

Interactive comment on “Biogeochemical properties and diagenetic changes during the past 3.6 Ma recorded by FTIR spectroscopy in the sediment record of Lake El’gygytgyn, Far East Russian Arctic” by C. Meyer-Jacob et al.

C. Meyer-Jacob et al.

carsten.meyer-jacob@emg.umu.se

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Dear Editor and Reviewers,

We would like to thank both reviewers for their reviews and valuable suggestions that will help improving our manuscript. Please find below our responses to the comments of both reviewers.

Yours sincerely, Carsten Meyer-Jacob

Response to comments by Reviewer #1 (anonymous)

C1653

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Reviewer comment: Firstly, I hold doubts that the content of this manuscript are well suited to CP. Although the remit of CP includes 'Development and Validation of New Proxies', in my mind, this relates to the development of techniques through which past climates can be inferred - namely considering the interaction between climate variability and sedimentary/ geochemical/biological systems. By contrast, the MVMR manuscript deals specifically with the development of a geochemical technique for the primary purpose of geochemistry. Although BSi, TOC etc. can be used to infer past environmental change, that leap is not covered in this paper and nor should it be. I therefore consider this manuscript would be better suited to a more technical geological/geochemical journal.

Author response: Seen as a single, independent publication, we agree with the reviewer that, because the technique provides primarily information about the geochemistry and only indirectly about the climate variability, a more technical journal focusing on geochemistry would be more suitable for the manuscript. However, our manuscript must be seen as part of the El'gygytgyn Special Issue, which in this context is well suited to be published in CP. Several studies of the sediment record from Lake El'gygytgyn refer to and/or rely on FTIR-inferred BSi concentrations (e.g. Melles et al., 2012, Brigham-Grette et al., 2013, Nowaczyk et al., 2013, Vogel et al., 2013). Variations of BSi concentrations in Lake El'gygytgyn are strongly tied to climate variability, in particular to temperature variations, affecting the nutrient (chemical weathering in the catchment) and light availability (duration of ice coverage) for primary production. A description and discussion of the technique performed on the entire sediment record as well as the resulting model performances is in our point of view important to understand and evaluate the application of this emerging technique in studies of the Lake El'gygytgyn sediment record. We believe that the Lake El'gygytgyn Special Issue in CP containing several publications referring to the here presented FTIR-calibrations (e.g. Nowaczyk et al., 2013, Snyder et al., 2013, Vogel et al., 2013) is the best suited forum for this discussion.

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Reviewer comment: In addition, I am not convinced that this manuscript is novel enough for a journal such as CP. As MVMR discuss, FTIR techniques have already been developed for, and applied to a variety of lake sedimentary systems. In some ways, this manuscript is essentially a repetition of those studies for a new site, and whilst this is an important and necessary step for future research, I do not consider it to be an extremely novel piece of research in it's own right.

Author response: We fully agree that the application of FTIRS to determine biogeochemical proxies in lake sediments itself is not novel. In this study, (1) we apply the method for the first time to a 318 m long and 3.6 Ma old sediment record affected by early diagenetic processes showing that the method is not restricted to young, unconsolidated sediment records. (2) In addition to this further proof of the broadness of the method applicability, (3) we are now able to expand the provided data set in a revised version of the manuscript. This FTIR-inferred data set covering the whole sediment record of Lake El'gygytgyn will provide information about environmental and climatic evolution in the Arctic during the past 3.6 Ma in high-resolution. Even though the BSi record is for the most part already published (Melles et al., 2012, Brigham-Grette et al., 2013, Nowaczyk et al., 2013), high-resolution FTIR-inferred concentrations for (4) TOC and (5) TIC are entirely new. Particularly, information on the occurrence of TIC in the thus far assumed to be carbonate-free lake system have not been published yet.

Reviewer comment: The real novelty of this research from a FTIR development perspective is the question of sediment diagenesis and the robustness of FTIR inferred parameters in the face of diagenetic alteration. The 3.6 Ma old sediments of El'gygytgyn provide a valuable resource with which to examine these questions, and MVMR highlight this importance in the introductory material. However, ultimately, the section which deals with diagenesis is very brief and warrants considerable expansion in my opinion. In particular, I was not convinced by the approach to assessing diagenetic change using FTIR - by 'calibrating' FTIR spectra against depth. Whilst diagenesis should be expected to increase with sediment depth, it is certainly not the only factor and the

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possibility that other factors could explain the FTIR spectral change with depth is discussed only briefly. I would have preferred a more detailed discussion and examination of specific diagenetic changes, such as the dehydration/maturation of silicate, as well as organic diagenetic processes and how they might affect the original FTIR -based inferences. Certainly, a FTIR based tool to explore diagenetic patterns would be of extreme value in it's own right.

