1 Sedimentological processes and environmental variability

- 2 at Lake Ohrid (Macedonia, Albania) between 637640 ka and
- 3 the present day

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Abstract

Lake Ohrid (Macedonia FYROM, Albania) is thought to be more than 1.2 million years old and hosthosts more than 300200 endemic species. As a target of the International Continental scientific Scientific Drilling Program (ICDP), a successful deep drilling campaign was carried out in 2013 within the scope of the Scientific Collaboration on Past Speciation Conditions in Lake Ohrid (SCOPSCO) project in 2013. Here, we present lithological, sedimentological, and (bio-)geochemical data from the upper 247.8 m composite depth of the overall 569 m long DEEP site sediment succession from the central part of the lake. According to an age model, which is based on 11 mine tephra layers (1st order tie points), and on tuning of biogeochemical proxy data to orbital parameters (2nd order tie points), and to the global benthic isotope stack LR04 (3rd order tie points), respectively, the analyzed sediment sequence covers the last 637 kyrs640 ka.

The DEEP site sediment succession consists of hemipelagic sediments, which are interspersed by several tephra layers and infrequent, thin (<5 cm) mass wasting deposits. The hemipelagic sediments can be classified into three different lithotypes. Lithotype 1 and 2 deposits comprise calcareous and slightly calcareous silty clay and are predominantly attributed to interglacial periods with high primary productivity in the lake during summer and reduced mixing during winter. The data suggest that high ion and nutrient concentrations in the lake water promoted calcite precipitation and diatom growth in the epilimnionepilmnion in during MIS15, 13, and 5. Following a strong primary productivity, highest interglacial temperatures can be reported for marine isotope stages (MIS) 11MIS11 and 5, whereas MIS15, 13, 9, and 7 were comparablyeomparable cooler.— Lithotype 3 deposits consist of clastic, silty clayey material and predominantly represent glacial periods with low primary productivity during summer and longer and intensified mixing during winter. The data imply that the most severe glacial conditions at Lake Ohrid persisted during MIS16, 12, 10, and 6 whereas somewhat warmer temperatures can be inferred for MIS14, 8, 4, and 23. Interglacial-like conditions occurred during parts of MIS14, and 8.

1 Introduction

In the lightLong sediment successions from lacustrine basins have been shown to provide valuable archives of recent local environmental variability and of global climate warming, it has become fundamentally important to understand the characteristics and shaping of individual glacial change during the Quaternary and Neogene (Prokopenko et al., 2006; Melles

et al., 2012; Stockhecke et al., 2014a). As lakes are highly sensitive to environmental change (e.g. Cohen, 2003), these lacustrine paleoclimate records commonly document external forcing mechanism via internal feedback processes in their sedimentological records. External forcing mechanisms are the global glacial/interglacial periodsclimatic variability, which characterize climate conditions during the Quaternary, as these differences can reveal information about external forcing and internal feedback mechanisms in the global climatic system (Lang and Wolff, 2011). The global glacial-interglacial variability has widely been studied on ice cores (e.g. -EPICA-members, 2004; NGRIP-members, 2004) and on marine sediment successions (e.g.; Lisiecki and Raymo, 2005). In ; Raymo et al., 2006). Additional external forcing mechanisms comprise orbital parameters and the effects of the local insolation on the terrestrial realms, longrealm. Lake basins thus have the potential to provide high-resolution, continuous paleoclimatic records are sparse and mostly restricted to loesspaleosol sequences (e.g. Chen et al., 1999), to speleothem records (Bar-Matthews and Ayalon, 2004; Wang et al., 2008) and to lacustrine sediments (e.g. Prokopenko et al., paleo-records of global climate change and its impact on regional environments. Long terrestrial paleo-records in 2006; Melles et al., 2012). In the eastern and southeastern Mediterranean region, long terrestrial paleo-records -have become available from Lake Van (Stockhecke et al., 2014a), 2014b) and from the Dead Sea (Stein et al., 2011), and from the Soreg Cave speleothem record (Bar-Matthews and Ayalon, 2004). 2011). In the central Mediterranean regionRegion, the only terrestrial paleo-recordrecords that continuously covers more than one million years year is the Tenaghi Philippon pollen record in northern Greece (cf. Fig. 1), which spans the last 1.3 million years and provides valuablefundamental insights into the vegetation history of the area (e.g. Tzedakis et al., 2006; Pross et al., 2015). The results from Tenaghi Philippon reveal that individual interglacial and glacial periods in the Mediterranean region can differ significantly in their duration and severity (e.g. Tzedakis et al., 2006; Fletcher et al., 2013).). However, analytical methods for paleoclimate reconstructions at Tenaghi Philippon have so far been restricted to pollen analyses. and the sensitivity of vegetation changes to short-term climate variability can be low (e.g. Panagiotopoulos et al., 2013). Lake Ohrid on the Balkan Peninsula is thought to be more than 1.2 million years old and has

