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A 250 ka oxygen isotope record from diatoms at Lake El'gygytgyn, far east Russian Arctic

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Abstract

In 2003 sediment core Lz1024 was drilled at Lake El'gygytgyn, far east Russian Arctic, in an area of the Northern Hemisphere which has not been glaciated for the last 3.6 Ma. Biogenic silica was used for analysing the oxygen isotope composition ($\delta^{18}O_{diatom}$) in the upper 13 m long section dating back about 250 ka with samples dominated by one taxa in the <10 µm fraction (*Cyclotella ocellata*). Downcore variations in $\delta^{18}O$ values show that glacial-interglacial cycles are present throughout the core and $\delta^{18}O_{diatom}$ values are mainly controlled by $\delta^{18}O_{precipitation}$. Changes reflect the Holocene Thermal Maximum, the Last Glacial Maximum and the interglacial periods corresponding to MIS 5e and MIS 7 with a peak-to-peak amplitude of $\delta^{18}O = 5.3$ ‰. Our record is the first continuous $\delta^{18}O_{diatom}$ record from an Arctic lake sediment core directly responding to precipitation and dating back more than 250 ka and correlates well with the stacked marine $\delta^{18}O$ LR04 ($r = 0.58$) and δD EPICA Dome-C record ($r = 0.69$). With $\delta^{18}O$ results indicating strong links to both marine and ice-core records, records from Lake El'gygytgyn can be used to further investigate the sensitivity of the Arctic climate to both past and future global climatic changes.

1 Introduction

1.1 The Arctic as an important area for paleoclimate reconstruction

The Arctic experienced the most rapid warming in the last 150 yr (Serreze et al., 2000; Kaufman et al., 2009; Bekryaev et al., 2010) with a continuation of this temperature trend above the global average projected for the 21st century (Serreze et al., 2000; Anisimov et al., 2007). Especially in climate-sensitive areas such as the Arctic (Serreze and Francis, 2006a, b; Miller et al., 2010; Serreze and Barry, 2011), longer, continuous terrestrial records for paleo-climate reconstructions are rare (Brigham-Grette et al., 2007; CCSP, 2009) due to the coverage of large areas by glaciers, e.g. during the Last Glacial Maximum (LGM) (Dyke and Prest, 1987; Lehman et al., 1991; Thiede, 2004) which destroyed sedimentary sequences in lakes especially in the western part of Siberia (Svendsen et al., 1999; Hubberten et al., 2004). The Beringia land bridge which connected Alaska (eastern Beringia) and northeast Russia (western Beringia) was exposed during the glacials (Hopkins, 1967, 1982; Brigham-Grette, 2001) linked to an eustatic sea-level drop due to emerging ice caps. However, due to its dry climate the Eastern Arctic experienced only valley glaciation (Glushkova, 2001) and the precipitation-controlled eastern margin of the Eurasian Ice Sheet never extended to Eastern Siberia (Svendsen et al., 2004; Melles et al., 2007).

Lake sediments are known as excellent archives for the reconstruction of past climate and environmental changes which may provide insights as to how regions may respond to future change. The longest lacustrine palaeoenvironmental record in Siberia exists from Lake Baikal reaching back to 35 Ma before present (Tapponnier and Molnar, 1979). However, Lake Baikal is located south of the Arctic circle and the $\delta^{18}O$ values of precipitation are influenced by south and southeast cyclones in July and August (Bezrukova et al., 2008). In an attempt to obtain long-term Quaternary lake records from the terrestrial, far east Russian Arctic drilling campaigns were conducted at Lake El'gygytgyn in an area of the Northern Hemisphere which has not been glaciated during at least the last five glacial/interglacial cycles and has the potential to be an archive of continuous and undisturbed sedimentation (Brigham-Grette et al., 2007; Melles et al., 2007).

1.2 The importance of $\delta^{18}O_{(diatom)}$ records

Oxygen isotope records from ice-cores (Greenland-Ice-Core-Project members, 1993; Grootes et al., 1993; Petit et al., 1999; EPICA members, 2004, 2006) or carbonate organisms (Zachos et al., 2001; Lisiecki and Raymo, 2005) are amongst the most important proxies for reconstructing paleoenvironmental conditions and paleoclimate. In regions of high latitude, where ice-records are not available or where carbonates are absent, as is the case for Beringia and Lake El'gygytgyn the oxygen isotope composition

from lacustrine biogenic silica, i.e. diatoms, often represents the best isotope proxy for reconstructing past climate changes (Leng and Marshall, 2004). By taking potential controls and effects into account, the analysis of oxygen isotopes in lacustrine biogenic silica provides one of the rare opportunities to gain a direct and continuous signal from paleo-precipitation beyond the LGM in the Eastern part of the Arctic. This can then be compared with other regional and global $\delta^{18}O$ records to better understand the links between West Beringia and the wider global climate system. The preparation of the samples (e.g. Juillet-Leclerc and Labeyrie, 1987; Shemesh et al., 1995; Morley et al., 2004), contamination assessment (Lamb et al., 2007; Brewer et al., 2008; Mackay et al., 2011; Swann and Patwardhan, 2011) as well as the oxygen isotope analysis for diatoms are often challenging and time-consuming (Leng and Barker, 2006; Swann and Leng, 2009). Recently, improved protocols have been developed for the purification of small fractions and a more reliable contamination correction (Chapligin et al., 2012). In addition, a faster dehydration and analytical technique has also been introduced (Chapligin et al., 2010). However, when analysing 250 ka old material, diagenetic changes pose a serious threat to the reliability of $\delta^{18}O$ values from biogenic silica. Additionally, the species-effect is still not well understood for diatoms.

This study aims to analyse the upper 13 m sequence of a sediment core from Lake El'gygytgyn and provide a continuous, 250 ka $\delta^{18}O$ record from diatoms for the Eastern terrestrial Arctic. Additionally, potential diagenetic changes and their impact on the oxygen isotope composition are addressed.

2 Materials and methods

2.1 Site description, material and age model

Lake El'gygytgyn is located in the far east Russian Arctic (67°30′ N, 172°05′ E) at 492 m a.s.l. (Fig. 1a) inside a crater structure formed by a meteorite impact circa 3.6 Ma ago (Layer, 2000). The lake is of circular shape, about 12 km in diameter, 170 m deep, cold-monomictic and ultra-oligotrophic (Nolan and Brigham-Grette, 2007). 50 streams drain into the lake, the Enmyvaam River is the only outflow in the southeast of the Lake and the total catchment area is 293 km^2 (Nolan and Brigham-Grette, 2007).

Several cores were drilled in the last decade (Fig. 1b) including the 16.5 m core Lz1024 drilled in 2003 (67°30.13′ N; 172°06.46′ E) examined in this study. A gravity corer (UWITEC Corp., Austria) was used for the water-sediment transition and changed to a percussion piston corer further down the sediment (Melles et al., 2005). In total, 96 samples spread over the first 13 m were chosen for analysis, covering the last three glacial-interglacial cycles. From 2 cm sections sub-samples with average dry weight of 1.9 g were taken. As the first test series of 10 samples distributed equidistantly downcore did not provide enough material after purification, two subsequent samples were merged and the average age and depth determined. The first age model for core Lz1024 was proposed by Juschus et al. (2007) using isochronous sediment layers and susceptibility variations to correlate core Lz1024 to the previously dated 13.5 m core PG1351 with the final age model and revised after tuning the magnetic susceptibility to the insolation at 70° N (Nowaczyk et al., 2002, 2007, 2012). The core base of Lz1024 was dated to a maximum age of 350 ka (Frank et al., 2012; Nowaczyk et al., 2012). However, the lower sequence is disturbed (V. Wennrich, personal communication, 2012) which is why the focus of this study is on the 250 ka record.

2.2 Methods

2.2.1 Preparation

Various steps are essential from coring to the final interpretation of the oxygen isotope composition from biogenic silica (overview in Fig. 2). One taxa dominates the diatom assemblage at Lake El'gygytgyn: *Cyclotella ocellata* (avg. size 5–10 µm, 96 to 100 % relative abundance) with minor occurrences of *Pliocaenicus seczkinae* (avg. size 20–35 µm, 1–4 %, relative abundance) (Cremer et al., 2005; Cherapanova et al., 2007). For this reason, the normally analysed >10 µm fraction did not provide enough diatom

material for oxygen isotope analyses in most core sections. Consequently, in an attempt to obtain an isotope record dominated by a single taxa, the <10 µm fraction was purified according to an 8-step method developed by Chapligin et al. (2012) which is similar to the 4-step method (Morley et al., 2004). After freeze-drying the samples were treated with H_2O_2 (32 %) and HCl (10 %) to remove organic matter and carbonates and wet sieved into <10 µm and >10 µm fractions. Four multiple heavy liquid separation (HLS) steps with varying densities (from 2.25 to 2.15 g cm^{-3}) were then applied using a sodium polytungstate (SPT) solution before being exposed to a mixture of $HClO_4$ (65 %) and HNO_3 (65 %) for removing any remaining micro-organics.