Author response: We agree with the reviewer that this section in the manuscript can be expanded. In a revised version of the manuscript, we will discuss the potential impact of diagenesis on the FTIR spectra of sediment samples in more detail. This will include the possible alteration, mainly dehydration, of specific inorganic, e.g. clay minerals, and organic compounds, such as biogenic silica and organic matter. We used the approach to calibrate the FTIR-spectral against the burial depth to show that the FTIR signature of a sample in general provides information about its burial depth/age and consequently about its diagenetic maturity. We are aware that other factors than diagenesis can cause a change in the FTIR spectra with increasing depth and will expand this in the discussion. However, the observed change in the FTIR spectra facilitating an approximate estimation of the burial depth strongly suggest to be caused by a constant, gradual process, as for instance diagenesis. To strengthen our interpretation, we will discuss other potential factors, such as differences in clay mineralogy and quality of organic matter in the context of the Lake El'gygytgyn sediment record that could have a similar impact on the FTIR spectra. With our study, we would like to point out that FTIRS is a potential tool to analyze diagenetically triggered processes in future research. To obtain more detailed information about those processes in the sediment by means of IR spectroscopy, the analysis of single sediment compounds by, for example, IR microscopy would most likely be necessary.

Reviewer comment: More detail would be appreciated on the way Partial Least Squares was used to develop predictive models in this context. For example, what determines the number of components used in each model? Are the wavelengths cho-

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sen dependent entirely on improving the statistical fit, or is any prior knowledge used in the selection of these wavelengths?

Author response: We agree with the reviewer and will add more information about development of the PLS models. The number of components was selected based on their significance. Previous studies have shown that models using wavelength ranges specific for the absorbance caused by a certain compound in the mid IR region can exhibit similar statistical performances as models based on the whole measured range (Rosén et al., 2010, 2011). Models based on the entire measured spectral range (in this case 3750-400cm⁻¹), however, seem to be more stable when the sediment composition of a sample differs from the composition of samples included in the calibration. This results from the fact that BSi, TOC, and TIC are measured as concentrations and therefore are related to the entire sediment composition. Due to the very distinct absorbance bands of carbonates, TIC models based on component specific wavelengths are relatively stable as well. In contrast, wavelength specific models for BSi and TOC are less accurate due to absorbance bands of other components overlapping the relatively broad bands of these two sediment compounds. We excluded the IR range between 400 and 450cm⁻¹ from the calibrations due to the lower signal-to-noise ratio obtained for this part of the measured IR spectrum.

Reviewer comment: The final interpretative section on the environmental significance of BSi, TOC and TIC changes is largely speculative, but no more so than other papers in this field. I question whether or not this section is entirely necessary, but in the most part found it useful to place the analyses in a paleoenvironmental context.

Author response: Due to the low sample resolution, we tried to keep the interpretation of the data to large scale patterns to minimize the speculative character. A more profound interpretation of the data will be possible by increasing the sample resolution in the revised version of the manuscript. However, we will further focus on the interpretation of large scale patterns, because a more detailed interpretation of climatic and environmental history at Lake El'gygytyn would be beyond the scope of this study.

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Reviewer comment: In Figure 6, AR-BSi and AR-TOC are plotted in a way that prevents the observation of any signal younger than 3 Ma due to the marked decline in these parameters. This should be re-plotted in a way that allows the reader to compare accumulation rates vs. % data for the whole record.

Author response: Figure 6 will be improved for the revised manuscript.

Response to comments by Reviewer #2 (anonymous)

Reviewer comment: 1. This paper is limited to an application of statistics in method. The FTIRS quantitative method for biogeochemical properties in sediment cores have been already established by Vogel et al. (2008), Rosen et al. (2010), Rosen et al. (2011), Melles et al. (2012).

Author response: This is a founded argument and we fully agree with the reviewer that, as also noted by reviewer #1, the application of FTIRS to determine biogeochemical proxies in lake sediments has already been established in studies by Vogel et al. (2008) and Rosén et al. (2010, 2011). The novel part of this study is the application of the technique to sediments affected by early diagenetic processes. Our results demonstrate that the method is not restricted to young, unconsolidated sediment records, thus highlighting its broad applicability. Further, the BSi concentrations and BSi accumulation rates, respectively, shown in Melles et al. (2012) and Brigham-Grette et al. (2013) are based on the model described in this manuscript. A discussion of the FTIR calibrations in these publications was not provided due to their focus on the reconstruction on the environmental and climatic history of Lake El'gygytgyn. However, a discussion of the background of the developed models is necessary to objectively assess the reliability of the shown data. We believe that the Lake El'gygytgyn Special Issue in CP is the best suited forum for this discussion, because further publications in the Special Issue refer or rely on the here described calibration (e.g. Nowaczyk et al., 2013, Snyder et al., 2013, Vogel et al., 2013).

