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Pliocene to Pleistocene climate and environmental history of Lake El’gygytgyn, Far East Russian Arctic, based on high-resolution inorganic geochemistry data

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Abstract

The 3.6 Ma sediment record of Lake El'gygytgyn, Far East Russian Arctic, represents the longest continuous climate archive of the terrestrial Arctic. Its elemental composition monitored by X-ray fluorescence scanning exhibits significant changes since the Mid-Pliocene caused by climate driven variations in the primary production, postsedimentary diagenetic processes, and current activity in the lake as well as weathering processes in its catchment.

During the Mid to Late Pliocene, warmer and wetter climatic conditions are reflected by elevated Si / Ti ratios, indicating enhanced diatom production in the lake. Prior to 3.3 Ma, this signal is highly masked by intensified detrital input from the catchment, visible in maxima of clastic-related proxies such as the K concentration. In addition, calcite formation in the early lake history points to enhanced nutrient flux into the lake caused by intensified weathering in its catchment. Its termination at ca. 3.3 Ma is supposed to be linked to the development of permafrost in the region triggered by a first cooling in the Mid-Pliocene.

After ca. 3.0 Ma the elemental data suggest a gradual transition to Quaternary-style glacial / interglacial cyclicity. In the early Pleistocene, the cyclicity was first dominated by variations on the 41 ka obliquity band but experienced a change to a 100 ka eccentricity dominance after the Middle Pleistocene Transition at ca. 1.2 to 0.7 Ma. This clearly demonstrates the sensitivity of the Lake El'gygytgyn record to orbital forcing.

A successive decrease of the baseline-levels of the redox-sensitive Mn / Fe ratio and magnetic susceptibility between 2.3 to 1.8 Ma reflects an overall change in the bottom water oxygenation due to an intensified occurrence of pervasive glacial episodes in the early Quaternary. The coincidence with major changes in the North Pacific and Bering Sea paleoceanography at ca. 1.8 Ma implies that the change in lake hydrology was caused by regional cooling and/or changes in the ocean-land moisture transport. Further rising TOC and TN values after ca. 1.6 Ma are attributed to a progressive intensification of the glacial intensity.

In the course of the Quaternary glacial/interglacial sequence eight so-called "super-interglacials" occur. Their exceptional warm conditions are reflected by extreme Si / Ti peaks accompanied by lows in Ti, K, and Fe, thus indicating an extraordinary high lake productivity.

1 Introduction

Geochemical analysis by X-ray fluorescence (XRF) scanning has become a well-accepted and intensively used analytical method to investigate the elemental composition of marine and terrestrial sediments (Rothwell and Rack, 2006). Although not as precise as conventional elemental analyses by inductively coupled plasma optical emission spectrometry (ICP-OES) or conventional XRF, XRF scanning has the advantages of non-destructive analyses combined with minimal sample preparation and short measuring time (Croudace et al., 2006). This makes XRF scanning an outstanding tool for measurements requesting high spatial resolution, as often the case in paleoclimatological and paleoenvironmental sciences (e.g. Brown, 2011; Kujau et al., 2010; Kylander et al., 2007; Yancheva et al., 2007).

The lake sediment sequence recovered from Lake El'gygytgyn in the Far East Russian Arctic (Fig. 1) within the framework of the International Continental Scientific Drilling Program (ICDP) in 2009 is considered as the most long-lasting continuous climate archive of the terrestrial Arctic. Sedimentation commenced about 3.6 Ma ago and was interrupted neither by inundation of Cenozoic glaciations nor by desiccation (Melles et al., 2012; Brigham-Grette et al., 2013). Previous work on pilot cores from the lake, covering the past 350 ka, has proven its unique potential for regional paleoclimate and environmental reconstructions (e.g. Brigham-Grette et al., 2007; Lozhkin et al., 2007a, b; Melles et al., 2007; Nowaczyk et al., 2007; Swann et al., 2010; Asikainen et al., 2007). This includes analysis of the inorganic geochemistry of the sediments, whose results reacts highly sensitive, for instance, to changes in the sediment flux into the lake and anoxia at the lake bottom (Minyuk et al., 2007, 2011), but also to hydrologically-driven changes in the sediment grain size (Wennrich et al., 2013a).

In this study, we present high-resolution XRF scanning data of the complete 318 m long lacustrine sediment sequence of Lake El'gygytgyn. Supported by complementary proxy analyses of the record (e.g., Melles et al., 2012; Andreev et al., 2013; Brigham-Grette et al., 2013; Francke et al., 2013; Gebhardt et al., 2013; Meyer-Jacob et al., 2013; Sauerbrey et al., 2013; Tarasov et al., 2013) the results of the geochemical analyses shed new light on variations in in-lake processes as well as changes in the lake catchment over the past 3.6 Ma that are supposed to be triggered by variations in the global, regional, and local climate.

2 Study site

Lake El'gygytgyn (67°30′ N, 172°05′ E; Fig. 1) is a high arctic lake located in central Chukotka, Far East Russian Arctic. The lake basin was formed by a meteorite impact 3.58 ± 0.04 Ma ago (Layer, 2000) that hit into Upper Cretaceous ignimbrites, tuffs and andesite-basalts of the Okhotsk-Chukchi Volcanic Belt (OCVB) (Belyi and Raikevich, 1994; Gurov et al., 2007). With its diameter of ca. 12 km and a surface area of ca. 110 km^2 (Nolan and Brigham-Grette, 2007) Lake El'gygytgyn fills the deepest part of the ca. 18 km wide impact crater (Gurov et al., 2007). Approximately 50 ephemeral streams drain the lake catchment of 293 km^2 confined by the crater rim (Nolan et al., 2003). The inlet streams annually deliver ca. 0.11 km^3 of water and 350 t of sediment to the lake, mainly during snowmelt (Fedorov et al., 2013). The Enmyvaam River as single outlet exits the lake into the south and flows towards the south-east via the Anadyr River into the Bering Sea (Nolan and Brigham-Grette, 2007).

Lake El'gygytgyn is located in an area that is influenced by both Siberian and North Pacific air-masses (Barr and Clark, 2011; Yanase and Abe-Ouchi, 2007). The climate at the lake is cold and dry, with mean annual air temperature and annual precipitation of −10.4 °C and 73 to 200 mm, respectively (Nolan and Brigham-Grette, 2007;

Nolan, 2013). A comparison of the local climate data with NCEP/NCAR reanalysis data yielded a good correspondence, indicating the local climate at the lake to well represent the regional climate patterns over western Beringia (Nolan, 2013). The wind pattern at Lake El'gygytgyn today is characterized by strong winds from the north or south, with a mean hourly wind speed of 5.6 $\mathrm{m\,s^{-1}}$ but peak values of up to 21.0 $\mathrm{m\,s^{-1}}$ (Nolan and Brigham-Grette, 2007).

Due to the cold Arctic climate, the oligo- to ultra-oligotrophic and cold-monomictic Lake El'gygytgyn (Cremer and Wagner, 2003) is fully ice-covered for almost nine months of the year, from mid October until early to mid July (Nolan et al., 2003). Since the ice cover prevents gas exchange with the atmosphere, the bottom waters become partially oxygen depleted during the ice-covered season (Cremer et al., 2005). Full mixis of the water body driven by descending warmer shore-waters and accompanied by complete bottom water oxygenation, initiates shortly after snowmelt and the initial ice break-up (Nolan and Brigham-Grette, 2007). During the ice-free season, a wind induced two-cell current system drives the circulation in Lake El'gygytgyn and supports the transport of coarse-grained material to the lake center (Nolan and Brigham-Grette, 2007; Wennrich et al., 2013a). Hydrological modelling approaches yielded a residence time of the modern lake water of ca. 100 yr (Fedorov et al., 2013).

