

## **Author comment to the reviews on Francke et al.**

The authors would like to express their thanks to the two anonymous reviewers of this MS, to P.C. Tzedakis, and to the anonymous reviewer#2 of Just et al. (2015) for their constructive comments and suggestions. We acknowledge that P.C. Tzedakis and the anonymous reviewer #2 of Just et al. took their time for an open discussion in order to provide comments on the age model of the analyzed sequence. We have considered all comments, and feel that the suggestions on the age model would significantly improve the chronological framework of the DEEP site sequence. Below, we provide (i) a response to the general annotations on the age model (**Part A**), and (ii) a point-to-point reply to the comments by the two anonymous reviewers of Francke et al. (**Part B**).

### **Part A: Chronological framework of the DEEP site sequence until 248 mcd**

All reviewers agree that the tephrostratigraphic tie points provide a robust basis for the chronology. The comments on the tuning approach reveal very opposing suggestions for an improvement of the age model. The anonymous reviewer #1 on the MS of Francke et al. suggests to exclude the second order tie points (TOC and TOC/TN versus orbital parameter), while the anonymous reviewer #2 of Just et al. and P.C Tzedakis expressed their concerns about the third order tie points (tuning TIC against the global benthic isotope stack LR04). Based on these recommendations, we suggest the following adjustments:

- 1. Three additional tephrochronological tie points discussed in detail by Leicher et al. (2015) will be included into the age model as first order tie points: POP2 at 40.468 mcd, SC5 at 195.566 mcd, and Tufo di Bagni Albule at 206.080 mcd. Furthermore, a new age for the P-11 tephra layer at 49.947 mcd following the discussion of Zanchetta et al. (2015) was used for the age-depth calculation.**

New tephrostratigraphic information published by Leicher et al. (this issue) surely improves the chronology of the DEEP site sequence. Only tephra layers, which could unambiguously be correlated to other records from the Mediterranean Region via geochemical finger print analyses of individual glass shards, were included in the age depth model. The ages of these tephra layers were obtained by tephrostratigraphy and tephrochronology (Leicher et al., this issue).

Zanchetta et al. (2015) provided a detailed evaluation of the chronostratigraphic position of the P-11 tephra layer in different records from the vicinity of Lake Ohrid. Their results suggest that the P-11 tephra layer is older than previously assumed. As the previously used age of the P-11 tephra is affected by some uncertainties ( $129 \pm 6$  ka), we follow Zanchetta et al. (2015) and incorporate the new age ( $133.5 \pm 2$  ka) into the age model.

## **2. The third order tie points (TIC against global benthic isotope stack LR04) have been excluded from the age model.**

P.C. Tzedakis and the anonymous reviewer #2 of Just et al. expressed their concerns about the use of the global benthic isotope stack LR04 as reference stack, as

- terrestrial and marine events are not necessarily synchronous
- radiometric-dated regional stacks have recently shown that benthic  $\delta^{18}$  changes are not globally synchronous (Stern and Lisiecki, 2014),
- the benthic  $\delta^{18}$ O records a mixed signal of sea water composition, deep water temperature, and ice volume changes,
- a direct response of the ITCZ to global ice volume variability is not straightforward, and
- circularity may arise when Lake Ohrid proxy data is compared to global climate variability inferred from LR04.

We agree with the concerns of the reviewers, and we acknowledge that the connection between global ice volume variability and TIC formation/preservation in Ohrid is probably more complex than previously thought. In addition, TIC formation/preservation in the DEEP site sequence is triggered by an on/off mode and the delayed increase of TIC at glacial to interglacial transitions has potentially more implication on the tuning approach as previously thought. As a large and hardly predictable error might be incorporated into the age model of the DEEP site sequence by tuning against LR04, we will remove all 3<sup>rd</sup> order tie points. Together, the 1<sup>st</sup> and 2<sup>nd</sup> order tie points account for a total of 42 age control points, which we believe is sufficient to provide a robust chronological framework to interpret the impact and magnitude of orbital scale climate change. This will also be shown in a new figure in the revised manuscript (replacing the previous figure 5), showing a direct comparison between the DEEP site sequence and the records from Soreq cave (rescaled age model from Grant et al., 2012) and from Tenaghi Philippon (Tzedakis et al., 2006).

