Interactive comment on “Inorganic data from El’gygytgyn Lake sediments: stages 6–11” by P. S. Minyuk et al.

Anonymous Referee #1

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Running comments on doi:10.5194/cpd-9-393-2013, Minyuk et al., Climate of the Past

Abstract

Please indicate what size fraction was analyzed, or if these are bulk samples.

Line 4: you probably determined more than presence/absence of elements; insert “concentrations” and accuracy (ppb or ppm?)

Line 5: replace “covering the timeframe between” with “dating from”

We have corrected the text:

“Major and rare element concentrations were determined using X-ray fluorescence spectroscopy (XRF) on the <250µm fraction from 617 samples dated ca. 440 and 125 ka, which approximates Marine Isotope Stages (MIS) 11 to 6.”

I hope it’s made clearer in the paper, but in the abstract I can’t tell if you are determining the interglacial or glacial status of samples by their geochemistry, or are relying on a different chronometer.

We left in the text:

“The elemental record from Lake El’gygytgyn can be divided into two groups or geochemical zones based on the variability of the inorganic compounds, elemental ratios, and LOI (Fig. 4). Each group is affected by different environmental conditions and climates associated with glacial/stadial or interglacial periods. These zones were correlated with marine isotope stages based on the age model developed for the El’gygytgyn record (Nowaczyk et al., 2007; Melles et al., 2012; Nowaczyk et al., 2013). Note that the age model (Melles et al., 2012; Nowaczyk et al., 2013) was used to help identify specific isotope stages, but boundaries of stages and substages were defined according to the inorganic geochemical data. Arabic numerals for the stages and substages in the figures and text follow Bassinot et al. (1994)”

Explain in the abstract why the similarities in structure of certain elemental profiles with other records is important during Stage 11.

We changed the sentence as: “The geochemical structure of MIS 11 shows similar characteristics as seen in MIS 11 records from Lake Baikal (southeastern Siberia) and Antarctic ice cores, thereby arguing for the influence of global forcings on these records”

Provide in the abstract one or two examples of the elemental ratios that indicate weathering or diagenesis.

We have added: “Elemental ratios (CIA, CIW, PIA, and Rb/Sr) indicate that glacial sediments are depleted in mobile elements, like Na, Ca, K and Sr.”

Introduction

Line 3: catchments area = catchment
Corrected

Line 4: The only outlet is via the Enmyvaam River to the south.
Corrected as: The only outlet is the Enmyvaam River that flows to the south.

Line 7 sites; make sure the sites are labeled on a map; otherwise just leave them out.

Few geochemical site numbers that were no mentioned in the text have been deleted from the map.
Lines 8-9: provide units for the measurement (mg/L?). Alkalinity is a useful measurement to provide.

We added unit: mg L$^{-1}$

Line 10: I have never heard the word “circumneutral”. Most people who are reading this will know how what the pH values mean with respect to neutrality. At least we can hope. I suggest combining the last two paragraphs. A lot of what is said in the first paragraph is duplicated in the Figure caption.

Section 1.2

We changed sentence as: “The pH values of 6.2–6.5 (Lz1024) and 5.7–5.9 (Lz1079) indicate that Lake El’gygytgyn is weakly acidic (Cremer and van de Vijver, 2006).”


We corrected sentence as:

“Based on the distribution of major and rare elements, the cores were divided into geochemical zones corresponding to Marine Isotopic Stages (MIS) 1–MIS 10.”

“1.2. Lithology and age model

Three lithofacies (Facies A, B, and C) dominate the pelagic Pleistocene sediments of Lake El’gygytgyn (Melles et al., 2011, 2012). These facies reflect different environmental settings and climate modes. Facies A consists of dark gray to black silt and clay, with fine, laminatae (<5 mm) characterized by a “wavy” structure. This facies is linked with glacial/stadial conditions and the presence of a perennial lake-ice cover. The latter resulted in a stratified water column with anoxic bottom waters, good preservation of the settled organic matter, and dissolution of magnetic minerals.

Facies B is composed of olive-gray to brown silt that is massive to faintly banded. Total organic matter (TOC) is low in this facies, but biogenic silica values and magnetic susceptibility (MS) are high. Sediment structure suggests the presence of bioturbation and oxygenated bottom water (Melles et al., 2011, 2012).

Facies C is defined by a distinct reddish brown appearance and the presence of laminaions that are faint, pale white in color and of a millimeter-to-centimeter scale thickness. This facies corresponds to times of warm super interglacial climate. “

Please tell us why sediments are MORE altered during glacials: this is counterintuitive.

In Introduction we point out that: “Sediment from the warm climatic stages is enriched in SiO$_2$, CaO, Na$_2$O, K$_2$O, and Sr, but is depleted in TiO$_2$, Al$_2$O$_3$, MgO, Fe$_2$O$_3$, and LOI. Glacial sediments are relatively low in mobile elements, such as Ca, Na, and K, but show higher values of the chemical index of alteration (CIA), the plagioclase index of alteration (PIA), and the Rb/Sr ratio (Minyuk et al., 2007, 2011).”

In the Introduction, there should be a paragraph about why the research for this paper was done even if it was done just to characterize the chemical signatures during a specific time period.

We added: “In this paper, we focus on the geochemical characterization of sediments from the upper part of ICDP core 5011-1, which spans MIS 6 to MIS 11. This interval encompasses great climatic variations from the maximum temperatures of the “super” interglacials
(MIS 11 and MIS 9) to the extreme cold of MIS 6 and MIS 8 (Melles et al., 2012; Matrosova, 2009; Lozhkin et al., 2013).”

It's also not clear how the chronology was derived. You may have to cite work in this compendium of papers.

We added:

“The age/depth model for the ICDP 5011-1 composite core is based on variations in several parameters including magnetostratigraphy and select sediment proxy data (Si/Ti, MS, TOC). The lake data were compared with, trends in the LR04 marine isotope stack (Lisiecki and Raymo, 2005) and curves of regional spring and summer insolation (Laskar et al., 2004) to achieve an age scheme for the El’gygytgyn record. See Melles et al. (2012) and Nowaczyk et al. (2013) for more details.”

Methods

Line 10. Using your numbers, I get about 1,000 samples should have some out of 2,000 cm of core sampled every 2 cm. This means there is about 60% core recovery? A scan of your profiles suggests that there is much less core loss than that. The upshot is that there should be more samples.

We specified as: “Sediments to be used in elemental analyses were taken at 2-cm intervals between 5.67 and 19.99 m of the composite core 5011-1 (Melles et al., 2011, 2012), yielding a total of 617 samples. Within this interval, deposits deemed to be the result of mass movement of slope sediments (Sauerbrey et al., 2013) were omitted (Wennrich et al., 2013b).”

Line 11. rock (not rocks)

Corrected

Line 12. Spectrometer (not spectrometers)

Corrected

Line 16. Can you write “layered with boric acid” rather than “layered with a boric acid base”? I am not qualified to review the technical parts of this paper

Corrected

Page 397, line 2, replace “achieved” with “determined”

Corrected

General: Detection limits should be provided in a table, and not included in the text.

We didn’t provide inorganic data in the Table format so we put detection limits in the text

Results

Should also include exogenic sources of sediment borne from Aeolian deposition. I can only imagine it gets pretty windy out there!

We changed the sentence as: “The geochemical characteristics of lacustrine sediments depend on many factors including the: 1) chemical composition of the provenance; 2) physical and chemical weathering processes in the catchment; 3) tectonic and eolian activity; 4) sorting during sediment transport and sedimentation; and 5) post-depositional diagenetic changes (e.g. Fralick and Kronberg, 1997).”

See also section 3.3. where eolian input discussed

The r2 data and Pearson coefficients are useful data to analyze. I also strongly recommend that you explore the structure of your data further using Principle Components Analysis. No doubt you will find
groups of elements that behave similarly. It should show the same kinds of things you have pointed out, but it goes a step further and shows the relatedness of all variables in one diagram (several kinds of plots are typically used). Using an analysis like this helps to identify the “best” pairs of elements for indicating changes in provenance and weathering. Perhaps you have already tried this and the results were too noisy to be of use! But it’s very easy to do: there are many “canned” stats programs that will run this with ease, such as SYSTAT or, easier still, the on-line program PAST.

We added the PCA data:

“Principal Component Analysis (PCA) was used to reduce the dimensions of a multivariate data set using the software program PAST (Hammer et al., 2001). This analysis was performed on a correlation matrix of major and trace elements, CIA, PIA, CIW, LOI, Rb/Sr, and magnetic susceptibility.