Lake El'gygytgyn today has a roughly bowl-shape morphology with a maximum water depth of 175 m (Nolan and Brigham-Grette, 2007). Multiple paleo-shorelines in the north and prominent lake terraces at 35–40 m, 9–11 m and 3–5 m above as well as 10 m below the modern water level point to significant lake-level variations throughout the lake history (Glushkova and Smirnov, 2007; Schwamborn et al., 2006, 2008; Juschus et al., 2011).

The surrounding of Lake El'gygytgyn is affected by 330 to 360 m deep continuous permafrost (Glushkova and Smirnov, 2007; Mottaghy et al., 2013), whose initial formation is supposed to be linked to a Mid-Pliocene cooling event (Brigham-Grette et al., 2013). Permafrost processes in the lake surrounding, such as cryogenic weathering, as well as slope dynamics and fluvial outwash are the main drivers of physical erosion in the catchment and sediment transport into the lake basin (Schwamborn et al., 2012) and thus, have strong influence on the composition of the lacustrine sediments.

3 Material and methods

3.1 Field work and core preparation

The 318-m thick sediment sequence of Lake El'gygytgyn was cored within the framework of the ICDP El'gygytgyn Drilling Project in spring 2009 (Melles et al., 2011, 2012; Brigham-Grette et al., 2013). Drilling was conducted from the artificially thickened lake-ice cover using a modified GLAD 800 system ("Russian GLAD 800") operated by the US consortium DOSECC (Melles et al., 2011). At drill site 5011-1 in the lake centre, a total of 3 overlapping holes, 1A, 1B, and 1C, were drilled to depths of 147, 112, and 525 meters below lake floor (m b.l.f.), respectively (Figs. 1c and 2). In hole 5011-1C, the base of the lacustrine sediments was reached at 318 m b.l.f.

The cores were treated according to a core handling protocol adapted from Ohlendorf et al. (2011). In the laboratories in Cologne, the plastic liners (Lexan or Butyrate) of the up to 1 m long core segments were split lengthwise with a manual core splitter. Subsequently, the sediment was cut into a work and an archive half using a guitar string. For the lower, more compacted sediments of Lake El'gygytgyn, a diamond band saw was used to cut both the plastic liner and the sediment at once. The surface of the core halves were carefully cleaned and levelled by scratching with standard microscope slides perpendicular to the core axes. After cleaning, high-resolution digital images of the fresh surfaces of both halves were taken using a MSCL-CIS benchtop core imaging system (Geotek Ltd.), and the cores were described for color, grain size, and sedimentary structure, leading to an initial facies definition (Melles et al., 2012; Brigham-Grette et al., 2013; Sauerbrey et al., 2013). Further measurements and the subsampling were conducted on the work halves, whereas the archive halves were stored for future analyses.

3.2 Composite profile compilation

Based on the visual core description, including the identification of prominent mass movement deposits (MMDs; Sauerbrey et al., 2013), tephra layers (Bogaard et al., 2013), and fossil redox layers, in combination with initial logging data, a core composite profile of the three holes of site 5011-1 was compiled for subsequent sampling. In detail, a layer-by-layer correlation of the overlapping core sections was performed, and, if possible, only the central part of a section was included in the composite to avoid disturbance at section cuts. Correlation between the ICDP drill cores and pilot core Lz1024 covering the past ca. 350 ky (Nowaczyk et al., 2013; Juschus et al., 2007; Frank et al., 2013) revealed that ICDP site 5011-1 start at a sub-bottom depth of 5.67 m b.l.f. The gap to the sediment surface was filled with core Lz1024 (Fig. 2). Between 5.67 and 104.80 m b.l.f. the core composite exclusively originates from holes 1A and 1B, whereas holes 1A, 1B and, 1C where spliced between 104.80 and 113.40 m b.l.f., and 1A and 1C where used between 113.40 and 145.70 m b.l.f. (Nowaczyk et al., 2013; Fig. 2). Below a composite depth of 145.70 m b.l.f. down to the base of the lacustrine sediments at 318 m b.l.f., only sediments of hole 1C where available, and thus, where included into the composite profile.

In order to investigate the long-term sedimentation history in Lake El’gygytgn, widely independent on short-term events, volcanic ash layers and MMDs with thicknesses exceeding 5 cm were defined as gaps and excluded from the composite profile. These intervals where afterwards omitted from the routine sampling. A detailed compilation of the sections used for the composite profile is presented in Table S1 in the Supplement.

3.3 XRF scanning

High-resolution elemental analyses of the sediments were performed by energy-dispersive X-ray fluorescence (XRF) on the working half of each core segment using an ITRAX core scanner (Cox Analytical, Sweden) at the University of Cologne. The ITRAX system is a multi-functional core-scanning instrument that enables to non-destructively record optical, radiographic, and chemical variations of sediment cores simultaneously with a spatial resolution down to 200 µm (Croudace et al., 2006). Each core has been scanned in 2 mm resolution twice, with the ITRAX equipped once with a 3.0 kW Molybdenum (Mo) and once with a 1.9 kW Chromium (Cr) tube in order to generate higher count rates and lower detection limits for heavier (Mn to U) and lighter elements (Al to Ti), respectively. In case of the Lake El'gygytgyn sediments, both tubes were set to a tube voltage of 30 kV and a current of 30 mA, with an integration time of 10 s. Element data recorded by the ITRAX is semi-quantitative, and is expressed as total counts (ct), i.e. integrated peak area, or as element ratios. Spectra evaluation and post-processing was performed with the software QSpec 6.5 (Cox Analytical, Sweden). Thereby, the used mathematical model was tuned to best fit the measured data by adjusting sample matrix characteristics, element composition, as well as tube and detector parameters.

The element-specific response to variations in the tube power, i.e. as a result of tube ageing during long-term measurements, were monitored by routinely scanning a standard reference glass of known composition after each core section (Ohlendorf et al., 2013). For elements of mid to high atomic number (Z) and heavy elements ($Z \geq 37$), the element intensities were corrected for drifts due to tube ageing or shifts in the signal after tube changes by normalizing with the Compton scatter. For lighter elements, calculating ratios of elements with comparable atomic numbers has shown to be more useful (Ohlendorf et al., 2013).

In addition to variations in the energy of the excitation source, the element intensities derived from the wet half cores, especially those of light elements such as Si, might be influenced by effects of the sediment matrix (Löwemark et al., 2011). In case of Si, an empirically determined matrix-correction based on an exponential attenuation function between the ratio of wet and dry element intensities and the ITRAX-derived ratio of Compton and Rayleigh scattering (inc/coh ratio) was applied using the formula

$$\mathrm{Si_{mc}} = \frac{\mathrm{Si_{raw}}}{3.2994 \cdot e^{0.505 \cdot \mathrm{inc/coh}}}, \quad (1)$$

with Si_{raw} being the raw and Si_{mc} the matrix-corrected Si integrals (Melles et al., 2012; Wennrich et al., 2013b). The relationship was determined by analysing a set of 329 samples from the Lake El'gygytgyn record by XRF scanning of both wet and untreated as well as freeze-dried and powered material, in combination with wavelength dispersive XRF (WDXRF) analyses of material fused with lithium tetraborate (Wennrich et al., 2013b). The inc/coh ratio used in the formula is in general dependent on the average atomic number of the sample, and thus, is reported to be indicative of organic matter content and/or matrix-induced density variations (Guyard et al., 2007).