2.2.2 Isotope analysis

Oxygen isotope analysis was performed with a PDZ Europa 2020 mass spectrometer (MS-2020; now supplied by Sercon Ltd., UK) following the method of Chapligin et al. (2010). Prior to isotope analyses, hydrous groups (H_2O, -OH) were removed from an initial sample weight of 1.5 to 2 mg using ramp degassing under inert gas flow conditions (inert Gas Flow Dehydration = iGFD technique) in a horizontal ceramic tube furnace flushed with helium (Chapligin et al., 2010). The dehydrated sample was then reacted by laser fluorination under BrF_5 atmosphere to liberate O_2 based on Sharp (1990). The oxygen was separated of by-products and directed to the mass spectrometer for isotope analysis. Every fifth sample was a biogenic working standard to verify the quality of the analyses. For this, the biogenic standard BFC (Leng et al., 2001; Leng and Sloane, 2008; Chapligin et al., 2010) calibrated within an inter-laboratory comparison was used (Chapligin et al., 2011). With a $\delta^{18}O$ values of +29.0 ± 0.3 ‰ BFC is the closest diatom working standard to the Lake El'gygytgyn samples ($\delta^{18}O$ values range between +19 and +26 ‰) available. Additionally, the international quartz standard NBS28 ($\delta^{18}O$ = +9.57 ‰; Hut, 1987; Gröning et al., 2007) was measured. Long-term standard measurements of $\delta^{18}O$ values in silica show standard deviations of $1\sigma = 0.15$ % for quartz and $1\,\sigma \leq 0.25$ % for biogenic silica working standards such as BFC (Chapligin et al., 2010). Replicate isotope analyses were performed for 49 samples from the core Lz1024 which show a mean standard deviation of 0.13 ‰ (1 σ, ranging between 0.00–0.41 ‰)

2.2.3 Contamination assessment and correction technique

The measured oxygen isotope composition ($\delta^{18}O_{measured}$) was corrected (to $\delta^{18}O_{corr}$) using geochemical mass-balancing (Swann and Leng, 2009; Chapligin, 2012).

$$\delta^{18}O_{corr} = (\delta^{18}O_{measured} - \%cont. \cdot \delta^{18}O_{cont.})/\%\ purity \quad (1)$$

where the percentage of purity was 100 % subtracted by the percentage of remaining contamination (% cont.). Determining % cont. by counting contamination particles/diatoms under a light microscope underestimates this parameter in the <10 µm fraction due to the presence of small, diffuse clay and silt particles (Chapligin et al., 2012). Thus, % cont. was calculated by dividing the sample percentage of Al_2O_3 by the Al_2O_3 percentage from a 100 % contamination end member according to Brewer et al. (2008), Swann and Leng (2008) and Mackay et al. (2011). Chapligin et al. (2012) tested different contamination assessment techniques to Lake El'gygytgyn sub-surface samples and found no significant difference between this method and calculating % cont. by multiplying the sample's Al_2O_3 percentage with a clay assemblage factor which depends on the Al_2O_3 percentage of the average clay types present in the core. Hence, the Al_2O_3 percentage for each sample was analysed by Energy-Dispersive X-ray Spectroscopy (EDS) (3–5 repetitions, diameter of excited-area size: 100–120 µm) and the % cont. and $\delta^{18}O_{cont.}$ end-members determined from a heavy fraction after the first heavy liquid separation containing no diatoms (verified under scanning-electron microscope, SEM) resulting in $Al_2O_{3\,<10\,\mu m}$ = 16.6 % and $\delta^{18}O_{cont.}$ = +6.5 ‰ (Chapligin et al., 2012).

2.2.4 Species assessment

The diatom assemblage in the <10 µm fraction of 40 purified samples equally distributed throughout the core was assessed by counting under light microscope (LM) (Chapligin et al., 2012, based on Morley et al., 2004, and Swann et al., 2008). Five random fields of view were selected along a transect in the middle of the slide and at least 200 valves as well as fragments were counted whenever possible. The biovolume was calculated by defining average area-sizes (Chapligin et al., 2012) for each species as it better reflects the actual proportion of each taxa when analysing for oxygen isotopes than using the number of valves.

2.2.5 FTIR analysis for studying diagenetic effects

The question of potential diagenetic changes and their impact on the oxygen isotope composition in the amorphous structure was addressed by performing diffuse reflectance Fourier Transform Infrared Spectroscopy (FTIRS) at Umeå University, Sweden. This method determines individual compounds in biogenic silica by recording the different characteristic vibration patterns (absorption peaks) of the chemical bonds present in the structure (siloxane bonds: Si-O-Si; silanol bonds: Si-OH; H_2O) over a certain wavelength window (Schmidt et al., 2001; Gendron-Badou et al., 2003; Moschen et al., 2006; Leng et al., 2009; Swann and Patwardhan, 2011). An FTIR spectrometer (Bruker IFS 66v/S) equipped with a diffuse reflectance accessory (Harrick Inc.) was used with 11 mg of sample material mixed with 500 mg KBr for the analysis under vacuum (4 mbar) conditions (Vogel et al., 2008; Rosén et al., 2010). 16 purified diatom samples from different core depths (first sample at 0.09 m, last sample at 12.35 m) were selected and scanned (64 scans per sample) with measurements taken every 4 cm^{-1} for the spectral region between 3750 and 400 cm^{-1}.

All wavelength absorption peaks >1500 cm^{-1} were removed as these peaks are not related to biogenic silica or linked to molecular vibrations of hydroxide (-OH stretching). Focusing on wavelengths <1500 cm^{-1} allows only the silica bonds from the diatom frustules to be examined. Common peak centers for amorphous silica are 450 cm^{-1}, 800 cm^{-1} and 1100 cm^{-1} for various modes of siloxane bonds and 945 cm^{-1} for silanol bonds (Gendron-Badou et al., 2003; Swann and Patwardhan, 2011). In our study the data was baseline-corrected and normalised, so that the area under each curve adds up to 100 %, with individual peaks separated by applying a Gaussian peak fitting (Fig. 4a) (Swann and Patwardhan, 2011) using the software Fytik, Version 0.9.3 (http://fityk.nieto.pl/). Peak types were then assigned (Si-OH and Si-O-Si) and the percentages calculated from the respective areas.

However, when using FTIR each Si-O-Si band has its own "sensitivity", so absolute unweighted calculations are not suitable for comparing individual samples. Therefore, the relative change in Si-OH bond determined by a single peak, was calculated. The highest peak area (top sample at 0.09 m, 1.3 ka) was set at 100 % (using the size of the un-normalised -Si-OH peak following peak fitting).

3 Results

3.1 Diatom assemblage

Five different types of diatoms and particles were counted for 40 samples downcore (*Cyclotella ocellata, Pliocaenicus seczkinae*, *Surirella* fragments, contamination particles and other diatom species) with an average of 236 ± 57 counts. The diatom assemblage in the analysed <10 µm fraction was almost mono-specific (Fig. 3, biovolume [%] with *Cyclotella ocellata* constituting >90 % of all diatom biovolume in 34 out of 40 samples, and 70–90 % in 4 samples). Only at 10.15 m and 10.75 m depth (203 and 208 ka) did the usually >10 µm sized species *Pliocaenicus seczkinae* predominate the <10 µm fraction (smaller frustules) with biovolume abundances of 52 % and 58 % respectively.

3.2 Contamination assessment and correction

Out of 96 samples, 80 contained sufficient material after all purification steps for both oxygen isotope measurements and contamination analysis (>5 mg). Chapligin et al. (2012) showed that the geochemical mass-balancing correction technique is reasonable for samples containing up to 2.5 % Al_2O_3 or <15 % contamination. From the 80 analysed samples 76 samples had an average Al_2O_3 percentage of 0.94 ± 0.16 % (Fig. 3, SiO_2 and Al_2O_3 [%], $\Delta^{18}O_{corr-measured}$). For four samples the Al_2O_3 percentage was >2.5 % and for one more sample the Al_2O_3 percentage of 2.3 % resulted in a high $\delta^{18}O$ value correction of >2.5 ‰. These samples were discarded from further interpretations.

Only a low correlation exists between the final mass of the sample after purification and Al_2O_3 percentage ($r^2 = 0.14$). However, all samples above 2.5 % Al_2O_3 had final masses below 10 mg which indicates that in horizons with low biogenic productivity (BSi <10 %) a purification resulting in enough cleaned sample material can be rather difficult.

3.3 $\delta^{18}O_{diatom}$ record

The $\delta^{18}O_{corr}$ values (henceforth simplified again to $\delta^{18}O$) throughout the 250 ka record range between +19.1 and +24.4 ‰ with an average of +21.7 ‰ (Fig. 3). The first sample (5 cm depth corresponding to 0.8 ka) shows a $\delta^{18}O$ value of +21.4 ‰ which is in good agreement with undated but younger sub-surface samples (Lz1032, 2–4 cm, $\delta^{18}O$ = +20.8 ‰) close to the Lz1024 drilling position (Chapligin et al., 2012). An increase to peak values of +23.1 ‰ (0.52 m depth, corresponding to 6.6 ka) and +23.4 ‰ (0.64 m, 8.4 ka) with a single spike of +23.9 ‰ (1.18 m, 15.0 ka) is observed. This is followed downcore by a significant decline to an absolute minimum in $\delta^{18}O$ of +19.1 ‰ at 1.61 m/23.1 ka. The $\delta^{18}O$ values continuously increase until +22.4 ‰ (1.98 m, 34.3 ka) with subsequent fluctuations within about 1.0 ‰ for the next 70 ka and prominent minima of +19.6 ‰ (3.36 m, 70.5 ka) and +20.0 ‰ (4.80 m, 107.3 ka) and average maxima with peaks of +23.3 ‰ (2.42 m, 54.6 ka) and +21.0 ‰ (~4.5 m, ~100 ka).

Measurements reveal an increase for the next 20 ka with a peak of +24.4 ‰ (5.85 m, 127.2 ka) before a progressive decrease down to +20.7 ‰ (7.35 m, 162.0 ka). This peak at 5.85 m (127.2 ka) is the absolute maximum of the record. Between 7.35 m and 9.56 m (162.2 ka and 187.6 ka) no measurements could be performed as the two samples within this period did not provide sufficient material. The $\delta^{18}O$ value of +20.1 ‰ at 9.56 m (187.6 ka) supports the decreasing trend. From the short-term minimum downcore a rapid increase until 197.6 ka was observed, plateauing until 209.3 ka with an average $\delta^{18}O$ = +23.2 ‰. Further downcore, a slight decline of 1.5 ‰ was detected until values increased again to a maximum of +23.6 ‰ (243.9 ka).