The first PC axis of the PCA results explains 40% of the total variance. It is positively correlated with Al\(_2\)O\(_3\), TiO\(_2\), Fe\(_2\)O\(_3\), MgO, Rb/Sr, CIA, PIA, CIW, Ni, and Cr and negatively correlated with SiO\(_2\). The second PC axis explains an additional 24% of the variability and is characterized by positive loadings of Ba, K, Rb, Sr, Na\(_2\)O, CaO, MS, and Sr. It is negatively correlated with P\(_2\)O\(_5\), MnO, and LOI. These results indicate the presence of three main data groups. SiO\(_2\) is clearly related to the super interglacial sediments, while Ba, K, Rb, Sr, Na\(_2\)O, CaO, MS, and Sr are related to the interstadial sediments. Al\(_2\)O\(_3\), TiO\(_2\), Fe\(_2\)O\(_3\), MgO, Rb/Sr, CIA, PIA, CIW, Ni, and Cr are associated with glacial sediments (Fig. 3 new).”

Page 398, line 15, then = than
Corrected

It might be useful to discuss enrichments of elements like SiO\(_2\) in terms of biogenic sequestration. The weathering of the volcanic rocks should bring into the basin dissolved silica, and this can either be bypassed and lost due to over flow, or captured (sequestered if buried in the sediment) by organisms, in this case diatoms.

We changed the text as:

“Maximum SiO\(_2\) values for the entire sequence were registered between 18.41–18.77 m and 15.77–16.11 m with peaks of 76.30% and 80.49%, respectively (Fig. 4). According to the age-depth model these horizons correlate to MIS 11.3 (424–390 ka) and MIS 9.3 (340–320 ka). The SiO\(_2\) enrichment in these zones is caused by elevated BSi and represents levels of high primary productivity in the lake (Cunningham et al., 2012; Vogel et al., 2013). The interval corresponding to MIS 11 exhibits the greatest peak in diatom concentrations (Snyder et al., 2013).”

Last line on pg 398 begins a sentence that is hard to follow. It would be very useful at some point to discuss the mineralogy of the sediments that you analyzed. This kind of information should be presented up front, rather than later on. The silica to aluminum ratio discussion is left (in my mind) a bit muddy because I’m not sure what phases these elements are in. You’ve mentioned biogenic silica, and that’s about it. What is the proportion of quartz to feldspar, for example? How much clay is there? The claims of “textural maturity” mean relatively little unless we know or can intuit what minerals will weather fastest.

We changed the text as:

“Large scale variations in the oxides SiO\(_2\) and TiO\(_2\) indicate a generally strong negative correlation (r = -0.74; Table 1). A strong linear correlation (R\(^2\) = 0.8) is especially valid for
samples from MIS 11.3 and 9.3 and less so for MIS 7.1 and 5.5, where SiO$_2$ exceeds 71% (Fig. 5a). These results indicate that BSi dilution is significant during the warmest interstadials. The linear correlation between SiO$_2$ and TiO$_2$ is very poor ($R^2 = 0.17$) in interstadial samples and is essentially nonexistent ($R^2 = 0.07$) for glacial sediments. This pattern suggests only negligible or no dilution of BSi (Fig. 5a) during cooler episodes in the El’gygytgyn record.

The SiO$_2$/Al$_2$O$_3$ ratio most resembles the SiO$_2$/TiO$_2$ ratio ($r = 0.89$; Fig. 6). SiO$_2$/Al$_2$O$_3$ ratios for interglacial and glacial sediments average 4.45 and 3.72, respectively, with a high linear correlation between SiO$_2$ and Al$_2$O$_3$ for interglacial sediments ($R^2 = 0.88$) and a poor correlation for glacial sediments ($R^2 = 0.26$; Fig. 5c).

A decrease in the SiO$_2$/Al$_2$O$_3$ ratio can be related either to a decrease in grain size or a lower textural maturity (e.g. Weltje and Eynatten, 2004). Von Eynatten et al. (2012) point out that mechanical processes, such as comminution, impact sediment composition. They further showed that increases in Al$_2$O$_3$ and decreases in SiO$_2$ concentrations occur with finer grain sizes. Thus, the low SiO$_2$/Al$_2$O$_3$ in the Lake El’gygytgyn data combined with an absence of Al$_2$O$_3$ dilution by BSi indicate that the glacial sediments consist of more fine-grained material as compared with either interstadial or interglacial sediments. This conclusion is supported by grain-size analysis which shows higher clay to fine silt content during glacial times (Francke et al., 2013). In contrast, a higher mean SiO$_2$/Al$_2$O$_3$ ratio of 4.70 obtained from bedrock samples of the Pykarvaam and Ergyvaam Formations indicate the lower maturity of the fresh rocks as compared to the lake sediments.”

But we didn’t study mineralogy of the sediments

Page 399, Section 3.1.2
The lead paragraph is bit misleading? The papers that I recognize are based on lacustrine systems that are much different that Lake E. If there is a study that has a similar setting, perhaps you could highlight that one, and discuss the similarities.

We changed paragraph as: “In lacustrine environments, Ti and Al have been shown to be good measures of the intensity of detrital input (e.g. Whitlock et al., 2008).”

Can you subtract out BSi from your analyses of Al vs silica? The results might lead to more meaningful data regarding relative weathering during glacial and interglacial.

We can’t subtract out BSi from total SiO$_2$ contents. But we point out that “The glacial/interstadial and interglacial samples, with the exception of those from the super interglacials, display a strong positive correlation between SiO$_2$/TiO$_2$ and Al$_2$O$_3$/TiO$_2$ ratios ($R^2 = 0.73–0.75$, Fig. 5a, 6). In intervals where fluctuations in the Al$_2$O$_3$/TiO$_2$ and the SiO$_2$/TiO$_2$ ratios coincide, the dilution of TiO$_2$ and Al$_2$O$_3$ by BSi is absent or negligible (Fig. 6).”

What mineral is the source of Ti? Ilmenite? It’s a common constituent in volcanic rocks. Its also magnetic, and your MS data may be able to correlate high Ti with high MS (but a certain kind that measures moments from coarser grains).

We have discussed this in subsection:

“Fe and Ti are the main elements in ferromagnetic minerals found in oxides, such as magnetite and titanomagnetite. In Lake El’gygytgyn sediments, the majority of the iron oxides are titanomagnetites that include Al, Si, and Mn impurities. Some titanomagnetites have characteristic cracks in the grains, which indicate low-temperature maghemitization. Other titanomagnetites are oxidized at high-temperatures, displaying lamellae of ilmenite and titanium magnetite. Chromite, ilmenite, and rutile also were found in the sediments.
To investigate the Fe and Ti mineralogy in Lake El’gygytgyn sediments, we examined the correspondence of both elements to various magnetic parameters. During glacial periods, sediments exhibit high Fe$_2$O$_3$ and TiO$_2$ but low MS; interglacial samples display the opposite pattern. Consequently, data on the Fe$_2$O$_3$–MS and TiO$_2$–MS diagrams show a scattered distribution (Fig. 7a, b) with low negative correlation coefficients (r) of -0.28 and -0.43 for Fe$_2$O$_3$ vs. MS, and TiO$_2$ vs. MS, respectively. This contradicts the idea that Ti and Fe were enriched in the detrital heavy-mineral fraction, which is mirrored by a generally positive correlation of TiO$_2$ and Fe$_2$O$_3$ to MS (e.g. Ortega et al., 2006; Parker et al., 2006; Reynolds et al., 2006; Vegas et al., 2010). MS includes both ferrimagnetic and paramagnetic components that can be distinguished by determining the induced magnetization. TiO$_2$ and Fe$_2$O$_3$ yield only a very poor correlation to the ferromagnetic component ($J_f$) (Fig. 7c, d), but a strong correlation to the paramagnetic component ($J_p$) of induced magnetization (Fig. 7e, f). Hence, high TiO$_2$ contents in the glacial-age samples can not be attributed to titaniferous minerals such as titanomagnetite, rutile, or ilmenite, which are typically found in lake sediments. These minerals would evoke a positive correlation of TiO$_2$ (Fe$_2$O$_3$) to MS and $J_f$. Most Ti and Fe, especially during cold intervals, should be concentrated in paramagnetic Fe- or Ti-bearing minerals. These minerals include chlorite (Mg$_{3.5}$Fe$_{1.5}$Al$_3$Si$_3$O$_{14}$), with Fe and Mg acting as the main elements (Boyle, 2002), or biotite. The importance of chlorite as a primary iron carrier in glacial sediments is indicated by the positive correlation of TiO$_2$ to MgO ($r = 0.83$) and Fe$_2$O$_3$ to MgO ($r = 0.65$). This conclusion is supported by a study of clay minerals deposited in Lake El’gygytgyn over the past 65 ka. This analysis indicated that cold stages typically are enriched in chlorite (Asikainen et al., 2007).”

