Oxygen isotope composition of diatoms as Late Holocene climate proxy at Two-Yurts Lake, Central Kamchatka, Russia

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Especially in combination with other proxies, the oxygen isotope composition of diatom silica (δ18Odiatom) from lake sediments is useful for interpreting past climate conditions. This paper presents the first oxygen isotope data of fossil diatoms from Kamchatka, Russia, derived from sediment cores from Two-Yurts Lake (TYL). For reconstructing Late Holocene climate change, palaeolimnological investigations also included diatom, pollen and chironomid analysis.

The most recent diatom sample (δ18Odiatom = +23.3‰) corresponds well with the present day isotopic composition of the TYL water (mean δ18O = −14.8‰) displaying a reasonable isotope fractionation in the system silica-water. Nonetheless, the TYL δ18Odiatom record is mainly controlled by changes in the isotopic composition of the lake water. TYL is considered as a dynamic system triggered by differential environmental changes closely linked with lake-internal hydrological factors.

The diatom silica isotope record displays large variations in δ18Odiatom from +27.3‰ to +23.3‰ from about −4.5 kyr BP until today. A continuous depletion in δ18Odiatom of 4.0‰ is observed in the past 4.5 kyr, which is in good accordance with other hemispheric environmental changes (i.e. a summer insolation-driven Mid- to Late Holocene cooling). The overall cooling trend is superimposed by regional hydrological and atmospheric–oceanic changes. These are related to the interplay between Siberian High and Aleutian Low as well as to the ice dynamics in the Sea of Okhotsk. Additionally, combined δ18Odiatom and chironomid interpretations provide new information on changes related to meltwater input to lakes. Hence, this diatom isotope study provides further insight into hydrology and climate dynamics of this remote, rarely investigated area.

1. Introduction

Among terrestrial climate archives, lake sediments have great potential to provide high resolution and continuous information on environmental change (Leng and Barker, 2006). Multi-proxy studies of lake sediment cores contribute to the reconstruction of Late Quaternary climate from the terrestrial perspective allowing for correlation with continuous archives such as marine sediments (LRO4 benthic stack: Lisiecki and Raymo, 2005) and ice cores of both hemispheres (i.e. NGRIP: Vinther et al., 2006; GISP2:Mayewski et al., 2004; EPICA Community, 2006). The use of oxygen isotopes in biogenic silica (diatoms) within aquatic sediments relates to milestone work by Labeyrie (1974) and Shemesh et al. (1992) and has become increasingly common since both, lacustrine and marine systems contain siliceous microfossils such as diatoms.

Diatoms are photosynthetic algae with cell walls composed of SiO2 with a characteristic morphology and two intricately-patterned valves. Their ubiquitous growth in almost all aquatic environments make the analysis of fossil diatoms in lake sediments a particularly useful method for reconstructing spatial and temporal ecological, environmental and climate changes at the local to regional scale (Battarbee et al., 2005). However, it is difficult to estimate the exact palaeoenvironmental parameters from diatom species distribution.

The oxygen isotope composition of diatom frustules (δ18Odiatom) extracted from lacustrine sediments is used as a tool to assess changes in temperature, precipitation patterns, or evaporation in lacustrine ecosystems (Jones et al., 2004; Leng and Marshall, 2004; Leng and Barker, 2006). A substantial number of such records from different parts of the world underline the potential for reconstructing past climate changes from the oxygen isotope composition of biogenic silica (δ18Osi).

However, a suitable lake for palaeoclimate reconstruction with oxygen isotopes in biogenic silica needs to be hydrologically known (Leng and Barker, 2006) including recent information on lake water temperature and isotope composition of the lake. Did the lake dry out or change its level during geological periods? What is the input signal to the lake and how did it change through time? What is the seasonality of precipitation to the lake? What is the hydrological balance (open/closed...
2. Regional setting

Two-Yurts Lake is situated at 56°49′2′′ N; 160°06′3′′ E in the Central Mountain Chain of Kamchatka at an elevation of 275 m a.s.l. (above sea level). The Central Kamchatka Mountain Chain is mostly built of Neogene to mid-Pleistocene volcanic rocks and extinct volcanoes (Solomina et al., 2007).

Two-Yurts Lake is oval-shaped and covers an area of 11.7 km² (Fig. 1). The mean water depth of this open through-flow lake system is about 25 m. TYL formed on a moraine of the Two-Yurts Lake Valley, located on the eastern slope of the Central Kamchatka Mountain Chain. There are three main inflows to TYL at the western part and one outflow at the eastern side. The basin of Two-Yurts Lake is embedded in a former glacial valley at the eastern slope of Kamchatka’s central mountain arc, the Sredinnyi Ridge. Mountain peaks and ridges closest to the lake reach about 1.100 m a.s.l. The local vegetation is characterised by stone birch forest and subalpine shrubs with dwarf birch and shrub pine (Krestov et al., 2008).