3.4 Diagenetic effects

In order to test the samples for diagenetic effects which could potentially alter $\delta^{18}O$ values with time FTIRS measurements were performed. The determined absolute percentage of Si-OH bonds ranges between 5.6 and 9.0 %. As absolute unweighted calculations are not suitable for comparing individual samples the change in Si-OH bond percentages relative to the highest peak area (top sample at 0.09 m, 1.3 ka set at 100 %) was calculated resulting in maximum values in the upper core section between 0–30 ka (average 88 %), a local minimum at 90 ka (64 %) and relatively constant values further downcore (average for the period between 90 ka and 230 ka = 68 %). A relative decrease of 2.9 % per 10 ka is observed in the first 90 ka (total decrease of 26 %) with a correlation between Si-OH percentage and age of $r^2 = 0.63$). For the relatively constant part of the Si-OH percentage record from 90 ka to 231 ka only a weak correlation exists ($r^2 = 0.30$). These numbers are not absolute and should only be used qualitatively to separate larger from smaller Si-OH layers. However, different calculations by peak height ratio (945 cm^{-1}, SiOH, vs. 800 cm^{-1}, inter-tetrahedral Si-O-Si bending vibrations) or peak area ratio (990–860 cm^{-1} vs. 860–750 cm^{-1}) confirmed this trend.

4 Discussion

4.1 $\delta^{18}O$ Isotope controls

4.1.1 Lake temperature, blooming period and $\delta^{18}O_{water}$

Various factors can influence the $\delta^{18}O$ values of lacustrine, biogenic silica (Fig. 5). The lake temperature in which the diatoms grow has an effect on the fractionation between $\delta^{18}O_{water}$ and $\delta^{18}O_{diatom}$ of about −0.2 ‰ per °C (Brandriss et al., 1998; Moschen et al., 2005; Dodd and Sharp, 2010; Dong and JingTai, 2010). Lake El'gygytgyn lacks a true thermocline as in winter the lake is thermally stratified, but only with a difference of 2.3 °C from the top to bottom of the water column (0.7 °C at 3 m water depth, 3 °C at 170 m depth). As soon as the ice melt begins, the first 30 m are mixed (at 1.4 °C, beginning of June) and in mid-July the lake is completely mixed with temperatures from July to Mid-October ranging between 2.2 °C to 3.8 °C (observations from 2002, Nolan and Brigham-Grette, 2007). Diatoms are phototrophic organisms and the major blooming period was assessed by Cremer et al. (2005) to the time from early spring (under-ice) through open-water conditions until the re-establishment of ice coverage in autumn with the highest increase of *Cyclotella ocellata* in the first meters of the photic zone between 1 June and 20 July. Thus, due to this short major blooming period variations in lake temperature should not exceed ±1 °C, equal to water temperature induced changes in $\delta^{18}O$ values of ±0.2 ‰ which is within the instruments error for biogenic silica ($1\sigma = 0.25$ ‰, Chapligin et al., 2010). Chapligin et al. (2012) has further shown that no significant isotopic differences exist in the water column throughout various times of the year, so only minor effects from seasonality are expected to be reflected in $\delta^{18}O_{diatom}$ values. With a deep photic zone of about 34 m (Dehnert and Juschus, 2008), good mixing conditions and a location in the cold Arctic environment, no significant impact on the $\delta^{18}O_{diatom}$ values from varying lake water temperature can be expected from different ages, samples or from taxa blooming in different seasons.

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

4.1.2 Lake hydrology, ice-cover and $\delta^{18}O_p$

Evaporation trends were not detected when analysing the $\delta^{18}O$ lake water profile at three different times of the year (May, August, November; Chapligin et al., 2012). Despite the fact that these observations account mainly for the recent system, the reconstructed differences in lake level (terraces: +35–40 m, middle Pleistocene; +9–11 m, late Pleistocene; +2–3 m, Holocene; Glushkova and Smirnov, 2007) and subsequent differences in evaporation rates can potentially change the hydrological conditions (i.e. the residence time) and cause a shift in $\delta^{18}O_{lakewater}$. However, changes in the extension of the photic zone should be considerably low throughout time. Hence $\delta^{18}O_{diatom}$ is basically influenced by $\delta^{18}O_{lakewater}$.

In a deep, well-mixed lake such as Lake El'gygytgyn with little evaporation and a defined small catchment area $\delta^{18}O_{lakewater}$ is mainly determined by the oxygen isotope composition of precipitation ($\delta^{18}O_p$). Precipitation is either directly going into the lake or is supplied via one of the small streams (Chapligin et al., 2012; Wilkie et al., 2012).

The residence time is about 100 yr (Fedorov, 2012) causing no major delays in the transfer of the $\delta^{18}O_p$ signal to $\delta^{18}O_{lakewater}$ for the last 100 yr as shown in the isotope mass balance model of the lake (Wilkie et al., 2012). The model additionally shows that this residence time buffers short-term changes and reduces the amplitude in $\delta^{18}O_{diatom}$ to approximately one third on a decadal scale (Wilkie et al., 2012). However, the low sedimentation rate only allowed for sampling on a centennial scale and for gaining average $\delta^{18}O_{diatom}$ values. Compared to this sample-related time resolution and the relatively low resolution from the $\delta^{18}O_{diatom}$ record (74 samples/250 ka), the residence time can have reduced the amplitude by "cutting off local maxima or minima" of the $\delta^{18}O_{diatom}$ record to a certain extent but considerably less than in the 100 yr model.

Modern lake water isotope composition of $\delta^{18}O_{AVG} = -19.8$ ‰ (Chapligin et al., 2012) matches the oxygen isotope composition of precipitation ranging between −14 and −34 ‰ for snow samples of single winter events (mean −23.2 ‰) and rain $\delta^{18}O$ values ranging from −15.9 ‰ to −12.4 ‰ (mean −14.3 ‰) (Wilkie et al., 2012).

Assuming a winter to summer precipitation ratio of 60 % to 40 % (Nolan and Brigham-Grette, 2007) the annual average of $\delta^{18}O$ values would be −19.3 ‰. Stream $\delta^{18}O$ values ranged from −24.2 ‰ to −16.7 ‰ (Wilkie et al., 2012).

Hence, the oxygen isotope composition of the diatom samples reflects $\delta^{18}O_{lakewater}$ which is mainly controlled by $\delta^{18}O_p$ (pathway via streams or directly on/into the lake). This is in accordance with Swann et al. (2010).

4.1.3 Air temperature, air mass source and continentality

The $\delta^{18}O$ precipitation signal could be affected by varying air mass sources, air temperature, and/or continentality. According to Dansgaard (1964) the mean annual air temperature (MAAT) at surface is directly related to the mean annual $\delta^{18}O_p$ signal (shift of +0.7 ‰ per °C; in high latitudes/continental regions +0.6 ‰ per °C, Rozanski et al., 1993). Due to the relatively stable lake water temperatures and the negligible effect from ΔT_{lake} we assume the effect of air temperature changes as predominant.

Nolan et al. (2012) identified modern synoptic weather patterns and climate trends affecting air temperatures from National Centers for Environmental Prediction (NCEP) global reanalysis data. Strong Aleutian lows and strong high pressure centres over the Arctic Ocean prevail in the winter bringing cold Arctic air and moisture from the East and North to Lake El'gygytgyn. Summers are characterized by weak low pressure systems over Siberia and broad high pressure systems to the south and east providing warm continental air and recycled moisture to the lake.

For this area and the lake system, the general warming or cooling trends for air temperature are more important in contrast to changes in storm tracks being negligible (Nolan et al., 2012). Furthermore, Nolan et al. (2012) suggest that these weather patterns have been relatively stable with time and are likely representative of this and other interglacial periods.

The modern day and interglacial mean annual air temperature is −10.3 °C (Nolan and Brigham-Grette, 2007) while mean annual air temperatures for glacials were assumed to be about −25 °C using the coldest value from modern day NCEP daily reanalysis

(Swann et al., 2010). Using the Dansgaard relationship of +0.6 ‰ per °C this temperature difference of about 15 °C is equivalent to a long-term amplitude in $\delta^{18}O_p$ by 9 ‰. This should be significantly higher when using MIS 5e interglacial temperatures instead of modern day temperatures.

If only condensation temperature controlled this peak-to-peak amplitude of $\Delta^{18}O = 5.3$ ‰, this would correspond to a mean annual air temperature change of about 9 °C between LGM and MIS 5e interglacial (according to Dansgaard, 1964).

Potentially, the change in the isotope signal due to air temperatures could be amplified by changes in continentality patterns. Lower sea levels and extended sea-ice in glacial periods increase the continentality of the location and the effect of the Rayleigh distillation and; thus, further decrease the $\delta^{18}O_p$. In contrast, there are three possibilities to explain a reduced amplitude.

1. The different lake temperature (about −0.2 ‰ per °C) and air temperature (about +0.6 ‰ per °C) factors cannot be mixed up and merged, as air temperature varies between glacial and interglacials from −10.3 °C to −25 °C while water temperatures at these latitudes in well mixed lakes with a depth of 170 m must have been always around 4 °C with only small variations (modern and interglacial lake temperatures about 2–4 °C; see Sect. 4.1.1). Hence, the effect from lake temperatures (e.g. potentially higher lake temperatures during the MIS 5e interglacial or the Greenland interstadial 1) would reduce the $\delta^{18}O_{diatom}$ values and, thus, the amplitude slightly (e.g. by 1 ‰ when assuming a maximum temperature difference of 4 to 5 °C).

2. The amplitude reduction from $\delta^{18}O_p$ to $\delta^{18}O_{water}$ could also originate from the lake residence time acting as a buffer for extreme variations in $\delta^{18}O_p$ over time (see Sect. 4.1.2). This effect could increase with longer residence time in cold phases generally characterized by lower temperature and humidity and thus potentially less moisture reaching the lake setting.

3. The global isotope-temperature relationship (Dansgaard et al., 1964) is based on recent precipitation from different regions. There is no detailed information if this $\delta^{18}O_p$ – MAAT relationship is valid for the region, nor if it might have changed through time. Additionally, every single $\delta^{18}O_{diatom}$ sample refers to centennial time scales, thus longer than the period considered by Dansgaard (1964). However, the reasonable order of magnitude of $\Delta^{18}O$ in the Lake El'gygytgyn isotope record indicates that air temperatures should be the main driver.