We didn’t study chemical composition of chlorite.

Page 400, line 2, seams = seems
Corrected

Line 18, intense = relatively intense. Weathering at this latitude is going to be very slow, so using an adjective like “intense” can be misleading.

We changed the paragraph as: “The TiO$_2$/Al$_2$O$_3$ (or Al$_2$O$_3$/TiO$_2$) ratio often has been used as an indicator of sediment provenance, but it also is a good measure of the degree of sediment alteration (Migdisov, 1960; Young and Nesbitt, 1998; Yudovich and Ketris, 2011). The TiO$_2$/Al$_2$O$_3$ ratio in the El’gygytgyn samples averages 0.037 and 0.045 in warm-stage and cold-stage sediments, respectively, and 0.032 in unweathered volcanic rocks. The Al$_2$O$_3$ vs. TiO$_2$ diagram shows a rather straight, linear trend for interglacial sediments ($R^2 = 0.55$), whereas cold sediments have a scattered, nearly vertical distribution ($R^2 = 0.24$) (Fig. 5e). We suggest that the higher TiO$_2$/Al$_2$O$_3$ ratios observed in glacial sediments are due to an enrichment in TiO$_2$ in the finer-grained sediments, as mentioned above. It may relate to the concentration of biotite as noted by Young and Nesbitt (1998) for Baffin Island sediments.”

Page 401. This page is difficult to follow partly because its hard to go from the text to the figures. The discussion about Ti in chlorite is interesting, but is hard to follow and hard to justify since there is no discussion about the phases (minerals). If there is chlorite, where is it coming from? In most cases I’m aware of, Ti often substitutes for Fe, and might comprise about 1% of the rock as an oxide, but the rocks are typically low-grade metamorphic rocks.

See above
Page 401, first sentence under 3.1.3. First sentence should read "Phosphate and manganese oxide concentrations have a relatively strong linear relationship ($r = 0.55$)."

Corrected

Line 25 – depth = depths, but I strongly recommend not listing the various depths: : :it’s a long (perhaps tedious) list, that perhaps would be better presented in a figure.

Corrected as “Peaks in $\text{P}_2\text{O}_5$ and MnO occurred in the early parts of cold stages (MIS 8.4, 7.4, 6.6, 6.4, and 6.2) with a single exception (18.85–18.39 m) that corresponds to the super interglacial MIS 11.3 (Fig. 4).”

Page 409, lines 2 and 3; replace “be the main drivers” with “control rates of”, and delete “rates in watersheds” on line 3

Corrected

Line 4, delete “rather”

Corrected

Line 5, insert “reconstruction of “before “maximum”

Corrected

Tell us how much warmer and wetter this period was compared to the mean Holocene instead of just say “higher than those” (line 6)

We changed the text as:

“Surprisingly, sediments from the super interglacial MIS 11.3 exhibit low weathering indices as compared to glacial sediments. Furthermore, weathering indices for MIS 11.3 are lower than Holocene values, even though the super interglacial was considerably warmer and wetter than the Holocene. That is, maximum summer temperature and annual precipitation of ~4°C to 5°C and ~300 millimeters, respectively, were reconstructed for MIS 11.3, whereas the mean temperature of the warmest month and mean annual precipitation during the Holocene thermal optimum were only ~1° to 2°C and ~50 mm higher than today (Melles et al., 2012). “

Line 10. Next two paragraphs. Reorganize and rewrite. If you are trying to convince the reader of something, start out with what you believe, and then follow with justifications, then caveats and less favored explanations. This is suggested because you want to be clear to your reader. I suggest starting this section “The greater surface area to volume ratio of clay particles probably accounts for the greater values of weathering indices for glacial versus interglacial lake sediment. (provide textural data, if you have it, rather than just descriptions). (The description of the various facies is OK, but diagrams would be better, especially if they are plotted with the indices). (It might be instructive to add a grain-size ratio to your multivariate analysis: : : you might find correlation among fine-grained sediment and particular elements, which of course are tied to mineralogy)."

Line 10. When you do your rewrite, keep in mind that glacial and interglacial are nouns: : : you treat them as adjectives in some places. You can fix this problem by simply adding “sediment” : : : then sediment is the noun, and gl and intergl are adjectives.
The argument that you make for no Aeolian input is not very strong if the composition of the loess or other Aeolian particles is the same or nearly the same. It seems strange that there would be very little dust falling into a large lake like Lake E especially with active glaciers all around (albeit not that close). The far distance from loess/dust sources indicate that the grain size of the Aeolian component might be quite small.

Line 29, tell us what kind of chlorite: : : there are several kinds, each with different compositions. I assume that Lake E chlorites are Fe and Mg-rich. But not all chlorites are.

Page 410. It took me a long while to sort out what was being said on this page. Start out a paragraph with a topical sentence, and then provide supporting discussion/data. The great amount of clay in
glacial sediment is a puzzlement given that the watershed was never glaciated. The bottom paragraph on pg. 410 reveals "the answer", and this should be presented at the beginning of the discussion. If I understand the argument, the finer-grained sediment is attributed to (year-round?) anoxia (due to year-round ice-cover?): : : the anoxia leads to dissolution of iron-bearing minerals (a well known phenomenon among folks who work with magnetic susceptibility), but apparently can lead to dissolution of silicate minerals as well. I would imagine this process would attack glassy or otherwise poorly crystallized volcanic rock fragments should they make their way into the lake. It would seem to me that SEM analysis of mineral particles might reveal if this process is actually occurring. I wonder if the process is bacterially mediated like many reactions involving magnetic minerals. It would also be interesting to pursue this: : : I have been working with sediment that were deposited under seasonally anoxic conditions: : : does this reduction of grain size occur at a fast-enough rate so that it can significantly alter grain-size distribution data? Obviously this occurs with magnetic minerals, but they make up only a small party of the mineral assemblage. If all feldspars, for example, are quickly irradiicated under anoxic conditions, this would be news (I think: : :!). The material in bold above should be presented at the beginning of this section. A lot of the rest of the discussion seems not necessary.

We have reorganized and rewritten this section as:

"3.3.Geochemical indices as proxy for environmental changes"

Geochemical indices commonly differ between glacial and interglacial intervals, suggesting that conditions in cold and warm periods exerted distinct influences on the sedimentary record. For example, glacial sediments show high values of CIA, CIW, Rb/Sr, Ba/Sr, LOI depleted by potassium, sodium, calcium, and strontium. Thus, these characteristics should be helpful in differentiating glacial and interglacial in the El’gygytgyn record.

Chemical weathering generally is considered to increase in warm and wet climates, although this process can also be active under cold climatic conditions (e.g. Darmody et al., 2000; Hall et al., 2002). Nonetheless, temperature and precipitation have been shown to be strong controls on the rates of chemical weathering (e.g. White and Blum, 1995).

Surprisingly, sediments from the super interglacial MIS 11.3 exhibit low weathering indices as compared to glacial sediments. Furthermore, weathering indices for MIS 11.3 are lower than Holocene values, even though the super interglacial was considerably warmer and wetter than the Holocene. That is, maximum summer temperature and annual precipitation of ~4°C to 5°C and ~300 millimeters, respectively, were reconstructed for MIS 11.3, whereas the mean temperature of the warmest month and mean annual precipitation during the Holocene thermal optimum were only ~1°C to 2°C and ~50 mm higher than today (Melles et al., 2012).

Hence, a simple application of chemical indices for inferring chemical weathering intensity within the El’gygytgyn catchment will be incorrect. Below we discuss and evaluate four scenarios that might account for the differences between chemical indices observed in the glacial and interglacial sediments from Lake El’gygytgyn.