already demonstrated its high sensitivity to environmental change and the potential to provide

high-resolution paleoenvironmental information for the last glacial/interglacial cycle (e.g.

Wagner et al., 2008; 2009, 2014; Vogel et al., 2010a). Given that Lake Ohrid is also a hotspot

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for endemism with more than 300200 endemic species in the lake (Föller et al., 2015Albrecht and Wilke, 2009), its sediments sediment records also have the potential to address evolutionary questions such as what the main triggers of speciation events are.

Based on up to 15 m long sediment cores, which were recovered between 2003 and 2011 (e.g. Wagner et al., An2009; Vogel et al., 2010a; Wagner et al., 2012), and on hydro-acoustic surveys carried out between 2004 and 2008 (e.g. Lindhorst et al., 2010), the Scientific Collaboration on Past Speciation Conditions in Lake Ohrid (SCOPSCO) project was established within the scope of the International Continental Scientific Drilling Program (ICDP). The main objectives of the SCOPSCO project are (1) to reveal the precise age and origin of Lake Ohrid, (2) to unravel the seismotectonic history of the lake area including effects of major earthquakes and associated mass wasting events, (3) to obtain a continuous record containing information on volcanic activities and climate changes in the central northern Mediterranean region, and (4) to better understand the impact of major geological/environmental events on general evolutionary patterns and shaping an extraordinary degree of endemic biodiversity as a matter of global significance.

The ICDP deep drilling campaign took place at Lake Ohrid in spring 2013 using the Deep Lake Drilling System (DLDS) operated by the Drilling, Observation and Sampling of the Earths Continental Crust (DOSECC) consortium. More than 2100 m of sediments were recovered from four different drill sites (Fig. 1)... The processing of the cores from the DEEP site from their central part of Lake Ohrid (Fig. 1) is still ongoing at the University of Cologne (Germany). Here, we present lithological, sedimentological, and (bio-)geochemical results from the upper part of the DEEP site sediment succession until 247.8 mcd (meter composite depth). According to an age model, which is based on 11 tephrochronological tie points and on tuning of biogeochemical proxy data against orbital parameters, the analyzed sequence covers the period since 637 ka. Here, we aim to provide a chronological framework for the deposits, confirm the completeness of the record, provide first insights into the sedimentological, paleoenvironmental and paleoclimatological history of Lake Ohrid, and form the basis of more detailed work in the future. Furthermore, our results enable a first characterization of glacial and interglacial severity since marine isotope stage (MIS) 16.5 which covers the period since 640 ka.

Site Information 2

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Lake Ohrid is located at the border of the Former Yugoslav Republic of Macedonia (FYROM) and Albania at an altitude of 693 m above sea level (m asl, Fig. 1A). The lake is approximately 30 km long₂ and 15 km wide and covers a surface area of 358 km². Due to its location in a tectonic, N-S trending graben system, the <u>lake basin</u>bathymetry is tub-shaped with a mean water depth of 150 m and a maximum water depth of 293 m (Fig. 1B). The water volume calculates to 55.4 km³. The lake is mainly fed by karstic inflow (55%, e.g. Matzinger et al., 2007; Vogel et al., 2010a, cf. Fig. 1), and by small rivers. The karstic inflow partly originates from Lake Prespa, located at an altitude of 848 m asl ca. 10 km to the east of Lake Ohrid (Fig. 1B). Both lakes are connected via karstic aquifers. The lake level of Ohrid is balanced by a surface outflow in the northern corner (Crim Drim River, 60%, Fig. 1B), and by evaporation (40%, Matzinger et al., 2006b2006a). The large water volume and the high proportion of karstic inflow induce an oligotrophic state inof Lake Ohrid. A complete overturn of the water column occurs approximately every 7 years (e.g. Matzinger et al., 2007), although the). The upper about 200 m of the water column are mixed every year. The catchment of Lake Ohrid comprises 2393 km² including Lake Prespa (Fig. 1B). Both lakes are separated by the up to 2300 m asl high Galicica Galicia mountain range (Fig. 1B). To the west of Lake Ohrid, the Mocra mountain chain risesreaches up to about 1500 m asl. The morphostructure with high mountains to the west and east of Lake Ohrid is mainly the result of a pull-apart like opening of the basin during the late phases of the Alpine orogeny (Aliaj et al., 2001; Hoffmann et al., 2010; Lindhorst et al., 2015). Several earthquakes in the area