Along these lines we would like to emphasize the work by Zanchetta et al. (2015). They show that for restricted time periods tuning of the DEEP site proxy data against an absolutely dated record from the vicinity of Lake Ohrid can provide robust age models for constrained time periods (using only absolute age control points). Such detailed studies for discrete time periods (here MIS5) can provide independent age models, which might even have the potential to highlight the synchronism or asynchronism of climatic events (Zanchetta et al., 2015). However, the application of this tuning approach is restricted to time periods, where absolute dated records are available, and therefore, is not applicable for the whole DEEP site record.

## **3. The positions of the 2<sup>nd</sup> order tie points (TOC, TOC/TN versus orbital parameters) were re-evaluated and the discussion about underlying**

**sedimentary processes is refined according to the suggestions of the anonymous reviewer #1 of Francke et al. and P.C. Tzedakis.**

The location of the TOC and TOC/TN age control points have been re-evaluated and adjusted on the basis of the new information from the tephrostratigraphy. This applies to the MIS6 to MIS5 transition, where a new age for the P-11 tephra layer was introduced, and to MIS15 and MIS13, where new tephrostratigraphic information has become available.

The anonymous reviewer #1 of Francke et al. expressed concerns about the tuning against orbital parameters as the interpretation of TOC and TOC/TN could be biased by (a) the impact of OM degradation (oxidation) in the water column and (b) the source of the OM. These two issues are discussed below:

**(a) Oxidation of OM in the water column:**

We agree with the reviewer that oxidation of OM starts in the water column, and thus, distinct lake level fluctuation might have a significant impact on OM preservation in the sediments. Remineralization of OM in the water column of Lake Ohrid has also recently been reported by Holtvoeth et al. (2015). However, the impact on the OM preservation and on TOC and TOC/TN strongly depends on the amplitude of the lake level fluctuations. Whereas for example at Lake Van in Turkey, a lake level low stand of 260 m below the current level has been reported for the Younger Dryas (e.g. Wick et al., 2003; Stockhecke et al., 2014 and references therein), lake level fluctuations at Lake Ohrid are likely less severe. Lacustrine terraces in the catchment, which would indicate lake level high stands, have not been observed around Lake Ohrid. The lowermost lake level since the penultimate glacial period occurred at the end of MIS6 and is indicated by a lacustrine terrace south of the city of Ohrid ca. 60 m below the modern lake level (Lindhorst et al., 2010). Given the fact that the MIS6/5 transition at the DEEP site occurs at ca. 50 mcd, the water depth column might not have changed significantly. This implies that climate-driven lake level fluctuations and their impact on TOC and TOC/TN at Lake Ohrid are probably only of minor importance. The high buffer capacity of Lake Ohrid against hydrological-induced lake level fluctuations can potentially be explained by the high amount of karstic inflow to Lake Ohrid. Furthermore, hydrological deficits in the lake during drier months could potentially be balanced by melting of ice caps in the catchment during spring. Nevertheless, a discussion about the impact of lake level fluctuations on TOC and TOC/TN will be included into the revised MS, as it improves the quality of the discussion.

**(b) Source of OM:** The anonymous reviewer #1 on Francke et al. expressed concerns about the source of the OM following the results of Holtvoeth et al. (2015), where it was shown that the OM preserved in the sediments of Lake Ohrid is predominantly of terrestrial origin. We would like to point out that the studies of Holtvoeth et al. (2015) focus on core Lz1120, which was retrieved close to the southern shoreline of Lake Ohrid in front of the Cerava River inflow (see Fig. 1 for coring location of Lz1120), and that the authors only focus on a short time period during the 8.2 cooling event. The coring

location might explain a high contribution of terrestrial OM to the sediments of Lz1120, whereas the amount of aquatic OM likely dominates the composition of the organic matter at the DEEP site, such as also shown by TOC/TN, which is mostly <10, except for some interglacial periods (e.g. during MIS11, 9, and 5). However, TOC/TN ratios can also be biased by various processes, which include:

