Interactive comment on "Inorganic data from El'gygytgyn 1 Lake sediments: stages 6–11" by P. S. Minyuk et al. 2

- **Anonymous Referee #1**
- 3 4 5 6 Received and published: 11 March 2013
- Running comments on doi:10.5194/cpd-9-393-2013, Minyuk et al., Cimate of the Past
- 7 Abstract
- 8 *Please indicate what size fraction was analyzed, or if these are bulk samples.*
- 9 Line 4: you probably determined more than presence/absence of elements; insert "concentrations" 10 and accuracy (ppb or ppm?)
- *Line 5: replace "covering the timeframe between" with "dating from"* 11
- 12 We have corrected the text:
- 13 "Major and rare element concentrations were determined using X-ray fluorescence
- 14 spectroscopy (XRF) on the <250µm fraction from 617 samples dated ca. 440 and 125 ka,
- 15 which approximates Marine Isotope Stages (MIS) 11 to 6."
- 16

17 *I* hope it's made clearer in the paper, but in the abstract *I* can't tell if you are determining the

- 18 interglacial or glacial status of samples by their geochemistry, or are relying on a different
- 19 chronometer.
- 20 We left in the text:
- 21 "The elemental record from Lake El'gygytgyn can be divided into two groups or geochemical
- 22 zones based on the variability of the inorganic compounds, elemental ratios, and LOI (Fig. 4).
- 23 Each group is affected by different environmental conditions and climates associated with
- 24 glacial/stadial or interglacial periods. These zones were correlated with marine isotope stages
- 25 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 26
- 27 et al., 2013) was used to help identify specific isotope stages, but boundaries of stages and
- 28 substages were defined according to the inorganic geochemical data. Arabic numerals for the 29 stages and substages in the figures and text follow Bassinot et al. (1994)"
- 30

31 Explain in the abstract why the similarities in structure of certain elemental profiles with other 32 records is important during Stage 11.

- We changed the sentence as: "The geochemical structure of MIS 11 shows similar 33
- 34 characteristics as seen in MIS 11 records from Lake Baikal (southeastern Siberia) and

35 Antarctic ice cores, thereby arguing for the influence of global forcings on these records"

- 36
- 37 Provide in the abstract one or two examples of the elemental ratios that indicate weathering or 38 diagenesis.
- 39 We have added: "Elemental ratios (CIA, CIW, PIA, and Rb/Sr) indicate that glacial
- 40 sediments are depleted in mobile elements, like Na, Ca, K and Sr."
- 41
- 42 Introduction 43 *Line 3: catchments area = catchment*
- 44 Corrected
- 45
- 46 *Line 4: The only outlet is via the Enmyvaam River to the south.*
- 47 Corrected as: The only outlet is the Enmyvaam River that flows to the south.
- 48
- 49 *Line* 7 *sites; make sure the sites are labeled on a map; otherwise just leave them out.*
- 50 Few geochemical site numbers that were no mentioned in the text have been **deleted** from the
- 51 map

- Lines 8-9; provide units for the measurement (mg/L?). Alkalinity is a useful measurement to provide.
 We added unit: mg l⁻¹
- 4

5 Line 10: I have never heard the word "circumneutral". Most people who are reading this will know

- 6 how what the pH values mean with respect to neutrality. At least we can hope. I suggest combining the
 7 last two paragraphs. A lot of what is said in the first paragraph is duplicated in the Figure caption.
 8 Section 1.2
- 9 We changed sentence as: "The pH values of 6.2–6.5 (Lz1024) and 5.7–5.9 (Lz1079) indicate 10 that Lake El'gygytgyn is weakly acidic (Cremer and van de Vijver, 2006)."
- 10 that Lake El gygytgyn is weakly acture (Cremer and van de vijver, 11
- 12 Line 28. "Core sequences": : : consider using "core segments".
- 13 We corrected sentence as:
- 14 "Based on the distribution of major and rare elements, the cores were divided into
- 15 geochemical zones corresponding to Marine Isotopic Stages (MIS) 1–MIS 10."
- 16
 17 Line 1, p 396. Suggest "Interglacial periods are represented by massive silt that is enriched in SiO2: :
- 18 : but depleted in TiO2: : : Glacial periods were represented by xxxx (tell us the lithology so it can
- 19 contrast with interglacial sediment), and are more chemically altered.
- 20 We added the additional subsection:

21 **"1.2.Lithology and age model**

- 22 Three lithofacies (Facies A, B, and C) dominate the pelagic Pleistocene sediments of Lake
- 23 El'gygytgyn (Melles et al., 2011, 2012). These facies reflect different environmental settings
- 24 and climate modes. Facies A consists of dark gray to black silt and clay, with fine, laminatae
- 25 (<5 mm) characterized by a "wavy" structure. This facies is linked with glacial/stadial
- 26 conditions and the presence of a perennial lake-ice cover. The latter resulted in a stratified
- 27 water column with anoxic bottom waters, good preservation of the settled organic matter, and
- 28 dissolution of magnetic minerals.
- 29 Facies B is composed of olive-gray to brown silt that is massive to faintly banded. Total
- 30 organic matter (TOC) is low in this facies, but biogenic silica values and magnetic
- 31 susceptibility (MS) are high. Sediment structure suggests the presence of bioturbation and
- 32 oxygenated bottom water (Melles et al., 2011, 2012).
- 33 Facies C is defined by a distinct reddish brown appearance and the presence of laminations
- 34 that are faint, pale white in color and of a millimeter-to-centimeter scale thickness. This facies
- 35 corresponds to times of warm super interglacial climate. "
- 37 Please tell us why sediments are MORE altered during glacials: this is counterintuitive.
- 38 In Introduction we point out that:
- 39 "Sediment from the warm climatic stages is enriched in SiO₂, CaO, Na₂O, K₂O, and Sr, but is
- 40 depleted in TiO₂, Al₂O₃, MgO, Fe₂O₃, and LOI. Glacial sediments are relatively **low** in
- 41 mobile elements, such as Ca, Na, and K, but show **higher** values of the chemical index of
- 42 alteration (CIA), the plagioclase index of alteration (PIA), and the Rb/Sr ratio (Minyuk et al.,
- 43 2007, 2011)."
- 44
- 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.
- 47 We added: "In this paper, we focus on the geochemical characterization of sediments from the
- 48 upper part of ICDP core 5011-1, which spans MIS 6 to MIS 11. **This interval encompasses**
- 49 great climatic variations from the maximum temperatures of the "super" interglacials

1 (MIS 11 and MIS 9) to the extreme cold of MIS 6 and MIS 8 (Melles et al., 2012;

2 Matrosova, 2009; Lozhkin et al., 2013)."

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

6 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

- 10 Raymo, 2005) and curves of regional spring and summer insolation (Laskar et al., 2004) to
- 11 achieve an age scheme for the El'gygytgyn record. See Melles et al. (2012) and Nowaczyk
- 12 et al. (2013) for more details."

14 Methods

- 15 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
- 20 a total of 617 samples. Within this interval, **deposits deemed to be the result of mass**
- 21 movement of slope sediments (Sauerbrey et al., 2013) were omitted (Wennrich et al.,
- 22 2013b)."
- 23
- 24 Line 11. rock (not rocks)
- 25 Corrected 26
- 27 *Line 12. Spectrometer (not spectrometers)*
- 28 Corrected 29
- 30 Line 16. Can you write "layered with boric acid" rather than "layered with a boric acid base"? I am
- 31 not qualified to review the technical parts of this paper
- 32 Corrected
- 33
- 34 Page 397, line 2, replace "achieved" with "determined"
- 35 Corrected
- 36
- 37 *General: Detection limits should be provided in a table, and not included in the text.*
- 38 We didn't provide inorganic data in the Table format so we put detection limits in the text
- 3940 *Results*
- Should also include exogenic sources of sediment borne from Aeolian deposition. I can only imagine it
 gets pretty windy out there!
- 43 We changed the sentence as: "The geochemical characteristics of lacustrine sediments depend
- 44 on many factors including the: 1) chemical composition of the provenance; 2) physical and
- 45 chemical weathering processes in the catchment; 3) tectonic and **eolian** activity; 4) sorting
- 46 during sediment transport and sedimentation; and 5) post-depositional diagenetic changes
- 47 (e.g. Fralick and Kronberg, 1997)."48
- 49 See also section 3.3. where eolian input discussed
- 50
- 51 The r2 data and Pearson coefficients are useful data to analyze. I also strongly recommend that you
- 52 explore the structure of your data further using Principle Components Analysis. No doubt you will find