22 (NEIC database, USGS) and mass wasting deposits, which occur in the lateral parts of Lake

Ohrid (Reicherter et al., 2011; Lindhorst et al., 2012; Wagner et al., 2012), document the

tectonic activity in the area until present day.

The oldest bedrock in the catchment of Lake Ohrid is of Devonian age, consists of metasedimentary rocksmetasediments (phyllites), and occurs in the northeastern part of the basin. Triassic carbonatecarbonates and siliciclastic rockssiliciclastics occur in the southeast, east, and northwest (e.g. Wagner et al., 2009; Hoffmann et al., 2010; Vogel et al., 2010b). Ultramafic metamorphic and magmatic rocks including ophiolites of Jurassic and Cretaceous age crop out in the west (Hoffmann et al., 2010). Quaternary lacustrine and fluvial deposits cover the plains to the north and to the south of Lake Ohrid (Hoffmann et al., 2010; Vogel et

32 al., 2010b).

- 1 The climate at Lake Ohrid is influenced both by continental and Mediterranean climate
- 2 conditions (Watzin et al., 2002). Between summer and winter, monthly average air
- 3 | temperatures range between +26°C and -1°C, respectively. The annual precipitation averages
- 4 to ca. 750 mm/yr⁻¹, with drier conditions during summer, and more precipitation during
- 5 winter. The prevailing wind directions are north and south and primarilyare controlled by the
- 6 topography of the Lake Ohrid valley (summarized by Wagner et al., 2009).

3 Material and Methods

3.1 Field work

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- 9 The DEEP site (5045-1) is the main drill site in the central part of the lake at a water depth of
- 10 243 m (Fig. 1B, N-41°02'57" N₂-E 020°42'54" E). The uppermost sediments at the DEEP
- site down to 1.5 m below lake floor (blf) were recovered in 2011 using a UWITEC gravity
- and piston corer (core Co1261), as these drilling techniques provide a good core quality for
- sub-surface sediments. In 2013, more than 1500 m of sediments were recovered from six
- different drill holes (5045-1A to 5045-1F) at the DEEP site. The distance between each drill
- 15 hole averages ca. 40 m. Holes 5045-1A and 5045-1E comprise <u>sub-</u>surface sediments down to
- 16 ca. 2.4 and 5 m blf, respectively. Holes 5045-1B and 5045-1C were drilled down to a
- penetration depth of 480 m blf. At hole 5045-1D, the maximum penetration of 569 m blf was
- 18 reached. Spot coring down to 550 m blf was conducted in hole 5045-1F in order to fill any
- 19 gaps present inof the other holes (see also Wagner et al., 2014). After core recovery, the
- 20 sediment cores were cut in (into-up to) one meter long segments and stored in darkness at
- 21 4°C.

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- 22 During the drilling campaign in 2013, onsite core processing comprised smear-slide analyses
- of core catcher material and magnetic susceptibility measurements on the whole cores in 2 cm
- 24 | resolution using a Multi-Sensor Core Logger (MSCL, GEOTEK Co.) equipped withand a
- 25 Bartington MS2C loop sensor (see also Wagner et al., 2014). Following the field campaign,
- the cores were shipped to the University of Cologne for further analyses.