In the generally maritime setting of Kamchatka, the study area represents Kamchatka’s most continental climate with coastal influence either from the Pacific side, about 150 km to the southeast, or from the Okhotsk Sea, 180 km to the west. The meteorological station at Petropavlovsk-Kamchatsky situated about 440 km to the SW of TYL yields an annual precipitation of 1335 mm and a mean annual air temperature (MAAT) of +1.9 °C (Fig. 2). This station has been included in the Siberian Network of Isotopes in Precipitation (SNIP; Kurita et al., 2004) displaying mean annual oxygen and hydrogen isotope compositions of −13.3‰ and −100.7‰, respectively, with an overall low annual temperature and isotope variability typical of coastal stations (Fig. 2).

3. Material and methods

3.1. Field work and age model

In September 2007, six sediment cores were taken from TYL with a raft and a tripod-supported UWITEC-piston corer system. We refer to two overlapping sediment cores taken at site PG1857 (Fig. 1). Sediment core PG1857-2 includes the upper section downcore from the surface bottom sediment, which has been spliced at a 189–191 cm core depth to sediment core PG1857-5 at a 59–61 cm core depth to gather a 3.5 m long composite section. The TYL age model at site PG1857 relies upon nine radiocarbon dates carried out at Poznan Radiocarbon Laboratory, Poland and tephra layers related to a reference ash stratigraphy of Kamchatka (Dirksen et al., 2013). The radiocarbon dates of sediment core PG1857-2 range between 0.14 and 2.55 cal yr BP and those of

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core PG1857-5 between 2.57 and 4.47 cal yr BP. The criteria for splicing were related to sedimentological changes (i.e. ash layers) and radiocarbon data (two dates confirming each other). Further information about the age model is discussed in detail in Nazarova et al. (2013) and Hoff et al. (this issue).

Water samples were taken with a 1.5-liter UWITEC water sampler from the surface and in two depth profiles (PG1852-2; PG1861-1) in the middle of Two-Yurts Lake (Table 1). Additionally, samples from two inflows (PG1864-2; PG1868-2) as well as from a small, unnamed lake ca. 1 km to the east of TYL (PG1858-4) were retrieved.

3.2. Water analysis

During field work, water temperatures, oxygen concentrations, pH and electrical conductivities were measured directly after sampling with a WTW Multi 340i probe. Water samples were filtered through 0.45 μm cellulose acetate filters for further major ion analysis and then subdivided for anion and cation analyses. Cation samples were then acidified with ultrapure nitric acid (65% HNO3). Anion concentrations were determined using Ion Chromatography (IC, Dionex DX-320), cation concentrations by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Perkin-Elmer Optima 3000XL) and HCO3⁻ by titration to pH 4.3 (Metrohm Basic Titrino 794). The analytical precision of major ion analyses is within ±10%.

The stable oxygen and hydrogen isotope compositions were measured using equilibration techniques and Finnigan MAT Delta-S mass-spectrometers (Meyer et al., 2000). They are given as δ values in per mil difference to V-SMOW (Vienna Standard Mean Ocean Water) with an analytical uncertainty (1σ) of better than ±0.8‰ and ±0.1‰ for δ18O and δD, respectively. All laboratory-based hydrochemical and stable isotope measurements were carried out at the Alfred Wegener Institute for Polar and Marine Research, Potsdam.

3.3. Diatom taxonomy and purification for stable isotope analysis

TYL sediment samples were freeze-dried and split into subsamples for micropalaeontological, sedimentological, and stable isotope studies. The sample preparation for quantitative diatom analyses (using light microscopy at 1000× magnification with a Zeiss AXIO A1 with an Achromplan 100× 1.4 Oil Ph3-objective and scanning electron microscopy) as well as diatom counting are described in detail in Hoff et al. (2012; this issue). Due to the predominance of two diatom species (Aulacoseira subarctica (O. Müller) Haworth and Stephanodiscus minutulus (Kützing) Cleve & Möller) in the samples of TYL we needed to count up to a number of 300 frustules including every diatom species except the dominant two species (which have been counted along).

Pure sample material is essential for analysing the isotopic composition of diatom frustules (δ18Odiatom). Therefore several physical and chemical preparation steps were conducted during the purification process based on Chapligin et al. (2012a): (1) organic matter and carbonates were removed by heating the sample to 50°C for at least 20 h, repeatedly adding concentrated hydrogen peroxide (H2O2, 35%) and in a last step hydrochloric acid (HCl, 10%). Chemical remains were rinsed with ultrapure water. (2) Clay and fine silt were eliminated by sieving the sample with a 10 μm sieve (hence, we refer to the size fraction >10 μm). (3) Diatom frustules were further concentrated by heavy liquid separation with sodium polytungstate (SPT). This process was repeated 4 times with different solutions of decreasing density (2.4–2.2 g/cm³), and SPT was discarded with ultrapure water. (4) Hardly soluble micro-organic coating or material trapped in the diatom frustules was removed by first heating the sample with ammonium chloride (NH4Cl) and acetic acid (CH3COOH) and then, with a mixture of nitric acid (HNO3) and perchloric acid (HClO4) before rinsing and drying the purified sample.