Reviewer comment: 2. The authors said that the FTIRS is rapid and cost-effective

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method. However, time resolution of the dataset in this paper is much lower than previous study (Melles et al., 2012). Moreover, the biogeochemical properties in Lake El'gygytgyn sediment cores during 2.8 Ma by FTIRS method have been also reported (Melles et al., 2012). I strongly recommend that the authors try to focus on high-time resolution analyses during Pliocene compared with the reported values from Quaternary. Then, I believe that the authors can discuss about climate and environmental changes in Far East Russian Arctic from 3.6 Ma to 2.8 Ma.

Author response: We will expand the data resolution, as suggested by the reviewer, throughout the entire sediment record. Even though the BSi record is for the most part already published (Melles et al., 2012; Brigham-Grette et al., 2013, Nowaczyk et al., 2013), high-resolution FTIR-inferred concentrations for TOC and TIC are so far unpublished. This will allow us a more profound interpretation of the long-term environmental and climatic evolution in the Arctic during the past 3.6 Ma. Our interpretations will further focus on large scale patterns, because a more detailed interpretation merely based on the FTIR-inferred proxies would be somewhat speculative and out of the scope of this study.

Reviewer comment: 3. In this paper (Figure 5), the error of FTIRS inferred burial depth is very large in the lower part of the core. The FTIRS inferred values at ~300m measured depth actually varied from ~200 to ~400 m. The authors should compare the values with other proxy for diagenetic changes.

Author response: As also suggested by reviewer #1, we will extend the discussion of this approach in the revised version and further discuss potential changes in the FTIR spectra related to diagenesis. Our intention with showing the relationship between FTIR spectral information and a sample's burial depth is to demonstrate the potential application of IR spectroscopy to obtain information about the maturity (age/burial depth) of a sediment sample, rather than presenting an implementable proxy for diagenesis in sediments at this point. In our point of view, FTIRS can potentially become a helpful tool in future research to assess sediment maturity and diagenetic processes.

However, further work, most likely on single sediment components to avoid spectral overlaps by different sediment constituent, will be necessary to provide more accurate FTIR-inferred information about the maturity of a sediment sample.

Minor comments:

Reviewer comment: Fig 1. The authors should not use the same figure as published one (Melles et al., 2012). It is just a copy, and it's completely same as previous study (Melles et al., 2012).

Author response: The figure has been modified after Melles et al. (2012), which we will point out in the revised version.

Reviewer comment: Fig 2. What is the meaning of comparison between Fig 2c and Fig 2d? If the authors discuss it based on literatures (Rosen et al., 2011; 1012), it could be just a repetition. If a 7-component TIC model is original way in this paper, the authors should show the detailed processes (How they can select the component?).

Author response: The developed TIC models are based on samples and their FTIR-spectra that have not been used in previous studies. Rosén et al. (2010, 2011) have shown that the use of component specific wavelengths in the calibration can yield a similar statistical performance as the use of the entire measured spectral range. Fig. 2c and 2d show the relationship between FTIR-inferred and conventionally measured TIC concentrations resulting from these two approaches and resulting different calibration models. Depending on the complexity of the sediment composition, the use of component specific wavelength does not always provide an improved or similar model performance. We will follow the suggestion of the reviewer and add information about the model development and particularly about the selection of components. The number of components depends on the complexity of the sediment composition, the characteristics of the proxy related absorbance bands in the FTIR spectra and the amount of spectral overlaps by other sediment components. Only significant PLC components were included into the calibration models.

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Reviewer comment: Fig 3. Fig 4. Please clarify the collected depth, age and sampling location of the BSi. Did they take the BSi samples from same core sediments (5011-1)?

Author response: Fig. 3 shows the loading plots of the FTIR calibration models for BSi, TOC, and TIC and is based on several sediment samples for core PG1351, Lz1024; 5011-1 distributed over the entire sediment record. We will add information on the origin of the samples and numbers of samples to the figure caption. Fig. 4 shows the FTIR spectra of purified BSi from a sediment sample of core Lz1024 from Lake El'gygytgyn. We will add this information as well as the sample depth and age.