3.4 TOC, TIC

The contents of total carbon (TC) and total inorganic carbon (TIC) were determined with a DimaTOC 100 carbon analyser (Dimatec Corp., Germany) in aqueous suspension. While TC was directly measured as CO_2 after combustion at 1150 °C, TIC was determined as CO_2 after treating with phosphoric acid (H_3PO_4). The total organic carbon (TOC) content was calculated from the difference between the measured TC and TIC contents.

3.5 Age-model

The age-depth model for the Lake El'gygytgyn composite profile is primarily based on well-dated polarity changes in the paleomagnetic inclination (Haltia and Nowaczyk, 2013) and the postulated age of the crater of 3.58 ± 0.04 Ma (Layer, 2000). It was further refined by tuning to both the 65° N summer insolation (Laskar et al., 2004) and the global marine isotope stack (Lisiecki and Raymo, 2005) using magnetic susceptibility (MS), TOC and biogenic silica (BSi) contents, pollen data, the Si/Ti ratio, colour hues, and grain-size parameters (Nowaczyk et al., 2013).

4 Results and discussion

4.1 Sediment facies

The Plio/Pleistocene core sequence of Lake El'gygytgyn is composed of a variaty of mainly clastic sediments that can be sub-divided into five different facies (A through E; Brigham-Grette et al., 2013). Sediments of facies A are characterized by their typical lamination that is build-up from alternating dark grey to black silt and clay horizons. The preservation of the laminated sediment texture is assigned to the lack of bioturbation due to anoxia during phases of multi-year lake ice coverage, which represent peak glacial conditions (Melles et al., 2007, 2012). In contrast to facies A, the majority of the sediments deposited during glacial to interstadial and interglacial periods consists of silts of facies B that have a massive to faintly banded texture. Laminated silts of reddish brown colour are attributed to facies C formed under peak interglacial conditions. In the Pliocene section of the core laminated intervals of grey silt to clay as well as sections of alternating grey to reddish-brown clay, silt and fine sand with intermittent brecciated intervals of facies D and E, respectively, occur (Brigham-Grette et al., 2013).

4.2 Element composition

As demonstrated in earlier studies for the past ca. 250, 340 and 440 ka, the elemental composition of the sediment record in Lake El'gygytgyn is highly variable and strongly fluctuates on glacial-interglacial timescales (Frank et al., 2013; Minyuk et al., 2007, 2011, 2013a; Nowaczyk et al., 2002, 2007). Further below, we present the results of selected indicative elements and element ratios and discuss their distribution in the entire Pliocene/Pleistocene sediment record with respect to changes in the detrital flux, bioproduction, sediment transport, and diagenetic sediment alteration.

4.2.1 Ti, K, Ca

Although being a minor element in Lake El'gygytgyn sediments, titanium in the younger sediments has shown to be a useful indicator of the climatic history of the lake and its catchment (Minyuk et al., 2007, 2013a). Throughout the entire lake sediment record, Ti exhibits a highly variable signal with typically lower values between ca. 5000 to 9000 ct during normal interglacials, peak minima down to ca. 3000 ct during peak interglacials, and maxima between 12 000 to 18 000 ct during cold stages (Fig. 3). As a relatively immobile element, titanium occurs as an abundant component in a variety of mineral phases (e.g., rutile, sphen, titano-magnetite, etc.), and thus, is commonly linked to detrital fluvial or eolian input (e.g., Haug et al., 2001; Yancheva et al., 2007). Therefore, it has been used in lacustrine sediments to reconstruct the intensities of catchment erosion and detrital input (Panizzo et al., 2008; Whitlock et al., 2008). In Lake El'gygytgyn sediments, correlation analyses of Ti intensities to grain-size results by Francke et al. (2013) yield a moderate to high correspondence to the fine silt fraction ($R = 0.68$; $n = 858$), but a weaker or even anti-correlation to other grain-size classes (Table 1). A similar enrichment of Ti in the fine fraction has been reported for the last 440 ka of the record and is explained by enhanced deposition of Ti-bearing chlorite during glacial conditions (Minyuk et al., 2013a). In interglacial sediments, in contrast, the clay mineralogy is rather dominated by smectite and illite (Asikainen et al., 2007). The Ti occurrence in these sediments has been mainly addressed to the presence of titanomagnetite (Murdock et al., 2013), whose generally low abundance likely explains the Ti depletion during warm stages. In addition, simultaneous minima in Ti, K, and Ca, but also in most other elements, during peak interglacials strongly suggest a significant dilution effect by biogenic opal especially in peak interglacial sediments (Melles et al., 2012). This dilution effect on the Ti signal is less visible in conventional XRF data (Minyuk et al., 2013a), thus suggesting that it is amplified in untreated sediments by higher water contents of the opal-rich sediment, leading to further scattering of the primary X-radiation.

Compared to titanium, potassium shows a smaller variability over the Lake El'gygytgyn sediment record (Fig. 3). Intensities range between 15 000 and 21 000 ct, except for some distinct lows during peak interglacials due to opal diution (e.g., MIS 11.3; ca. 3400 ct). The long-term trend yield rather constant K values back to ca. 2.0 Ma, whereas in the older sediments, two periods with significantly reduced K counts occur between 2.60 to 2.00 and ca. 3.48 to 3.10 Ma (Fig. 3).

Potassium in the Lake El'gygytgyn sediments partly derives from orthoclase ($KAlSi_3O_8$), which abundantly occurs as phenocrysts in both rhyolithic and andesitic volcanic rocks of the lake catchment (Belyi, 2010; Gurov et al., 2005). Bulk mineral analyses of modern lake sediments and bedrock samples yielded orthoclase contents of up to 8.4 and 10.4 %, respectively (Wennrich et al., 2013a). According to these results as well as downcore investigations, these feldspars are enriched in the coarse fraction of Lake El'gygytgyn sediments as a result of cryogenic weathering in the active layer of the permafrost (Schwamborn et al., 2012; Wennrich et al., 2013a). The transport of coarse material to deeper parts of the lake is reported to be triggered by the existence of a wind-induced current system, which is restricted to interglacial periods (Francke et al., 2013; Wennrich et al., 2013a). Another important K source in Lake El'gygytgyn sediments is illite ($K_{0.65}Al_{2.0}[Al_{0.65}Si_{3.35}O_{10}]$*(OH); Minyuk et al., 2007), which accounts for up to 12.8 % of the mineral spectrum in surface samples (Wennrich et al., 2013a), and it is regarded to be the major clay mineral in the sediments, predominantly deposited during warm stages (Asikainen et al., 2007). This mixture of fine-grained illite and coarse-grained feldspar is supposed to cause a lacking grain-size dependency of K contents (Table 1).

Like potassium, calcium shows relatively small fluctuations throughout most of the record (Fig. 3). In contrast to K, however, Ca rather constantly decreases from ca. 14 000 ct in the latest Pliocene deposits down to ca. 5000 ct in the youngest Quaternary section, with pronounced minima of only ca. 3400 ct during the Quaternary peak interglacials. In addition, Ca exhibits strongly increased values of up to ca. 210 000 in the Mid-Pliocene sediments formed prior to ca. 3.25 Ma.