4.2 Comparison with other Lake El'gygytgyn records

4.2.1 $\delta^{18}O_{diatom}$ Holocene study

Apart from this study Swann et al. (2010) examined the oxygen isotope composition of diatoms for the first 23 ka at Lake El'gygytgyn in relatively high resolution (Fig. 6). Differences exist between the two studies and a relatively constant offset of 3.4 ± 1.0 ‰, $n = 16$ was observed. The studies are compared and simplified in the following section to study1 (Swann et al., 2010) and study2 (our data). While for study1 the 5–75 µm fraction was used (comprised of *Cyclotella ocellata* and *Pliocaenicus costatus*) to provide enough material for isotope analysis, in study2 the <10 µm fraction was used in order to obtain single-species samples of *Cyclotella ocellata*. Differences in diatom assemblages (and different living conditions between both species) between the two studies could have caused the different $\delta^{18}O$ values, although numerous studies have found no evidence of a species-dependent isotope fractionation in diatoms (Schmidt et al., 1997, 2001; Brandriss et al., 1998; Moschen et al., 2005). Chapligin et al. (2012) analysed the *Pliocaenicus*-dominated >10 µm fraction vs. the *Cyclotella*-dominated <10 µm fraction for sub-surface samples from Lake El'gygytgyn and detected no significant difference in $\delta^{18}O_{diatom}$ values between the two size fractions after contamination correction.

The purity of diatoms in a sample could cause differences in $\delta^{18}O$ values between both studies. The % cont. in study1 was assessed by counting under a light microscope, resulting in a mean sample purity of 95.9 ± 1.9 % (1 σ), while study2 showed a purity of 94.6 ± 3.4 %. Study1 did not correct the measured values for contamination where as study2 did. However, higher contamination should cause lower $\delta^{18}O$ values for study1 which is not the case.

Different dehydration techniques were applied in both laboratories (step-wise fluorination = SWF; inert Gas Flow Dehydration = iGFD), but an inter-laboratory comparison showed for both techniques results within standard deviation on various biogenic working standards (Chapligin et al., 2011) between the two laboratories. The removal of Si-OH groups in Nickel cylinders by using SWF as applied in study1 could potentially remove oxygen from clay structures whereas iGFD removes just H_2O and -OH groups. However, study2 corrected for contamination, so a significant difference due to different dehydration techniques can also be excluded. Both studies show different analytical reproducibility (mean SD (1 σ) = 0.34 ‰ for study1 vs. 0.13 ‰ for study2) but a similar trend can be observed. In both records, $\delta^{18}O$ values increase until 8–10 ka corresponding to the HTM (study1: +27.0 to +27.4 ‰, increase between 3–10.7 ka; study2: +23.4 ‰ peak at 8.4 ka) and decrease until 20–22 ka corresponding to the LGM (study1: +22.4 to +22.5 ‰ at 21.4–21.6 ka; study2: +19.1 to +20.3 ‰ at 21.2–23.1 ka). Hence, no obvious reason for the offset in $\delta^{18}O$ values between the two studies could be observed, but both records show similar trends indicating that conclusions on palaeoclimatic changes can be drawn based on relative $\delta^{18}O$ changes in the individual studies.

4.2.2 Biogenic silica, TiO_2, magnetic susceptibility

For a longer time-series, we compared measurements of biogenic silica (BSi [%]), TiO_2 [%] and magnetic susceptibility analysed on the same core (Lz1024; Frank et al., 2012) to our $\delta^{18}O$ record (Fig. 7). BSi can be generally used as a proxy for nutrient availability and bioproductivity or primary production (Colman et al., 1995). TiO_2 is commonly used as a proxy for clastic sediment supply from fluvial (Haug et al., 2001) or eolian (Yancheva et al., 2007) transport and often related to weathering (Minyuk et al., 2011). To compare the $\delta^{18}O$ record with both data sets (BSi record, Rosén et al., 2010; TiO_2,

Frank et al., 2012) we interpolated between sample depths to get comparable data. Both, BSi and TiO_2 records do not correlate well with the $\delta^{18}O$ record ($\delta^{18}O$ vs. BSi, $r = -0.14$; $\delta^{18}O$ vs. TiO_2, $r = -0.33$). The anti-correlation of the overall record is mainly due to the first three meters of the core and the high peak of BSi at the time interval corresponding to the LGM. This can be explained by enhanced weathering (maximum in TiO_2 percentage) and a subsequent nutrient availability (maximum in BSi percentage) accompanied by a minimum in $\delta^{18}O$ values.

Magnetic susceptibility in lake sediments reflects the concentration of magnetic mineral phases which is controlled by preservation in Lake El'gygytgyn sediments (Nowaczyk et al., 2007). Anoxic bottom and pore waters dissolve the respective mineral phases while keeping preserved under oxic conditions. Thus, high and low magnetic susceptibility values can represent interglacials and glacials but a high organic content during interglacials can also induce anoxic bottom water conditions.

None of the compared proxies are directly related to temperature and precipitation and hence, only weak correlations exist between these proxies and the diatom $\delta^{18}O$ signal. It is remarkable though, that $\delta^{18}O$ peaks often occur earlier than TiO_2 minima or BSi maxima percentages (cf. $\delta^{18}O$ at 5.50–6.22 m depth vs. TiO_2 and BSi at 5.30–5.80 m; $\delta^{18}O$, 2.40–2.70 m vs. TiO_2 and BSi, 2.40–2.00 m) which could indicate a more direct atmospheric signal responsible for $\delta^{18}O$ while there is a delayed reaction in the more indirect proxy records.

4.3 Comparison with other regional and global climate records

The diatom $\delta^{18}O$ record was compared with prominent climate curves such as the global marine $\delta^{18}O$ benthic stack LR04 (Lisiecki and Raymo, 2005; henceforth simplified to LR04) and the glacial $\delta^{18}O$ record from the North Greenland Ice Core Project (NGRIP; North-Greenland-Ice-Core-Project members, 2004; henceforth simplified to NGRIP). As this latter record ends at ~123 ka the δD Dome-C record from the European Project for Ice Coring in Antarctica (EPICA; EPICA members, 2004, 2006;

henceforth simplified to EPICA) was used for comparison further downcore as well as the mean monthly (July) insolation at 67° N (Laskar et al., 2004) being indicative for the main diatom blooming period (Fig. 8).

For comparing the EPICA, the LR04 record and the mean monthly (July) insolation at 67° N with our $\delta^{18}O$ record we interpolated between sample ages. The correlation of the diatom $\delta^{18}O$ record and the stacked $\delta^{18}O$ LR04 record (Fig. 9; $r = +0.58$) and δD EPICA record (Fig. 9; $r = +0.69$) are significant ($p < 0.05$) indicating that a clear precipitation driven climate signal is preserved in the $\delta^{18}O$ record from diatoms at Lake El'gygytgyn.

The correlation between the diatom $\delta^{18}O$ record and the mean monthly (July) insolation at 67° N is $r = +0.56$. When correlating this record to the different Milankovitch cycles, the 41 ka cycle caused by the obliquity of the ecliptic is clearly the best fit ($r = +0.62$; eccentricity: $r = +0.29$; precession: $r = -0.38$). Hence, solar forcing, especially the 41 ka obliquity cycle, seems to be the main forcing factor on longer timescales for $\delta^{18}O$ in diatoms at Lake El'gygytgyn. On the one hand, this further supports the proposed age model, on the other hand this shows the potential of $\delta^{18}O$ in diatoms at Lake El'gygytgyn as a long-term climate archive back to 3.6 Ma.

4.4 Paleoclimate reconstruction

Glacial-interglacial cycles are clearly visible in the presented $\delta^{18}O_{diatom}$ record at Lake El'gygytgyn dating back to 250 ka. This includes prominent minima and maxima such as the Holocene Thermal Maximum (HTM, $\delta^{18}O \sim +23$ ‰, 8.9 ka). A post-HTM cooling trend can be observed, while in the pre-HTM time the Younger Dryas stadial (Greenland Stadial 1) has not been identified in the $\delta^{18}O$ record which might be due to the relatively low resolution. However, in the higher resolved $\delta^{18}O$ record of Swann et al. (2010) a local minimum in the Younger Dryas exists, but is not clearly visible within the general trend. The LGM ($\delta^{18}O = +19.1$ ‰, 23.1 ka) reflects the absolute minimum of the record and corresponds to minima in the $\delta^{18}O$ NGRIP, δD EPICA Dome-C and stacked $\delta^{18}O$ LR04 records (Fig. 8) as well as in the July insolation record from 67° N.

However, the LGM minimum in the Lake El'gygytgyn $\delta^{18}O$ record is earlier than those in LR04 and EPICA (20–18 ka), whereas the insolation minimum at 67° N occurs at the same time (~23 ka). Despite the relatively low resolution, two maxima in the MIS 3 interstadial can be distinguished. These maxima generally coincide with the mid MIS 3 warm phase (+22.4 ‰, 34.3 ka) and early MIS 3 warm phase (+23.3 ‰, 54.6 ka) as stated for Siberia (e.g. Swann et al., 2005). The colder MIS 4 is reflected by relatively lower $\delta^{18}O$ values between 120 and 60 ka. The local minimum ($\delta^{18}O = +19.6$ ‰), verified by multiple data points, occurs at ~70 ka and matches the NGRIP and the insolation minimum. After the LGM minimum it is the second lowest minimum reflecting a cold time period. The MIS 4 is preceeded by a characteristic maximum corresponding to the MIS 5e interglacial (+24.4 ‰, 127.2 ka) being the absolute maximum of the record. Again, this maximum correlates well with the maxima of the EPICA and the insolation record. However, the increase towards higher $\delta^{18}O$ values occurs earlier than in the other records and already at ~133 ka the values are close to the peak maximum. Further maxima are present in the time interval corresponding to MIS 7.1 and 7.3 (plateau ~+23.0 ‰, ~209–203 ka) as well as MIS 7.5 (+23.6 ‰, 243.9 ka). The intermediate period of MIS 7.2 could not be detected despite the analysis of four samples within this time. Hence, the $\delta^{18}O$ record shows a plateau which is more similar to the weakly developed minima of the EPICA and LR04 records than to the distinct minimum of the insolation record at ~206 ka. The $\delta^{18}O$ minimum corresponding to MIS 7.4 (+21.5 ‰, ~231 ka) correlates well with the EPICA, LR04 and insolation minima. The time corresponding to MIS 7.5 is reflected by the local $\delta^{18}O$ maximum (+23.6 ‰, 243.9 ka) which occurs slightly earlier than in the EPICA, LR04 and insolation record (~240 ka).