- A selective early diagenetic loss of N might result in elevated TOC/TN ratios (Cohen, 2003), which can potentially explain the high TOC/TN ratios up to 16 during peak interglacial periods MIS11, MIS9, and MIS5.
- Very low TOC/TN ratios around 4, which correspond to overall very low TOC concentrations at the DEEP site in glacial periods, are even lower than the so-called Redfield Ratio of 6.6, which is indicative for aquatic plant material (cf. also Leng et al., 1999; Holtvoeth et al., 2015). Potential explanations for these low TOC/TN ratios are the clay-bound ammonium supply from the catchment along with ongoing organic carbon degradation (Leng et al., 1999; Holtvoeth et al., 2015). This process would decrease the organic carbon concentration, while the TN concentration remains fairly stable or might even increase and thus, result in low TOC/TN ratios. As already discussed in the manuscript, this is in agreement with the findings of Holtvoeth et al. (2015), where it is shown that the described process can substantially decrease the TOC/TN ratio in the sediments of Lake Ohrid.

In summary, TOC/TN as a proxy for the source of OM encompasses several limitations and issues. Therefore, we will build the discussion about the source of the OM on the recent findings by Lacey et al. (2015a), where it was shown that the OM is mostly of pure algal material in the deep parts of the Ohrid basin. Lacey et al. (2015a) focus on a Late Glacial to Holocene record from the LINI drill site, retrieved ca. 4 km NW of the DEEP site in a water depth of ca. 260 m. In addition, a high contribution of terrestrial OM in the sediments of the DEEP site sequence is unlikely due to the coring location and the relatively small inlet streams in combination with the high contribution of karstic inflow. In addition, we also would like to add that the aquatic origin of the OM during peak interglacial periods (where TOC/TN is between 10 and 16) is supported by unpublished  $\delta^{13}\text{C}_{\text{org}}$  data (pers. com. G. Zanchetta).

P.C. Tzedakis pointed out that the 2<sup>nd</sup> order tie points coincide with the perihelion passage in March. If the highest proportion of the radiation is delivered in March, the comparable high surface albedo during spring results in a substantial loss of this annual radiation (following the arguments of Tzedakis). This might result in low temperatures at the latitude of Lake Ohrid. Cold and dry conditions during the perihelion passage in March are also reported from the Tenaghi Philippon pollen record. The described process would support the tuning of TOC and TOC/TN versus orbital parameters. Lower temperatures promote a lower productivity and improved mixing in the lake and thus, low TOC and TOC/TN. We thank P.C. Tzedakis for this suggestion, which surely improves the quality of the manuscript.

#### **4. The error of the second order tie points was increased to $\pm 2,000$ years**

In order to account for potential inaccuracies in the tuning process, we will increase the error of each age control point to  $\pm 2,000$  years. Comparable errors are also discussed in absolute dated records such as in the older part of the Soreq speleothem record, in many other records from the North Atlantic and Europe (e.g. Koutsodendris et al., 2014), and also in the younger part of the global benthic isotope stack LR04, which was tuned against variations in Northern Hemisphere insolation (Lisiecki and Raymo, 2005).

The comparison of the age model of the DEEP site sequence to the Tenaghi Philippon pollen and the Soreq cave speleothem records show that the chronologies are in broad agreement within the respective error bars (see new Fig. 5). Differences compared to the Tenaghi Philippon pollen record occur between at the transition from MIS12 to MIS11, as the MIS12/11 transition occurs slightly earlier at Lake Ohrid. However, MIS 12 is chronologically well constrained in the DEEP site sequence by the Pozzolane Rosse tephra layer, which has an age of  $457 \pm 2$  ka. The sedimentation rates at the DEEP site at the end of MIS12 are already reduced by half the rates before and after this period (sedimentation rates will be shown in Fig. 7). A shift towards younger ages of the MIS12 to MIS11 transition would result in even lower sedimentation rates, which is not supported by sedimentological and lithological information.