- 1 groups of elements that behave similarly. It should show the same kinds of things you have pointed
- 2 out, but it goes a step further and shows the relatedness of all variables in one diagram (several kinds
- 3 of plots are typically used). Using an analysis like this helps to identify the "best" pairs of elements
- 4 5 6 7 for indicating changes in provenance and weathering. Perhaps you have already tried this and the
- results were too noisy to be of use! But its 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.
- 8 We added the PCA data:
- 9 10 "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 11
- performed on a correlation matrix of major and trace elements, CIA, PIA, CIW, LOI, Rb/Sr, 12
- 13 and magnetic susceptibility.
- 14 15
- 16 The first PC axis of the PCA results explains 40% of the total variance. It is positively correlated with Al₂O₃, TiO₂, Fe₂O₃, MgO, Rb/S, CIA, PIA, CIW, Ni, and Cr and negatively 17 18 correlated with SiO₂. The second PC axis explains an additional 24% of the variability and is 19 characterized by positive loadings of Ba, K, Rb, Sr, Na₂O, CaO, MS, and Sr. It is negatively 20 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, Sr, Na₂O, 21
- 22 CaO, MS, and Sr are related to the interstadial sediments. Al₂O₃, TiO₂, Fe₂O₃, MgO, Rb/Sr,
- 23 CIA, PIA, CIW, Ni, and Cr are associated with glacial sediments (Fig. 3 new)." 24
- 25 Page 398, line 15, then = than
- 26 Corrected 27
- 28 It might be useful to discuss enrichments of elements like SiO2 in terms of biogenic sequestration. The
- 29 weathering of the volcanic rocks should bring into the basin dissolved silica, and this can either be
- 30 bypassed and lost due to overflow, or captured (sequestered if buried in the sediment) by organisms,
- 31 in this case diatoms.
- 32 We changed the text as:
- 33 "Maximum SiO₂ 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 34
- 35 age-depth model these horizons correlate to MIS 11.3 (424-390 ka) and MIS 9.3 (340-320
- ka). The SiO₂ enrichment in these zones is caused by elevated BSi and represents levels of 36
- 37 high primary productivity in the lake (Cunningham et al., 2012; Vogel et al., 2013). The
- 38 interval corresponding to MIS 11 exhibits the greatest peak in diatom concentrations (Snyder 39 et al., 2013)."
- 40
- 41 Last line on pg 398 begins a sentence that is hard to follow. It would be very useful at some point to
- 42 discuss the mineralogy of the sediments that you analyzed. This kind of information should be
- 43 presented up front, rather than later on. The silica to aluminum ratio discussion is left (in my mind) a 44 bit muddy because I'm not sure what phases these elements are in. You've mentioned biogenic silica,
- 45 and that's about it. What is the proportion of quartz to feldspar, for example? How much clay is
- 46 there? The claims of "textural maturity" mean relatively little unless we know or can intuit what
- 47 minerals will weather fastest.
- 48 We changed the text as:
- 49 "Large scale variations in the oxides SiO₂ and TiO₂ indicate a generally strong negative
- 50 correlation (r = -0.74; Table 1). A strong linear correlation ($R^2 = 0.8$) is especially valid for

- 1 samples from MIS 11.3 and 9.3 and less so for MIS 7.1 and 5.5, where SiO₂ exceeds 71%
- 2 (Fig. 5a). These results indicate that BSi dilution is significant during the warmest
- 3 interglacials. The linear correlation between SiO₂ and TiO₂ is very poor ($R^2 = 0.17$) in
- 4 interstadial samples and is essentially nonexistent ($R^2 = 0.07$) for glacial sediments. This
- 5 pattern suggests only negligible or no dilution of BSi (Fig. 5a) during cooler episodes in the 6 El'gygytgyn record.
- 7 The SiO₂/Al₂O₃ ratio most resembles the SiO₂/TiO₂ ratio (r = 0.89; Fig. 6). SiO₂/Al₂O₃ ratios
- 8 for interglacial and glacial sediments average 4.45 and 3.72, respectively, with a high linear
- 9 correlation between SiO₂ and Al₂O₃ for interglacial sediments ($R^2 = 0.88$) and a poor
- 10 correlation for glacial sediments ($R^2 = 0.26$; Fig. 5c).
- 11 A decrease in the SiO₂/Al₂O₃ ratio can be related either to a decrease in grain size or a lower
- 12 textural maturity (e.g. Weltje and Eynatten, 2004). Von Eynatten et al. (2012) point out that
- 13 mechanical processes, such as comminution, impact sediment composition. They further
- 14 showed that increases in Al_2O_3 and decreases in SiO_2 concentrations occur with finer grain
- 15 sizes. Thus, the low SiO_2/Al_2O_3 ratios in the Lake El'gygytgyn data combined with an
- 16 absence of $A1_2O_3$ dilution by BSi indicate that the glacial sediments consist of more fine-
- 17 grained material as compared with either interstadial or interglacial sediments. This
- 18 conclusion is supported by grain-size analysis which shows higher clay to fine silt content 10 during classical times (Francisco et al. 2012). In contrast, a higher many SiO (ALO) ratio of 4.70
- during glacial times (Francke et al., 2013). In contrast, a higher mean SiO_2/Al_2O_3 ratio of 4.70 obtained from bedrock samples of the Pykarvaam and Ergyvaam Formations indicate the
- 20 obtained from bedrock samples of the Pykarvaam and Ergyvaam Formations indi-21 lower maturity of the fresh rocks as compared to the lake sediments."
- 21 lower maturity of the fresh rocks as compared to the lake sediments."
- 23 But we didn't study mineralogy of the sediments
- 24 25 Page 399, Section 3.1.2
- 26 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
- 28 highlight that one, and discuss the similarities.
- 29 We changed paragraph as: "In lacustrine environments, Ti and Al have been shown to be
- 30 good measures of the intensity of detrital input (e.g. Whitlock et al., 2008)."
- 31
- 32 Can you subtract out BSi from your analyses of Al vs silica? The results might lead to more
- 33 meaningful data regarding relative weathering during glacials and interglacials.
- 34 We can't subtract out BSi from total SiO₂ contents. But we point out that "The glacial/interstadial
- 35 and interglacial samples, with the exception of those from the super interglacials, display a
- 36 strong positive correlation between SiO₂/TiO₂ and Al₂O₃/TiO₂ ratios ($R^2 = 0.73-0.75$, Fig. 5a,
- 37 6). In intervals where fluctuations in the Al₂O₃/TiO₂ and the SiO₂/TiO₂ ratios coincide,
- 38 the dilution of TiO₂ and Al₂O₃ by BSi is absent or negligible (Fig. 6)."
- 39
- 40 What mineral is the source of Ti? Illmenite? It's a common constituent in volcanic rocks. Its also
- 41 magnetic, and your MS data may be able to correlate high Ti with high MS (but a certain kind that
- 42 *measures moments from coarser grains).*
- 43 We have discussed this in subsection:
- 44 "Fe and Ti are the main elements in ferromagnetic minerals found in oxides, such as
- 45 magnetite and titanomagnetite. In Lake El'gygytgyn sediments, the majority of the iron
- 46 oxides are titanomagnetites that include Al, Si, and Mn impurities. Some
- 47 titanomagnetites have characteristic cracks in the grains, which indicate low-
- 48 temperature maghemitization. Other titanomagnetites are oxidized at high-
- 49 temperatures, displaying lamellae of ilmenite and titanium magnetite. Chromite,
- 50 ilmenite, and rutile also were found in the sediments.