3.2 Laboratory work

- A first correlation of the individual core segments to provide a preliminary composite profile
- 29 for the DEEP site sequence was established based on the magnetic susceptibility data of the
- 30 whole cores from holes 5045-1B, 5045-1C, 5045-1D, and 5045-1F. Cores
- 31 <u>incorporated included</u> into the composite profile were then split lengthwise and described for

color, grain-size, structure, macroscopic components, and calcite content (reaction with 10% 1 2 HCl). High-resolution line scan images were taken using the MSCL (GEOTEK Co.). X-ray 3 Fluorescence (XRF) scanning was carried out at 2.5 mm resolution and with an integration 4 time of 10 s using an ITRAX core scanner (Cox Analytical, Sweden). The ITRAX core 5 scanner was equipped with a chromium (Cr) X-Ray source and was run at 30 kV and 30 mA. 6 Data processing was performed with the software QSpec 6.5 (Cox Analytical, Sweden, cf. 7 Wennrich et al., 2014). In order to account for inaccuracies and to validate the quality of the 8 XRF--scanning data, conventional wavelength dispersive XRF (WDXRF, Philips PW 2400, 9 Panalytical Cor., The Netherlands) was conducted at 2.56 m resolution. The optical and 10 lithological information (layer by layer correlation) were then combined with XRF scanning 11 data tofor a fine-tune tuning of the core correlation by using the Corewall software package 12 (Correlator 1.695 and Corelyzer 2.0.1). 13 If an unequivocal core correlation was not possible, additional core sections from other drill 14 holes in the respective depths were opened, likewise analyzed, and used to refine for a 15 refinement of the core correlation. In the composite profile, the field depth measurements 16 based on 'meters below lake floor' (m blf) were replaced by 'meters composite depth' (mcd). 17 The DEEP site composite profile down to 247.8 mcd comprises two sections of core Co1261 18 for the uppermost 0.93 mcd and aim total of 386 core sections from holes 5045-1B, 5045-1C, 19 5045-1D, and 5045-1F (Fig. 2, Table 1). The overall recovery of the composite profile 20 calculates to 99.97%, as no overlapping sequences were found between core run numbers 80 21 and 81 in hole 5045-1C. The length of the core catcher (8.5 cm) between these two runs led to 22 one gap between 204.719 and 204.804 mcd. At 16 cm resolution, 2 cm thick slices (40.7 cm³) were removed from the core half and 23 24 separated into four sub-samples to establish a multiproxy data set. Intermediate intervals (8 25 cm distance to the 2 cm thick slices) were subsampled for high-resolution studies by pushing 26 two cylindrical plastic vials (diameter = 0.9 cm, height = 4 cm, volume = 2.5 cm³) into the 27 core halves. In addition, samples for paleomagnetic analyses were taken in cubic plastic cubesboxes (volume of 6.2 cm³) at 50 cm resolution until 100 mcd, and at 48 cm resolution 28 29 below this depth (cf. Just et al., 2015this issue). 30 All sub-samples (8 cm resolution) were freeze-dried, and the water content was calculated by 31 the difference in weight before and after drying. For every other sample, an aliquot of about 32 100 mg was homogenized and ground to <63 μm. For the measurement of total carbon (TC) and total inorganic carbon (TIC) using a DIMATOC 100 carbon analyzer (Dimatec Corp., 33

1 Germany), 40 mg of this aliquot was dispersed with an ultrasonic disperser in 10 ml DI water. 2 TC was measured as released CO₂ after combustion at 900°C. The TIC content was determined as CO₂ after treating the dispersed material with phosphoric acid (H₃PO₄) and 3 4 combustion at 160°C. The total organic carbon (TOC) content was calculated from the 5 difference between TC and TIC. For the measurement of total sulfur (TS) and total nitrogen 6 (TN), 10 mg of the ground material was analyzed using an elemental analyzer (vario MICRO 7 cube, Elementarelementar Corp.) after combustion at 1150°C. 8 Biogenic silica (bSi) concentrations were determined at 32 cm resolution by means of Fourier 9 Transform Infrared Spectroscopy (FTIRS) at the Institute of Geological Sciences, University 10 of Bern, Switzerland. For sample preparation, 11 mg 0.011 g of each sample was mixed with 500 mg0.5 g of oven-dried spectroscopic grade potassium bromide (KBr,)-(Uvasol®, Merck 11 12 Corp.) and subsequently homogenized using a mortar and pestle. A Bruker Vertex 70 equipped with a liquid nitrogen cooled MCT (Mercury-Cadmium-TellurideDTGS 13 14 (Deuterated Triglycine Sulfate) detector, a KBr beam splitter, and a HTS-XT accessory unit (multi-sampler) was used for the measurement. Each sample was scanned 64 times at a 15 resolution of 4 cm⁻¹ (reciprocal centimeters) for the wavenumber range from 3750 to <u>520</u>450 16 cm⁻¹ in diffuse reflectance mode. After the measurements, a linear baseline correction was 17 18 applied to normalize the recorded FTIR spectra and to remove baseline shifts and tilts by setting two points of the recorded spectrum to zero (3750 and 2210-2200 cm⁻¹). The 19 20 determination of bSi from FTIR spectral information relies on spectral variations in synthetic 21 sediment mixtures with known bSi concentrations and calibration models between the FTIR 22 spectral information and the corresponding bSi concentrations based on partial least squares 23 regression (PLSR, Wold et al., 2001 and references therein). For details and information 24 regarding ground truthing groundtruthing of the calibration see Meyer-Jacob et al. (2014). For grain-size analyses at 64 cm resolution, 1.5 g of the sample material was treated with 25 26 27 28