According to the presented $\delta^{18}O_{diatom}$ record of Lake El'gygytgyn similar temperatures occurred in the time of the HTM, MIS 3 and MIS 7, where as the MIS 5e interglacial was significantly warmer than the Holocene. In the global marine LR04 record abrupt warming and slow cooling trends were observed whereas in our $\delta^{18}O$ record both warming and cooling processes seem to occur with the same speed. However, the reason for the different reaction time is not yet understood but may be linked to the fast reaction time of the lake water to climate change.

4.5 Diagenetic effect

Diagenetic effects could severely influence the oxygen isotope composition on longer time scales by preferentially incorporating ^{18}O from exchangeable Si-OH bonds into the Si-O-Si structure which results in higher δ^{18}O values (Brandriss et al., 1998; Schmidt et al., 2001; Moschen et al., 2006). Despite the relative decrease of silanol bonds of 0.6 %/10 ka and a total of 20 % for the whole 250 ka record (Fig. 4b; top sample: 9 cm, 1.4 ka, 100 %; deepest sample: 12.35 m, 231 ka, 76 %) no general trend in the oxygen isotope composition of the samples (+0.2 ‰/100 ka, $r^2 = 0.03$) towards higher δ^{18}O values could be detected in the 250 ka record (Fig. 3). The results support the theory from Moschen et al. (2006) that a rapid signal alteration during sedimentation is followed by only minor post-sedimentary diagenetic changes which are not detectable in the δ^{18}O data. This makes the Lake El'gygytgyn diatom record suitable for further downcore δ^{18}O analyses.

5 Conclusions

Samples from the upper 13 m (dating back about 250 ka) of the 16.5 m sediment core drilled at Lake El'gygytgyn (far east Russian Arctic) were analysed for the oxygen isotope composition of biogenic silica (diatoms). For this purpose the <10 µm fraction was used showing mostly a mono-specific diatom assemblage of *Cyclotella ocellata*. Sample purity was analysed by EDS and $\delta^{18}O_{diatom}$ values corrected using geochemical mass-balancing. Despite a decreasing trend in silanol group percentages of about 25 % from the topmost sample downcore detected by FTIRS, this diagenetic change is not reflected in the δ^{18}O record. The $\delta^{18}O_{diatom}$ signal is clearly controlled by the δ^{18}O signal from precipitation (driven by temperature at the point

of condensation in the atmosphere) with downcore variations indicating that glacial-interglacial cycles are present throughout the whole core. The Holocene Thermal Maximum (HTM; δ^{18}O∼+23 ‰; 8.9 ka), the Last Glacial Maximum (LGM; +19.1 ‰, 23.1 ka) as well as the MIS 5e interglacial (+24.4 ‰, 127.2 ka) and the interval corresponding to MIS 7.1, 7.3 (plateau around +23.0 ‰, ∼209–203 ka) and MIS 7.5 (+23.6 ‰, 243.9 ka) are clearly visible. A peak-to-peak amplitude of 5.3 ‰ between the MIS 5e absolute maximum and the LGM absolute minimum was detected. This shift would be equal to a change in mean annual air temperature of about 9 °C when assuming that changes in $\delta^{18}O_p$ and $\delta^{18}O_{lakewater}$ are governed by atmospheric temperature at the point of condensation (+0.6 ‰ per °C) for high latitudes. However, variations in moisture source and continentality could be still masked within this difference.

Generally the δ^{18}O record tends to peak earlier than the weathering (TiO_2 [%]) or bioproductivity (BSi [%]) proxy records indicating that δ^{18}O precipitation signal rapidly responds to global/regional climate change while TiO_2 reacts on enhanced weathering in cold periods or BSi percentages increase after warmer time intervals with a certain delay. The correlations of the δ^{18}O record with the δ^{18}O benthic stack LR04 ($r = 0.58$) and the δD EPICA Dome-C record ($r = 0.69$) are significant and show the sensitivity of Lake El'gygytgyn and the wider Arctic climate system to global climate conditions. However, when comparing Lake El'gygytgyn to these global records, the LGM, MIS 7.5 and the δ^{18}O values increase towards the MIS 5e occur earlier. From the Milankovitch cycles the 41 ka obliquity cycle correlates best with the δ^{18}O record and is most likely one of the main forcing factors on longer timescales for δ^{18}O in diatoms at Lake El'gygytgyn. This is the longest continuous terrestrial δ^{18}O record from the Arctic directly reflecting δ^{18}O precipitation signals. The work will be expanded to sediment core 5011-1 (dating back to about 3.6 Ma), which was drilled within the ICDP program at Lake El'gygytgyn in early 2009.

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References

Bekryaev, R. V., Polyakov, I. V., and Alexeev, V. A.: Role of Polar Amplification in Long-Term Surface Air Temperature Variations and Modern Arctic Warming, J. Climate, 23, 3888–3906, 2010.

Bezrukova, E., Krivonogov, S. K., Takahara, H., Letunova, P. P., Shichi, K., Abzaeva, A. A., Kulagina, N. V., and Zabelina, Y. S.: Lake Kotokel as a stratotype for the late glacial and Holocene in southeastern Siberia, Dokl. Earth Sci., 420, 658–663, 2008.

Brandriss, M. E., O'Neil, J. R., Edlund, M. B., and Stoermer, E. F.: Oxygen isotope fractionation between diatomaceous silica and water, Geochim. Cosmochim. Ac., 62, 1119–1125, 1998.

Brewer, T. S., Leng, M. J., Mackay, A. W., Lamb, A. L., Tyler, J. J., and Marsh, N. G.: Unravelling contamination signals in biogenic silica oxygen isotope composition; the role of major and trace element geochemistry, J. Quaternary Sci., 23, 321–330, 2008.

Brigham-Grette, J.: New perspectives on Beringian Quaternary paleogeography, stratigraphy, and glacial history, Quaternary Sci. Rev., 20, 15–24, 2001.

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

CCSP: Past Climate Variability and Change in the Arctic and at High Latitudes, A report by the U.S. Climate Change Science Program and Subcommittee on Global Change Research, coordinating lead authors: Alley, R. B., Brigham-Grette, J., Miller, G. H., Polyak, L., and White, J. W. C., US Geological Survey, Reston, VA, 257 pp., 2009.

Chapligin, B., Meyer, H., Friedrichsen, H., Marent, A., Sohns, E., and Hubberten, H. W.: A high-performance, safer and semi-automated approach for the $\delta^{18}O$ analysis of diatom silica and new methods for removing exchangeable oxygen, Rapid Commun. Mass Sp., 24, 2655–2664, 2010.

Chapligin, B., Leng, M. J., Webb, E., Alexandre, A., Dodd, J. P., Ijiri, A., Lücke, A., Shemesh, A., Abelmann, A., Herzschuh, U., Longstaffe, F. J., Meyer, H., Moschen, R., Okazaki, Y., Rees, N. H., Sharp, Z. D., Sloane, H. J., Sonzogni, C., Swann, G. E. A., Sylvestre, F., Tyler, J. J., and Yam, R.: Inter-laboratory comparison of oxygen isotope compositions from biogenic silica, Geochim. Cosmochim. Ac., 75, 7242–7256, 2011.

Chapligin, B., Meyer, H., Bryan, A., Snyder, J., and Kemnitz, H.: Assessment of purification and contamination correction methods for analysing the oxygen isotope composition from biogenic silica, Chem. Geol., 300–301, 185–199, 2012.

Cherapanova, M. V., Snyder, J. A., and Brigham-Grette, J.: Diatom stratigraphy of the last 250 ka at Lake El'gygytgyn, northeast Siberia, J. Paleolimnol., 37, 155–162, 2007.

Colman, S. M., Peck, J. A., Karabanov, E. B., Carter, S. J., Bradbury, J. P., King, J. W., and Williams, D. F.: Continental climate response to orbital forcing from biogenic silica records in Lake Baikal, Nature, 378, 769–771, 1995.

Cremer, H., Wagner, B., Juschus, O., and Melles, M.: A microscopical study of diatom phytoplankton in deep crater Lake El'gygytgyn, Northeast Siberia, Algol. Studies, 116, 147–169, 2005.

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

Dehnert, A. and Juschus, O.: Rezente Sedimentation im Elgygytgyn-See, NE Sibirien, abgeleitet aus der Zusammensetzung von Oberflächensedimenten, Leipziger Geowissenschaften, Leipzig, 35–51, 2008.

Dodd, J. P. and Sharp, Z. D.: A laser fluorination method for oxygen isotope analysis of biogenic silica and a new oxygen isotope calibration of modern diatoms in freshwater environments, Geochim. Cosmochim. Ac., 74, 1381–1390, 2010.