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In close resemblance to K, Ca is primarily associated with feldspars, mainly oligoclase and andesine (both (Na,Ca)[Al(Si,Al)Si_2O_8]) from the catchment bedrocks, and Ca-bearing smectite as a typical interglacial clay mineral (Asikainen et al., 2007), thus explaining the low grain-size dependency of the Ca signal (Table 1). The strongly enriched Ca values in the sediments deposited prior to 3.25 Ma are traced back to additional calcite ($CaCO_3$) accumulation in the early lake history. This suggestion is confirmed by simultaneously enhanced TIC contents (up to 4.9 %; Fig. 3) and the detection of calcite by FTIRS analyses in the basal lake sediments (Meyer-Jacob et al., 2013). The occasional occurrence of TIC in the younger sediments (Fig. 3), in contrast, is supposed to reflect the formation of other carbonate minerals, like siderite or rhodochrosite, since TIC and Ca show only low to lacking correspondence and calcite was not identified by FTIRS analyses in these sediments. The deposition of calcite restricted to the early lake history may be associated with an initial supply from the underlaying impactites and volcanic bedrocks, which, according to analyses on respective rocks in the drill core from ICDP Site 5011-1C contain calcitic vein fillings (Raschke et al., 2013a, b).

4.2.2 Si

Silicon is the main component in the elemental spectrum of the Lake El'gygytgyn sediments. Si concentrations determined by wave-length dispersive XRF in the uppermost ca. 440 ka of the Lake El'gygytgyn record ($n = 340$) range from 57.0 to 80.5 % (Minyuk et al., 2013a). The Si_{mc} intensities from XRF scanning derived after application of the empirical correction function for combined matrix effects to the Si_{raw} data (Melles et al., 2012; Wennrich et al., 2013b) well correlate to these data, yielding a coefficient of determination (R^2) of 0.57. The Si_{mc} intensities throughout the entire record vary between ca. 170 and 6900 ct (Fig. 3). During the late Pliocene and early Quaternary (< 2.7 Ma), Si_{mc} intensities show rather constant long-term averages, but slightly depressed counts between ca. 1.9 to 1.6 Ma. Further-on, strong short-term fluctuations that can be attributed to glacial/interglacial variations. The early lake history prior to

3.0 Ma, in contrast, is reflected by strongly decreased $\mathrm{Si_{mc}}$ values. A ten-fold higher sedimentation rate during this interval (Nowaczyk et al., 2013; Fig. 3) points to dilution by enhanced clastic input, which, in turn, can be traced back due to an increased precipitation, steeper relief of the young crater, and reduced or absent permafrost within the catchment (Sauerbrey et al., 2013; Brigham-Grette et al., 2013).

Si in lakes is related to either detrital or biological sources (Peinerud, 2000). In the sediment record of Lake El'gygytgyn, the biogenic silica (BSi) content varies from less than 5 % up to 56.1 % (Melles et al., 2012). It is primarily formed by diatom frustules, making the BSi concentration a valuable proxy for in-lake biological primary production. To discriminate detrital and biological Si sources in the elemental composition, the $\mathrm{Si_{mc}}$ intensities were corrected for titanium that exclusively occur in the clastic sediment fraction. Previous studies have demonstrated the Si/Ti ratio to be a reliable indicator of the BSi content (e.g., Brown, 2011; Brown et al., 2007; Johnson et al., 2011; Cartapanis et al., 2013). In the Quaternary section of the Lake El'gygytgyn record, the $\mathrm{Si_{mc}}$/Ti (in the following mentioned simply as Si/Ti) ratio exhibits a systematic variability with lows between 0.2 to 0.4 during cold stages, moderate values between 0.4 to 0.8 during interstadials and normal interglacials, and peaks exceeding 0.8 during peak interglacials (e.g., MIS 11.3, MIS 31, MIS 87; Fig. 3). The absolute Si/Ti maximum of 1.92 occurs during MIS 11.3 at 404.5 ka.

The Si/Ti ratio has been shown to strongly correlate with the BSi content ($r^2 = 0.88$), thus suggesting Si/Ti to be primarily modulated by variations in the primary production of the lake (Melles et al., 2012). The pronounced variability of the aquatic primary production on glacial/interglacial timescales is supposed to be controlled by both orbital-induced changes in the ice cover of the lake but also long-term changes in the weathering intensity within the lake catchment as a trigger of nutrient flux into the lake.

4.2.3 Mn and Fe

Although chemically very similar, iron and manganese exhibit different distribution patterns in the sediments of Lake El'gygytgyn (Fig. 4). Mn intensities are relatively constant throughout the record, with an average of 693 ct, but pronounced maxima (exceeding 1000 ct) during some glacial periods. Fe intensities, in contrast, are characterised by a much stronger variability on glacial to interglacial timescales, with higher values of usually up to ca. 80 000 ct during cold stages and lows down to 20 000 ct during warmer periods. Thereby, Fe behaves very similar to typical detrital elements, like Ti or K, as also demonstrated by a positive TiO_2–Fe_2O_3 correlation in the upper 440 ka of the El'gygytgyn record (Minyuk et al., 2013a) and similar distribution of Ti and Fe in surface sediments of the lake (Wennrich et al., 2013a). Extraordinary low Fe intensities during MIS 11.3 are supposed to be the consequence of particularly pronounced dilution by biogenic opal. During peak glacials, very pronounced short-term Fe peaks of up to 200 000 ct occur that are synchronous with lows in MS (Fig. 4), which indicates the formation of non-ferromagnetic mineral phases.

In aquatic environments both Fe and Mn have shown to react sensitively to changes in the redox condition, but with different E_h stability fields of both Fe and Mn (Davison, 1993). In fully oxygenated surface and downcore sediments of Lake El'gygytgyn, prevailing during interglacial climates, iron occurs in a variety of different phases including magnetite, titanomagnetite, haematite, chromite, and ilmenite, as well as Fe (oxyhydr)oxides (Nowaczyk et al., 2002; Wennrich et al., 2013a; Minyuk et al., 2013a). Manganese oxides and hydroxides often co-precipitate with Fe (oxyhydr)oxides (Hongve, 1997), and thus, are assumed to account for a majority of the Mn. The Mn/Fe ratio as proxy for syn- and post-depositional redox conditions in the bottom waters and sediment in lacustrine systems, (e.g., Koinig et al., 2003; Naeher et al., 2013) usually has higher values between 0.01 and 0.03 in oxic sediments of Lake El'gygytgyn (Fig. 4).

During full glacial periods with reducing bottom and pore-water conditions as a result of a perennial ice cover (Melles et al., 2007, 2011, 2012), in contrast, magnetite becomes widely dissolved. Under such conditions, chlorite and biotite are supposed to be the major Fe-bearing minerals (Minyuk et al., 2013a), which is also visible in a high correlation of Fe to the fine silt ($R = 0.59$) and very fine silt fraction ($R = 0.52$; Table 1). Furthermore, anoxia promotes the additional diagenetic formation of abundant vivianite and, to a lesser extent, siderite (Murdock et al., 2013; Minyuk et al., 2013b). Due to the higher solubility of Mn under less oxic conditions (Davison, 1993), glacial sediments of Facies A typically exhibit lower Mn/Fe ratios (Fig. 4). Coinciding peaks of Mn and the Mn/Fe ratio (up to 0.2) during single peak glacial phases at 1460, 1382, 1255, 965, 230, and 187 ka points to exceptional Mn enrichment. Supported by synchronous peaks in TIC (cf. Fig. 3), this enrichment is supposed to be caused by the formation of rhodochrosite ($MnCO_3$) that is usually linked to anoxia (Frederichs et al., 2003; Murdock et al., 2013).