- To investigate the Fe and Ti mineralogy in Lake El'gygytgyn sediments, we examined the 1
- 2 correspondence of both elements to various magnetic parameters. During glacial periods,
- 3 sediments exhibit high Fe_2O_3 and TiO_2 but low MS; interglacial samples display the opposite
- 4 pattern. Consequently, data on the Fe₂O₃-MS and TiO₂-MS diagrams show a scattered
- 5 distribution (Fig. 7a, b) with low negative correlation coefficients (r) of -0.28 and -0.43 for
- 6 Fe₂O₃ vs. MS, and TiO₂ vs. MS, respectively. This contradicts the idea that Ti and Fe were
- 7 enriched in the detrital heavy-mineral fraction, which is mirrored by a generally positive
- 8 correlation of TiO₂ and Fe₂O₃ to MS (e.g. Ortega et al., 2006; Parker et al., 2006; Reynolds et 9 al., 2006; Vegas et al., 2010). MS includes both ferrimagnetic and paramagnetic components
- 10 that can be distinguished by determining the induced magnetization.
- 11 TiO_2 and Fe_2O_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 12
- 13 (Fig. 7e, f). Hence, high TiO₂ contents in the glacial-age samples can not be attributed to
- 14 titaniferous minerals such as titanomagnetite, rutile, or ilmenite, which are typically
- 15 found in lake sediments. These minerals would evoke a positive correlation of TiO₂ (Fe₂O₃)
- 16 to MS and J_{f.}. Most Ti and Fe, especially during cold intervals, should be concentrated in
- 17 paramagnetic Fe- or Ti-bearing minerals. These minerals include chlorite
- 18 (Mg_{3.5}Fe_{1.5}Al₂Si₃O₁₄), with Fe and Mg acting as the main elements (Boyle, 2002), or
- 19 biotite. The importance of chlorite as a primary iron carrier in glacial sediments is indicated
- 20 by the positive correlation of TiO₂ to MgO (r = 0.83) and Fe₂O₃ to MgO (r = 0.65). This conclusion is supported by a study of clay minerals deposited in Lake El'gygytgyn over the 21
- past 65 ka. This analysis indicated that cold stages typically are enriched in chlorite
- 22 23 (Asikainen et al., 2007)."
- 24
- 25 We didn't study chemical composition of chlorite.
- 26 27 Page 400, line 2, seams = seems
- 28
- Corrected 29
- 30 *Line 18, intense = relatively intense. Weathering at this latitude is going to be very slow, so using an* 31 adjective like "intense" can be misleading.
- 32 We changed the paragraph as: "The TiO_2/Al_2O_3 (or Al_2O_3/TiO_2) ratio often has been used as an 33 indicator of sediment provenance, but it also is a good measure of the degree of sediment
- 34 alteration (Migdisov, 1960; Young and Nesbitt, 1998; Yudovich and Ketris, 2011). The
- 35 TiO₂/Al₂O₃ ratio in the El'gygytgyn samples averages 0.037 and 0.045 in warm-stage and
- 36 cold-stage sediments, respectively, and 0.032 in unweathered volcanic rocks. The Al₂O₃ vs.
- TiO₂ diagram shows a rather straight, linear trend for interglacial sediments ($R^2 = 0.55$), 37
- whereas cold sediments have a scattered, nearly vertical distribution ($R^2 = 0.024$) (Fig. 5e). 38
- 39 We suggest that the higher TiO_2/Al_2O_3 ratios observed in glacial sediments are due to an
- 40 enrichment in TiO₂ in the finer-grained sediments, as mentioned above. It may relate to the 41 concentration of biotite as noted by Young and Nesbit (1998) for Baffin Island sediments. "
- 42 43
- 44 Page 401. This page is difficult to follow partly because its hard to go from the text to the figures. 45 The discussion about Ti in chlorite is interesting, but is hard to follow and hard to justify since there is 46 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
- 47 48 rocks are typically low-grade metamorphic rocks.
- 49 See above
- 50

- Page 401, first sentence under 3.1.3, First sentence should read "Phosphate and manganese oxide" 1 2 3 concentrations have a relatively strong linear relationship (r = 0.55).
- Corrected
- 4 5

Line 25 - depth = depths, but I strongly recommend not listing the various depths: : : it's a long 6 (perhaps tedious) list, that perhaps would be better presented in a figure.

- 7 Corrected as "Peaks in P₂O₅ and MnO occurred in the early parts of cold stages (MIS 8.4, 7.4,
- 8 6.6, 6.4, and 6.2) with a single exception (18.85–18.39 m) that corresponds to the super 9 interglacial MIS 11.3 (Fig. 4)."
- 10

Page 409, lines 2 and 3; replace "be the main drivers" with "control rates of", and delete "rates in 11 12 watersheds" on line 3

- 13 Corrected
- 14
- 15 *Line 4, delete "rather"* Corrected
- 16 17
- 18 *Line 5, insert "reconstruction of "before "maximum"*
- 19 Corrected
- 20

21 Tell us how much warmer and wetter this period was compared to the mean Holocene instead of just

- 22 say "higher than those" (line 6)
- 23 We changed the text as:
- 24 "Surprisingly, sediments from the super interglacial MIS 11.3 exhibit low weathering indices
- 25 as compared to glacial sediments. Furthermore, weathering indices for MIS 11.3 are lower
- 26 than Holocene values, even though the super interglacial was considerably warmer and wetter
- 27 than the Holocene. That is, maximum summer temperature and annual precipitation of ~4°C
- 28 to 5°C and ~300 millimeters, respectively, were reconstructed for MIS 11.3, whereas the
- 29 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). "
- 30
- 31 32 *Line 10. Next two paragraphs. Reorganize and rewrite. If you are trying to convince the reader of*
- 33 something, start out with what you believe, and then follow with justifications, then caveats and less
- 34 favored explanations. This is suggested because you want to be clear to your reader. I suggest starting
- 35 this section "The greater surface area to volume ratio of clay particles probably accounts for the
- 36 greater values of weathering indices for glacial versus interglacial lake sediment. (provide textural
- 37 data, if you have it, rather than just descriptions). (The description of the various facies is OK, but
- 38 diagrams would be better, especially if they are plotted with the indices). (It might be instructive to
- 39 add a grain-size ratio to your multivariate analysis: : : you might find correlation among fine-grained
- 40 sediment and particular elements, which of course are tied to mineralogy).
- 41 *Line 10. When you do your rewrite, keep in mind that glacial and interglacial are nouns: : : you treat*
- 42 them as adjectives in some places. You can fix this problem by simply adding "sediment": : : then
- 43 sediment is the noun, and gl and intergl are adjectives.
- 44 The argument that you make for no Aeolian input is not very strong if the composition of the loess or
- 45 other Aeolian particles is the same or nearly the same. It seems strange that there would be very little
- 46 dust falling into a large lake like Lake E especially with active glaciers all around (albeit not that
- 47 close). The far distance from loess/dust sources indicate that the grain size of the Aeolian component
- 48 might be quite small.
- 49 Line 29, tell us what kind of chlorite: : : there are several kinds, each with different compositions. I
- 50 assume that Lake E chlorites are Fe and Mg-rich. But not all chlorites are.
- 51 Page 410. It took me a long while to sort out what was being said on this page. Start out a paragraph
- 52 with a topical sentence, and then provide supporting discussion/data. The great amount of clay in

1 glacial sediment is a puzzlement given that the watershed was never glaciated. The bottom paragraph

- 2 on pg. 410 reveals "the answer", and this should be presented at the beginning of the discussion. If I
- 3 understand the argument, the finer-grained sediment is attributed to (year-round?) anoxia (due to
- 4 5 vear-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
- 6 7 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
- 8 9 if the process is bacterially mediated like many reactions involving magnetic minerals. It would also
- 10 be interesting to pursue this: :: I have been working with sediment that were deposited under season-
- 11 ally anoxic conditions: : : does this reduction of grain size occur at a fast-enough rate so that it can
- 12 significantly alter grain-size distribution data? Obviously this occurs with magnetic minerals, but they
- 13 make up only a small party of the mineral assemblage. If all feldspars, for example, are quickly
- 14 irradicated under anoxic conditions, this would be news (I think: : :!). The material in bold above
- 15 should be presented at the beginning of this section. A lot of the rest of the discussion seems not 16 necessary.
- 17
- 18 We have reorganized and rewritten this section as:

19 "3.3.Geochemical indices as proxy for environmental changes

- Geochemical indices commonly differ between glacial and interglacial intervals, suggesting 20
- that conditions in cold and warm periods exerted distinct influences on the sedimentary 21
- 22 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 23 24 helpful in differentiating glacials and interglacials in the El'gygytgyn record.
- 25 Chemical weathering generally is considered to increase in warm and wet climates, although
- 26 this process can also be active under cold climatic conditions (e.g. Darmody et al., 2000; Hall
- 27 et al., 2002). Nonetheless, temperature and precipitation have been shown to be strong
- 28 controls on the rates of chemical weathering (e.g. White and Blum, 1995).
- 29 Surprisingly, sediments from the super interglacial MIS 11.3 exhibit low weathering indices
- 30 as compared to glacial sediments. Furthermore, weathering indices for MIS 11.3 are lower
- 31 than Holocene values, even though the super interglacial was considerably warmer and wetter
- 32 than the Holocene. That is, maximum summer temperature and annual precipitation of $\sim 4^{\circ}$ C
- 33 to 5°C and ~300 millimeters, respectively, were reconstructed for MIS 11.3, whereas the
- 34 mean temperature of the warmest month and mean annual precipitation during the Holocene
- thermal optimum were only $\sim 1^{\circ}$ to 2° C and ~ 50 mm higher than today (Melles et al., 2012). 35
- 36 Hence, a simple application of chemical indices for inferring chemical weathering intensity
- 37 within the El'gygytgyn catchment will be incorrect. Below we discuss and evaluate four
- 38 scenarios that might account for the differences between chemical indices observed in the
- 39 glacial and interglacial sediments from Lake El'gygytgyn.
- 40 1. Grain-size is considered an important factor that can influence the expected relationship
- between sediment composition and geochemical indices (e.g. van Evnatten et al., 2012). In 41
- 42 the El'gygytgyn sediments, sand content does not exceed 15.5%, and the average silt and clay
- 43 contents are ca. 69.2 and 27.7%, respectively. Mean grain size varies between 2.5 µm and 9.3
- um and is higher in interglacial sediments (Franke et al., 2013). Geochemical data from 44 45 volcanic rocks and sediments show a strong dependence of geochemical indices and
- 46 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 47
- 48 investigate the dependence of geochemical data and grain-size in the El'gygytgyn record, one
- 49 sample from MIS 7 was separated into two size fractions (<40 μ m and > 40 μ m). The < 40