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3.4. Stable isotope analysis

Oxygen isotope analysis on biogenic silica was performed with a PDZ Europa 2020 mass spectrometer (MS-2020; now supplied by Sercon Ltd., UK) according to the method presented in Chapligin et al. (2010). Hydrous groups (H₂O, OH) were removed from clean diatom sample material (1.5 to 2 mg) using inert Gas Flow Dehydration (iGFD) in a horizontal ceramic tube furnace flushed with helium (Chapligin et al., 2010). The dehydrated sample was fully reacted by laser fluorination under BrF₅ atmosphere to quantitatively generate O₂ according to Sharp (1990). The O₂ was separated from its by-products (such as SiF₄), trapped in a molecular sieve, then transferred into the mass spectrometer for oxygen isotope analysis. 20% of the samples were biogenic working standards to verify the accuracy of the mass spectrometer for oxygen isotope analysis. The O₂ was separated from its by-products (such as SiF₄), trapped in a molecular sieve, then transferred into the mass spectrometer for oxygen isotope analysis. 20% of the samples were biogenic working standards to verify the accuracy of the mass spectrometer for oxygen isotope analysis. The O₂ was separated from its by-products (such as SiF₄), trapped in a molecular sieve, then transferred into the mass spectrometer for oxygen isotope analysis. 20% of the samples were biogenic working standards to verify the accuracy of the mass spectrometer for oxygen isotope analysis. The O₂ was separated from its by-products (such as SiF₄), trapped in a molecular sieve, then transferred into the mass spectrometer for oxygen isotope analysis. 20% of the samples were biogenic working standards to verify the accuracy of the mass spectrometer for oxygen isotope analysis.

Fig. 2. Meteorological background data from Petropavlovsk–Kamchatky (mean monthly temperature: red; mean monthly precipitation: blue). Additionally, the intra-annual variability of δ¹⁸O and δ excess for precipitation at this station are given. (For interpretation of the references to colours in this figure legend, the reader is referred to the web version of this article.)

where the percentage of purity was 100% subtracted by the percentage of remaining contamination (%cont.). Accordingly, %cont. was calculated by dividing the sample percentage of Al₂O₃ by the Al₂O₃ percentage from a 100% contamination end member according to Brewer et al. (2008), Swann et al. (2008) and Mackay et al. (2011). Al₂O₃ percentages for each sample were analysed by Energy-dispersive X-ray Spectroscopy (EDS) (3–5 replications, diameter of excited-area size: 100–120 µm). Finally, the %cont. and δ¹⁸Ocorr were calculated using the end-members δ¹⁸Ocorr. = +7.34‰ and Al₂O₃corr. = 15% (Chapligin et al., 2012a). In Table 2, the results of the EDS analyses are summarized showing the geochemical characteristics of diatoms at TYL. The high purity in the diatom samples at TYL is documented by SiO₂ concentrations always >98.1% (>99% in 29 out of 42 samples) and Al₂O₃ < 0.9% (<0.3% in 34 out of 42 samples). This leads to a small mean correction value for δ¹⁸Omeasured compared to δ¹⁸Ocorr of +0.28‰ and did not change the overall course of the measured TYL diatom isotope record (Fig. 4). Only at around 3.5 kyr BP, the contamination is slightly higher (max. δ¹⁸O correction of +1.0‰), which smoothened the δ¹⁸Ocorr record (Fig. 4, Table 2). In the following, we refer to δ¹⁸Ocorr when interpreting δ¹⁸Odiatom in detail. Furthermore, as Kamchatka is known as a volcanically strongly active region, contamination with tephras needs to be taken into account when interpreting δ¹⁸Odiatom records. Lamb et al. (2007) describe several methods of assessing tephras contamination including light microscopy as well as geochemistry, i.e. K₂O concentrations below 0.1% (which comprises all our samples except one). We therefore assume our samples as clean without major tephras sherd contamination. This is further substantiated by careful examination under the SEM (Fig. 5).

4. Results

4.1. Water analysis

Two water-depth profiles (PG1852-2 and PG1861-1) were taken in the centre of TYL on 11 and 16 September 2007, respectively (Table 1). The lake water temperatures varied between 8.9 and 10.3 °C and were similar in both profiles. The TYL water shows fresh-water conditions with low salinity (total dissolved ions: 40–44 mg/l, conductivity: ±54 µS/cm) and an ion composition with Na >> Ca >> Mg ≥ K, and HCO₃ ≥ SO₄ ≥ Cl (Table 1), pointing to waters supplied by river runoff and precipitation (e.g. Wetzel, 2001). Overall high Si concentrations (>6.0 mg/l) reflect the presence of volcanic rocks and soils in the catchment, which are prone to leaching.

The results of stable water isotope analyses are summarized in Table 1 and presented in a δ¹⁸O–δD diagram (Fig. 3) with respect to the Global Meteoric Water Line (GMWL: δD = 8 · δ¹⁸O + 10), in which fresh surface waters (Craig, 1961) are correlated on a global scale. Modern TYL water depth profiles show a constant isotopic composition of δ¹⁸Owater = −14.8‰; δDwater = −110‰ and δ excesswater = 9.5‰, respectively. These values point to a well-mixed water column lacking any isotopic stratification, at least in late summer 2007 (compare Table 1). The strong wind activity during field work and uniform hydrochemical parameters in the water column substantiate this assumption. TYL water isotope data are situated close to the Global Meteoric Water Line (GMWL) (Fig. 3), suggesting the absence of evaporation effects. In contrast, a smaller closed-system lake near TYL shows a marked offset from the GMWL (Fig. 1 and 3) indicative of evaporation effects. The two main river inflows display slightly higher temperatures than the lake (12.7–13.5 °C), with a chemical composition roughly consistent with the lake-water chemistry (Table 1). Since the stable isotopic composition of one inflow (δ¹⁸O = −15.2‰; δD = −110.9‰) is also similar to that of the TYL water, we assume that the tributaries contribute a significant amount of water and ions to TYL.