1. Grain-size is considered an important factor that can influence the expected relationship between sediment composition and geochemical indices (e.g. van Eynatten et al., 2012). In the El’gygytgyn sediments, sand content does not exceed 15.5%, and the average silt and clay contents are ca. 69.2 and 27.7%, respectively. Mean grain size varies between 2.5 μm and 9.3 μm and is higher in interglacial sediments (Franke et al., 2013). Geochemical data from volcanic rocks and sediments show a strong dependence of geochemical indices and granulometry. Volcanic rocks and impactites display the lowest values of CIA, PIA, and CIW. In finer sediments, the values of geochemical indices increase (Fig. 9). To further investigate the dependence of geochemical data and grain-size in the El’gygytgyn record, one sample from MIS 7 was separated into two size fractions (<40 μm and > 40 μm). The < 40
µm fraction (90% of the total sample weight) is depleted in CaO, Na₂O, and K₂O and displays higher CIA (64.58), PIA (70.18) and CIW (74.97) indices as compared to the coarser size fraction. The values of CIA, PIA and CIW for >40 µm fraction (10% of sample weight) are 57.15, 60.21, and 67.22, respectively. Cold and warm periods experienced different sedimentological regimes. A perennial ice cover on the lake during peak glacial times restricted the transport of coarse-grained, less-altered sediments to the basin. However, this situation enabled finer particles to be transported to the center of the lake through cracks in the ice or through the formation of moats around the shore during summer (Asikainen et al., 2007). During interglacials, the greater precipitation would have increased the transport energy of streams draining into the lake that in turn, would carry coarser clastic material to the basin. Additionally, the longer ice-free period combined with wind-induced lake currents would result in a greater redistribution of clastic material within the basin (Francke et al., 2013). Asikainen et al. (2007) noted that chloride is the typical clay mineral in glacial sediments, whereas smectite and illite are more abundant during interglacials. An abundance of chlorite would increase certain geochemical indices; for example, the CIA and CIW for chlorite is 100 (Nesbitt and Young, 1982; Fedo et al., 1995).

2. Variations in the sediment geochemistry between glacial and interglacial periods can be caused by changes in sediment provenance. However, this explanation can be excluded in the case of Lake El’gygytgyn, because it is a closed basin with a very restricted watershed that is bordered by a distinct crater rim (Fig. 1). The highly altered material found in the El’gygytgyn record possibly was transported by eolian processes, originating in remote regions. Fedorov et al. (2012) showed that streams are the major agents for carrying clastic materials to the basin during spring and summer under modern climate condition. Total eolian supply amounts to only 4–5% of the total sediment input. Prevailing local winds on the lake are from the north and south. They are strong and persistent, and this likely plays an important role in controlling lake shape (Nolan et al., 2007). Past wind direction was likely the same. Today large areas of eolian sediment are absent in the El’gygytgyn catchment and in areas immediately to the north and south of the lake. In other regions of Chukotka and in Yakutia, silt-dominated Pleistocene sediments are widespread. They are associated with ice-rich permafrost and are referred to as ice complex or yedoma deposits. There are different explanations for the origin of the ice-complex sediments, including an eolian genesis (Tomirdiaro and Chernen’ky, 1987). Geochemical data of the ice-complex are available from the Anadyr River to the south of the lake and along the Arctic lowlands to the north (Tomirdiaro, 1974; Tomirdiaro and Chernen’ky, 1987). As part of our analysis, we compared the geochemical data from the predominant volcanic rocks and pebbles and from lake and ice-complex sediments. On the ternary Al₂O₃-(CaO+Na₂O)-K₂O and CaO-(Al₂O₃-K₂O)-Na₂O diagrams, the various El’gygytgyn data plot parallel to the (CaO+Na₂O)-Al₂O₃ and Na₂O-(Al₂O₃-K₂O) axes, respectively, clearly indicating local volcanic rocks to be the major source of clastic material deposited on the lake floor. In contrast, the ice complex data form a separate group on the diagrams. These results suggest that any eolian input into the lake during glacial intervals must have been derived from the product of local weathering products of the volcanic rocks. This scenario is unlikely.

3. During the warm and wet interglacials, the chemical weathering was increased and as result the surface waters were enriched in mobile elements, such as Ca, Na, K, and Sr. The consequent increase in stream and overland water flow into the lake resulted in a higher total content of these elements in the lake sediments. In this case, low values of CIA, PIA, CIW, and Rb/Sr reflect the high degree of chemical weathering. A similar scenario has been suggested for the Heqing paleolake basin (An et al., 2011), Daihai Lake (Jin et al., 2001), and
Barkol Lake (Zhong et al., 2012). However, Lake El’gygytgyn is extremely oligotrophic, meaning that the water is low in anions and cations (< 1 mg l\(^{-1}\)) and has a low conductivity based on measurements carried out in May (prior to snow melt) and in August (following snow and ice melt and subsequent lake water) at Lake El’gygytgyn (Cremer and van de Vijver, 2006). Therefore, dissolved Ca\(^{2+}\), Na\(^{+}\), and K\(^{+}\) contributed only slightly to the total contents of these elements in the sediments. In contrast, at Barkol Lake the water content of Ca, Na, and K was – 444.8 mg l\(^{-1}\), – 62089.39 mg l\(^{-1}\), and – 1117.35 mg l\(^{-1}\), respectively (Zhong et al., 2012). Thus, this scenario is also unlikely to explain the El’gygytgyn patterns.

4. Diagenetic processes can obscure the detrital geochemical signals. Glacial facies at Lake El’gygytgyn supposedly accumulated under anoxic bottom-water conditions (Melles et al., 2007, 2012), resulting in the dissolution of magnetic minerals (Nowaczyk et al., 2007). The formation of authigenic vivianite, Fe-Mn aggregates, pyrite, and greigite indicates a strong post-depositional alteration of sediments during anoxia. This process can also lead to the partial dissolution of silicates, which is accompanied by a loss of cations as was reported for Sea of Okhotsk sediments (Wallmann et al., 2008). A similar cation depletion in anoxic glacial sediments might explain the high indices of CIA, CIW, and PIA. However, additional mineralogical investigations are required to confirm such a scenario.

In summary, our data indicate that geochemical indices and selected elemental ratios mirror sedimentation conditions and, possibly, diagenetic processes that are triggered by environmental and climate changes during glacial and interglacials.

Page 411
Delete “Obtained data indicate”. Start with “Our”. It seems that the “controlling mechanism” is anoxia, and should be mentioned in the concluding statement of this section.
Corrected

Section 4.
First paragraph. This would be much more effectively presented as part of a figure. Just point out the substages in a figure, then you don’t need the first paragraph. You may already have.
We have shown the substages on figures

Line 11. Why are you pointing out the vivianite and the ice-rafted sand grains? This is a discussion, so you should, perhaps, make an interpretation (about the vivianite and sand), and then back it up with evidence.

Line 14. Again, you are giving us evidence for something, but not directly telling us what the interpretation is. Presumably the higher BSi levels are related to higher paleoproductivity (in Lake Baikal and Lake E). Start out a section with this interpretation, and follow it up with the evidence. If the special issue that this chapter belongs to has an article about diatoms, you may want to cross-reference your data. The diatom article will, no doubt, make use of a BSi curve.

Line 18. This paragraph needs rethinking and reorganization. What are your points about this paragraph? Clearly it needs to be broken up into at least two paragraphs. You need to tell us your interpretation first. “High BSi values indicate relatively high paleoproductivity during deposition of SS 11.3, especially in the middle. The high silica values mute the concentrations of other elements (list), but, curiously?, values of LOI, Cr and Ni are abnormally high. (do you have an explanation for this?)”

Page 412. Very interesting material, but again, I suggest that you reorganize the paragraph so your interpretation is given first. The reader will have a much easier time digesting all of this information, and that is what we are striving for. Start a paragraph pointing out alternating anoxic and oxic conditions are indicated by , and perhaps go beyond this and tell us why this is important. I would think that this signature could be attributed to ice-cover vs. ice-free conditions, and indicates high climatic variability.
4. Geochemical zonation

Down-core changes in major and trace elements and in elemental ratios display a strong geochemical zonation that corresponds to marine isotopic stages (Fig. 4, 6). The samples analyzed in this study represent a wide range of climate conditions, varying from the climatic optima of MIS 11 and MIS 9 to the frigid glacial environments of MIS 6, MIS 8, and MIS 10 (Lozhkin and Anderson, 2013; Lozhkin et al., 2013). Vegetation types present during MIS 11 indicate greater summer warmth and annual precipitation as compared to modern (Lozhkin and Anderson, 2013; Melles et al., 2012, Tarasov et al., 2013). Pollen-based reconstructions of mean temperatures for July and January were +12 to 16°C and -20 to -24°C, respectively, and mean annual precipitation was ~550 to 600 millimeters. The following interglacials and interstadials were cooler in comparison to MIS 11, and sediment data show a decreasing trend in SiO$_2$. Mean summer temperatures during MIS 9.3 ranged from +12 to 14°C (Lozhkin et al., 2013). Simultaneously, sediments of MIS 9.3 contain less SiO$_2$ as compared to MIS 11 (Fig. 4). During MIS 7 mean July temperature was +2.4°C (Matrosova, 2009), and the warm substages of MIS 7 display low concentrations of SiO$_2$. During glacial intervals, mean July and January temperatures were +2 to 3°C and -24 to -25°C, respectively (Matrosova, 2009). Glacial sediments are characterized by the highest content of TiO$_2$, Fe$_2$O$_3$, and MgO and by the lowest values of SiO$_2$ (Fig. 4). Below we give a detailed description of MIS 11 and MIS 7.4 sediments, which represent the warmest and coldest stages within the core interval reported here.