1 µm fraction (90 % of the total sample weight) is depleted in CaO, Na₂O, and K₂O and 2 displays higher CIA (64.58), PIA (70.18) and CIW (74.97) indices as compared to the coarser 3 size fraction. The values of CIA, PIA and CIW for >40 μ m fraction (10 % of sample weight) 4 are 57.15, 60.21, and 67.22, respectively. Cold and warm periods experienced different 5 sedimentological regimes. A perennial ice cover on the lake during peak glacial times 6 restricted the transport of coarse-grained, less-altered sediments to the basin. However, this 7 situation enabled finer particles to be transported to the center of the lake through cracks in 8 the ice or through the formation of moats around the shore during summer (Asikainen et al., 9 2007). During interglacials, the greater precipitation would have increased the transport 10 energy of streams draining into the lake that in turn, would carry coarser clastic material to 11 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., 12 13 2013). Asikainen et al. (2007) noted that chlorite is the typical clay mineral in glacial 14 sediments, whereas smectite and illite are more abundant during interglacials. An abundance 15 of chlorite would increase certain geochemical indices; for example, the CIA and CIW for 16 chlorite is 100 (Nesbitt and Young, 1982; Fedo et al., 1995). 17 2. Variations in the sediment geochemistry between glacial and interglacial periods can be

18 caused by changes in sediment provenance. However, this explanation can be excluded in the 19 case of Lake El'gygytgyn, because it is a closed basin with a very restricted watershed that is 20 bordered by a distinct crater rim (Fig. 1). The highly altered material found in the 21 El'gygytgyn record possibly was transported by eolian processes, originating in remote 22 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 23 24 supply amounts to only 4–5% of the total sediment input. Prevailing local winds on the lake 25 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. 26 27 Today large areas of eolian sediment are absent in the El'gygytgyn catchment and in areas 28 immediately to the north and south of the lake. In other regions of Chukotka and in Yakutia, 29 silt-dominated Pleistocene sediments are widespread. They are associated with ice-rich 30 permafrost and are referred to as ice complex or *vedoma* deposits. There are different 31 explanations for the origin of the ice-complex sediments, including an eolian genesis 32 (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 33 34 (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-35 complex sediments. On the ternary Al₂O₃-(CaO+Na₂O)-K₂O and CaO-(Al₂O₃-K₂O)-Na₂O 36

- 37 diagrams, the various El'gygytgyn data plot parallel to the (CaO+Na₂O)–Al₂O₃ and Na₂O–
- $(Al_2O_3-K_2O)$ axes, respectively, clearly indicating local volcanic rocks to be the major source
- 39 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
- 41 during glacial intervals must have been derived from the product of local weathering products 42 of the velocity rocks. This scenario is unlikely
- 42 of the volcanic rocks. This scenario is unlikely.
- 43 3. During the warm and wet interglacials, the chemical weathering was increased and as result
- 44 the surface waters were enriched in mobile elements, such as Ca, Na, K, and Sr. The
- 45 consequent increase in stream and overland water flow into the lake resulted in a higher total
- 46 content of these elements in the lake sediments. In this case, low values of CIA, PIA, CIW,
- 47 and Rb/Sr reflect the high degree of chemical weathering. A similar scenario has been
- 48 suggested for the Heqing paleolake basin (An et al., 2011), Daihai Lake (Jin et al., 2001), and

- 1 Barkol Lake (Zhong et al., 2012). However Lake El'gygytgyn is extremely oligotrophic,
- 2 meaning that the water is low in anions and cations ($< 1 \text{ mg } 1^{-1}$) and has a low conductivity
- 3 based on measurements carried out in May (prior to snow melt) and in August (following
- 4 snow and ice melt and subsequent of lake water) at Lake El'gygytgyn (Cremer and van de
- 5 Vijver, 2006). Therefore, dissolved Ca^{2+} , Na^+ , and K^+ contributed only slightly to the total
- 6 contents of these elements in the sediments. In contrast, at Barkol Lake the water content of
- 7 Ca, Na, and K was $-444.8 \text{ mg } l^{-1}$, $-62089.39 \text{ mg } l^{-1}$, and $-1117.35 \text{ mg } l^{-1}$, respectively
- 8 (Zhong et al., 2012). Thus, this scenario is also unlikely to explain the El'gygytgyn patterns.

9 4. Diagenetic processes can obscure the detrital geochemical signals. Glacial facies at Lake

- 10 El'gygytgyn supposedly accumulated under anoxic bottom-water conditions (Melles et al.,
- 11 2007, 2012), resulting in the dissolution of magnetic minerals (Nowaczyk et al., 2007). The
- 12 formation of authigenic vivianite, Fe-Mn aggregates, pyrite, and greigite indicates a strong
- 13 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 similiar cation depletion in anoxic
- 15 Sea of Oknolsk sequences (wallhall et al., 2008). A similar cation depiction in anoxic 16 glacial sediments might explain the high indices of CLA. CUW and DLA. However, addition
- 16 glacial sediments might explain the high indices of CIA, CIW, and PIA. However, additional 17 mineralogical investigations are required to confirm such a scenario
- 17 mineralogical investigations are required to confirm such a scenario.
- 18 In summary, our data indicate that geochemical indices and selected elemental ratios mirror
- 19 sedimentation conditions and, possibly diagenetic processes that are triggered by
- 20 environmental and climate changes during glacials and interglacials. "
- 22 Page 411
- 23 Delete "Obtained data indicate". Start with "Our". It seems that the "controlling mechanism" is
- 24 anoxia, and should be mentioned in the concluding statement of this section.
- 25 Corrected
- 26
- 27 Section 4.
- 28 First paragraph. This would be much more effectively presented as part of a figure. Just point out the
- 29 substages in a figure, then you don't need the first paragraph. You may already have.
- 30 We have shown the substages on figures
- 31

32 Line 11. Why are you pointing out the vivianite and the ice-rafted sand grains? This is a discussion, so

- 33 you should, perhaps, make an interpretation (about the vivianite and sand), and then back it up with 34 evidence.
- 35 Line 14. Again, you are giving us evidence for something, but not directly telling us what the
- 36 interpretation is. Presumably the higher BSi levels are related to higher paleoproductivity (in Lake
- 37 Baikal and Lake E). Start out a section with this interpretation, and follow it up with the evidence. If
- 38 the special issue that this chapter belongs to has an article about diatoms, you may want to cross-
- 39 reference your data. The diatom article will, no doubt, make use of a BSi curve.
- 40 Line 18. This paragraph needs rethinking and reorganization. What are your points about this
- 41 paragraph? Clearly it needs to be broken up into at least two paragraphs. You need to tell us your
- 42 interpretation first. "High BSi values indicate relatively high paleoproductivity during deposition of
- 43 SS 11.3, especially in the middle. The high silica values mute the concentrations of other elements
- 44 *(list), but, curiously?, values of LOI, Cr and NI are abnormally high. (do you have an explanation for this?)*"
- 46 Page 412. Very interesting material, but again, I suggest that you reorganize the paragraph so your
- 47 interpretation is given first. The reader will have a much easier time digesting all of this information,
- 48 and that is what we are striving for. Start a paragraph pointing out alternating anoxic and oxic
- 49 conditions are indicated by : : :., and perhaps go beyond this and tell us why this is important. I would
- 50 think that this signature could be attributed to ice-cover vs. ice-free conditions, and indicates high
- 51 *climatic variability*.

Line 17. Delete this paragraph? It points out that upper 11.3 is transitional, and unless you have
something to say about this in terms of an interpretation, the observations that are made are easily
seen in the figures and don't really need to be pointed out.