hydrogen peroxide (H₂O₂, 30%), hydrochloric acid (HCl, 10%), sodium hydroxide (NaOH, 1M) in order to remove authigenic matter), and Na₄P₂O₇ for sample dispersion. Prior to the analyses, the sample material was dispersed on a shaker for 12h12 h and underwent one minute of ultrasonic treatment. Sample aliquots were then measured three times with a Saturn DigiSizer 5200 laser particle analyzer equipped with a Master Tech 52 multisampler (Micromeritics Co., USA) and the individual results were averaged. Data processing was carried out by using the GRADISTATv8 program (Blott and Pye, 2001).).

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4 Results and Discussion

4.1 Lithology

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- 3 The sediments from the DEEP site sequence down to 247.8 mcd consist of fine-grained
- 4 hemipelagic sediments, which are sporadically interspersed by more coarse-grained event
- 5 layers. From the top to the bottom of the sequence, the water content decreases from a
- 6 maximum of 70% to a minimum of 32% due to compaction by overlying deposits (for
- detailed studies on the sediment compaction at the DEEP site see Baumgarten et al., 2015).

8 4.1.1 Hemipelagic sediments

- 9 The hemipelagic deposits of the DEEP site sequence were subdivided into three lithotypes
- 10 | (Fig. 2, 3) based on information from the visual core descriptions. This includes variations in
- 11 the calcite content (reaction with 10% HCl), and the sediment color and structure.
- 12 The sediments of **lithotype 1** (calcareous silty clay, Fig. 2), 3) show strong to very strong
- 13 reactions with 10% HCl, have very dark greenish grey to greenish grey colors, and appear
- 14 massive, bioturbated, or mottled (cf. finely laminated. Fig. 3A to 3D). Silt to gravel-sized
- vivianite concretions occur irregularly distributed within lithofacies 1 and can be identified by
- 16 a color change from grey/white to blue after core opening.
- 17 The strong to very strong reaction with 10% HCl and TIC contents between 2.0% and 9.7%
- imply that calcite (CaCO₃) is abundant in lithotype 1 sediments. Changes in color correspond
- 19 to different calcite and TOC contents in the deposits (Fig. 3). The TOC content can be used as
- an indicator offer the amount of finely dispersed organic matter (OM) in lacustrine deposits
- 21 (e.g. Cohen, 2003; Stockhecke et al., 2014b2014a). In the sediments of lithotype 1, bright
- colors (greenish grey) are commonly correlated with massive layers and are indicative for
- 23 high calcite and low OM contents. Dark (very dark greenish grey, dark greenish grey)
- 24 lithotype 1 deposits appear mottledbioturbated and have lower calcite and higher OM
- 25 concentrations. Laminated successions occur only in the upper meter of the DEEP site
- 26 sequence. The bSi content varies between 1.9% and 42.5% contents in the sediments of
- 27 lithotype 1 vary between 1.9 and 42.5% and is a measure for the amount of suggest that
- diatom frustules in the sediments of Lake Ohrid (Vogel et al., 2010a). Additional
- 29 contributions to the bSi content come from sponge spicules, which were observed in in smear
- 30 slides. Extraordinary high bSi concentrations of up to 42.5% are restricted to discrete
- 31 <u>layersean be abundant</u>. Low potassium intensities (K, Fig. 2) correspond to minima in the fine