Dong, L. and JingTai, H.: Temperature-induced fractionation of oxygen isotopes of diatom frustules and growth water in Lake Sihailongwan in Northeast China, Chinese Sci. Bull., 55, 3794–3801, 2010.
Dyke, A. S. and Prest, V. K.: Late Wisconsinan history of the Laurentide ice sheet, Geogr. Phys. Quatern. XLI, 41, 237–263, 1987.
EPICA members: Eight glacial cycles from an Arctic ice core, Nature, 429, 623–628, 2004.
EPICA members: One-to-one coupling of glacial climate variability in Greenland and Antarctica, Nature, 444, 195–198, doi:10.1038/nature05301, 2006.
Fedorov, G., Nolan, M., Brigham-Grette, J., Bolshiyanov, D., Schwamborn, G., and Juschus, O.: Lake El'gygytgyn water and sediment balance 1 components overview and its implications for the sedimentary record, in preparation, 2012.
Frank, U., Nowaczyk, N. R., Minyuk, P., Vogel, H., Rosen, P., and Melles, M.: A 350 ka record of climate change from Lake El'gygytgyn, far eastern Russian Arctic: Refining the pattern of climate modes by means of cluster analysis, in preparation, 2012.
Gendron-Badou, A., Coradin, T., Maquet, J., Fröhlich, F., and Livage, J.: Spectroscopic characterization of biogenic silica, J. Non-Cryst. Solids, 316, 331–337, 2003.
Glushkova, O. Y.: Geomorphological correlation of Late Pleistocene glacial complexes of Western and Eastern Beringia, Quaternary Sci. Rev., 20, 405–417, 2001.
Glushkova, O. Y. and Smirnov, V. N.: Pliocene to Holocene geomorphic evolution and paleogeography of the El'gygytgyn Lake region, NE Russia, J. Paleolimnol., 37, 37–47, 2007.
Greenland-Ice-Core-Project members: Climate instability during the last interglacial period recorded in the GRIP ice core, Nature, 364, 203–207, 1993.
Grootes, P. M., Stuiver, M., White, J. W. C., Johnsen, S., and Jouzel, J.: Comparison of oxygen isotope records from the GISP2 and GRIP Greenland ice cores, Nature, 366, 552–554, 1993.
Haug, G. H., Hughen, K. A., Sigman, D. M., Peterson, L. C., and Röhl, U.: Southward Migration of the Intertropical Convergence Zone Through the Holocene, Science, 293, 1304–1308, 2001.
Hopkins, D. M. E.: The Bering Land Bridge, Stanford University Press, Stanford, 1967.
Hopkins, D. M., Matthews Jr., J. V., Schweger, C. E., and Young, S. B.: Paleoecology of Beringia, Academic Press, New York, 489 pp., 1982.
Hubberten, H. W., Andreev, A., Astakhov, V. I., Demidov, I., Dowdeswell, J. A., Henriksen, M., Hjort, C., Houmark-Nielsen, M., Jakobsson, M., Kuzmina, S., Larsen, E., Lunkka, J. P., Lyså,

A., Mangerud, J., Möller, P., Saarnisto, M., Schirrmeister, L., Sher, A. V., Siegert, C., Siegert, M. J., and Svendsen, J. I.: The periglacial climate and environment in northern Eurasia during the Last Glaciation, Quaternary Sci. Rev., 23, 1333–1357, 2004.
Juillet-Leclerc, A. and Labeyrie, L.: Temperature dependence of the oxygen isotopic fractionation between diatom silica and water, Earth Planet. Sc. Lett., 84, 69–74, 1987.
Juschus, O., Preusser, F., Melles, M., and Radtke, U.: Applying SAR-IRSL methodology for dating fine-grained sediments from Lake El'gygytgyn, north-eastern Siberia, Quat. Geochronol., 2, 187–194, 2007.
Kaufman, D. S., Schneider, D. P., McKay, N. P., Ammann, C. M., Bradley, R. S., Briffa, K. R., Miller, G. H., Otto-Bliesner, B. L., Overpeck, J. T., Vinther, B. M., and Arctic Lakes 2k Project Members: Recent Warming Reverses Long-Term Arctic Cooling, Science, 325, 1236–1239, 2009.
Lamb, A. L., Brewer, T. S., Leng, M. J., Sloane, H. J., and Lamb, H. F.: A geochemical method for removing the effect of tephra on lake diatom oxygen isotope records, J. Paleolimnol., 37, 499–516, 2007.
Laskar, J., Robutel, P., Joutel, F., Gastineau, M., Correia, A. C. M., and Levrard, B.: A long-term numerical solution for the insolation quantities of the Earth, Astron. Astrophys., 428, 261–285, 2004.
Layer, P. W.: Argon-40/argon-39 age of the El'gygytgyn impact event, Chukotka, Russia, Meteorit. Planet. Sci., 35, 591–599, 2000.
Lehman, S. J., Jones, G. A., Keigwin, L. D., Andersen, E. S., Butenkoi, G., and Ostmo, S. R.: Initiation of Fennoscandian ice-sheet retreat during the last deglaciation, Nature, 349, 513–516, 1991.
Leng, M. J. and Barker, P. A.: A review of the oxygen isotope composition of lacustrine diatom silica for palaeoclimate reconstruction, Earth-Sci. Rev., 75, 5–27, 2006.
Leng, M. J. and Marshall, J. D.: Palaeoclimate interpretation of stable isotope data from lake sediment archives, Quaternary Sci. Rev., 23, 811–831, 2004.
Leng, M. J. and Sloane, H. J.: Combined oxygen and silicon isotope analysis of biogenic silica, J. Quaternary Sci., 23, 313–319, 2008.
Leng, M. J., Barker, P., Greenwood, P., Roberts, N., and Reed, J.: Oxygen isotope analysis of diatom silica and authigenic calcite from Lake Pinarbasi, Turkey, J. Paleolimnol., 25, 343–349, 2001.

Leng, M. J., Swann, G. E. A., Hodson, M. J., Tyler, J. J., Patwardhan, S. W., and Sloane, H. J.: The Potential use of Silicon Isotope Composition of Biogenic Silica as a Proxy for Environmental Change, Silicon, 1, 65–77, 2009.
Lisiecki, L. E. and Raymo, M. E.: A Pliocene-Pleistocene stack of 57 globally distributed benthic δ^{18}O records, Paleoceanography, 20, PA1003, doi:10.1029/2004PA001071, 2005.
Mackay, A. W., Swann, G. E. A., Brewer, T. S., Leng, M. J., Morley, D. W., Piotrowska, N., Rioual, P., and White, D.: A reassessment of late glacial – Holocene diatom oxygen isotope record from Lake Baikal using a geochemical mass-balance approach, J. Quaternary Sci., 26, 627–634, 2011.
Melles, M., Minyuk, P. S., Brigham-Grette, J., and Juschus, O.: The Expedition El'gygytgyn Lake 2003 (Siberian Arctic), Ber. Polarforsch. Meeresforsch., ISSN 1618-3193, 509, 2005.
Melles, M., Brigham-Grette, J., Glushkova, O. Y., Minyuk, P. S., Nowaczyk, N. R., and Hubberten, H.: 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, J. Paleolimnol., 37, 89–104, 2007.
Melles, M., Brigham-Grette, J., Minyuk, P., Koeberl, C., Andreev, A., Cook, T., Fedorov, G., Gebhardt, C., Haltia-Hovi, E., Kukkonen, M., Nowaczyk, N., Schwamborn, G., Wennrich, V., and Party, E. G. S.: The El'gygytgyn Scientific Drilling Project – conquering Arctic challenges through continental drilling, Scientific Drilling, 11, 29–40, 2011.
Miller, G. H., Alley, R. B., Brigham-Grette, J., Fitzpatrick, J. J., Polyak, L., Serreze, M. C., and White, J. W. C.: Arctic amplification: can the past constrain the future?, Quaternary Sci. Rev., 29, 1779–1790, 2010.
Minyuk, P., Borkhodoev, V., and Goryachev, N.: Geochemical characteristics of sediments from Lake El'gygytgyn, Chukotka Peninsula, as indicators of climatic variations for the past 350 ka, Dokl. Earth Sci., 436, 94–97, 2011.
Morley, D. W., Leng, M. J., Mackay, A. W., Sloane, H. J., Rioual, P., and Battarbee, R. W.: Cleaning of lake sediment samples for diatom oxygen isotope analysis, J. Paleolimnol., 31, 391–401, 2004.
Moschen, R., Lücke, A., and Schleser, G. H.: Sensitivity of biogenic silica oxygen isotopes to changes in surface water temperature and palaeoclimatology, Geophys. Res. Lett., 32, L07708, doi:10.1029/2004GL022167, 2005.
Moschen, R., Lücke, A., Parplies, J., Radtke, U., and Schleser, G. H.: Transfer and early diagenesis of biogenic silica oxygen isotope signals during settling and sedimentation of diatoms

in a temperate freshwater lake (Lake Holzmaar, Germany), Geochim. Cosmochim. Ac., 70, 4367–4379, 2006.
Nolan, M. and Brigham-Grette, J.: Basic hydrology, limnology, and meteorology of modern Lake El'gygytgyn, Siberia, J. Paleolimnol., 37, 17-35, 2007.
Nolan, M., Cassano, E., and Cassano, J.: Synoptic climatology and recent climate trends at Lake El'gygytgyn, Chukotka, Clim. Past Discuss., in press, 2012.
North-Greenland-Ice-Core-Project members: High-resolution record of Northern Hemisphere climate extending into the last interglacial period, Nature, 431, 147–151, 2004.
Nowaczyk, N. R., Minyuk, P., Melles, M., Brigham-Grette, J., Glushkova, O., Nolan, M., Lozhkin, A. V., Stetsenko, T. V., Andersen, P. M., and Forman, S. L.: 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, 2002.
Nowaczyk, N., Melles, M., and Minyuk, P.: A revised age model for core PG1351 from Lake El'gygytgyn, Chukotka, based on magnetic susceptibility variations tuned to northern hemisphere insolation variations, J. Paleolimnol., 37, 65–76, 2007.
Nowaczyk, N. R., Haltia-Hovi, E. M., Ulbricht, D., Wennrich, V., Kukkonen, M., Rosén, P., Vogel, H., Meyer-Jacob, C., Andreev, A., and El'gygytgyn Scientific Party: Orbital tunes from Lake El'gygytgyn sediments, in preparation, 2012.
Petit, J. R., Jouzel, J., Raynaud, D., Barkov, N. I., Barnola, J. M., Basile, I., Bender, M., Chappellaz, J., Davis, M., Delaygue, G., Delmotte, M., Kotlyakov, V. M., Legrand, M., Lipenkov, V. Y., Lorius, C., Pepin, L., Ritz, C., Saltzman, E., and Stievenard, M.: Climate and atmospheric history of the past 420 000 years from the Vostok ice core, Antarctica, Nature, 399, 429–436, 1999.
Rosén, P., Vogel, H., Cunningham, L., Reuss, N., Conley, D., and Persson, P.: Fourier transform infrared spectroscopy, a new method for rapid determination of total organic and inorganic carbon and biogenic silica concentration in lake sediments, J. Paleolimnol., 43, 247–259, 2010.
Rozanski, K., Araguás-Araguás, L., and Gonfiantini, R.: Isotopic patterns in modern global precipitation, in: Climate Change in Continental Isotope Records, edited by: Swart, P., McKenzie, J. A., Lohmann, K. C., and Savin, S., American Geophysical Union, 1–36, 1993.
Schmidt, M., Botz, R., Stoffers, P., Anders, T., and Bohrmann, G.: Oxygen isotopes in marine diatoms: A comparative study of analytical techniques and new results on the isotope composition of recent marine diatoms, Geochim. Cosmochim. Ac., 61, 2275–2280, 1997.