4.1 Geochemical structure of MIS 11

MIS 11 is known to be the warmest and longest interglacial interval of the past 500 ka (e.g. Howard, 1997) and has been subdivided into several substages: 11.1, 11.22, 11.23, 11.24, and 11.3 (Bassinot et al. 1994). On the basis of the El’gygytgyn geochemical data, however, stage 11.3 can be further divided into three zones (Fig. 10), each representing different sedimentation conditions. The lower zone (zone a; 428.4-418.7 ka) is transitional between MIS 12 and MIS 11 and marks the initial warming. This zone is characterized by gradual increases in SiO$_2$, Na$_2$O, K$_2$O, CaO, and Sr, and decreases in TiO$_2$, Al$_2$O$_3$, MgO, Fe$_2$O$_3$, LOI, CIA, and CIW as characteristic of all warm stages. At this time, the lake had a semipermanent ice-cover, lake waters were mixed, and more coarse material was supplied to the center of the basin. In the earliest stages of warming, anoxic conditions probably still existed on the lake bottom, resulting in favorable circumstances for the formation of large vivianite nodules (Fig. 10). During the spring, the lake supported a thick ice-cover, but active snow melt caused a significant amount of debris to be carried by streams and deposited on the surface of the ice (Fedorov et al., 2012). As visible in large amounts of rock fragments (Fig. 10), coarse-grained sand and gravel are supposed to be delivered to the center part of the lake by ice-floes. Zone a is characterized by a distinct peak in the geochemical data. These curves resemble both the distribution of biogenic silica in Lake Baikal (Prokopenko et al., 2006, 2010) and the temperature reconstructions derived from Antarctic ice-cores marked as event 11.33 (Spahni et al., 2005). The similarity in trends from such distant sites argues for the influence of global forcings on these records.
The middle zone (zone b; 418.7-401.1 ka) of substage 11.3 exhibits a sharp increase in SiO$_2$ owing to a pronounced BSi maximum (Melles et al. 2012). This increase represents high bioproductivity during the sediment deposition. A simultaneous drop to minimum values in TiO$_2$, Al$_2$O$_3$, and MgO, and lesser but significant decreases in Na$_2$O, CaO, K$_2$O, Rb, Sr, Zr, and Ba, can presumably be traced to dilution by high amounts of biogenic silica. On the other hand, values of LOI markedly increase during zone b, an increase which is common during glacial intervals. High LOI reflects enhanced primary production and incomplete decomposition of organic matter in the oxygenated bottom water. A few peaks in Cr and Ni occur in this zone. However, they do not coincide with those of other elements, and further detailed mineralogical investigations are needed to explain this pattern. Our data indicate that during zone b, the warmest period of substage 11.3, sedimentation conditions in the lake varied. The sharp parallel variations in P$_2$O$_5$, MnO, and Fe$_2$O$_3$ in zone b are underscored by high correlation coefficients of 0.93, 0.86, and 0.94 for P$_2$O$_5$/MnO, Fe$_2$O$_3$/MnO, and Fe$_2$O$_3$/P$_2$O$_5$, respectively. These elements are typically contained in fine-grained vivianite, whose presence in the El’gygytgyn samples was verified by examination of smear-slides. In contrast to glacial sediments, vivianite nodules > 0.25 mm do not occur in zone b. The curve of high SiO$_2$ exhibits a saw-toothed pattern and is out of phase with the P$_2$O$_5$, MnO, and Fe$_2$O$_3$ curves (Fig. 10). This relationship is clearly shown by a highly negative correlation coefficient of -0.50 between SiO$_2$ and Fe$_2$O$_3$. Furthermore, numerous peaks in Fe$_2$O$_3$ and corresponding maxima in the MnO/Fe$_2$O$_3$ ratio indicate these levels are associated with reducing environments. These data suggest that the laminations observed in the MIS 11.3 sediments were formed by alternating layers of: (1) biogenic sediments greatly enriched in SiO$_2$ that were deposited on the lake bottom under oxidizing conditions; and (2) sediments that were less enriched in SiO$_2$ but still contained abundant Fe, P, and Mn which probably formed under anoxic conditions. Even in the oxidized horizons, MS is low, presumably because of the dilution of magnetic minerals by BSi. However, in contrast to the low MS minima in anoxic glacial sediments, the low paramagnetic component of magnetization indicates the dissolution of magnetic minerals was negligible. Zone b lacks a coarse-grained component (e.g., sand or gravel), which implies only minor ice-floe activity occurred at that time. The alternation of oxic and anoxic horizons suggests that when anoxic condition occurred at the water-sediment interface bioproductivity was high. This increase probably reflects the presence of favorable, highly oxygenated conditions in the middle and upper parts of the water column and increased decomposition of organic matter on the lake bottom. The uppermost zone of substage 11.3 (zone c; 401.1-395.5 ka) represents decreasing biological productivity. It also is characterized by a gradual decrease in SiO$_2$ and LOI, and a simultaneous increase in TiO$_2$, MgO, Fe$_2$O$_3$, Al$_2$O$_3$ and other elements. Furthermore, there is an absence of P$_2$O$_5$ and MnO peaks, vivianite nodules, and coarse sediments. Finer-grained sediments progressively increase up-core, but the record does not display any sharp changes in sedimentation. In the upper part of MIS 11 (depth 18.07-17.11 m), the accumulation of biogenic silica was insignificant, although sedimentation conditions were variable. The SiO$_2$ content ranges between 66.92 and 69.97% (mean 68.65%) and exhibits only minor fluctuations. However, the TiO$_2$ curve displays four distinct minima at depths of 17.87 (392.1 ka), 17.73 (389.1 ka), 17.61 (385.7 ka), and 17.29 (373.4 ka) m. These depths correspond to peak values in CIA, PIA, and CIW. The common occurrence of coarse sand and gravel in substage 11.2 might indicate enhanced ice-floe activity.
Page 413. Start this paragraph “The lowest BSi values, reflecting the lowest paleoproductivity, occurred during interpreted MIS 6.6. and 7.4. These zones also have relatively high values of Ti: etc., suggesting biogenically mediated diagenesis of transition metals and organic matter under anoxic conditions”. Then give details as you see fit.

We have reorganized this paragraph


Line 2 – stages 6-11 are not the “last 500,000 yrs”. I don’t know if this will be covered in another chapter, but your paper should stand alone in terms of presenting evidence critical to your interpretations. So there are two things you need to do early on: : : what is the basis for “glacial” and “interglacial”? It doesn’t appear to be the data you present on its own merit. Your data can support the glacial vs. interglacial interpretation. But please indicate the basis upon which these basic and essential distinctions are made. Second, what is the chronology based upon? Do you have tephrochronology? Magne-tostratigraphy? I wouldn’t necessarily just cite a chapter or paper, but provide at least rudimentary information to the reader about what the timeframe is based upon.

Last paragraph: : : you also attributed the loss of mobile elements to diagenesis of silicate minerals, and creation of somewhat finer-grained material: : : I thought that was a fascinating suggestion which could be backed up by SEM work on grain surfaces (searching for evidence of chemical erosion).

We changed the Conclusion as:

“The inorganic geochemistry of Lake El’gygytgyn sediments indicates distinct down-core variations in elemental composition over the past ca. 125-430 ka. The correspondence of these variations to glacial and interglacial periods is based on complementary biological and geochemical indicators. Interglacial sediments show high content of SiO₂, Na₂O, CaO, K₂O, and Sr but low values for Al₂O₃, Fe₂O₃, TiO₂, and MgO. Glacial sediments, in contrast, exhibit opposite trends. Peaks in P₂O₅ and MnO coincide with an increased abundance of fine-grained vivianite, which indicates times of dominating reducing conditions in the sediment and/or bottom waters. Super interglacial stages 9.3 and 11.3 are enriched in SiO₂ due to the increased flux of biogenic silica, a reflection of maximum diatom production. The geochemical structure of MIS 11 shows very similar characteristics that have been documented in similar-age records from Lake Baikal and Antarctica. Among the glacials substages, MIS 7.4 and MIS 6.6 are the most marked. They are characterized by the lowest SiO₂ values, suggesting low or absent diatom productivity, and very high TiO₂, Fe₂O₃, MgO, Al₂O₃ and Zr. Peaks in Fe₂O₃ coincide with high MnO/Fe₂O₃ ratios, indicating reducing condition in the sediments and/or bottom water.