- 1 fraction (<4 μm, Fig. 2) of the grain size classes and imply a low abundance of siliciclastic
- 2 minerals in the bulk sediment composition of lithotype 1 depositssediments (cf. Arnaud et al.,
- 3 2005; Wennrich et al., 2014).
- 4 Lithotype 2 (slightly calcareous silty clay) sediments exhibit a moderate reaction with 10%
- 5 HCl, are greenish black and very dark greenish grey in color, and appear mottled bioturbated
- 6 or massive (cf. Fig. 3E to 3H).- Vivianite concretions occur irregularly, and yellowish brown
- 7 layers exhibityield high amounts of siderite (FeCO₃) crystals in smear-slidesslide samples
- 8 (Fig. 2, 4).
- 9 The occurrence of siderite in the DEEP site sediments was confirmed by means of XRD,
- EDX, and FTIRS spectroscopy (Lacey et al., 2015b).
- 11 TIC contents between 0.5% and 2% indicatemoderate reaction with 10% HCl implies that
- 12 calcite is less abundant in lithotype 2 sediments. which is consistent with TIC contents
- 13 between 0.5 and 2%. Distinct peaks in the TIC content correspond to peaks in Fe and Mn
- counts and to the occurrence of the yellowish brown siderite layers (Fig. 4). The greenish
- 15 black sediment successions of lithotype 2 sediments are mottledbioturbated and have high
- amounts of OM, as indicated by TOC contents of up to 4.5%. Brighter, very dark greenish
- 17 grey sections can be massive or mottledbioturbated and have lower TOC contents (Fig. 3).
- 18 The amount of diatom frustules is moderate to high, as inferred from bSi contents between
- 19 2% and 27.9%. The bulk sediment composition%, and the amount of clastic matter is
- 20 balanced by moderate amounts of clastic material (Fig. 2, K-intensities).
- 21 The bright, greenish grey sediments of **lithotype 3** (silty clay)do not show a reaction with
- 22 10% HCl, are mottledbioturbated and intercalated with massive sections of up to several
- 23 decimeters thickness (Fig. 31 to 3L3). Vivianite concretions occur irregularly, and yellowish
- brown siderite layers are abundant (Fig. 2).
- 25 The TIC values of lithotype 3 sediments rarely exceed 0.5%, which infers negligible calcite
- 26 | contents. Occasional peaks, and matches the null reaction to 10% HCl. Peaks in TIC >, which
- 27 occasionally exceed 0.5% can be attributed to the occurrence of siderite layers (Fig. 2, 4).
- TOC ranges between 0.4% and 4.8% (Fig.2), with higher values >2.5% close to the lower and
- 29 upper boundaries of lithotype 3 sediment sections, and between 3.21 mcd and 2.89 mcd (Fig.
- 2). The amount of bSi is mostly between 1.68% and 14.5%, except for several peaks of up to
- 31 41.3% just above tephra layers. High potassium intensities throughout most parts of lithotype
- 32 3 sediments indicate high clastic matter contents and correspond to high percentages of the
- fine fraction ($<4\mu m$, Fig. 2).

4.1.2 Event Layers

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The macroscopic event layers were classified as tephra depositdeposits if a high proportion ofexelusively glass shards were observed in the smear slides, and as mass movement depositdeposits (MMD) if predominantly coarse grains and detrital siliciclasticminerogenic components or a mixture of glass shards from different tephras occurred (cf. Fig 2, 3). Tephra layers in the DEEP site sequence appear as up to 15 cm thick layers and as lenses (cf. Leicher et al., 2015. this issue). Most of the tephra layers are between 0.5 cm and 5 cm thick (e.g. Fig. 3H and 3P).3, 1D-18H-3, 85 to 82 cm section depth, 1D-6H-2, 23 to 21 cm section depth). Tephrostratigraphic work including geochemical analyses of glass shards enabled the correlation of eight tephra layers from the DEEP site sequence to known volcanic eruptions in the central Mediterranean Region (cf. table 2, Leicher et al., this issue). In addition, a distinct peak in the K intensitiesconcentration in the DEEP site sequence at 2.775773 mcd was identified as the Mercato crypto tephra layer (cf. Tabletable 2) by a correlation of the K XRF curve from the DEEP site to the curve of coreto those of cores Co1202 (Sulpizio et al., 2010; Vogel et al., 2010c) and Co1262 (Wagner et al., 2012, for locations of the cores see Fig. 1). Tephrostratigraphic investigation including geochemical and morphological analyses of glass shards enabled the correlation of 13 tephra layers from the DEEP site sequence to known volcanic eruptions or distal1). In cores Co1202 and Co1262, glass shards that co-occurred with a significant potassium peak were identified as the Mercato crypto tephra from the central Mediterranean region (cf. Table 2 and Leicher et al., 2015). layer and glass shards were also found in the DEEP site, where the corresponding K peak was identified. The MMDs in the DEEP site sequence are between 0.1 cm and 3 cm thick, and consist of very coarse silt to fine sand-sized material (cf. also Fig. 3M, 3N, and 3O3). A higher frequency of MMDsMMD's occurs between 117 mcd and 107 mcd, and between 55 mcd and 50 mcd, respectively. Most of the MMDs show MMD's appear normal gradation graded (Fig. 3N3, 1C-68H-2, 70 to 68 cm section depth), or appear as lenses (Fig. 30).3, 1D-24H-2, 41 to 39 cm section depth). In some very thin MMDs, the gradation is graded structures are only weakly expressed. The MMD in core 1F-4H-3 (Fig. 3M2, 3, 17 to 14 cm section depth) differs from all other MMDs in the DEEP site sequence as it is the only one with a clay layer at the top, and a 1.5 cm thick, poorly sorted, clay to fine sand-sized section at the bottom. In the overlapping core sections from holes 5045-1B, 5045-1C, and 5045-1D, the basal, poorly sorted part of the MMD in 1F-4H-3 is not preserved.