During the field campaign in 2007, it did not rain and no precipitation samples could be taken. Therefore, the oxygen and hydrogen
isotope composition of precipitation ($\delta^{18}O_{\text{prec}}$; $\delta^{18}O_{\text{measured}}$) for Kamchatka has been derived from the GNIP database (IAEA/WMO, 2013). The mean annual isotopic composition of precipitation at Petropavlovsk-Kamchatsky (WMO 3258300, N52°58'48"; E 158°39'00", height 24 m a.s.l.) is $\delta^{18}O_{\text{prec}} = -13.5 \pm 0.8\%$ (GNIP), which is only slightly higher (heavier) than the Two-Yurts Lake $\delta^{18}O$ lake water with $-14.8\%$ (located further inland at 280 m a.s.l.). Additionally, $\delta^{18}O_{\text{lake}}$ plots near the local meteoric water line (LMWL) based on mean monthly precipitation at Petropavlovsk-Kamchatsky ($\delta^{18}O_{\text{lake}} = 6.72 \delta^{18}O_{\text{LMWL}} - 11.7\%$; Figs. 2 and 3), but here rather corresponds to cold seasons $\delta^{18}O_{\text{prec}}$. Thus, we assume, that $\delta^{18}O_{\text{lake}}$ in fact should roughly correspond to $\delta^{18}O_{\text{prec}}$, potentially biased to slightly more negative values (lighter) due to higher continentality and/or altitude of TYL or due to seasonality effects.

4.2. Diatom analysis

Within the sediments of the Two-Yurts Lake, 131 diatom species were identified (Hoff et al., this issue). The most abundant species throughout the core were Actinocyclus minutulus and Stephanodiscus medius (max. 13.8%), Cyclotella ocellata Pantocek (max. 18.5%), Stephanodiscus alpinus Håkansson (max. 41.4%) and A. subarctica f. recta (O. Müller) Krammer (max. 3.7%). A multivariate, depth-constrained cluster analysis was performed leading to a differentiation into five diatom assemblage zones (DAZ 1–5; Fig. 4; further details in Hoff et al., this issue). Since the first DAZ involves diatoms below a hiatus, they have not been used in this paper. We therefore discuss DAZ 2 to 5 only. DAZ 2 is characterised by the highest abundances in A. subarctica and S. medius only being present in this zone. DAZ 3 contains high abundances of S. alpinus, whereas S. medius and C. ocellata are present in only very small abundances. DAZ 4 displays the highest abundances for C. ocellata, which is only present in this interval. The uppermost DAZ 5 is characterised by the highest abundances of A. subarctica f. recta.

4.3. Stable oxygen isotopes in diatoms

The $\delta^{18}O_{\text{diatom}}$ record (Fig. 4) exhibits varying isotopic compositions between $\pm 23.3\%$ and $\pm 27.3\%$. The oldest part of the core displays the highest $\delta^{18}O_{\text{diatom}}$ values ($\pm 3.6$ kyr BP; mean $\delta^{18}O_{\text{diatom}} = \pm 27.0\%$; N = 5) and can be distinguished from the middle ($\pm 3.6$–$6$ kyr BP;
mean $\delta^{18}O_{\text{diatom}} = +25.5\%$; N = 27) and the younger parts (< 1.8 kyr BP; mean $\delta^{18}O_{\text{diatom}} = +24.3\%$; N = 9) of the record. Roughly, the lower part of the record is characterised by $\delta^{18}O_{\text{diatom}}$ of $>+26.5\%$; the middle section of between $+24.5$ and $+26.5\%$ and the uppermost part of the investigated cores by the lowest $\delta^{18}O_{\text{diatom}}$ values of $<-24.5\%$. Accordingly, the TYL diatom isotope record is characterised by an overall decreasing $\delta^{18}O_{\text{diatom}}$ trend with time to $+23.3\%$ for the topmost two samples, corresponding to a decrease of approximately $-0.8\%$/kyr between $-4.5$ kyr BP and today.

5. Discussion

5.1. Stable oxygen isotope signals in diatoms

The oxygen isotope composition of lacustrine diatom silica ($\delta^{18}O_{\text{diatom}}$) is controlled by several interacting environmental factors (Leng and Barker, 2006). These factors comprise lake water temperature ($T_{\text{lake}}$), disequilibrium ("vital") effects as well as the isotopic composition of the lake water ($\delta^{18}O_{\text{lake}}$) being affected by precipitation and further hydrological parameters (i.e. evaporation and inflow/outflow ratio).