4 Line 20. Give us an interpretation of the significance of these data, then provide the evidence.

5

7

6 We have reorganized the paragraph 4, 4.1. as:

4. "Geochemical zonation

8 Down-core changes in major and trace elements and in elemental ratios display a strong 9 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 10 11 optima of MIS 11 and MIS 9 to the frigid glacial environments of MIS 6, MIS 8, and MIS 10 12 (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 13 14 and Anderson, 2013; Melles et al., 2012, Tarasov et al., 2013). Pollen-based reconstructions 15 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 16 interstadials were cooler in comparison to MIS 11, and sediment data show a decreasing trend 17 in SiO₂. Mean summer temperatures during MIS 9.3 ranged from +12 to 14° C (Lozhkin et 18 19 al., 2013). Simultaneously, sediments of MIS 9.3 contain less SiO₂ as compared to MIS 11 20 (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 21 and January temperatures were +2 to 3°C and -24 to -25° C, respectively (Matrosova, 2009). 22 23 Glacial sediments are characterized by the highest content of TiO₂, Fe₂O₃, and MgO and by 24 the lowest values of SiO₂ (Fig. 4). Below we give a detailed description of MIS 11 and MIS 25 7.4 sediments, which represent the warmest and coldest stages within the core interval 26 reported here.

27 **4.1 Geochemical structure of MIS 11**

28 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 29 11.3 (Bassinot et al. 1994). On the basis of the El'gygytgyn geochemical data, however, 30 31 substage 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 32 33 MIS 12 and MIS 11 and marks the initial warming. This zone is characterized by gradual 34 increases in SiO₂, Na₂O, K₂O, CaO, and Sr, and decreases in TiO₂, Al₂O₃, MgO, Fe₂O₃, LOI, CIA, and CIW as characteristic of all warm stages. At this time, the lake had a semipermanent 35 ice-cover, lake waters were mixed, and more coarse material was supplied to the center of the 36 37 basin. In the earliest stages of warming, anoxic conditions probably still existed on the lake 38 bottom, resulting in favorable circumstances for the formation of large vivianite nodules (Fig. 39 10). During the spring, the lake supported a thick ice-cover, but active snow melt caused a 40 significant amount of debris to be carried by streams and deposited on the surface of the ice 41 (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 42 43 is characterized by a distinct peak in the geochemical data. These curves resembles both the distribution of biogenic silica in Lake Baikal (Prokopenko et al., 2006, 2010) and the 44 45 temperature reconstructions derived from Antarctic ice-cores marked as event 11.33 (Spahni 46 et al., 2005). The similarity in trends from such distant sites argues for the influence of global 47 forcings on these records.

1 The middle zone (zone b; 418.7-401.1 ka) of substage 11.3 exhibits a sharp increase in SiO₂ 2 owing to a pronounced BSi maximum (Melles et al. 2012). This increase represents high 3 bioproductivity during the sediment deposition. A simultaneous drop to minimum values in 4 TiO₂, Al₂O₃, and MgO, and lesser but significant decreases in Na₂O, CaO, K₂O, Rb, Sr, Zr, 5 and Ba, can presumably be traced to dilution by high amounts of biogenic silica. On the other 6 hand, values of LOI markedly increase during zone b, an increase which is common during 7 glacial intervals. High LOI reflects enhanced primary production and incomplete 8 decomposition of organic matter in the oxygenated bottom water. A few peaks in Cr and Ni 9 occur in this zone. However, they do not coincide with those of other elements, and further 10 detailed mineralogical investigations are needed to explain this pattern. 11 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 P₂O₅, MnO, and Fe₂O₃ in zone b 12 13 are underscored by high correlation coefficients of 0.93, 0.86, and 0.94 for P₂O₅/MnO, 14 Fe₂O₃/MnO, and Fe₂O₃/P₂O₅, respectively. These elements are typically contained in fine-15 grained vivianite, whose presence in the El'gygytgyn samples was verified by examination of 16 smear-slides. In contrast to glacial sediments, vivianite nodules > 0.25 mm do not occur in 17 zone b. The curve of high SiO₂ exhibits a saw-toothed pattern and is out of phase with the 18 P₂O₅, MnO, and Fe₂O₃ curves (Fig. 10). This relationship is clearly shown by a highly 19 negative correlation coefficient of -0.50 between SiO₂ and Fe₂O₃. Furthermore, numerous 20 peaks in Fe₂O₃ and corresponding maxima in the MnO/Fe₂O₃ ratio indicate these levels are 21 associated with reducing environments. These data suggest that the laminations observed in 22 the MIS 11.3 sediments were formed by alternating layers of: (1) biogenic sediments greatly 23 enriched in SiO_2 that were deposited on the lake bottom under oxidizing conditions: and (2) 24 sediments that were less enriched in SiO₂ but still contained abundant Fe, P, and Mn which 25 probably formed under anoxic conditions. Even in the oxidized horizons, MS is low, 26 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 27 28 magnetization indicates the dissolution of magnetic minerals was negligible. Zone b lacks a 29 coarse-grained component (e.g., sand or gravel), which implies only minor ice-floe activity 30 occurred at that time. 31 The alternation of oxic and anoxic horizons suggests that when anoxic condition occurred at 32 the water-sediment interface bioproductivity was high. This increase probably reflects the 33 presence of favorable, highly oxygenated conditions in the middle and upper parts of the 34 water column and increased decomposition of organic matter on the lake bottom. 35 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 SiO₂ and LOI, and a 36 37 simultaneous increase in TiO₂, MgO, Fe₂O₃, Al₂O₃ and other elements. Furthermore, there is 38 an absence of P₂O₅ and MnO peaks, vivianite nodules, and coarse sediments. Finer-grained 39 sediments progressively increase up-core, but the record does not display any sharp changes 40 in sedimentation. 41 In the upper part of MIS 11 (depth 18.07-17.11 m), the accumulation of biogenic silica was 42 insignificant, although sedimentation conditions were variable. The SiO₂ content ranges between 66.92 and 69.97% (mean 68.65%) and exhibits only minor fluctuations. However, 43 44 the TiO₂ curve displays four distinct minima at depths of 17.87 (392.1 ka), 17.73 (389.1 ka), 45 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 46 47 indicate enhanced ice-floe activity.

- Page 413. Start this paragraph "The lowest BSi values, reflecting the lowest paleoproductivity, 1
- occurred during interpreted MIS 6.6. and 7.4. These zones also have relatively high values of Ti: ::
- 2 3 etc., suggesting biogenically mediated diagenesis of transition metals and organic matter under
- anoxic conditions". Then give details as you see fit.
- 4 5 6 7 We have reorganized this paragraph
- Page 414. Conclusions.
- 8 9 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
- 10 interpretations. So there are two things you need to do early on: : : what is the basis for "glacial" and
- 11 "interglacial"? It doesn't appear to be the data you present on its own merit. Your data can support
- 12 the glacial vs. interglacial interpretation. But please indicate the basis upon which these basic and
- 13 essential distinctions are made. Second, what is the chronology based upon? Do you have
- 14 tephrochronology? Magne-tostratigraphy? I wouldn't necessarily just cite a chapter or paper, but 15
- provide at least rudimentary information to the reader about what the timeframe is based upon. 16 Last paragraph: :: you also attributed the loss of mobile elements to diagenesis of silicate minerals,
- 17 and creation of somewhat finer-grained material: :: I thought that was a fascinating suggestion which
- 18 could be backed up by SEM work on grain surfaces (searching for evidence of chemical erosion).
- 19
- 20 We changed the Conclusion as:
- 21 "The inorganic geochemistry of Lake El'gygytgyn sediments indicates distinct down-core
- 22 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 23
- 24 geochemical indicators. Interglacial sediments show high content of SiO₂, Na₂O, CaO, K₂O,
- 25 and Sr but low values for Al₂O₃, Fe₂O₃, TiO₂, and MgO. Glacial sediments, in contrast,
- exhibit opposite trends. Peaks in P₂O₃ and MnO coincide with an increased abundance of 26
- 27 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 28
- 29 due to the increased flux of biogenic silica, a reflection of maximum diatom production. The
- 30 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 31
- 32 substages, MIS 7.4 and MIS 6.6 are the most marked. They are characterized by the lowest
- 33 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 34
- 35 condition in the sediments and/or bottom water.
- Geochemical indices and some elemental ratios indicate a higher alteration of glacial 36
- 37 sediments as compared to interglacial sediments accompanied by a depletion of mobile
- 38 elements, such as Na, Ca, K, and Sr. This alteration might be caused by the sedimentation
- 39 regime and/or post-depositional diagenetic processes."
- 40
- 41 Tables.
- 42 Table 1. "Pearson correlation coefficients for : "
- 43 Corrected
- 44
- 45 Figures.
- 46 Figure 1. It would make it much easier for the reader if you gave a lithologic synopsis for each
- 47 geological unit. Then there would be no need to reiterate this information in the text.
- 48 We did 49
- 50 The latitude line for 67"30" is missing, probably because it conflicts with other labels. I suggest
- 51 placing tick marks for lat long on the periphery of the figure.
- 52 In a heavy line, provide an outline of the watershed.