4.2 Sedimentary Processes

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4.2.1 Hemipelagic sediments

Although a detailed examination of the sediment bedding structures in the DEEP site sediments was frequently difficult due to secondary oxidation structures (cf. Fig. 3), the mottled and massive appearance and the lack of lamination imply that anoxic bottom water conditions did not occur. As massive structures commonly correspond to high calcite concentrations in the sediments (high TIC), they can be explained by a high abundance of calcite crystals in the sediments. Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) analyses on carbonate crystals from sediment traps (Matter(e.g. Wagner et al., 2009; Leng et al., 2010) and from sediment cores spanning the last 40,000 kyrs (e.g.), the calcite in the sediments of Wagner et al., 2009; Leng et al., 2010) show that the majority of carbonates in Lake Ohrid sediments areis mainly endogenic calciteand the amount of detrital carbonates is considered to be negligible despite the high abundance of limestones in the catchment. Only minor contributions to the calcite content come from biogenic sources, for example from ostracod valves (Vogel et al., 2010a), detrital carbonates only occur in trace amounts (Lacey et al., 2015b). 2010a). Endogenic calcite deposition in the sediments of Lake Ohrid is predominately triggered by photosynthesis-induced formation of calcite crystals in the epilimnion (e.g. Wagner et al., 2009; Vogel et al., 2010a). The precipitation occurs at warm temperatures during spring and summer, as long Ca²⁺ and HCO³⁻ ions are not short in supply (e.g. Matzinger et al., 2007; Wagner et al., 2009; Vogel et al., 2010a). High Ca²⁺ and HCO³⁻ concentrations in Lake Ohrid are triggered by the intensity of chemical weathering and limestone dissolution in the catchment, the karst discharge volumeamount of incoming water, and the evaporation of lake water (Vogel et al., 2010a). The calcium carbonate concentration in the sediments also depends on the preservation of the endogenic calcite. Dissolution of calcite in at the sediment surface and lower parts of the water column, at the sediment water interface, and in the upper sediment column can be caused by oxidation of OM, which triggers H₂CO₃ release from the surface sediments and a lowering of the lake-water pH (Müller et al., 2006; Vogel et al., 2010a). SEM analyses on indicate that microbial dissolution of endogenic calcite can be observed in the DEEP site sediments, in addition, indicates the presence of microbial dissolution sequence (Lacey et al., 2015b2015). The high TIC contents in lithotype 1 imply high photosynthesis—induced precipitation of endogenic calcite, high temperatures during spring and summer, good calcite preservation in the sediments, and a somewhat higher buffering of the lake water pH. Lower primary productivity, lower temperatures, and a somewhat strongerprobably at least partly dissolution of calcite can be inferred from the TIC contentrecord in lithotype 2 and 3 sediments. In lithotype 2 and 3, siderite layers (FeCO₃) also contribute to the TIC content (cf. Fig. 2, 4). In neighboring Lake Prespa, siderite formation has been reported to occur in the surface sediments close to the redox boundary under rather acidicacid and reducing conditions (Leng et al., 2013). In Lake Ohrid, DEEP site lithotype 2 and 3 sediments contain discrete horizons of authigenic siderite crystals and crystal clusters nucleating within an unconsolidated clay matrix (Lacey et al., 2015b2015). The open-packed nature of the matrix and growth relationships between crystals suggest that, as also observed in Lake Prespa, siderite formed in the pore spaces of the surface sediments close to the sediment-water interface, similar to other ancient lakes such as Lake Baikal (Berner, 1981; LaceyGranina et al., 2015b2004).