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Schmidt, M., Botz, R., Rickert, D., Bohrmann, G., Hall, S. R., and Mann, S.: Oxygen isotopes of marine diatoms and relations to opal-A maturation, Geochim. Cosmochim. Ac., 65, 201–211, 2001.
Serreze, M. C. and Barry, R. G.: Processes and impacts of Arctic amplification: A research synthesis, Global Planet. Change, 77, 85–96, 2011.
Serreze, M. C. and Francis, J. A.: The Arctic Amplification Debate, Climatic Change, 76, 241–264, 2006a.
Serreze, M. C. and Francis, J. A.: The Arctic on the fast track of change, Weather, 61, 65–69, 2006b.
Serreze, M. C., Walsh, J. E., Chapin, F. S., Osterkamp, T., Dyurgerov, M., Romanovsky, V., Oechel, W. C., Morison, J., Zhang, T., and Barry, R. G.: Observational Evidence of Recent Change in the Northern High-Latitude Environment, Climatic Change, 46, 159–207, 2000.
Sharp, Z. D.: A laser-based microanalytical method for the in situ determination of oxygen isotope ratios of silicates and oxides, Geochim. Cosmochim. Ac., 54, 1353–1357, 1990.
Shemesh, A., Burckle, L. H., and hays, J. D.: Late Pleistocene oxygen isotope records of biogenic silica from the Atlantic sector of the Southern Ocean, Paleoceanography, 10, 179–196, 1995.
Svendsen, J. I., Astakhov, V. I., Bolshiyanov, D. Y., Demidov, I., Dowdeswell, J. A., Gataullin, V., Hjort, C., Hubberten, H. W., Larsen, E., Mangerud, J. A. N., Melles, M., MÖLler, P. E. R., Saarnisto, M., and Siegert, M. J.: Maximum extent of the Eurasian ice sheets in the Barents and Kara Sea region during the Weichselian, Boreas, 28, 234–242, 1999.
Svendsen, J. I., Alexanderson, H., Astakhov, V. I., Demidov, I., Dowdeswell, J. A., Funder, S., Gataullin, V., Henriksen, M., Hjort, C., Houmark-Nielsen, M., Hubberten, H. W., Ingólfsson, Ó., Jakobsson, M., Kjær, K. H., Larsen, E., Lokrantz, H., Lunkka, J. P., Lyså, A., Mangerud, J., Matiouchkov, A., Murray, A., Möller, P., Niessen, F., Nikolskaya, O., Polyak, L., Saarnisto, M., Siegert, C., Siegert, M. J., Spielhagen, R. F., and Stein, R.: Late Quaternary ice sheet history of northern Eurasia, Quaternary Sci. Rev., 23, 1229–1271, 2004.
Swann, G. E. A. and Leng, M. J.: A review of diatom δ^{18}O in palaeoceanography, Quaternary Sci. Rev., 28, 384–398, 2009.
Swann, G. E. A. and Patwardhan, S. V.: Application of Fourier Transform Infrared Spectroscopy (FTIR) for assessing biogenic silica sample purity in geochemical analyses and palaeoenvironmental research, Clim. Past, 7, 65–74, doi:10.5194/cp-7-65-2011, 2011.

Swann, G. E. A., Mackay, A. W., Leng, M. J., and Demory, F.: Climatic change in Central Asia during MIS 3/2: a case study using biological responses from Lake Baikal, Global Planet. Change, 46, 235–253, 2005.
Swann, G. E. A., Leng, M. J., Sloane, H. J., and Maslin, M. A.: Isotope offsets in marine diatom delta (super 18) O over the last 200 ka, J. Quaternary Sci., 23, 389–400, 2008.
Swann, G. E. A., Leng, M. J., Juschus, O., Melles, M., Brigham-Grette, J., and Sloane, H. J.: A combined oxygen and silicon diatom isotope record of Late Quaternary change in Lake El'gygytgyn, North East Siberia, Quaternary Sci. Rev., 29, 774–786, 2010.
Tapponnier, P. and Molnar, P.: Active Faulting and Cenozoic Tectonics of the Tien Shan, Mongolia, and Baykal Regions, J. Geophys. Res., 84, 3425–3459, 1979.
Thiede, J.: Quaternary Environments of the Eurasian North (QUEEN), Quaternary Sci. Rev., 23, 1225–1511, 2004.
Vogel, H., Rosén, P., Wagner, B., Melles, M., and Persson, P.: Fourier transform infrared spectroscopy, a new cost-effective tool for quantitative analysis of biogeochemical properties in long sediment records, J. Paleolimnol., 40, 689–702, 2008.
Wilkie, K., Chapligin, B., Meyer, H., Burns, S., Petsch, S., and Brigham-Grette, J.: Modern isotope hydrology and controls on δD of plant leaf waxes at Lake El'gygytgyn, NE Russia, in preparation, 2012.
Yancheva, G., Nowaczyk, N. R., Mingram, J., Dulski, P., Schettler, G., Negendank, J. F. W., Liu, J., Sigman, D. M., Peterson, L. C., and Haug, G. H.: Influence of the intertropical convergence zone on the East Asian monsoon, Nature, 445, 74–77, 2007.
Zachos, J., Pagani, M., Sloan, L., Thomas, E., and Billups, K.: Trends, Rhythms, and Aberrations in Global Climate 65 Ma to Present, Science, 292, 686–693, 2001.

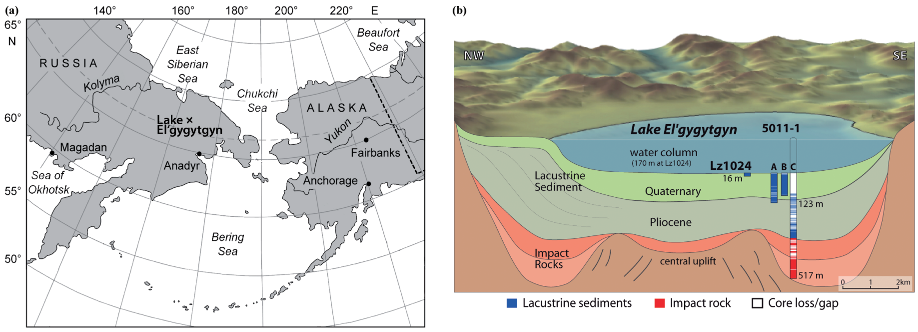

Fig. 1. (a) Geographical position of Lake El'gygytgyn and **(b)** drilling locations (Melles et al., 2011).

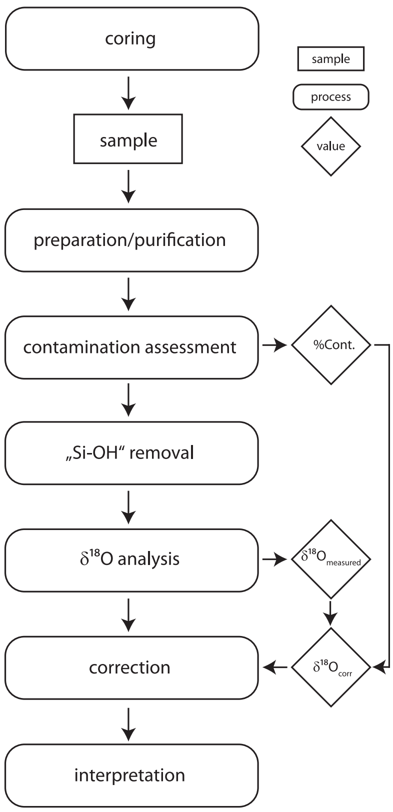

Fig. 2. Method outline from coring to final interpretation.

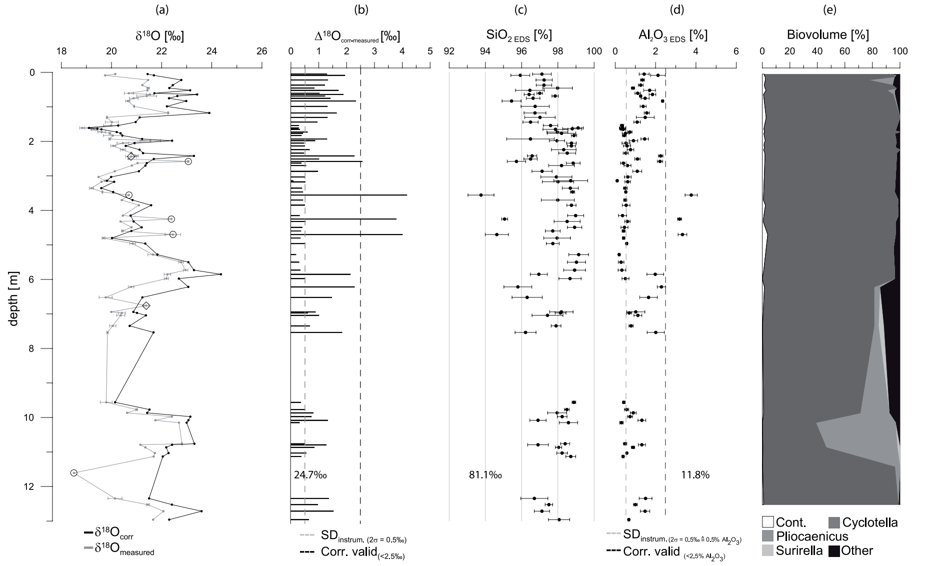

Fig. 3. **(a)** Uncorrected (grey) and corrected (black) δ^{18}O record from the <10µm fraction. Highly contaminated samples (encircled) or samples without correction data (open diamonds) were excluded. **(b)** A correction was performed according to Al_2O_3 percentages and the difference between measured and corrected δ^{18}O values displayed. **(c)** SiO_2 percentages and **(d)** Al_2O_3 percentage of the sample analysed by EDS. **(e)** Five different categories (Contamination particles, different species) were counted for 40 samples and expressed in biovolume [%].