The short-term variability of the Mn/Fe record of Lake El'gygytgyn is overprinted by long-term gradual Mn/Fe decrease from a higher level between ca. 3.6 and 2.3 Ma to a steady-state that was reached after ca. 1.8 Ma ago (Fig. 4). This indicates a gradual trend to less oxic conditions at the lake bottom, likely due to a progressive change in the lake hydrology with a gradual drop in the bottom water oxygenation. A lower bottom water oxygenation is also confirmed by a simultaneous baseline reduction visible in the MS and a shift toward higher TOC and TN contents (Fig. 4), presumably due to a reduction of organic matter decay.

4.2.4 Rb and Sr

Rubidium and Strontium as trace elements abundantly occur in the sediments of Lake El'gygytgyn. Modern surface sediments of the lake are characterized by Sr contents between ca. 51 and 116 ppm (Wennrich et al., 2013a). In the upper part of the sediment record between ca. 440 to 125 ka Rb and Sr concentrations are up to 154 and 249 ppm, respectively (Minyuk et al., 2013a). The XRF scanner analyses yield mean Rb and Sr count rates between 176 to 548 and 177 to 1417, respectively.

In Lake El'gygytgyn sediments Sr is supposed to be mainly associated with the occurence of Na-Ca-feldspars and K-feldspars from the surrounding acidic and andesitic volcanic rocks (Wennrich et al., 2013a) substituting sodium, calcium, or potassium (El Bouseily and El Sokkary, 1975; Cherniak and Watson, 1994). Due to its similar ionic radius, Rb, in contrast, preferably replaces K (Chang et al., 2013), and thus, is commonly found in K-feldspars as well as micas and clay minerals (Kylander et al., 2011; Fralick and Kronberg, 1997). Hence Rb is typically enriched in the fine-grained sediment fraction of weathering products of silicates (Koenig et al., 2011; Dypvik and Harris, 2001).

The resulting Rb/Sr ratio of the XRF scanner measurements show highly variable values with mean values varying between 0.12 to 2.60 (Fig. 5). In general, higher values occur during glacial periods and lows during interglacial periods, thus, proving the previously stated climate dependency of the Rb/Sr ratio in the Mid to Late Quaternary section of the Lake El'gygytgyn core (Minyuk et al., 2011, 2013a).

Thereby, Rb/Sr displays an obvious cyclicity over the past 3.6 Ma with higher frequencies for the interval prior to ca. 0.7 Ma and a remarkable decrease for sediments younger than ca. 0.7 Ma.

The Rb/Sr (or Sr/Rb) ratio is commonly used as an indicator of the weathering intensity of the bedrock in different kinds of sediments records (e.g., Chang et al., 2013; Jin et al., 2001; Dasch, 1969; Heymann et al., 2013), but has also been interpreted in terms of grain-size variations of Siberian lakes Teletskoye and El'gene-Kyuele (Kalugin et al., 2007; Biskaborn et al., 2013). Previous studies of Lake El'gygytgyn sediments attributed variations in the Rb/Sr ratio on an interglacial/glacial timescales mainly to an enhanced Sr-depletion due to higher chemical alteration, which in term, is controlled by grain-size (Minyuk et al., 2011, 2013a). The comparison of our high-resolution Rb/Sr data with grain-size data determined on sediments from ICDP Site 5011-1 (Francke et al., 2013) yield a moderate to good correlation of Rb/Sr to the mean grain-size ($R = -0.64$; Table 1) with a high correlation to fine and a high anti-correlation to coarse grain-size classes (Table 1), thus strongly supporting the grain-size dependency. The climate-driven grain-size variability in Lake El'gygytgyn sediments is supposed to be triggered by the occurrence and absence of a wind-driven current system during interglacials and glacials, respectively, delivering coarser material to the lake center (Francke et al., 2013; Wennrich et al., 2013a). Thus, variations in the Rb/Sr on a longer timescale presumably mirror changes in the current activity in Lake El'gygytgyn, which are mainly controlled by the presence/absence of a perennial ice cover at the lake (Asikainen et al., 2007; Francke et al., 2013).

5 Interpretation

The elemental composition of the sediment succession of Lake El’gygytgyn has shown to be influenced by the flux of detrital material into the lake, by the sediment transport within the water column as well as by lake-internal processes, such as the primary diatom production, redox processes at the lake bottom and in the sub-surface sediments. Since most of these processes are triggered by regional to global climate variations due to orbital forcing, high-resolution elemental data can be used as suitable proxies to reconstruct the environmental and climatic history of Lake El’gygytgyn and its catchment of the past 3.6 Myr.

5.1 Mid to Late Pliocene (3.6–2.8 Ma)

The early history of Lake El’gygytgyn is characterized by a high flux of clastic material into the lake as visible in elevated K values during the first about 10 000 yr after the lake formation at ca. 3.58 Ma and in the ten-fold higher sedimentation rate until 3.3 Ma (Nowaczyk et al., 2013; Fig. 3). Higher sediment flux from the catchment is assumed to be the result of the steeper relief of the young crater (Sauerbrey et al., 2013), and is supposed to be amplified by a higher annual precipitation of ca. 600 mm yr^{-1} and the absence of permafrost in the catchment (Brigham-Grette et al., 2013; Tarasov et al., 2013). Greater seasonal in-lake productivity during the Mid-Pliocene warmth as evoked by higher BSi accumulation rates and larger diatom frustules (Brigham-Grette et al., 2013) is neither noticeable in the Si/Ti ratios nor in the TOC contents (Figs. 3 and 4), since the signal is hardly masked by detrital dilution. Higher Mn/Fe ratios during this period suggest well-oxygenated bottom water conditions, thus, pointing to a shortened seasonal lake ice cover. Calcite formation and/or deposition in the basal part of the core as indicated by simultaneously intensified Ca and TIC contents (Fig. 3) required an oversaturation of bottom or pore waters with both Ca^{2+} and CO_3^{2-} ions, which is excluded for modern Lake El'gygytgyn waters characterized by low cation and anion concentrations (Cremer et al., 2005). Thus, the calcite formation can presumably be traced back to an enhanced ion (and nutrient) flux into the lake due to intensified chemical weathering in the lake catchment. This would have been promoted by a 7 to 8 °C warmer and ca. 400 mm wetter regional climate and reduced or absent permafrost during the Mid-Pliocene as postulated by Brigham-Grette et al. (2013).

Dropping Ca and TIC values at ca. 3.25 Ma (Fig. 3) correspond fairly well with the end of the M2 cooling event at 3.264 Ma (Lisiecki and Raymo, 2005; Fig. 3) and a change to cold adapted trees around the lake that have been linked to permafrost onset after the so-called Mammoth event at ca. 3.3 Ma (Brigham-Grette et al., 2013; Andreev et al., 2013). As the formation of rhododochrosite in the later record suggest at least the temporary saturation of CO_3^{2-} in the bottom sediments (Murdock et al., 2013), Ca^{2+} seams to be the limiting factor for calcite formation. Hence, the termination of calcite formation is supposed to point to a slow-down of the chemical weathering, and thus, the Ca^{2+} flux into the lake, presumably due to initial permafrost formation. Simultaneously, decreasing sedimentation rates (Fig. 3) and a reduced mass movement frequency and turbidite thickness after 3.3 Ma (Sauerbrey et al., 2013) further imply a certain landscape stabilization in the catchment.