5.1.1. Lake water temperature

The $\delta^{18}O_{\text{diatom}}$ composition is strongly dependent on $T_{\text{lake}}$ during diatom growth (Brandris et al., 1998; Schmidt et al., 2001; Dodd and Sharp, 2010). The temperature relationship of the silica–water fractionation is described with a relatively constant $\delta^{18}O$-temperature coefficient of $-0.2\%/\degree C$ (Dodd et al., 2012). Several experimental studies describe the temperature-dependency of the silica–water fractionation, expressed in different fractionation factors ($\alpha$ (silica–water); e.g. Julliet-Leclerc and Labeyrie, 1987; Dodd and Sharp, 2010). A compilation of different fractionation factors (Dodd et al., 2012), leads to an average $\alpha$ (silica–water) value of $1.038 \pm 0.004$, taking under consideration isotope fractionation at a modern Two-Yurts Lake water temperature of $-10\degree C$ (as measured in the field). Based on this, the measured $\delta^{18}O_{\text{diatom}}$ of $+23\%$ leads to an expected modern lake water isotopic composition of Two-Yurts Lake of $\delta^{18}O_{\text{lake}} = -15 \pm 2\%$, which corresponds well to the measured $\delta^{18}O_{\text{lake}}$ of $-14.8\%$. Consequently, the uppermost sample of core PG1857, as the most recent sample, displays a $\delta^{18}O_{\text{diatom}}$ of about $+23.3\%$ coinciding with the present day isotopic composition of the TYL.

However, the temperature of the lake water alone can be excluded as a controlling factor on the changing oxygen isotope composition of the TYL diatoms. Following the $\delta^{18}O_{\text{diatom}}-T_{\text{lake}}$ correlation (Brandris et al., 1998), such a wide isotopic range of $\Delta^{18}O = 4.0\%$ would be equivalent to a $T_{\text{lake}}$ difference of up to $-20\degree C$ lower temperature and, hence, would correspond to negative $T_{\text{lake}}$. Although some diatom species are able to grow even under lake ice cover, even well adapted diatoms are not able to grow in large amounts in TYL in a hypothetically frozen milieu. Particularly, the Late Holocene is known to have been a rather warm period verified by different proxy studies, though not reaching temperatures of the mid-Holocene Climate Optimum. Furthermore, the spliced sections of the core delineate an overall decreasing trend in $\delta^{18}O_{\text{diatom}}$ Values. In general such a decreasing trend in $\delta^{18}O_{\text{diatom}}$ values with time would infer increasing $T_{\text{lake}}$, assuming that $T_{\text{lake}}$ would be the major determining factor for the isotopic composition of the $\delta^{18}O_{\text{diatom}}$ record. Since this scenario delineates the opposite of what is known about the mid- and Late Holocene of Kamchatka, we assume a minor relevance of the lake water temperature changes for the $\delta^{18}O_{\text{diatom}}$ trend.

5.1.2. Evaporation and hydrology

Closed lake systems (such as the small lake presented in Figs. 1 and 3) are generally more influenced by evaporative effects than open through-flow systems, such as Two-Yurts Lake. Furthermore, enhanced evaporation would shift the isotopic composition of the remaining lake water towards more positive (isotopically heavier) values and below the Global Meteoric Water Line (GMWL). Such evaporative enrichment is not observed in the $\delta^{18}O_{\text{lake}}$ of TYL (Table 1, N = 15), with measured $\delta^{18}O_{\text{lake}}$ and $\delta^{18}O_{\text{lake}}$ close to the GMWL (Fig. 3), indicating that presently evaporation does not remarkably affect the Two-Yurts Lake system. This assumption is supported by the modern water depth of $-25$ m and the geological setting of the lake. The recent water body is almost completely bordered by steep slopes, allowing for changes in the water depth without significant changes of the surface area of the lake. Nonetheless, there are at least two palaeo-lake terraces around TYL pointing to higher lake levels in the past (Dirksen et al., 2013), but spanning a small area only. The higher lake level might have resulted from landslides retaining the water, whereas shortly after these events retrograde erosion might have led to a lowering of the lake level. A significantly lower lake level in the past seems unlikely because bathymetric investigations provided no hints of fossil lake terraces situated under the recent lake level. Therefore, we assume no major variations in lake extent and depth. Hence, evaporation effects are assumed to be of minor importance at TYL and accordingly, we suggest the precipitation signal ($\delta^{18}O_{\text{prec}}$) to be most relevant for the isotopic composition of the lake water.

5.1.3. Vital effects

Although Swann et al. (2007, 2008) found a small vital effect (isotopic-species effect) in diatom oxygen isotopic composition, studies on both marine (Shemesh et al., 1995) and freshwater diatoms (Shemesh and Petaeit, 1998; Roqsveit et al., 1999; Shemesh et al., 2001; Chaplin et al., 2012b), established that vital effects do not influence the isotopic composition of diatoms. As the Two-Yurts Lake contains predominantly two main diatom species (A. subarctica and S. minutus) in the >10 μm fraction, which are consistently present throughout the core, we assume that $\delta^{18}O_{\text{diatom}}$ is not being affected by isotopic-species effects. This is supported by the observation that none of the DAZ boundaries (Fig. 4) corresponds to major changes (i.e. minima/maxima) in the $\delta^{18}O_{\text{diatom}}$ record.
Hence, we assume the changes in the isotopic composition of the lake water ($\delta^{18}O_{\text{lake}}$) to be the most important control on the $\delta^{18}O_{\text{diatom}}$ record. The $\delta^{18}O_{\text{lake}}$ at TYL is mainly influenced by the $\delta^{18}O_{\text{prec}}$ signal rather than by evaporative effects. Changes in $\delta^{18}O_{\text{prec}}$ are again linked to either air temperature changes and/or changes in the atmospheric circulation patterns (Leng and Barker, 2006).