#### **Part B: Point to point reply to the reviewer of Francke et al.**

##### **Point to point reply to the comments of the anonymous reviewer #1:**

##### **General comment 1: More information about the sediment bedding patterns shall be added**

The interpretation and discussion of the results is mainly built on the proxy data and the sediment composition for two reasons:

- The sediment bedding patterns described as “mottled” (replacing “bioturbated” in the manuscript, see below) and “massive” do not significantly differ between the three different lithotypes 1 to 3. Most prominent changes in the sedimentology, which are related to environmental change, can be traced back to variations in the sediment composition, and are reflected in TIC, bSi, TOC, K, and sediment color.
- Variations between mottled and massive sediments are rare in some intervals (i.e. in the sediments of lithotype 3) or occur on centimeter to decimeter scales in other intervals. A detailed description of each change between mottled and massive sections for the whole record would go way beyond the scope of this paper, but may be included in subsequent studies. Furthermore, a comparable

high number of core sections from the DEEP site sequence were unfortunately already oxidized all the way to the core center before core opening, although the cores had been sealed tightly with tape in the field. This oxidation overprints the original sediment bedding structures and hampers a more detailed examination of the sediment bedding patterns.

We will follow the suggestion of the reviewer and provide more information about the sediment bedding patterns:

- (1) We will replace the term “bioturbated” with the term “mottled”, as “bioturbated” already refers to a discussion and/or interpretation.
- (2) A discussion about the sediment bedding patterns will be included in the section 4.2.1 (Hemipelagic sediments). The term “laminated” sediments, which only occur until ca. 0.3 mcd, is probably misleading for the description of the DEEP site sediments. We will remove “laminated” from the core descriptions. The lack of laminated sediment successions implies that anoxic bottom water conditions did not occur at the DEEP site. Changes between mottled and massive sections correspond to changes in the sediment color and sediment composition. Massive sections commonly correspond to successions with high TIC concentrations and are probably a result of a high abundance of calcite crystals in the sediments.
- (3) We considered moving Figure 3 before Figure 2, however, position of the figure is due to the need to refer to Figure 2 in chapter 3.2 (Laboratory work). We will carefully evaluate the position of Figures 2 and 3 during type setting.

**General comment 2: Impact of lake level fluctuations and the source of OM on TOC and TOC/TN**

Please see part A, number 3 of this author comment.

**Minor comments from reviewer 1:**

**The manuscript sometimes would benefit from some shortening. For instance the description and reaction of the sediment to 10 % HCl. It is mostly a repetition to the TIC results.**

We removed the information about the reaction with HCl.

**Page 15111: title should be “. . .and the present” and not “and present day”**

We changed this accordingly.

**Page 15115, line 24: add 248 m**

We changed this accordingly.

**Page 15117, line 9: add water depth**

We changed this accordingly.

**Page 15121, line 6: In Figure 2 the lithotypes have names such as calcareous silty clay. Please add those to all three cases.**

We added the names of the three lithotypes to the text.

**Page 15121, line 8: at to each sub-lithotype the reference to the corresponding image in Fig. 3 (same for page 15121/line27 and 15122/11). It would be easier to read and more informative to label the images in Fig. 3 with A, B etc. and give the composite depth in the figure caption instead of the long label of the section.**

We changed this accordingly and changed the figure label to A, B, C. etc. Information about the sediment depth (mcd) will be provided in the supplement.

**Page 15121, line 21: "...42 %"..this is a lot.**

Yes indeed. These extraordinary high bSi concentration mostly occur above tephra layer and are likely a result of volcanic ash induced Si fertilization, which trigger exceptional diatom blooms in the lake. We also refer to Jovanovska et al. (2015), where the impact of the Y-5 tephra deposition on diatom community and diatom concentration is studied in more detail.

**Page 15121, line 22: "...low abundance.." – low compared to which fraction (bulk, allochthonous)?**

Compared to the bulk sediment composition. We clarified this in the text.

**Page 15121, line 22: delete "...and diatom frustules can be abundant."**

Such as done for TIC, TOC, and K, we would like to indicate in the description of the sediment composition for what the proxy data is indicative for. A reader who is not familiar with the data might be confused if this explanation is missing. Therefore, we would prefer to leave this information in the text, but we re-write this sentence.

**Page 15122, line 8: re-write sentence "BSi contents are moderate to high (2 to 27.9%) and clastic contents are moderate (Fig. 2, K-intensities)."**

Re-written.

**Page 15122, line 11: be more specific in separating MMDs and tephtras by referring to the individual images of Fig. 3**

We changed this accordingly.