Protracted favourable conditions in the lake due to a warmer and moist climate until after 3.0 Ma (Brigham-Grette et al., 2013) are clearly evidenced by high Si/Ti and TOC values (Figs. 3 and 4). High diatom production as also indicated by high BSi accumulation rates (Brigham-Grette et al., 2013) obviously strongly dilute the clastic input into the lake resulting in lows of all clastic related elements, like K, Ca, and Ti (Fig. 3). A gradual lowering of the Si/Ti ratio and a contemporaneous increase in clastic elements after the MIS KM2 (3.15–3.119 Ma; Lisiecki and Raymo, 2005) until ca. 3.0 indicate a deterioration of the in-lake bioproduction and induce a transitional period to Quaternary-style variations of in-lake processes. This shift predates a stepwise cooling

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in summer temperatures as reconstructed from pollen data after ca. 3.02 Ma (Brigham-Grette et al., 2013) but coincides with a shift to more open landscapes after MIS KM2 (Tarasov et al., 2013) and a drop in winter temperatures after 3.25 Ma (Brigham-Grette et al., 2013).

5.2 Plio-Pleistocene transition (2.8–1.5 Ma)

After the Mid-Pliocene warmth, the interval between 2.8 to 1.5 Ma marks a transitional phase from relatively uniform Mid-Pliocene conditions to the high-amplitude variability of the Quaternary. The most striking feature in the element data of this interval is the onset of a pronounced glacial-to-interglacial cyclicity visible in most geochemical proxies, either for clastic input, grain-size distribution, redox-conditions or primary production at ca. 2.67 Ma, thus displaying an overall change in the lake but also in its catchment. This change to a higher variability just slightly postdates a drop in precipitation and winter temperatures at 2.73 Ma reconstructed from pollen data (Brigham-Grette et al., 2013; Tarasov et al., 2013; Andreev et al., 2013), and the onset of subarctic Northern Pacific stratification interpreted to have triggered an intensified Northern Hemisphere glaciation (e.g., Haug et al., 2005).

The regular glacial/interglacial variability is interrupted by periods of exceptionally elevated diatom production as visible in Si/Ti ratios > 0.8 and the occurrence of sediment facies C during MIS 93, 91, 87, 77, and 55 at ca. 2.38, 2.34, 2.30, 2.26, and 1.60 Ma (Fig. 3). These “super-interglacials” mark periods of unusual Arctic warming at Lake El’gygytgyn that are widely synchronous to major retreats in the West Antarctic Ice Sheet as interpreted from Ross Sea sediments (Melles et al., 2012; Naish et al., 2009). Extreme peaks in the BSi content of the sediments are supposed to have strongly diluted the clastic contents (Minyuk et al., 2013a) causing the majority of proxies related to detrital clastic input into the lake, like Ti, K, Rb, and Ca to have minima (Figs. 3 and 5).

During MIS 104 (2.602–2.598 Ma) typical finely laminated silt and clay of facies A for the first time occurs in the sediment sequence of Lake El’gygytgyn (Melles et al., 2012;

Fig. 4). Facies A sediments are addressed to sedimentation processes under a perennial ice cover (Melles et al., 2007, 2011) implying that during MIS 104 for the first time mean annual temperatures at the lake fell below a critical threshold of 5.5±1.0 °C below modern that is required to initiate multi-year lake ice and to eliminate oxygen exchange with the atmosphere (Nolan, 2013). This is clearly confirmed by results of pollen analyses yielding a substantial cooling in the surrounding of Lake El'gygytgyn during this interval (Melles et al., 2012; Andreev et al., 2013) that is also seen in the Lake Baikal record (Demske et al., 2002). Low Mn/Fe ratios and MS as well as high TOC contents during periods of facies A sedimentation (Fig. 4) clearly point to anoxia at the lake bottom with reduced organic matter decay, magnetite dissolution, and the formation of vivianite and rhodochrosite (Nowaczyk et al., 2002; Murdock et al., 2013; Minyuk et al., 2013b). Low Si/Ti in combination with high Ti, K, and Rb/Sr (Figs. 3 and 5) further indicate a diminished primary production under the perennial lake ice, and thus, clastic dominated fine-grained sediments during these peak glacial periods.

The progressive appearance of facies A in the Lake El'gygytgyn sediments after ca. 2.3 Ma until ca. 1.8 Ma, accompanied by a gradual baseline-level drop of Mn/Fe and MS, and a rise in TOC and TN (Fig. 4) suggest a overall change in the lake hydrology and a reduced level of bottom water oxygenation likely due to a higher frequency of pervasive glacial episodes (Melles et al., 2012). The termination of this gradual trend at ca. 1.8 Ma as indicated by knick points in both the Mn/Fe and MS record (Fig. 4) is interpreted to mark the full establishment of glacial/interglacial cycles in the lake region (Melles et al., 2012), which well fits a period of accelerated glacial erosion in British Columbia (Shuster et al., 2005). Furthermore, the timing also coincides with major changes in the paleoceanography of the adjacent marine realm. The central Bering Sea simultaneously experienced a major drop in opal accumulation but an increase in MS at 1.8 Ma that is interpreted as a result of a change in ocean circulation (März et al., 2013). In the sub-Arctic North Pacific the onset of a major subpolar cooling at ca. 1.8 Ma induced a temperature drop of 4–5 °C until 1.2 Ma (Martínez-Garcia et al., 2010). This cooling might have caused both a cooling of the Western Beringian landmass and a drop in the ocean-land moisture transport.

5.3 Quaternary climate variability

The elemental composition of the Quaternary section of the Lake El'gygytgyn record is marked by a notable cyclicity especially in the Ti, Fe, but also the Rb/Sr and Si/Ti signals (Figs. 3 and 5), whose correspondence to variations in the benthic marine isotope stack LR04 (Lisiecki and Raymo, 2005; Fig. 3) clearly demonstrate its glacial-to-interglacial nature. The apparent shift in the frequency of the glacial/interglacial variability between ca. 1.2 and 0.7 Ma that is visible especially in the Rb/Sr ratio and in the mean grain size (Francke et al., 2013; Fig. 5) might therefore correspond to the change from a 41 ka obliquity to 100 ka eccentricity dominance in the glacial/interglacial frequency during the Middle Pleistocene Transition (MPT; Clark et al., 2006). This and the correspondence of the Si/Ti ratio to the isotope stack (Fig. 3) clearly evidence internal lake processes and processes in the catchment as indirect indicators of the regional climate at Lake El'gygytgyn to be strongly triggered by orbital forcing (Nowaczyk et al., 2013).

Beyond the glacial/interglacial variability, the gradually rising TOC and TN contents in combination with a more frequent occurrence of facies A during the past 1.5 to 1.6 Ma (Fig. 4) strongly imply an intensification of the glacial intensity. Longer anoxic periods under a perennial ice cover presumably prohibited the organic matter mineralization during pronounced peak glacial period, with especially the easily removable nitrogen effectively buried in the sediment.

Similar to the early Quaternary "super interglacials", three periods of extraordinary high Si/Ti ratios accompanied by low detrital clastic parameters during MIS 49, 31, and 11.3 at ca. 1.48, 1.07, and 0.40 Ma clearly exceed the range of normal glacial/interglacial cyclicity. Pollen-based climate reconstructions yielded MIS 31 and MIS 11.3 as warmest and wettest of all "super-interglacials", with maximum summer temperatures and annual precipitation of 4 to 5 °C and ca. 300 mm higher even than during the Holocene thermal maximum (Melles et al., 2012). Warmer climate and an associated higher nutrient flux from the catchment into the lake during both MIS 31 and MIS 11.3 (Snyder et al., 2013; Vogel et al., 2013), in combination with a supposed reduced ice-coverage, promoted a maximum in-lake productivity as indicated by peaks in Si/Ti, but also in BSi, as well as the diatom concentration and diversity (Snyder et al., 2013; Vogel et al., 2013). Higher nutrient flux was presumably supported by an enhanced soil formation due to a dense vegetation cover dominated by boreal evergreen conifer and cool-temperate broadleaf forests (Tarasov et al., 2013; Vogel et al., 2013). The elevated Mn/Fe ratio during the "super-interglacials" and simultaneous lows in clastic-bound elements clearly evidence the remarkably reduced MS during these periods (Fig. 4) to be mainly driven by dilution with high biogenic components rather than by magnetite dissolution as derived for the full glacial lows (Nowaczyk et al., 2002, 2007).