5.2. Implementation of other regional information

5.2.1. Chironomids

Chironomid analyses (Nazarova et al., 2013) at TYL provide additional insight about the likeliness of $\delta^{18}O_{\text{prec}}$ being the most relevant control for the $\delta^{18}O_{\text{diatom}}$ record. The application of transfer functions on the fossil chironomid assemblages in sediment cores PG1857-2/-5 yielded an estimate of temporal changes in palaeo July air temperatures ($T_{\text{air July}}$) in central Kamchatka in the range of $\sim2$–$3$ °C (Fig. 4 and 6). The used transfer function was inferred from modern chironomid training data sets from lakes of eastern Siberia (Nazarova et al. 2008, 2011). The chironomid-based $T_{\text{air July}}$ exhibit a threefold pattern of change with colder intervals ($\sim12$–$13$ °C) before about 3.9 kyr BP and after about 1.2 kyr BP. Between 3.9 and 1.2 kyr BP, the chironomid-based climate reconstruction yielded warmer temperatures ($T_{\text{air July}} > 14$ °C) (Figs. 4, 6) interrupted by a short cool phase around 2.8 kyr BP visible in both records ($\delta^{18}O_{\text{diatom}}$ and chironomid-based $T_{\text{air July}}$). Both display a similar overall decreasing trend towards the upper part of the core. Hypothesizing that the decrease in $\delta^{18}O_{\text{diatom}}$ of about 4.0‰ would have been caused solely by changes in $\delta^{18}O_{\text{prec}}$, this would correspond to a mean annual air temperature (MAAT) decrease of about 3 °C (Dansgaard, 1964). This is in the same order of magnitude as the chironomid-based temperature reconstruction and could be explained by Late Holocene cooling.
The lower part of the core, however, shows a decrease in the δ¹⁸Odiatom record between 4.5 and 3.5 kyr BP inversely correlated to chironomid Tair July (Nazarova et al., 2013; Fig. 6). Whereas the chironomid-based Tair July infers a warming, the δ¹⁸Odiatom record rather corresponds to decreasing air temperatures for this period. This overall inverse behaviour of both proxy time series can best be explained by changes in water supply from the hinterland to the lake.

5.2.3. Diatom assemblages

Brooks and Birks (2001) describe that Tair July reconstructions based on chironomids might become critical during periods with increased glacier formation due to a strong increase of the gradient between air temperature and lake water temperatures. Relatively high air temperatures may result in lower lake temperatures because of an increased input of cold meltwaters originating from the hinterland, i.e. glaciers. Then reconstructed Tair July would indicate a colder regime than it actually has been. Thus, we assume that the reconstructed values of Tair July for the lower part of the core may be too low.

Additionally, the isotopic composition of an inflow draining into a lake is relatively depleted in heavy isotopes when originating from higher altitudes (e.g. from a spring or a glacier with temporal melting events). The enhanced formation of glaciers could decrease the input of winter precipitation (and relatively increase summer precipitation) into the lake by conserving it within a newly formed glacier. Since summer precipitation has an enriched isotopic composition compared to winter precipitation (Fig. 2), this would shift the δ¹⁸Olake to a more positive (‘heavier’) isotopic composition. This could, at least partly explain the relatively high δ¹⁸Odiatom values in the older part of the record (Fig. 6). The decrease in δ¹⁸Odiatom and increasing chironomid-derived Tair July after 4 kyr would then reflect increased meltwater input until the glaciers – if they existed at this time – were gone. A similar phenomenon with decreasing δ¹⁸Odiatom due to greater meltwater input from higher altitudes has been described for Lake Kotokel in the Lake Baikal area (Kostrova et al., 2013). The subsequent decrease in δ¹⁸Odiatom (after 4 kyr BP) could be related to melting of the glacier in the hinterland as supported by a simultaneous increase in Tair July from the chironomid-based reconstruction. We suggest that the glacier advances that Savoskul (1999) described for south Kamchatka at around 5 kyr BP might have included the hinterland of Two-Yurts Lake. Therefore, we assume that changes in the δ¹⁸Oprec signal are mainly responsible for the general trend in the δ¹⁸Odiatom record, whereas changes in water supply in the catchment (see Fig. 1; and Hoff et al., this issue) (i.e. from a melting glacier) could reverse and superimpose this pattern.