- 1 We corrected and added the watershed line
- 2
 3 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!
- 4 multivariate analysis!
 5 Figure 4. Same comment as above.
- 6 For Figures 3 and 4. I think that a plot of age should be provided, not just depth and MIS. I suggest 7 plotting age next to depth. Or at the very least, provide an age-depth
- 8 model.
- 9 We added additional figure of PCA;
- 10 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.*
- 13 Corrected
- 14
- 15 Figures 8 and 9: : : nicely presented!
- 16 Thank you
- 17 18

Interactive comment on "Inorganic data from El'gygytgyn Lake sediments: stages 6–11" by P. S.

21 Minyuk et al.

22 Anonymous Referee #2

- 23 Received and published: 2 April 2013
- 24
- 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
- 29 elements than those in interglacial is interesting and surprising, despite never being clearly explained.
- 30 However, the discussion is wandering, incomplete, and deeply flawed scientifically, and it is nearly
- 31 unreadable. Overall, I cannot recommend it for publication. Even making allowances for the fact that
- 32 the authors' first language is not English, the manuscript is in poor shape. Almost half the sentences
- 33 have grammatical errors, commonly involving misuse of articles; agreements among subjects, objects,
- 34 and verbs; and verb tense. Beyond grammatical problems, ideas are poorly expressed or are
- 35 expressed in language that is idiomatically incorrect. For example, in the title, what are "inorganic
- 36 data?" presumably this means inorganic elemental analyses of sediment geochemistry. And "sand
- 37 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.
- 40 Perhaps the biggest weakness of the paper is that the differences in geochemistry between the glacial
- 41 and interglacial intervals are never adequately explained. The paper argues convincingly that neither
- 42 differential weathering nor different source area are sufficient to explain the observations. Grain-size
- 43 effects and diagenetic processes are offered as alternatives, but clear explanations of how these
- 44 *factors would produce the observed geochemical differences are not given.*
- 45 A few specific comments and questions will illustrate the level of problems with the manuscript. This is
 46 by no means a complete list.

- 48 We have edited the text, reorganized of the MS and changed the title of MS as:
- 49 "Inorganic geochemistry data from Lake El'gygytgyn sediments: marine
- 50 isotope stages 6–11"
- 51

- 1 1. Why was the interval from MIS 6 to 11 chosen? As the penultimate interglaciation, the absence of 2 MIS 5 is especially troubling. This choice seems quite fundamental, but is never mentioned.
- 3 In the Introduction we refined:

4 "In this paper, we focus on the geochemical characterization of sediments from the upper part 5 of ICDP core 5011-1, which spans MIS 6 to MIS 11. This interval encompasses great climatic 6 variations from the maximum temperatures of the "super" interglacials (MIS 11 and MIS 9) to 7 the extreme cold of MIS 6 and MIS 8 (Melles et al., 2012; Matrosova, 2009; Lozhkin et al., 8 2013)." 9

- 10 2. P395:7-9. No units are given with the water chemistry.
- 11 Corrected 12

18

13 3. Two different XRF methods were used to analyze for major and minor elements, yielding data that 14 are expressed in weight percentages and parts per million, respectively. I suppose this is sufficient for 15 comparison purposes, but it would have been nice if the analyses were recalculated to a common scale 16 and if there were some discussion of this.

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

19 4. Sec. 3.1.1. Because biogenic silica is such an important component of the sediments, it is absolutely 20 essential that the published BSi data be plotted along with the other geochemical data, including SiO_2 21 and Si/Ti in Figures 3, 5, 7, and 9. The dilution effect of BSi is mentioned in passing several times, but 22 in reality, it has a major effect on all of the data, and it is never discussed in a coherent way. 23

- 24 We agree that dilution effect of BSi has effect on all of the data. But we point out that dilution is
- 25 significant only for warmest interglacials.
- 26 For example:
- 27 "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 28
- samples from MIS 11.3 and 9.3 and less so for MIS 7.1 and 5.5, where SiO₂ exceeds 71% 29
- 30 (Fig. 5a). These results indicate that BSi dilution is significant during the warmest
- 31 interglacials. The linear correlation between SiO₂ and TiO₂ is very poor ($R^2 = 0.17$) in
- interstadial samples and is essentially nonexistent ($R^2 = 0.07$) for glacial sediments. This 32
- 33 pattern suggests only negligible or no dilution of BSi during cooler episodes in the
- 34 El'gygytgyn record (Fig. 5a)."
- 35 or:
- 36 "...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 37 38 due to dilution by extremely high BSi values."
- 39
- 40 5.P398:20-25. There is no mention of the complications involved with BSi, such as volcanic
- 41 amorphous silica or non-diatom productivity. Presumably these are covered by Melles et al. (2012).
- 42 Our gaol was not to study the mineralogy of bedrocks or sediments or amorphous silica. So we have
- 43 no any data on inorganic amorphous silica concentrations in the sediments. But we agree that it is
- 44 necessary to take into account the concentracions of volcanic amorphous silica that according to (Bely
- 45 and Belaya, 1998) occur in volcanic rocks of the El'gygytgyn area. We do not know sponges from 46 Lake as well as phytolites from vegetation. But there is a positive correlation between Si/Ti of
- 47 sediments from super interstadials and total diatoms (=productivity) (Snyder et al., 2013).
- 48

- 1 The original use of Si/Ti as an index of biogenic silica was in Lake Malawi (Brown et al.), which is not 2 referenced.
- 3 We referenced:
- 4 "The Si/Ti ratio is positively correlated with biogenic silica. This ratio has been previously
 5 used as a relative indicator of the biogenic component in sediments of Lake Malawi (Brown)
- 6 et al., 2007), Lake Baikal (Tanaka et al., 2007), and Lake El'gygytgyn (Melles et al., 2012). "
- 7
- 8 After discussing Si/Ti, the text switches to SiO_2/TiO_2 , which should be similar, but which is not the 9 same.
- 10 We agree similar. And our analysis is **quantitative** analysis.
- 11

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

- 15 Yes: "... results indicate that BSi dilution is significant during the warmest interglacials. The 16 linear correlation between SiO₂ and TiO₂ is very poor ($R^2 = 0.17$) in interstadial samples and 17 is essentially nonexistent ($R^2 = 0.07$) for glacial sediments. This pattern suggests only
- 18 negligible or no dilution of BSi during cooler episodes in the El'gygytgyn record (Fig. 5)."
- 19 20 However, I don't know how to interpret the correlation between SiO_2/TiO_2 and TiO_2/Al_2O_3 The most 21 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.
 23
- We changed the figure 5 (now figure 6) where was used Al_2O_3/TiO_2 instead TiO_2/Al_2O_3 and we point out:
- ²⁶ "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_2O_3/TiO_2 ratios
- 28 ($R^2 = 0.73-0.75$, 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)."
- 31

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.

- 35 We discuss relation between grain size and geochemistry in Section 3.3 (see below).
- 36
 37 8. P400: 1. A weak correlation between Si and Ti would imply strong and variable dilution by BSiâ^{*}A^{*}
- 38 *This line says just the opposite.*
- 39 We have adited this part of the text
- 40
- 9. P400: 18. I think that significant removal of Al by weathering in this frigid environment is highly
 unlikely.
- 43 We agree, and changed text as: "The Al_2O_3 vs. TiO₂ diagram shows a rather straight, linear trend
- 44 for interglacial sediments ($R^2 = 0.55$), whereas cold sediments have a scattered, nearly vertical
- 45 distribution ($R^2 = 0.024$) (Fig. 5e). We suggest that the higher TiO₂/Al₂O₃ ratios observed in
- 46 glacial sediments are due to an **enrichment in TiO_2** in the finer-grained sediments, as
- 47 mentioned above. It may relate to the concentration of biotite as noted by Young and Nesbit
- 48 (1998) for Baffin Island sediments."
- 49

10. P400: 27. 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

- 4 *incomplete here.*
- 5 We studied the magnetic mineralogy by optical, microzond, SEM, EDS, thermomagnetic 6 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
- 8 titanomagnetite. In Lake El'gygytgyn sediments, the majority of the iron oxides are
- titanomagnetites that include Al, Si, and Mn impurities. Some titanomagnetites have
- 10 characteristic cracks in the grains, which indicate low-temperature maghemitization. Other
- 11 titanomagnetites are oxidized at high-temperatures, displaying lamellae of ilmenite and
- 12 titanium magnetite. Chromite, ilmenite, and rutile were also found in the sediments."
- 13
- 14 We found and studied vivianite, pyrite, greigite, iron, Fe-Mn agregares.
- 15
 16 11. P402: 3. There is a good story here concerning redox conditions and vivianite, but was vivianite
 17 actually observed or measured (the ms doesn't say)? Vivianite is readily identifiable in smear slides.
- 18 We do not discuss the presence of vivianite in the sediments; just refer to (Minyuk et al., 2013).
- 19 Electron microprobe analyses, electron microscopy and energy dispersive spectroscopy,
- 20 optical (smear slide studies) were used to identify diagnostic mineral.
- 21 *12. 3.1.4.* This discussion of Cr and Ni is very hard to follow, and I am not sure it adds much to the story.
- 23
- 24 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
- 27