6 Conclusions

High-resolution inorganic elemental analyses by XRF core scanning have been conducted on the complete 318 m long lacustrine sediment sequence of Lake El'gygytgyn/Far East Russian Arctic. Their results shed new light on the climate and environmental evolution since the Mid Pliocene formation of the lake 3.58 Ma ago as visible in changes of lake productivity, postsedimentary diagenetic processes, and current activity in the lake as well as weathering processes in its catchment.

1. Fluctuations in titanium, potassium, and calcium indicate major changes in the detrital clastic content of the sediment that are driven by glacial/interglacial variations in the weathering intensity in the lake surrounding and the clastic supply to the lake centre, but also by dilution with biogenic opal. A calcium enrichment in the Mid Pliocene section can be traced back to calcite formation in the early lake history. The termination of the calcite formation after ca. 3.3 Ma is supposed to be

associated with a drop in the Ca flux into the lake due to permafrost onset after the M2 cooling event.

2. Besides detrital sources, silicon in Lake El’gygytgyn sediments mainly derives from diatom production in the water column. A strong interglacial/glacial variability of the Si/Ti ratio as proxy of the biogenic opal content is caused by climate-driven changes in the lake productivity due to a variable seasonal ice coverage of the lake and the nutrient flux from the catchment. Extreme Si/Ti maxima during eight Quaternary “super-interglacials” reflect periods of an exceptional warming.

3. Manganese and iron signals in the sediment record are strongly modulated by redox-dependent diagenetic alteration processes in the bottom water and subsurface sediments. The redox-sensitive Mn/Fe ratio exhibits a drop in the baseline level between 2.3 to 1.8 Ma due to changes in the lake hydrology that are supposed to be linked to a progressive intensification of the glacial intensity in the North Pacific region.

4. The rubidium to strontium ratio of the Lake El’gygytgyn sediments strongly correlates with their grain-size distribution. Changes in the Rb/Sr cyclicity between ca. 1.2 and 0.7 Ma are triggered by a shift in the glacial/interglacial frequency from the 41 ka obliquity band to a 100 ka eccentricity dominance during the Middle Pleistocene transition.

Supplementary material related to this article is available online at http://www.clim-past-discuss.net/9/5899/2013/cpd-9-5899-2013-supplement.pdf.

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Table 1. Correlation of selected elements measured by XRF core scanning with the mean grain size and grain-size classes of samples from Lake El'gygytgyn ($n = 858$). Correlation coefficients above 0.5 and below −0.5 are indicated by italic numbers.

	Si	Ti	K	Ca	Mn	Fe	Mn/Fe	Rb	Sr	Rb/Sr
Mean (µm)	0.03	*−0.50*	−0.06	0.21	−0.03	−0.48	0.16	−0.09	0.21	*−0.64*
Medium sand	0.02	−0.01	0.02	0.01	−0.01	−0.04	0.00	−0.03	−0.02	−0.03
Fine sand	−0.02	−0.06	−0.09	−0.12	−0.01	−0.09	0.02	−0.07	−0.03	−0.09
Very fine sand	0.10	−0.45	0.02	0.31	−0.02	−0.43	0.17	−0.07	0.20	*−0.58*
Very coarse silt	−0.01	*−0.63*	−0.11	0.16	−0.08	*−0.56*	0.12	0.00	0.30	*−0.70*
Coarse silt	0.02	−0.42	−0.12	0.17	−0.04	−0.42	0.12	−0.10	0.18	*−0.58*
Medium silt	−0.04	0.40	−0.11	−0.14	0.12	0.27	0.02	−0.23	−0.25	0.19
Fine silt	−0.05	*0.68*	0.03	−0.27	0.11	*0.59*	−0.10	−0.04	−0.32	*0.66*
Very fine silt	0.00	*0.56*	0.15	−0.14	0.04	*0.52*	−0.15	0.05	−0.25	*0.68*

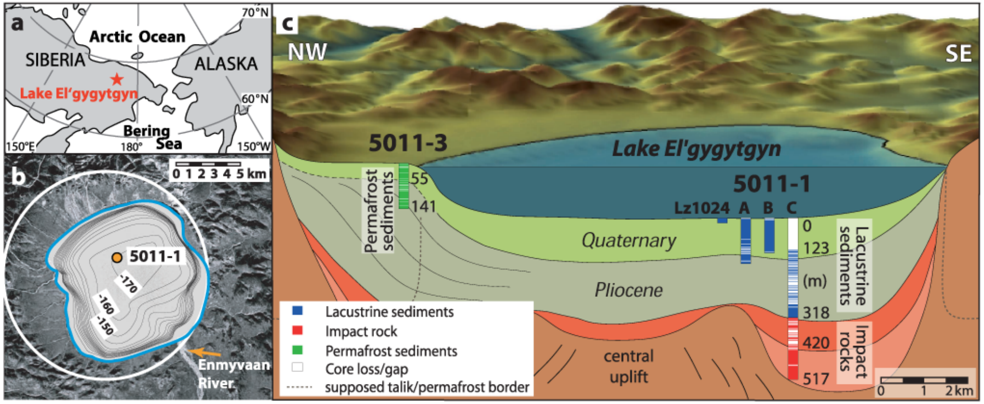

Fig. 1. (a) Map showing the location of Lake El'gygytgyn in the western Beringian Arctic, **(b)** arial image of the El'gygytgyn impact crater, bathymetry of Lake El'gygytgyn, and location of ICDP drill site 5011-1. The white circle shows the dimensions of the crater rim, **(c)** schematic cross-section of the El'gygytgyn basin stratigraphy with location and recovery of ICDP sites 5011-1 and 5011-3 (modified after Melles et al., 2011). At site 5011-1, three holes (1A, 1B, and 1C) were drilled to replicate the Quaternary and uppermost Pliocene sections. Lz1024 is a 16 m long percussion piston core taken in 2003 that fills the stratigraphic gap between the lake sediment surface and the top of drill cores 1A and 1B.