Geochemical indices and some elemental ratios indicate a higher alteration of glacial sediments as compared to interglacial sediments accompanied by a depletion of mobile elements, such as Na, Ca, K, and Sr. This alteration might be caused by the sedimentation regime and/or post-depositional diagenetic processes.”

Tables.

Table 1. “Pearson correlation coefficients for : ”

Corrected

Figures.

Figure 1. It would make it much easier for the reader if you gave a lithologic synopsis for each geological unit. Then there would be no need to reiterate this information in the text.

We did

The latitude line for 67”30” is missing, probably because it conflicts with other labels. I suggest placing tick marks for lat long on the periphery of the figure.

In a heavy line, provide an outline of the watershed.
We corrected and added the watershed line

Figure 3. I sure hope that this is published so that its easier to read!! This is a good reason to do the multivariate analysis!

Figure 4. Same comment as above.

For Figures 3 and 4, I think that a plot of age should be provided, not just depth and MIS. I suggest plotting age next to depth. Or at the very least, provide an age-depth model.

We added additional figure of PCA;

We added the ages to depth on figures 3 and 4 (now 4 and 6) as well as lithofacies

Figure 7. I do not see any arrows.

Corrected

Figures 8 and 9: : : nicely presented!

Thank you

Interactive comment on “Inorganic data from El’gygytgyn Lake sediments: stages 6–11” by P. S. Minyuk et al.

Anonymous Referee #2

Received and published: 2 April 2013

This manuscript attempts to present a data set of inorganic geochemical analyses of sediments from a selected time interval in Lake El’gygytgyn cores. The data set itself appears to be valid and valuable. Some of the ideas related to the data are also interesting. For example, the observation that samples from the glacial intervals are more depleted in mobile elements than those in interglacial is interesting and surprising, despite never being clearly explained. However, the discussion is wandering, incomplete, and deeply flawed scientifically, and it is nearly unreadable. Overall, I cannot recommend it for publication. Even making allowances for the fact that the authors’ first language is not English, the manuscript is in poor shape. Almost half the sentences have grammatical errors, commonly involving misuse of articles; agreements among subjects, objects, and verbs; and verb tense. Beyond grammatical problems, ideas are poorly expressed or are expressed in language that is idiomatically incorrect. For example, in the title, what are “inorganic data?” – presumably this means inorganic elemental analyses of sediment geochemistry. And “sand and gravel that are supposed to be formed by ice-rafting” does not idiomatically mean what is intended. Many of these problems could be greatly improved by a thorough editing, but much of the discussion is unfocussed and poorly organized, which cannot be easily fixed.

Perhaps the biggest weakness of the paper is that the differences in geochemistry between the glacial and interglacial intervals are never adequately explained. The paper argues convincingly that neither differential weathering nor different source area are sufficient to explain the observations. Grain-size effects and diagenetic processes are offered as alternatives, but clear explanations of how these factors would produce the observed geochemical differences are not given.

A few specific comments and questions will illustrate the level of problems with the manuscript. This is by no means a complete list.

We have edited the text, reorganized of the MS and changed the title of MS as:

“Inorganic geochemistry data from Lake El’gygytgyn sediments: marine isotope stages 6–11”
1. Why was the interval from MIS 6 to 11 chosen? As the penultimate interglaciation, the absence of MIS 5 is especially troubling. This choice seems quite fundamental, but is never mentioned.

In the Introduction we refined:

“In this paper, we focus on the geochemical characterization of sediments from the upper part of ICDP core 5011-1, which spans MIS 6 to MIS 11. This interval encompasses great climatic variations from the maximum temperatures of the “super” interglacials (MIS 11 and MIS 9) to the extreme cold of MIS 6 and MIS 8 (Melles et al., 2012; Matrosova, 2009; Lozhkin et al., 2013).”

2. P395:7-9. No units are given with the water chemistry.

Corrected

3. Two different XRF methods were used to analyze for major and minor elements, yielding data that are expressed in weight percentages and parts per million, respectively. I suppose this is sufficient for comparison purposes, but it would have been nice if the analyses were recalculated to a common scale and if there were some discussion of this.

We left ppm units for rare elements since these units are most often used in the literature.

4. Sec. 3.1.1. Because biogenic silica is such an important component of the sediments, it is absolutely essential that the published BSi data be plotted along with the other geochemical data, including SiO₂ and Si/Ti in Figures 3, 5, 7, and 9. The dilution effect of BSi is mentioned in passing several times, but in reality, it has a major effect on all of the data, and it is never discussed in a coherent way.

We agree that dilution effect of BSi has effect on all of the data. But we point out that dilution is significant only for warmest interglacials.

For example:

“Large scale variations in the oxides SiO₂ and TiO₂ indicate a generally strong negative correlation (r = -0.74; Table 1). A strong linear correlation (R² = 0.8) is especially valid for samples from MIS 11.3 and 9.3 and less so for MIS 7.1 and 5.5, where SiO₂ exceeds 71% (Fig. 5a). These results indicate that BSi dilution is significant during the warmest interglacials. The linear correlation between SiO₂ and TiO₂ is very poor (R² = 0.17) in interstadial samples and is essentially nonexistent (R² = 0.07) for glacial sediments. This pattern suggests only negligible or no dilution of BSi during cooler episodes in the El’gygytgyn record (Fig. 5a).”

or:

“…Rb is in general negatively correlated to Zr (r = -0.66), except in sediments from super interglacial stages 9.3 and 11.3 when both elements exhibit a parallel distribution presumably due to dilution by extremely high BSi values.”

5.P398:20-25. There is no mention of the complications involved with BSi, such as volcanic amorphous silica or non-diatom productivity. Presumably these are covered by Melles et al. (2012).

Our goal was not to study the mineralogy of bedrocks or sediments or amorphous silica. So we have no data on inorganic amorphous silica concentrations in the sediments. But we agree that it is necessary to take into account the concentrations of volcanic amorphous silica that according to (Bely and Belaya, 1998) occur in volcanic rocks of the El’gygytgyn area. We do not know sponges from Lake as well as phytolites from vegetation. But there is a positive correlation between Si/Ti of sediments from super interstadials and total diatoms (=productivity) (Snyder et al., 2013).
The original use of Si/Ti as an index of biogenic silica was in Lake Malawi (Brown et al.), which is not referenced.

We referenced:

“The Si/Ti ratio is positively correlated with biogenic silica. This ratio has been previously used as a relative indicator of the biogenic component in sediments of Lake Malawi (Brown et al., 2007), Lake Baikal (Tanaka et al., 2007), and Lake El’gygytgyn (Melles et al., 2012). “

After discussing Si/Ti, the text switches to SiO₂/TiO₂, which should be similar, but which is not the same.

We agree – similar. And our analysis is quantitative analysis.

6. P399:1-5. I don’t understand most of this paragraph. The difference in correlation between Si and Ti in glacial and interglacials is interesting, and it may mean that BSi dilution is only significant in the warmest of the interglacials.

Yes: “… results indicate that BSi dilution is significant during the warmest interglacials. The linear correlation between SiO₂ and TiO₂ is very poor (R² = 0.17) in interstadial samples and is essentially nonexistent (R² = 0.07) for glacial sediments. This pattern suggests only negligible or no dilution of BSi during cooler episodes in the El’gygytgyn record (Fig. 5).”

However, I don’t know how to interpret the correlation between SiO₂/TiO₂ and TiO₂/Al₂O₃. The most stable element is in the denominator of the first ratio and the numerator of the second. The discussion of this relationship being due to alteration of sediment is not only vague, it seems simplistic.

We changed the figure 5 (now figure 6) where was used Al₂O₃/TiO₂ instead TiO₂/Al₂O₃ and we point out:

“The glacial/interstadial and interglacial samples, with the exception of those from the super interglacials, display a strong positive correlation between SiO₂/TiO₂ and Al₂O₃/TiO₂ ratios (R² = 0.73–0.75, Fig. 5a, 6). In intervals where fluctuations in the Al₂O₃/TiO₂ and the SiO₂/TiO₂ ratios coincide, the dilution of TiO₂ and Al₂O₃ by BSi is supposed to be absent or negligible (Fig. 6).”