5.2.4. Palynology

The spliced record from TYL sediments has been subdivided into four pollen assemblage zones since – 4.5 kyr BP (compare Hoff et al., this issue; PAZ 4–7). Between 4.5 and 3.3 kyr BP, pollen data indicate a warm and wet climate dominated by stone birch forest (corresponding better to δ¹⁸Odiatom than DAZ). Between 3.3 and 2.6 kyr BP, white birch forest advanced suggesting drier and/or more continental climate conditions with a maximum forest expansion around ca. 2.7 kyr BP. From 2.6 to 1.3 kyr BP pollen assemblages indicate retreating forests, more moderate temperatures and wetter conditions. Since the beginning of the youngest PAZ starting after 1.3 kyr, forest retreated further and shrublands expanded suggesting cooler, but still wet climate conditions. Consequently the overall climate deterioration is also visible in the TYL pollen record, whereas the boundaries of the PAZ do not correspond with marked δ¹⁸Odiatom changes.

5.3. The TYL δ¹⁸Odiatom record in the north hemispheric context

The character of the diatom isotope record obtained for TYL is similar to that obtained for Lake Kotokel (Kostrova et al., 2013), Kola Peninsula (Jones et al., 2004), Lake Baikal (Mackay et al., 2011) and Swedish Lapland (Lake 850: Shemesh et al., 2001). All curves show a general Mid to Late Holocene depletion in δ¹⁸Odiatom through the cores from 4.5 kyr BP to the present, which is in line with many other climate reconstructions of the northern hemisphere (Wanner et al., 2008). Ice cores δ¹⁸O records i.e. from Greenland (N-GRIP; Vinther et al., 2006; Fig. 6) and the Canadian Arctic (Agassiz ice core; Fisher et al., 1995) display decreasing trends throughout the Holocene. Furthermore, palynological climate reconstructions from the Siberian Arctic also show a Mid to Late Holocene cooling trend (Andreev et al., 2001, 2004). The main driver of this Mid to Late Holocene cooling is assumed to be the decreasing summer insolation (Laskar et al., 2004; Fig. 6; 60°N). We therefore conclude that the overarching trend in the TYL δ¹⁸Odiatom record is mainly driven by summer insolation changes. However, besides the overall decrease in δ¹⁸Odiatom throughout the Mid to Late Holocene, several minor minima and maxima are visible in the TYL record.

The Holocene climate has not been stable as demonstrated in numerous high-resolution palaeoclimate studies (Mayewski et al., 2004; Wanner et al., 2008 and references therein). For the Mid to Late Holocene, Mayewski et al. (2004) identified five periods of significant rapid climate change (RCC) during the time periods of 6.5, 4.2–3.8, 3.5–2.5, 2.1–1.0 and 0.6–0.15 kyr BP, displaying marked changes in temperature and major atmospheric circulation patterns. During several of the RCC phases, the TYL δ¹⁸Odiatom record shows distinct minima or maxima, i.e. the absolute maximum around 4 kyr BP followed by a strong decrease in δ¹⁸Odiatom at about 3.7 kyr, which might be an evidence of Neoglacial cooling. The absolute minimum at 0.2–0.3 kyr BP might correspond to the negative climate anomaly known as Little Ice Age (LIA). Hence our record is broadly in line with palaeotemperatures inferred from the GRIP borehole in Greenland (Dahl-Jensen et al., 1998).

A smaller minimum is observed in the TYL δ¹⁸Odiatom record around 3 kyr BP followed by a maximum around 2.5 kyr. The TYL δ¹³Cminima around 3.0 (and also 0.3) kyr BP occur in RCC phases of a stronger than normal Siberian High (Mayewski et al., 2004 and references therein; Fig. 6).

Itaki and Ikehara (2004) demonstrated that the position of the two most important air pressure systems for Kamchatka – the Aleutian Low and the Siberian High – directly affect the moisture sources as well as the amount of precipitation. A drastic shift towards a decreasing ventilation of the Okhotsk Sea Intermediate Water (OSIW) was described around 3.5 kyr BP. This shift reflects a change of the relative position between the Aleutian Low and the Siberian High (Itaki and Ikehara, 2004). Before 3.5 kyr BP, the regional air pressure systems were arranged in a north Aleutian Low mode, accompanied by...
enhanced ventilation of the OSIW, warmer temperatures and prevailing northerly winds on Kamchatka. In contrast, the south Aleutian Low mode has been described between 3 and 2 kyr BP and 0.3 to 0.4 kyr BP and is accompanied by decreased ventilation, colder temperatures and mainly easterly winds. The abrupt change of the air mass origin at 3.5 kyr BP bears the potential to shift $\delta^{18}O_{\text{prec}}$ and hence $\delta^{18}O_{\text{lake}}$ and $\delta^{18}O_{\text{diatom}}$ to lower values in Kamchatka lakes during the south Aleutian Low mode. As a clear shift about 3.5 kyr BP is visible in the Two-Yurts Lake $\delta^{18}O_{\text{diatom}}$ record (Fig. 6), changes of moisture origin and/or pathways may be at least partly responsible for the $\delta^{18}O_{\text{diatom}}$ in Kamchatkan lakes.