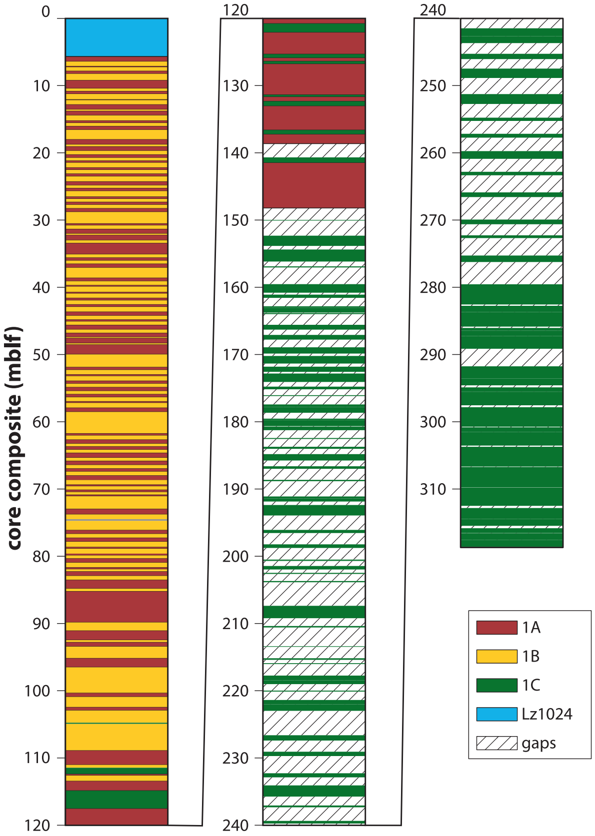

Fig. 2. Core composite profile of the lacustrine basin infill of Lake El'gygytgyn illustrating the origin of the used interval from holes 1A, 1B, 1C, and pilot core Lz1024. Shaded section are gaps in the composite profile.

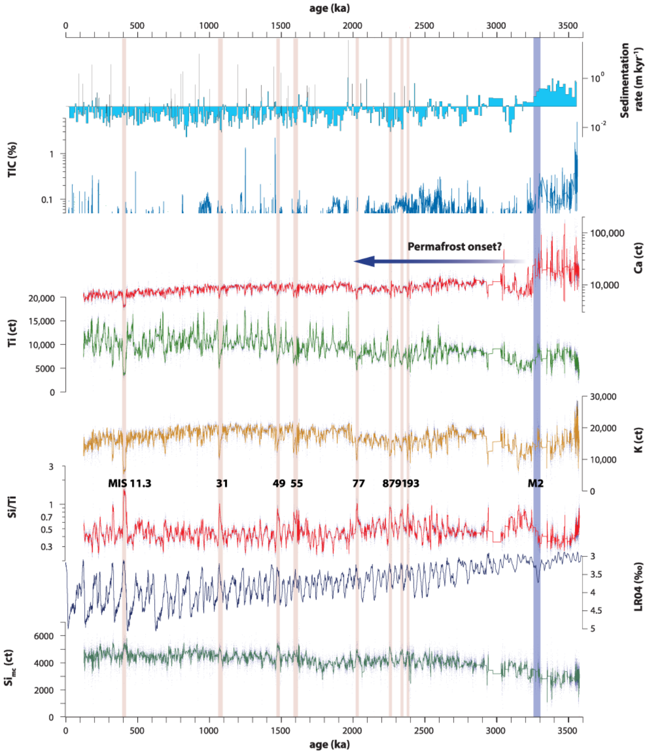

Fig. 3. Matric corrected Si intensity (Si$_{mc}$), Si/Ti ratios, K, Ti and Ca intensity determined by XRF core scanning as well total inorganic carbon (TIC) content and sedimentation rate in the sediment record from Lake El'gygytgyn vs. age compared with the LR04 global marine isotope stack. XRF data are plotted as raw data (blue dots) and 101 point weighted running average (coloured lines). "Super-interglacials" at Lake El'gygytgyn and the Mid Pliocene M2 cooling event are highlighted with red and blue bars, respectively.

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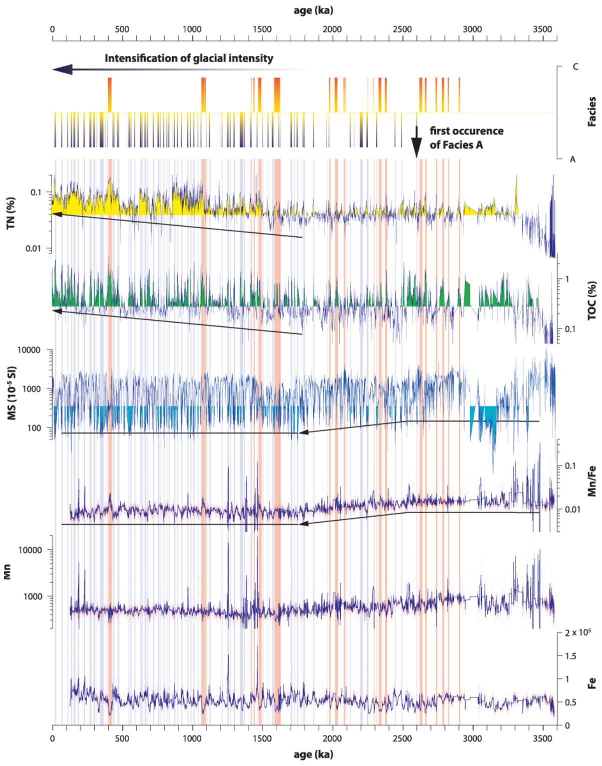

Fig. 4. XRF scanning Fe and Mn intensities and Mn/Fe ratios as well magnetic susceptibility (MS; Nowaczyk et al., 2013), total organic carbon (TOC), total nitrogen (TN) contents, and the occurrence of sediment facies A and C in the sediment record from Lake El'gygytgyn vs. age. XRF data are plotted as raw data (blue dots) and 101 point weighted running average (coloured lines). Magnetic susceptibility data is smoothed by 500 yr weighted running mean to improve the signal-to-noise ratio. Blue and red bars mark the occurrence of sediment facies A and C.

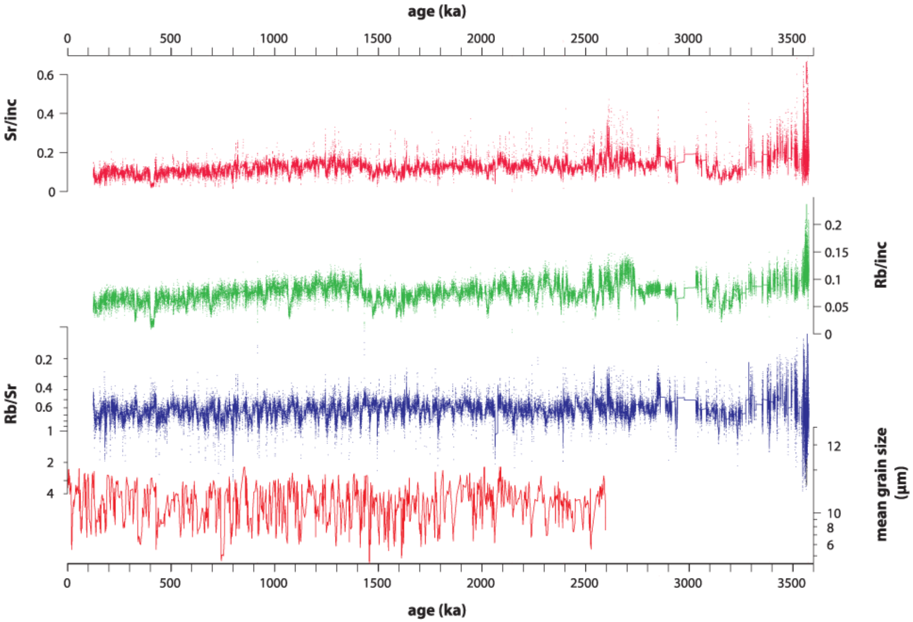

Fig. 5. Mean grain size, incoherent scatter normalized Rb (Rb/inc) and Sr intensities (Sr/inc), and Rb/Sr ratios derived by XRF scanning in the sediment record from Lake El'gygytgyn vs. age. XRF data are plotted as raw data (dots) and 101 point (Sr; Rb/Sr) or 201 point weighted running average (coloured lines).

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Interactive Discussion