13 3.1.5. 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 uset being, but there are furgingle until a K/Ti) that are easier to

- has been used as an index of weathering, but there are far simpler ratios (e.g. K/Ti) that are easier to
 interpret.
- 33 At first, these elements are trace elemenents which were measured by different method and
- 34 equipment then major elements (much faster measuring).
- 35 Secondly, we indicated:
- 36 "The first PC axis of the PCA results explains 40% of the total variance. It is positively
- 37 correlated with Al₂O₃, TiO₂, Fe₂O₃, MgO, Rb/Sr, CIA, PIA, CIW, Ni, and Cr and negatively
- 38 correlated with SiO₂. The second PC axis explains an additional 24% of the variability and is
- 39 characterized by positive loadings of Ba, K, Rb, Zr, Na₂O, CaO, MS, and Sr. It is negatively
- 40 correlated with P_2O_5 , MnO, and LOI. These results indicate the presence of three main data
- 41 groups. SiO₂ is clearly related to the super interglacial sediments, while Ba, K, Rb, Zr, Na₂O,
- 42 CaO, MS, and Sr are related to the interstadial sediments. Al₂O₃, TiO₂, Fe₂O₃, MgO, Rb/Sr,
- 43 CIA, PIA, CIW, Ni, and Cr are associated with glacial sediments (Fig. 3)."
- 44
- 45 *14. 3.2. Geochemical indices. The first paragraph of this section is a good description of what these*
- 46 indices are and how they can be used, but the subsequent discussion is useless. Why discuss every
- 47 index that has ever been proposed? Most are redundant and only a few have real meaning for
- 48 El'gygytgyn.
- 49 We have reduced the indices
- 50

- 1 15. P408: 20-23. This is one of the key observations of the paper, even if it is not in correct English.
- 2 *However, a convincing alternative to weathering is never described.*
- 3 16. P409: 29. The difference in clay minerals between glacial and interglacial sediments might be
- 4 5 important for the geochemistry, but what produced the difference in clays, if not weathering?
- Secondary clay mineral formation in this environment is highly unlikely.
- 6 7 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
- 8 cations. This is a key uncertainty in suggesting diagenesis as an explanation for the differences
- 9 between glacials and interglacials.
- 10 We have reorganized the discussion on indices:

3.3 "Geochemical indices as proxy for environmental changes 11

- 12 Geochemical indices commonly differ between glacial and interglacial intervals, suggesting
- 13 that conditions in cold and warm periods exerted distinct influences on the sedimentary
- 14 record. For example, glacial sediments show high values of CIA, CIW, Rb/Sr, Ba/Sr, LOI
- 15 depleted by potassium, sodium, calcium, and strontium. Thus, these characteristics should be
- helpful in differentiating glacials and interglacials in the El'gygytgyn record. 16
- 17 Chemical weathering generally is considered to increase in warm and wet climates, although
- 18 this process can also be active under cold climatic conditions (e.g. Darmody et al., 2000; Hall
- 19 et al., 2002). Nonetheless, temperature and precipitation have been shown to be strong
- 20 controls on the rates of chemical weathering (e.g. White and Blum, 1995).
- 21 Surprisingly, sediments from the super interglacial MIS 11.3 exhibit low weathering indices
- 22 as compared to glacial sediments. Furthermore, weathering indices for MIS 11.3 are lower
- 23 than Holocene values, even though the super interglacial was considerably warmer and wetter
- 24 than the Holocene. That is, maximum summer temperature and annual precipitation of ~4°C
- 25 to 5°C and ~300 millimeters, respectively, were reconstructed for MIS 11.3, whereas the
- 26 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). 27 Hence, a simple application of chemical indices for inferring chemical weathering intensity 28
- 29 within the El'gygytgyn catchment will be incorrect. Below we discuss and evaluate four
- 30 scenarios that might account for the differences between chemical indices observed in the
- 31 glacial and interglacial sediments from Lake El'gygytgyn.
- 32 1. Grain-size is considered an important factor that can influence the expected relationship
- between sediment composition and geochemical indices (e.g. van Evnatten et al., 2012). In 33
- 34 the El'gygytgyn sediments, sand content does not exceed 15.5%, and the average silt and clay
- 35 contents are ca. 69.2 and 27.7%, respectively. Mean grain size varies between 2.5 µm and 9.3
- um and is higher in interglacial sediments (Franke et al., 2013). Geochemical data from 36
- 37 volcanic rocks and sediments show a strong dependence of geochemical indices and
- 38 granulometry. Volcanic rocks and impactites display the lowest values of CIA, PIA, and
- 39 CIW. In finer sediments, the values of geochemical indices increase (Fig. 9 new). To further
- 40 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 ($<40 \mu m$ and $>40 \mu m$). The <4041
- 42 μ m 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 43 44 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 45
- sedimentological regimes. A perennial ice cover on the lake during peak glacial times 46
- 47 restricted the transport of coarse-grained, less-altered sediments to the basin. However, this
- 48 situation enabled finer particles to be transported to the center of the lake through cracks in
- 49 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

4 would result in a greater redistribution of clastic material within the basin (Francke et al.,

5 2013). Asikainen et al. (2007) noted that chlorite is the typical clay mineral in glacial

6 sediments, whereas smectite and illite are more abundant during interglacials. An abundance

7 of chlorite would increase certain geochemical indices; for example, the CIA and CIW for

8 chlorite is 100 (Nesbitt and Young, 1982; Fedo et al., 1995).

9 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 10 11 case of Lake El'gygytgyn, because it is a closed basin with a very restricted watershed that is 12 bordered by a distinct crater rim (Fig. 1). The highly altered material found in the 13 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 14 15 materials to the basin during spring and summer under modern climate condition. Total eolian 16 supply amounts to only 4–5% of the total sediment input. Prevailing local winds on the lake 17 are from the north and south. They are strong and persistent, and this likely plays an important 18 role in controlling lake shape (Nolan et al., 2007). Past wind direction was likely the same. 19 Today large areas of eolian sediment are absent in the El'gygytgyn catchment and in areas 20 immediately to the north and south of the lake. In other regions of Chukotka and in Yakutia, 21 silt-dominated Pleistocene sediments are widespread. They are associated with ice-rich 22 permafrost and are referred to as ice complex or *vedoma* deposits. There are different 23 explanations for the origin of the ice-complex sediments, including an eolian genesis 24 (Tomirdiaro and Chernen'ky, 1987). Geochemical data of the ice-complex are available from 25 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 26

- 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 $(CaO+Na_2O)-Al_2O_3$ and Na_2O-

30 $(Al_2O_3-K_2O)$ 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

32 separate group on the diagrams. These results suggest that any contain input into the lake 33 during glacial intervals must have been derived from the product of local weathering products

34 of the volcanic rocks. This scenario is unlikely.

35 3. During the warm and wet interglacials, the chemical weathering was increased and as result

36 the surface waters were enriched in mobile elements, such as Ca, Na, K, and Sr. The

37 consequent increase in stream and overland water flow into the lake resulted in a higher total

38 content of these elements in the lake sediments. In this case, low values of CIA, PIA, CIW,

39 and Rb/Sr reflect the high degree of chemical weathering. A similar scenario has been

40 suggested for the Heqing paleolake basin (An et al., 2011), Daihai Lake (Jin et al., 2001), and

- 41 Barkol Lake (Zhong et al., 2012). However Lake El'gygytgyn is extremely oligotrophic,
- 42 meaning that the water is low in anions and cations $(< 1 \text{ mg } l^{-1})$ 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
- 44 show and ice ment and subsequent of lake water) at Lake Er gygytgyn (Cremer and van de 45 Vijver, 2006). Therefore, dissolved Ca^{2+} , Na^+ , and K^+ contributed only slightly to the total
- 46 contents of these elements in the sediments. In contrast, at Barkol Lake the water content of
- 47 Ca, Na, and K was $-444.8 \text{ mg } l^{-1}$, $-62089.39 \text{ mg } l^{-1}$, and $-1117.35 \text{ mg } l^{-1}$, respectively
- 48 (Zhong et al., 2012). Thus, this scenario is also unlikely to explain the El'gygytgyn patterns.