7. P399: 10-12. An assumed relation between grain size and geochemistry is referred to several times, but it is never explained. In this low temperature environment, it is not clear why there should be such a relationship.

We discuss relation between grain size and geochemistry in Section 3.3 (see below).

8. P400: 1. A weak correlation between Si and Ti would imply strong and variable dilution by BSia’A’ This line says just the opposite.

We have adited this part of the text

9. P400: 18. I think that significant removal of Al by weathering in this frigid environment is highly unlikely.

We agree, and changed text as: “The Al₂O₃ vs. TiO₂ diagram shows a rather straight, linear trend for interglacial sediments (R² = 0.55), whereas cold sediments have a scattered, nearly vertical distribution (R² = 0.024) (Fig. 5e). We suggest that the higher TiO₂/Al₂O₃ ratios observed in glacial sediments are due to an enrichment in TiO₂ in the finer-grained sediments, as mentioned above. It may relate to the concentration of biotite as noted by Young and Nesbit (1998) for Baffin Island sediments.”
The discussion of the relation between Fe and Ti contents and magnetic properties is a good idea, and the relation to MS is fairly straightforward. However, magnetic mineralogy and its relation to magnetic measurements and elemental chemistry is a very complex subject that is incomplete here.

We studied the magnetic mineralogy by optical, microzont, SEM, EDS, thermomagnetic methods. These data have not been published yet. Nevertheless we add to text: “Fe and Ti are the main elements in ferromagnetic minerals found in oxides, such as magnetite and titanomagnetite. In Lake El’gygytgyn sediments, the majority of the iron oxides are titanomagnetites that include Al, Si, and Mn impurities. Some titanomagnetites have characteristic cracks in the grains, which indicate low-temperature maghemitization. Other titanomagnetites are oxidized at high-temperatures, displaying lamellae of ilmenite and titanium magnetite. Chromite, ilmenite, and rutile were also found in the sediments.”

We found and studied vivianite, pyrite, greigite, iron, Fe-Mn aggregares.

There is a good story here concerning redox conditions and vivianite, but was vivianite actually observed or measured (the ms doesn’t say)? Vivianite is readily identifiable in smear slides. We do not discuss the presence of vivianite in the sediments; just refer to (Minyuk et al., 2013).

Electron microprobe analyses, electron microscopy and energy dispersive spectroscopy, optical (smear slide studies) were used to identify diagnostic mineral.

Ni and Cr is separate group of elements (as P₂O₅ and MnO) and not correlated with other elements (see also PCA data, fig. 3). We point out that enrichment in these elements is in the glacial sediments.

Why are Zr, Rb, Sr, and Ba discussed as a group? Zr behaves much like Ti, and Sr behaves like Ca (as implied by the correlations mentioned in the text), but why discuss them together? Rb/Sr has been used as an index of weathering, but there are far simpler ratios (e.g. K/Ti) that are easier to interpret.

At first, these elements are trace elements which were measured by different method and equipment then major elements (much faster measuring).

Secondly, we indicated:

“The first PC axis of the PCA results explains 40% of the total variance. It is positively correlated with Al₂O₃, TiO₂, Fe₂O₃, MgO, Rb/Sr, CIA, PIA, CIW, Ni, and Cr and negatively correlated with SiO₂. The second PC axis explains an additional 24% of the variability and is characterized by positive loadings of Ba, K, Rb, Zr, Na₂O, CaO, MS, and Sr. It is negatively correlated with P₂O₅, MnO, and LOI. These results indicate the presence of three main data groups. SiO₂ is clearly related to the super interglacial sediments, while Ba, K, Rb, Zr, Na₂O, CaO, MS, and Sr are related to the interstadial sediments. Al₂O₃, TiO₂, Fe₂O₃, MgO, Rb/Sr, CIA, PIA, CIW, Ni, and Cr are associated with glacial sediments (Fig. 3).”

Geochemical indices. The first paragraph of this section is a good description of what these indices are and how they can be used, but the subsequent discussion is useless. Why discuss every index that has ever been proposed? Most are redundant and only a few have real meaning for El’gygytgyn.

We have reduced the indices.
15. P408: 20-23. This is one of the key observations of the paper, even if it is not in correct English. However, a convincing alternative to weathering is never described.

16. P409: 29. The difference in clay minerals between glacial and interglacial sediments might be important for the geochemistry, but what produced the difference in clays, if not weathering? Secondary clay mineral formation in this environment is highly unlikely.

17. P410: 27. Major changes in redox sensitive elements and related mineralogy can occur without changing much of the rest of the geochemistry, such as the weathering indices or the depletion of cations. This is a key uncertainty in suggesting diagenesis as an explanation for the differences between glacials and interglacials.

We have reorganized the discussion on indices:

3.3 “Geochemical indices as proxy for environmental changes

Geochemical indices commonly differ between glacial and interglacial intervals, suggesting that conditions in cold and warm periods exerted distinct influences on the sedimentary record. For example, glacial sediments show high values of CIA, CIW, Rb/Sr, Ba/Sr, LOI depleted by potassium, sodium, calcium, and strontium. Thus, these characteristics should be helpful in differentiating glacial and interglacials in the El’gygytgyn record. Chemical weathering generally is considered to increase in warm and wet climates, although this process can also be active under cold climatic conditions (e.g. Darmody et al., 2000; Hall et al., 2002). Nonetheless, temperature and precipitation have been shown to be strong controls on the rates of chemical weathering (e.g. White and Blum, 1995).

Surprisingly, sediments from the super interglacial MIS 11.3 exhibit low weathering indices as compared to glacial sediments. Furthermore, weathering indices for MIS 11.3 are lower than Holocene values, even though the super interglacial was considerably warmer and wetter than the Holocene. That is, maximum summer temperature and annual precipitation of ~4°C to 5°C and ~300 millimeters, respectively, were reconstructed for MIS 11.3, whereas the mean temperature of the warmest month and mean annual precipitation during the Holocene thermal optimum were only ~1°C to 2°C and ~50 mm higher than today (Melles et al., 2012). Hence, a simple application of chemical indices for inferring chemical weathering intensity within the El’gygytgyn catchment will be incorrect. Below we discuss and evaluate four scenarios that might account for the differences between chemical indices observed in the glacial and interglacial sediments from Lake El’gygytgyn.

1. Grain-size is considered an important factor that can influence the expected relationship between sediment composition and geochemical indices (e.g. van Eynatten et al., 2012). In the El’gygytgyn sediments, sand content does not exceed 15.5%, and the average silt and clay contents are ca. 69.2 and 27.7%, respectively. Mean grain size varies between 2.5 μm and 9.3 μm and is higher in interglacial sediments (Franke et al., 2013). Geochemical data from volcanic rocks and sediments show a strong dependence of geochemical indices and granulometry. Volcanic rocks and impactites display the lowest values of CIA, PIA, and CIW. In finer sediments, the values of geochemical indices increase (Fig. 9 new). To further investigate the dependence of geochemical data and grain-size in the El’gygytgyn record, one sample from MIS 7 was separated into two size fractions (<40 μm and > 40 μm). The <40 μm fraction (90% of the total sample weight) is depleted in CaO, Na2O, and K2O and displays higher CIA (64.58), PIA (70.18) and CIW (74.97) indices as compared to the coarser size fraction. The values of CIA, PIA and CIW for >40 μm fraction (10% of sample weight) are 57.15, 60.21, and 67.22, respectively. Cold and warm periods experienced different sedimentological regimes. A perennial ice cover on the lake during peak glacial times restricted the transport of coarse-grained, less-altered sediments to the basin. However, this situation enabled finer particles to be transported to the center of the lake through cracks in the ice or through the formation of moats around the shore during summer (Asikainen et al.,
2. Variations in the sediment geochemistry between glacial and interglacial periods can be caused by changes in sediment provenance. However, this explanation can be excluded in the case of Lake El’gygytgyn, because it is a closed basin with a very restricted watershed that is bordered by a distinct crater rim (Fig. 1). The highly altered material found in the El’gygytgyn record possibly was transported by eolian processes, originating in remote regions. Fedorov et al. (2012) showed that streams are the major agents for carrying clastic materials to the basin during spring and summer under modern climate condition. Total eolian supply amounts to only 4–5% of the total sediment input. Prevailing local winds on the lake are from the north and south. They are strong and persistent, and this likely plays an important role in controlling lake shape (Nolan et al., 2007). Past wind direction was likely the same. Today large areas of eolian sediment are absent in the El’gygytgyn catchment and in areas immediately to the north and south of the lake. In other regions of Chukotka and in Yakutia, silt-dominated Pleistocene sediments are widespread. They are associated with ice-rich permafrost and are referred to as ice complex or yedoma deposits. There are different explanations for the origin of the ice-complex sediments, including an eolian genesis (Tomirdiaro and Chernen’ky, 1987). Geochemical data of the ice-complex are available from the Anadyr River to the south of the lake and along the Arctic lowlands to the north (Tomirdiaro, 1974; Tomirdiaro and Chernen’ky, 1987). As part of our analysis, we compared the geochemical data from the predominant volcanic rocks and pebbles and from lake and ice-complex sediments. On the ternary Al$_2$O$_3$–(CaO+Na$_2$O)–K$_2$O and CaO–(Al$_2$O$_3$–K$_2$O)–Na$_2$O diagrams, the various El’gygytgyn data plot parallel to the (CaO+Na$_2$O)–Al$_2$O$_3$ and Na$_2$O–(Al$_2$O$_3$–K$_2$O) axes, respectively, clearly indicating local volcanic rocks to be the major source of clastic material deposited on the lake floor. In contrast, the ice complex data form a separate group on the diagrams. These results suggest that any eolian input into the lake during glacial intervals must have been derived from the product of local weathering products of the volcanic rocks. This scenario is unlikely.