**Page 15123, line 1: just refer to Fig. 3X and 3X and delete all other details. It would be easier to read and pick up in the image.**

We changed this accordingly.

**Page 15123, line 9-12: repetition of the sentence above, re-write**

We changed this accordingly.

**Page 15123, line 26: “sediments of Lake Ohrid” - specify the sediments for which this analysis were done. Recent or Holocene?**

SEM and XRD investigation have been conducted on sediment cores covering the last 40,000 years, and on calcite crystals from sediment traps. We specify this in the text. Please see also the reply on the comment about the “Groundtruthing of the data” by the anonymous reviewer #2 of Francke et al. (Part B of this author comment).

**Page 15124, line 17: “can be observed” or has been observed?**

Has been observed.

**Page 15125, line 16: From Lake Baikal it is known that oxidation of OM occurs to a large share in the water column during settling next to OM mineralization at the water- sediment interface (Mueller et al., 2015). The time OM spends in oxic part of the water column, the more it is degraded. The thickness of the water column is critical.**

We agree that the time OM spends in oxic conditions is critical for the degradation. Please see comments in part A, number 3 of this author comment.

**Page 15125, line 23-26: At odds with the statement in line 5 that TOC/TN imply origin of OM. Please check.**

Please see part A, no 3 of this author comment. The TOC/TN ratio and the source of the OM are discussed in detail there.

**Page 15126, line 15: delete “, as”**

Changed accordingly.

**Page 15127, line 4: specify long time periods: years, decades, ..?**

Sediments may be stored in soils, paleo-riverbeds or alluvial fans up to several thousands of years. We specified this information.

**Page 15127, line 16: delete “At Lake Ohrid..”**

Deleted.

**Page 15127, line 19: delete “strong”**

Deleted.

**Page 15127, line 25: add “identified”**

Added.

**Page 15128, line 3-4: repetition**

We deleted the repetition in section 4.1.2..

**Page 15128, line 9: sentence needs to be better embedded in context**



We re-write this sentence.

**Page 15128, line 16: “would have prevented”**

We changed this accordingly.

**Page 15128, line 19: Do you actually mean “tephrostratigraphy” instead of “radiometric ages”? The tephras found within the cores were not directly dated if I understood correctly.**

The term “radiometric ages” was misleading. We corrected this accordingly.

**Page 15129, line 29: This teleconnection has been shown and should be referenced.**

This section is deleted. Please see general comments on the age model.

**Page 15146: add “composite” in table caption. A elegant way to cut down this table would be to give the numbers of columns 3 and 4 in parenthesis in column A and B.**

Thank you for the idea. We changed this accordingly.

**Page 15147: Its unclear why cal. 14C ages if this are recalculated Ar/Ar-dated tephrostratigraphic tie points?**

The tephra layers were not directly dated in the sediments of Lake Ohrid, but  $^{39}\text{Ar}/^{40}\text{Ar}$  and radiocarbon ages were transferred from other records. We clarified this in the table caption. Please see Leicher et al. (2015) for tephrostratigraphic results of the DEEP site sequence.

**Fig. 1: add legend for bathymetry, spell out FYROM in caption, delete “pollen record”**

We changed this accordingly.

**Fig. 2: add y-axis label**

Added.

**Fig. 3: add A, B, C to images and mcb on the image, in the caption or main text body**

We change the description to A, B, C etc.. The sediment depth (mcd) and the core labels will be provided in the supplement.

**Fig. 4: would be nice to be complemented with a SEM image of Siderite**

SEM images of the siderite and a discussion about the diagenetic processes can be found in Lacey et al. (2015b). We added this information in the figure caption.

**Fig. 5: This figure is hard to read due to all the vertical lines. TOC/TN tie points are weak and suggested (see above to be deleted) in order to improve the age model**

**and leave room for upcoming findings. Add y-axis labels. Lacks specification of definition of “local” and winter season length.**

Please see general comments on the age model. Fig. 5 will be replaced.