- 1 4. Diagenetic processes can obscure the detrital geochemical signals. Glacial facies at Lake
- 2 El'gygytgyn supposedly accumulated under anoxic bottom-water conditions (Melles et al.,
- 3 2007, 2012), resulting in the dissolution of magnetic minerals (Nowaczyk et al., 2007). The
- 4 formation of authigenic vivianite, Fe-Mn aggregates, pyrite, and greigite indicates a strong
- 5 post-depositional alteration of sediments during anoxia. This process can also lead to the
- 6 partial dissolution of silicates, which is accompanied by a loss of cations as was reported for
- 7 Sea of Okhotsk sediments (Wallmann et al., 2008). A similiar cation depletion in anoxic
- 8 glacial sediments might explain the high indices of CIA, CIW, and PIA. However, additional
- 9 mineralogical investigations are required to confirm such a scenario.
- 10 In summary, our data indicate that geochemical indices and selected elemental ratios mirror
- sedimentation conditions and, possibly diagenetic processes that are triggered by
- 12 environmental and climate changes during glacials and interglacials."
- 14 18. 4. Stages 11, 6.6, and 7.4. Why were these stages chosen for detailed discussion?
- 16 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
- 24 of mean temperatures for July and January were +12 to 16° C and -20 to -24° C, respectively,
- and mean annual precipitation was \sim 550 to 600 millimeters. The following interglacials and
- 26 interstadials were cooler in comparison to MIS 11, and sediment data show a decreasing trend
- 27 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
- 29 (Fig. 4). During MIS 7 mean July temperature was +2.4° C (Matrosova, 2009), and the warm
- 30 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
- 32 Glacial sediments are characterized by the highest content of 110₂, Fe₂O₃, and MgO and by 33 the lowest values of SiO₂ (Fig. 4). Below we give a detailed description of MIS 11 and MIS
- 34 7.4 sediments, which represent the warmest and coldest stages within the core interval
- 35 reported here."
- 36

1 Figure 1. Location (A) and geological map (B) of the El'gygytgyn area adapted from Bely 2 and Raikevich (1994) and Bely and Belaya (1998). 3 4 Figure 2. Diagram of total alkali and silica (Le Maitre et al., 2002) for volcanic rocks from the 5 El'gygytgyn area. Geochemical data are from Bely and Belaya (1998). 6 7 Figure 3. Principal components analysis of the Lake El'gygytgyn sediments. Red, blue and 8 rose symbols are samples from interglacial, glacial, and super interglacial sediments, 9 respectively. 10 Figure 4. Graphs of selected elements plotted by depth and age. Yellow, orange and blue bars 11 represent interglacials, super interglacials, and glacials, respectively. Marine isotopic stages 12 13 (MIS) follow Bassinot et al. (1994). Note that SiO_2 is plotted on a reversed scale. Lithofacies 14 A, B and C are shown in blue, yellow, and red, respectively. 15 16 Figure 5. Scatterplots of: a) SiO₂ versus TiO₂; b) SiO₂/TiO₂ versus Al₂O₃/TiO₂; c) Al₂O₃ 17 versus SiO₂; d) Fe₂O₃ versus TiO₂; e) TiO₂ versus Al₂O₃; f) Fe₂O₃ versus Al₂O₃; g) Fe₂O₃ 18 versus MnO; and h) Ni versus Cr. Red (blue) symbols indicate interglacial (glacial) samples. 19 Violet squares are samples where SiO₂ content exceeds 71%. Orange squares indicate 20 samples from MIS 11, whereas green squares are samples from MIS 6.6 and 7.4. 21 22 Figure 6. Distribution of selected geochemical indices and ratios plotted by depth and age. 23 Yellow, orange and blue bars represent interglacials, super interglacials and glacials. 24 respectively. Marine isotopic stages (MIS) follow Bassinot et al. (1994). Lithofacies A, B and 25 C are shown by blue, yellow, and red, respectively. 26 27 Figure 7. Diagrams showing variations in TiO₂ and Fe₂O₃ versus magnetic susceptibility and 28 ferromagnetic and paramagnetic components of induced magnetization. Red (blue) symbols 29 indicate samples from interglacial (glacial) sediments. 30 31 Figure 8. Ternary diagrams showing weathering trends in volcanic rocks, lake sediments, and 32 ice complex: a) (CaO+Na₂O)-Al₂O₃-K₂O diagram (Nesbitt and Young, 1984); and b) CaO-33 (Al₂O₃-K₂O)-Na₂O diagram (Fedo et al., 1995). Arrow indicates the weathering trends. 34 35 Figure 9. Geochemical indices (CIA, PIA, CIW) from impactites (n = 9), volcanic rocks (n = 9)19) (Belv and Belava, 1998), pebbles comprised of volcanic rocks (n = 11) (Feldman et al., 36 37 1980), coarse sand (n = 2), fine sand (n = 1), interglacial sediments (n = 228), and glacial 38 sediments (n = 387). 39 40 Figure 10. Geochemical structure of MIS 11. Note that TiO₂ is plotted using a reversed scale. 41 42 Figure 11. Geochemical structure of MIS 7.4. Note that SiO₂ is plotted using a reversed scale. 43

Table 1 Pearson (r) correlation coefficients for major and trace elemental analyses from Lake
 El'gygytgyn sediments

2 El gygytgyn sediments SiQa AlaQa TiQa FeaQa MnQ MnQ CaQ NaaQ KaQ PaQa Rb Zr Sr Ba Ni Cr															
	SiO ₂	Al ₂ O ₃ TiO ₂	Fe_2O_3	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	Rb	Zr	Sr	Ba	Ni	Cr
SiO ₂	1.00														
AI_2O_3	-0.89	1.00													
TiO ₂	-0.74	0.62 1.00													
Fe ₂ O ₃	-0.82	0.49 0.69	1.00												
MnO	-0.26	0.01 0.22	0.51	1.00											
MgO	-0.81	0.77 0.83	0.65	0.08	1.00										
CaO	0.12	-0.04 -0.34	-0.38	-0.29	-0.29	1.00									
Na ₂ O	-0.04	0.02 0.10	-0.17	-0.12	-0.14	0.55	1.00								
K ₂ O	-0.47	0.64 -0.06	0.01	-0.31	0.22	0.49	0.31	1.00							
P_2O_5	-0.21	-0.16 0.03	0.56	0.55	-0.01	-0.25	-0.22	-0.29	1.00						
Rb	-0.66	0.82 0.19	0.22	-0.19	0.47	0.18	0.02	0.89	-0.22	1.00					
Zr	-0.63	0.55 0.82	0.48	0.13	0.55	0.01	0.53	0.22	-0.09	0.25	1.00				
Sr	0.19	-0.07 -0.38	-0.49	-0.34	-0.42	0.83	0.71	0.56	-0.31	0.23	0.08	1.00			
Ва	-0.47	0.55 0.13	0.07	-0.20	0.21	0.56	0.49	0.86	-0.22	0.69	0.38	0.62	1.00		
Ni	012	0.07 0.21	0.14	0.09	0.12	-0.02	0.06	-0.04	0.01	-0.04	0.22	-0.05	0.01	1.00	
Cr	-0.38	0.25 0.60	0.47	0.21	0.50	-0.32	009	-0.20	0.12	-0.04	0.42	-0.41	-0.11	0.78	1.00

Table 2 Pearson (r) correlation coefficients for selective elemental ratios and indices from
 Lake El'gygytgyn sediments

Lake Li Sysytsyn seaments										
	CIA	CIW	PIA	Rb/Sr	SiO ₂ /TiO ₂	SiO_2/AI_2O_3	Ba/Sr	LOI	MS	J_p
CIA	1.00									
CIW	0.97	1.00								
PIA	0.99	0.99	1.00							
Rb/Sr	0.86	0.90	0.89	1.00						
SiO ₂ /TiO ₂	-0.57	-0.52	-0.54	-0.51	1.00					
SiO ₂ /Al ₂ O ₃	-0.58	-0.59	-0.59	-0.60	0.89	1.00				
Ba/Sr	0.73	0.75	0.74	0.85	-0.63	-0.64	1.00			
LOI	0.35	0.38	0.37	0.31	0.37	0.26	0.12	1.00		
MS	-0.66	-0.57	-0.61	-0.44	0.29	0.18	-0.35	-0.43	1.00	
Jp	0.73	0.67	0.70	0.59	-0.46	-0.41	0.51	0.37	-0.88	1.00



Figure 1



Figure 2



Figure 3



Figure 4



Figure 5



1

Figure 6



Figure 7



Figure 8



Figure 9



Figure 10



Figure 11