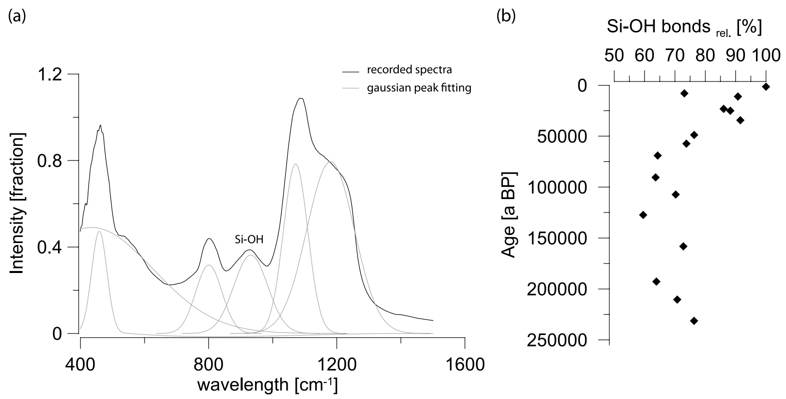

Fig. 4. Assessment of potential diagenetical changes. **(a)** gaussian peak fitting and peak centres for all silica modes, the Si-OH bond peak is located at about 945 cm^{-1}. **(b)** FTIRS analysis of 16 samples downcore.

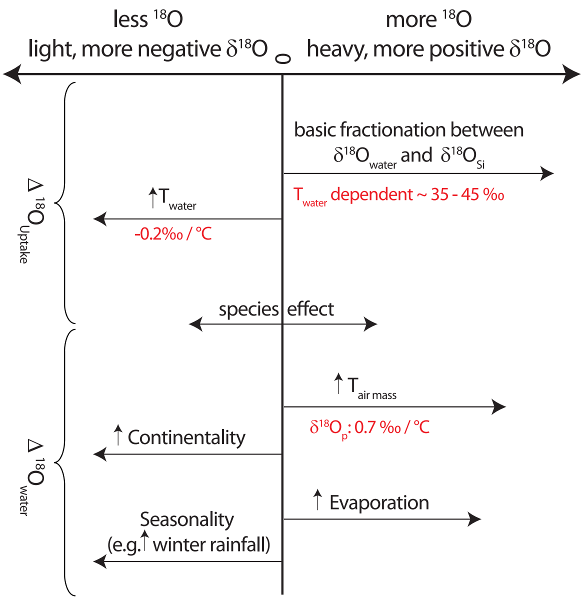

Fig. 5. $\delta^{18}O_{diatom}$ controls in the lacustrine environment.

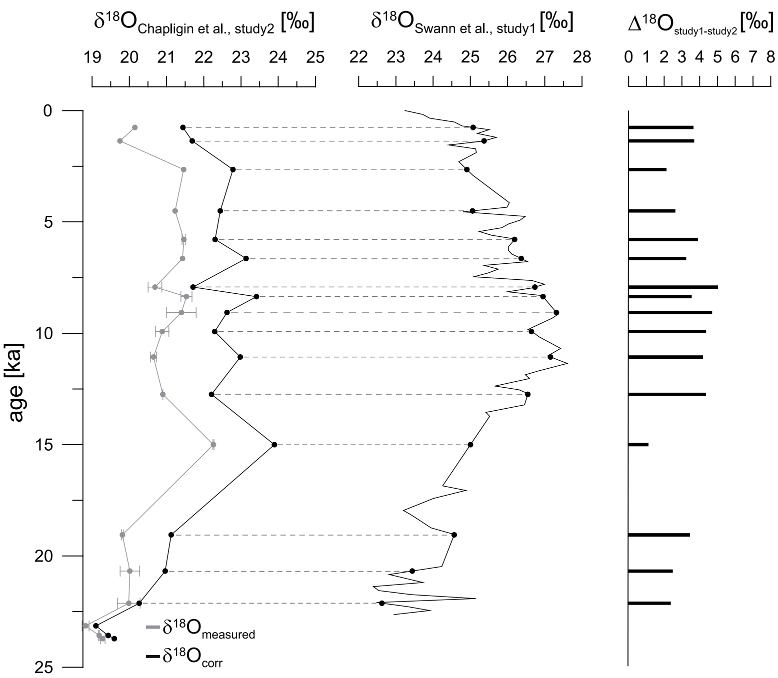

Fig. 6. Both existing studies on $\delta^{18}O_{diatom}$ values from Lake El'gygytgyn until the LGM. Left: our study, uncorrected (grey) and corrected (black) $\delta^{18}O$ record; middle: study by Swann et al. (2010); right: the resulting offsets between the two studies.

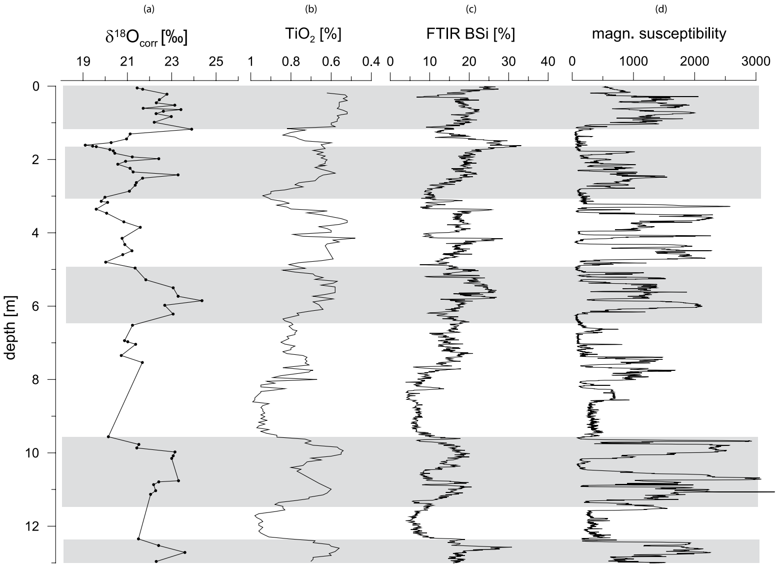

Fig. 7. Comparison of the **(a)** $\delta^{18}O_{diatom}$ record with other Lake El'gygytgyn records: **(b)** TiO_2 [%], **(c)** BSi [%] (both Frank et al., 2012) analysed with FTIRS (Rosén et al., 2010) and **(d)** magnetic susceptibility for core Lz1024.

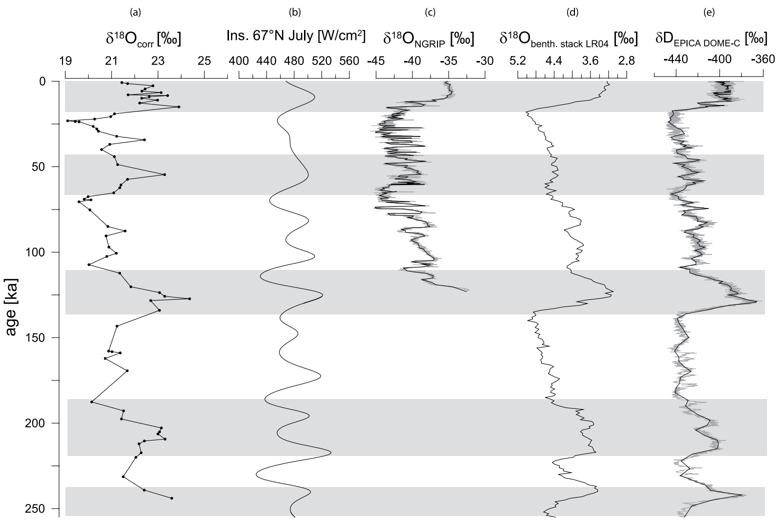

Fig. 8. (a) The $\delta^{18}O_{diatom}$ record is plotted versus **(b)** July insolation at 67° N (Laskar et al., 2004), **(c)** $\delta^{18}O$ from the ice-core record NGRIP (North-Greenland-Ice-Core-Project members, 2004), **(d)** the stacked marine oxygen isotope record LR04 (Lisiecki and Raymo, 2005) and **(e)** δD from EPICA Dome-C ice-core record (EPICA members, 2004, 2006). For both ice-core records: complete record in grey; spline smoothing in black. Warmer periods corresponding to MIS 1, MIS 3, MIS 5 and MIS 7 (7.1/7.3 and 7.5) are marked in grey.

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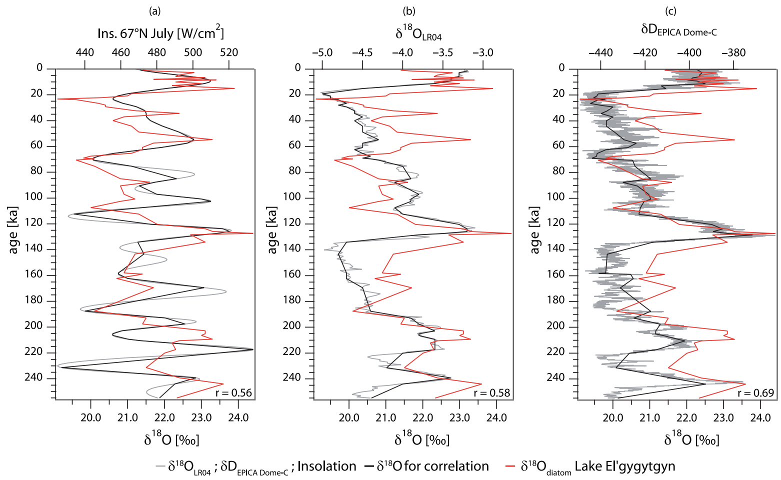

Fig. 9. Correlation between the $\delta^{18}O_{diatom}$ record and **(a)** mean monthly Insolation (July) at 67° N **(b)** the $\delta^{18}O$ record from the marine LR04 stack and **(c)** the $\delta D_{EPICADome\text{-}C}$ record.