3. During the warm and wet interglacials, the chemical weathering was increased and as result the surface waters were enriched in mobile elements, such as Ca, Na, K, and Sr. The consequent increase in overland water flow into the lake resulted in a higher total content of these elements in the lake sediments. In this case, low values of CIA, PIA, CIW, and Rb/Sr reflect the high degree of chemical weathering. A similar scenario has been suggested for the Heqing paleolake basin (An et al., 2011), Daihai Lake (Jin et al., 2001), and Barkol Lake (Zhong et al., 2012). However Lake El’gygytgyn is extremely oligotrophic, meaning that the water is low in anions and cations (< 1 mg l$^{-1}$) and has a low conductivity based on measurements carried out in May (prior to snow melt) and in August (following snow and ice melt and subsequent of lake water) at Lake El’gygytgyn (Cremer and van de Vijver, 2006). Therefore, dissolved Ca$^{2+}$, Na$^{+}$, and K$^+$ contributed only slightly to the total contents of these elements in the sediments. In contrast, at Barkol Lake the water content of Ca, Na, and K was – 444.8 mg l$^{-1}$, – 62089.39 mg l$^{-1}$, and – 11173.35 mg l$^{-1}$, respectively (Zhong et al., 2012). Thus, this scenario is also unlikely to explain the El’gygytgyn patterns.
4. Diagenetic processes can obscure the detrital geochemical signals. Glacial facies at Lake El’gygytgyn supposedly accumulated under anoxic bottom-water conditions (Melles et al., 2007, 2012), resulting in the dissolution of magnetic minerals (Nowaczyk et al., 2007). The formation of authigenic vivianite, Fe-Mn aggregates, pyrite, and greigite indicates a strong post-depositional alteration of sediments during anoxia. This process can also lead to the partial dissolution of silicates, which is accompanied by a loss of cations as was reported for Sea of Okhotsk sediments (Wallmann et al., 2008). A similar cation depletion in anoxic glacial sediments might explain the high indices of CIA, CIW, and PIA. However, additional mineralogical investigations are required to confirm such a scenario.

In summary, our data indicate that geochemical indices and selected elemental ratios mirror sedimentation conditions and, possibly, diagenetic processes that are triggered by environmental and climate changes during glacial and interglacial.

18. 4. Stages 11, 6.6, and 7.4. Why were these stages chosen for detailed discussion?

In the first paragraph we have tried to explain:

“Down-core changes in major and trace elements and in elemental ratios display a strong geochemical zonation that corresponds to marine isotopic stages (Fig. 4, 6). The samples analyzed in this study represent a wide range of climate conditions, varying from the climatic optima of MIS 11 and MIS 9 to the frigid glacial environments of MIS 6, MIS 8, and MIS 10 (Lozhkin and Anderson, 2013; Lozhkin et al., 2013). Vegetation types present during MIS 11 indicate greater summer warmth and annual precipitation as compared to modern (Lozhkin and Anderson, 2013; Melles et al., 2012, Tarasov et al., 2013). Pollen-based reconstructions of mean temperatures for July and January were +12 to 16°C and -20 to -24°C, respectively, and mean annual precipitation was ~550 to 600 millimeters. The following interglacials and interstadials were cooler in comparison to MIS 11, and sediment data show a decreasing trend in SiO₂. Mean summer temperatures during MIS 9.3 ranged from +12 to 14°C (Lozhkin et al., 2013). Simultaneously, sediments of MIS 9.3 contain less SiO₂ as compared to MIS 11 (Fig. 4). During MIS 7 mean July temperature was +2.4°C (Matrosova, 2009), and the warm substages of MIS 7 display low concentrations of SiO₂. During glacial intervals, mean July and January temperatures were +2 to 3°C and -24 to -25°C, respectively (Matrosova, 2009). Glacial sediments are characterized by the highest content of TiO₂, Fe₂O₃, and MgO and by the lowest values of SiO₂ (Fig. 4). Below we give a detailed description of MIS 11 and MIS 7.4 sediments, which represent the warmest and coldest stages within the core interval reported here.”
Figure 1. Location (A) and geological map (B) of the El’gygytgyn area adapted from Bely and Raikevich (1994) and Bely and Belaya (1998).

Figure 2. Diagram of total alkali and silica (Le Maitre et al., 2002) for volcanic rocks from the El’gygytgyn area. Geochemical data are from Bely and Belaya (1998).

Figure 3. Principal components analysis of the Lake El’gygytgyn sediments. Red, blue and rose symbols are samples from interglacial, glacial, and super interglacial sediments, respectively.

Figure 4. Graphs of selected elements plotted by depth and age. Yellow, orange and blue bars represent interglacials, super interglacials, and glacial sediments, respectively. Marine isotopic stages (MIS) follow Bassinot et al. (1994). Note that SiO$_2$ is plotted on a reversed scale. Lithofacies A, B and C are shown in blue, yellow, and red, respectively.

Figure 5. Scatterplots of: a) SiO$_2$ versus TiO$_2$; b) SiO$_2$/TiO$_2$ versus Al$_2$O$_3$/TiO$_2$; c) Al$_2$O$_3$ versus SiO$_2$; d) Fe$_2$O$_3$ versus TiO$_2$; e) TiO$_2$ versus Al$_2$O$_3$; f) Fe$_2$O$_3$ versus Al$_2$O$_3$; g) Fe$_2$O$_3$ versus MnO; and h) Ni versus Cr. Red (blue) symbols indicate interglacial (glacial) samples. Violet squares are samples where SiO$_2$ content exceeds 71%. Orange squares indicate samples from MIS 11, whereas green squares are samples from MIS 6.6 and 7.4.

Figure 6. Distribution of selected geochemical indices and ratios plotted by depth and age. Yellow, orange and blue bars represent interglacials, super interglacials and glacial sediments, respectively. Marine isotopic stages (MIS) follow Bassinot et al. (1994). Lithofacies A, B and C are shown by blue, yellow, and red, respectively.

Figure 7. Diagrams showing variations in TiO$_2$ and Fe$_2$O$_3$ versus magnetic susceptibility and ferromagnetic and paramagnetic components of induced magnetization. Red (blue) symbols indicate samples from interglacial (glacial) sediments.

Figure 8. Ternary diagrams showing weathering trends in volcanic rocks, lake sediments, and ice complex: a) (CaO+Na$_2$O)-Al$_2$O$_3$-K$_2$O diagram (Nesbitt and Young, 1984); and b) CaO-(Al$_2$O$_3$-K$_2$O)-Na$_2$O diagram (Fedo et al., 1995). Arrow indicates the weathering trends.

Figure 9. Geochemical indices (CIA, PIA, CIW) from impactites (n = 9), volcanic rocks (n = 19) (Bely and Belaya, 1998), pebbles comprised of volcanic rocks (n = 11) (Feldman et al., 1980), coarse sand (n = 2), fine sand (n = 1), interglacial sediments (n = 228), and glacial sediments (n = 387).

Figure 10. Geochemical structure of MIS 11. Note that TiO$_2$ is plotted using a reversed scale.

Figure 11. Geochemical structure of MIS 7.4. Note that SiO$_2$ is plotted using a reversed scale.
Table 1 Pearson (r) correlation coefficients for major and trace elemental analyses from Lake El’gygytgyn sediments

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