Reviewer comment: Fig 5. It is difficult to see Figure 5 in this paper. What is "Burial depth" on the top of figures? The authors can express as "measured burial depth (m)" just below the horizontal axis. Anyway, it is not necessary to show the information on the top of figure, because the authors have already described it in the figure legend.

Author response: We will incorporate the suggested changes.

Reviewer comment: Page 2492 line7 and Page 2493 line25. In this paper, the authors should clearly show the age model for core 5011-1. The authors refer to Nowaczyk et al ("in preparation") for the age model. I believe that nobody can refer to the manuscript "in preparation".

Author response: The age model has now been published in CPD (Nowaczyk, N. R., Haltia, E. M., Ulbricht, D., Wennrich, V., Sauerbrey, M. A., Rosén, P., Vogel, H., Francke, A., Meyer-Jacob, C., Andreev, A. A., and Lozhkin, A. V.: Chronology of Lake El'gygytgyn sediments, *Clim. Past Discuss.*, 9, 3061-3102, doi:10.5194/cpd-9-3061-2013, 2013) and the citation will be changed.

Reviewer comment: Page 2496 lines4-14 and Page 2498 lines8-20. The information has been reported (Vogel et al., 2008; Rosen et al., 2010; 2011), so it should be shown in Introduction section. The authors should try to show original novel results in CPD.

Author response: We fully agree with the reviewer that the correlation between IR

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absorbance bands of carbonate and the most important wavelength ranges for the TIC calibration model has been shown by Vogel et al. (2008) and Rosén et al. (2010, 2011). The reported loadings in our study are based on a new set of samples and consequently show slight differences to the loadings presented in other studies. We refer to these studies to highlight the stability of FTIR calibrations. We will clarify this in the revised manuscript.

Reviewer comment: Page 2500 lines19-20. In my opinion, the authors should show the XRD results in this paper. It is not original data for your research? If it is only citations from others, they should show it in the Introduction section.

Author response: We agree with the reviewer and we will clarify in the introduction that IR spectroscopy allows not only a quantification of biogeochemical proxies but also a differentiation between different mineral phases, especially for carbonates.

Reviewer comment: Page 2501 lines3-6. Why the TIC values increased at 223 ka? Please make discussion about it.

Author response: We will add this to the discussion.

Reviewer comment: Page 2501 lines15-19. The authors concluded that "biological activity was strongly impaired..." However, AR values of "TOC" during the initial sedimentation period (<3.54 Ma) are higher than those in Quaternary (Figure 6). Please clarify the source of TOC in the period (<3.54 Ma).

Author response: We fully agree and will clarify this in the text. The increased TOC accumulation rates are a result of the extremely high sedimentation rate in the basal part of the record. The TOC concentrations during this period are generally very low (only up to 0.1%). Taking the prediction error (RMSECV) of the model of 0.09% into account and the fact that this part of the record is free of macrofossils, it is likely that the increase in the TOC accumulation rates is an artifact of the high sedimentation rate and the measuring inaccuracy of the method.

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Reviewer comment: Page 2501 line 20-Page 2502 line 10. Although the AR values varied largely during 3.6-3.3 Ma, the authors explain it by only warming. How can the authors explain these fluctuations?

Author response: The BSi indicated bioproductivity in Lake El'gygytyn seems to be strongly tied to temperature variations affecting the duration of the ice coverage as well as the chemical weathering in the catchment (nutrient supply). Pollen-based temperature and precipitation reconstructions from Lake El'gygytyn (Brigham-Grette et al., 2013) show large variations during the period 3.6 to 3.3 Ma. We will, based on now available multiproxy data, add a short discussion about further possible processes causing these fluctuations. However, based only on the FTIR-inferred proxies, a further interpretation of the fluctuations of the accumulation rates would be relatively speculative.

Reviewer comment: Page 2502 lines15-17. I guess this sentence is a speculation without any proof. Please show the large scale cycles in the figure.

Author response: Several previous studies (Melles et al., 2007, 2012, Brigham-Grette et al., 2013, Cunningham et al., 2013, in press, Vogel et al., 2013) have shown that changes in BSi concentrations during the Quaternary are following glacial-interglacial cycles and are mainly caused by changes in temperature. By adding high-resolution data, we will be able to show these large scale cycles.

Reviewer comment: Page 2502 lines21-22. The authors comment is right. Please try to show the age model and make high-time resolution dataset for climate changes during the period.

Author response: We agree with the reviewer and we will add data in higher resolution. The age model by Nowaczyk et al. (2013) is now published.

Interactive comment on Clim. Past Discuss., 9, 2489, 2013.

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