**Fig. 6: green and purple dots are hard to differentiate**

We changed this accordingly

**Fig. 7: add x-axis label**

We changed this accordingly

**Point to point reply to the comments of the anonymous reviewer 2:**

**Introduction: the first paragraph of the introduction on the meaning of palaeolimnology is too general. Please start with open questions concerning Mediterranean palaeoenvironmental history. Lake Ohrid can help to unravel those. The introduction repeats the goals of the SCOPSCO project, but does not mention the specific goals of the paper.**

We will change the introduction accordingly.

**Page 15116, line 26: Is it important to know that Macedonia once belonged to Former Yugoslav Republic? Avoid political issues.**

“Former Yugoslav Republic of Macedonia” or “FYROM” is the official name with which the country is member of United Nations. The name “Macedonia” might be misleading, as it equals the name of a region in Greece.

**Page 15116, lines24-25: The geological exposures comprise lithified formations, correction to metasedimentary rocks and siliciclastic rocks instead of metasediments and siliciclastics**

We changed this accordingly.

**Groundtruthing of data: There is a better way to give evidence of carbonates in the record, rather than by acid treatment (HCL) and element data (XRF). XRD may provide direct evidence of siderite and calcite. This only needed for a few representative samples. Or use published data from cited papers.**

Several studies already focused on the TIC and calcite formation in the epilimnion of Lake Ohrid, including XRD and SEM analyses on calcite crystals from sediment traps (Matter et al., 2010) and from the sediments of Lake Ohrid (Wagner et al., 2008; Wagner et al., 2009; Leng et al., 2010; Matter et al., 2010). The presence of siderites in the sediments of the DEEP site sequence has been proved by Lacey et al. (2015b) by XRD, EDX, and FTIRS spectroscopy. We will add the relevant literature.

**The interpretation of Zr/K ratios is not straightforward. As stated, Zr is usually included in the heavy mineral zircon. Zircon grains are usually enriched in the fine-sand fraction, not in clay. Potassium can be related to both feldspars and mica, but normally is included in sheet silicates of the clay fraction (as in gamma-ray logs).**

This is in agreement with p. 1526, line 25 to page 1526, line 29.

**The Zr/K ratio seems to be positively correlated with clay concentrations, but not at all in Fig. 4. Show scatter plot. Thus the grain-size signal might be overprinted by other sedimentary processes, such as changes in sediment provenance. Zircon often is enriched in aeolian sedimentary components. Maybe, sediment supply changed from proximal to distal sources during glacial stages. This has to be discussed.**

Various processes, which encompass the grain size of the source material in the catchment, variations of the transportation energy in the inlet streams, the flow velocity of lake internal currents (Vogel et al., 2010b), lake level fluctuations, and the shoreline distance can affect the grain size distribution at the DEEP site. These processes might explain deviations from the good correspondence between Zr/K and the <4 $\mu$ m grain size fraction. Therefore, we do not postulate that there is a good correlation between the two parameters. We rather aim to highlight the good match between relative minima and maxima of Zr/K and the <4 $\mu$ m grain size fraction.

Changes in the sediment provenance to more distal sources (wind transportation) are likely not a main trigger for variations of the Zr/K ratio and of the <4 $\mu$ m grain size fraction. This is supported by the highlighted good match between high Zr/K ratios and high percentages of the <4 $\mu$ m grain size fraction in glacial periods. If high Zr/K ratio would indicate enhanced aeolian supply, high Zr/K ratios would rather match low percentages of the <4 $\mu$ m grain size fraction, as wind transported material is commonly enriched in the (coarser) silt-sized fractions. A negligible impact of wind-transported material on Zr intensities in the sediments of Lake Ohrid also corresponds to the findings of previous studies on a short core from the northern part of the lake, where the Zr/Ti ratio was used as an indicator for the strength of lake internal surface currents (Vogel et al., 2010a). In addition, the good match between the Zr/K ratio and the S-ratio (cf. Fig.7) supports the interpretation of the elemental ratio. The S-ratio represents the hematite + goethite versus magnetite concentration. Goethite is the most widespread pedogenetically formed magnetic mineral. It is assumed that high Zr/K ratios

correspond to the input of “old” soils, where pedogenetically minerals have formed and K is depleted. Since the high Zr/K values co-occur with low S-Ratios (relative increase in goethite + hematite) the two proxies support each other (see Just et al., 2015 for more details about the S-ratio).

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