This is further substantiated by observations from the Yukon region (Anderson et al., 2005). The maximum in TYL $\delta^{18}O_{\text{diatom}}$ around 2.5 kyr BP corresponds to an eastward shift of the Aleutian Low as indicated by a $\delta^{18}O$ anomaly in the Jellybean carbonates (Anderson et al., 2005). We hypothesize that the shift in position of the Aleutian Low might have weakened the dominant pressure centre over eastern Asia i.e. in Kamchatka and influenced the regional atmospheric moisture transport.

Furthermore, the TYL diatom $\delta^{18}O$ record shows similarities to the stalagmite $\delta^{18}O$ record from Dongge Cave, China (Yuan et al., 2004) such as a marked change around 2.5 kyr BP with a decrease in both $\delta^{18}O$ records. The $\delta^{18}O$ records from Chinese stalagmites are interpreted as an indicator of the Pacific monsoon intensity (Tarasov et al., 2009), which weakened since the Mid Holocene. Kamchatka’s regional atmospheric moisture transport seems to be influenced by the interplay of the changing conditions in the dominant air pressure centres (Siberian High, Aleutian Low) with TYL $\delta^{18}O_{\text{diatom}}$ record presumably being indicative of moisture source changes.

In summary, the TYL diatom oxygen isotope record presented in this paper is linked to changes in the northern hemispheric climate, which are responsible for the transport of heat and moisture to Kamchatka. The $\delta^{18}O_{\text{diatom}}$ record of TYL core shows that the Holocene has been a period of variable climate conditions with an overall Mid to Late Holocene cooling trend likely triggered by summer insolation. Several known Holocene climate features including periods of RCC such as the LIA as well as changing atmospheric pressure conditions are visible as minima/maxima in the TYL record and, hence, might explain parts of the variability in $\delta^{18}O_{\text{diatom}}$.

6. Conclusions

For reconstructing Holocene climate change, a $\delta^{18}O_{\text{diatom}}$ record from fossil diatoms from Two-Yurts Lake (Kamchatka, Russia) has been investigated. We used spliced sections of two sediment cores (PG1857-2/PG1857-5) from Two-Yurts Lake, Kamchatka for palaeolimnological investigations also including diatom, pollen and chironomid analyses.

For the most recent diatom sample at TYL (0.2–0.3 kyr BP; $\delta^{18}O_{\text{diatom}} = +23.3\%$), the isotope fractionation between water and silica ($\Delta^{18}O_{\text{diatom-water}} = +38.1\%$) is in the right order of magnitude when being related to the isotopic composition of recent lake water (mean $\delta^{18}O_{\text{lake}} = -14.8\%$) and recent water temperature (~10 °C). Nonetheless, the TYL $\delta^{18}O_{\text{diatom}}$ record is mostly controlled by internal-changes in the isotopic composition of the lake water ($\delta^{18}O_{\text{lake}}$) and hence by air temperature, hydrology and atmospheric circulation pattern changes.

Fig. 6. Stable oxygen isotope composition of diatoms from Two-Yurts Lake (corrected for contamination) compared to other north hemispheric climate reconstructions such as (b) the July air temperatures reconstructed from chironomids at TYL (Nazarova et al., 2013); (c) the GISP2 K- record indicative for the strength of the Siberian High (Mayewski et al., 2004); (d) the Jellybean carbonate $\delta^{18}O$ anomaly indicative for the position of the Aleutian Low (Anderson et al., 2005); (e) N-GRIP Greenland oxygen isotope record (Vinther et al., 2006); (f) July insolation at 60°N. Laskar et al. (2004).

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The downcore $\delta^{18}O_{\text{diatom}}$ record documents Holocene climate dynamics in Kamchatka. We interpreted an overall decrease in $\delta^{18}O_{\text{diatom}}$ from $+27.3\%$ to $+23.3\%$ between about $-4.5$ kyr BP and today as a Late Holocene cooling trend. This gross pattern is also detectable in other TYL proxy information from bioindicators (such as diatom assemblage, pollen and chironomid data), and in good accordance with other north hemisphere environmental changes (i.e., a summer insolation-driven Mid- to Late Holocene cooling). Late Holocene climate variability in the TYL $\delta^{18}O_{\text{diatom}}$ record yields evidence for a Neoglacial cooling starting at $3.7$ kyr BP, with the Little Ice Age (LIA) as the coldest phase in the past $4.5$ kyr.

However, the TYL $\delta^{18}O_{\text{diatom}}$ record not only reflects global climatic changes but also accounts for local to regional environmental features. The comparison with other bioindicator proxy data (i.e., the chironomid-based lake water temperature record) especially demonstrates the complex interaction of different controls for changing environmental conditions at TYL, Kamchatka. These include site-specific factors such as hydrological changes (i.e., enhanced inflow of snow meltwater) superimposing general, i.e., northern hemisphere climatic trends.

Furthermore, the $\delta^{18}O_{\text{diatom}}$ record is linked with atmospheric–oceanic changes such as the interplay between Siberian High and Aleutian Low air pressure centers, as well as with the sea ice dynamics in the Sea of Okhotsk.

In summary, the interpretation of $\delta^{18}O_{\text{diatom}}$ data from lacustrine sediments yields important and unique information on past climate and hydrology changes for the remote and sparsely investigated area of Kamchatka, Russia.

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