The OM in lithotype 2 and 3 the sediments of the DEEP site sequence is predominately of aquatic origin with minor contributions of allochthonous OM supply, as indicated by TOC/TN ratios below 1016 (cf. Meyers and Ishiwatari, 1995; Wagner et al., 2009). In lithotype 1 sediments, TOC/TN occasionally exceeds 10, which could imply some contributions of terrestrial OM. However, due to the coring location in the central part of Lake Ohrid and the relatively small inlet streams, a substantial supply of allochthonous OM to the DEEP site is rather unlikely. The Thus, high TOC/TN ratios are therefore most likely a result of early digenetic selective loss of N (cf. e.g. Cohen, 2003). The aquatic origin of the OM in the sediments of the deep basin of Lake Ohrid is also in agreement with the results of Rock Eval pyrolysis from the nearby LINI drill site (Lacey et al., 2015a, see Fig. 1 for coring location). This implies that phases characterized by higher TOC contents are representative for a somewhat elevatedin the sediments imply a strong primary productivity. This finding is confirmed in Lake Ohrid, which is also displayed by high amounts of diatom frustules in the sediments (Wagner et al., 2009) and, accordingly, in high biogenic silica (bSi) contents. Enhanced (Vogel et al., 2010a). A high productivity in the lake requires high temperatures and sufficient nutrient supply to the epilimnion. The nutrient supply to Lake Ohrid is mainly triggered by river inflow (e.g. Matzinger et al., 2006a; Matzinger et al., 2006b; Matzinger et al., 2007; Wagner et al., 2009; Vogel et al., 2010a), karstic inflow from Lake Prespa (Matzinger et al., 2006a2006b; Wagner et al., 2009), and by nutrient recycling from the surface sediments (Wagner et al., 2009). Phosphorous recycling from the surface sediments is promoted by anoxic bottom water conditions and mixing can transport phosphorous from the bottom water to the epilimnion (e.g. Wagner et al., 2009). Mixing also leads to oxidation of

OM at the sediment surface and, thus, to lower TOC contents. TOC preservation in the sediments can also be modified by lake level fluctuations, as oxidation of OM starts in the water column during settling (Cohen, 2003; Stockhecke et al., 2014b). However, distinct climate induced lake level fluctuations such as described for the Younger Dryas at Lake Van in Turkey (Wick et al., 2003; Stockhecke et al., 2014b and references therein) have not been observed at Lake Ohrid in previous studies covering the last glacial-interglacial cycle (cf. e.g. Vogel et al., 2010a; Wagner et al., 2010). This can potentially be explained by the hydrological conditions at the lake, the large water volume, and the relative high contribution of karstic groundwater inflow to the hydrological budget of Lake Ohrid. Hence, lower (higher-However, mixing also leads to oxidation of OM at the sediment surface and, thus, to lower TOC contents. Hence, low (high) TOC content are be related to an overall lower (higher) productivity and/or to more (less) oxidation of OM and improved (restricted) mixing conditions.

Overall high TOC and bSi contents in lithotype 1 sediments imply a-high productivity as a result of and high temperatures in at Lake Ohrid. Less productivity and/or oxidation of OM can be inferred for sediments of lithotype 2 and 3 from low TOC and bSi contents, and from TOC/TN ratios <4 (cf. Leng et al., 1999). When TOC is At Lake Ohrid, low such as in lithotype 3 sediments, TOC/TN <4 can be a result of OM degradation (decreasing organic C concentration) and clay-bound ammonium supply from the catchment (increasing N concentration). such as also observed in core Lz1120 from the southeastern parteorner of the lake (Holtvoeth et al., 2015).

Good OM preservation, low oxygen availability, and overall poor mixing conditions could have favored sulfide formation, such as pyrite, in lithotype 1 sediments. Sulfide Pyrite formation can be indicated by a low TOC/TS ratio (cf. Müller, 2001; Wagner et al., 2009). In lithotype 1 sediments, the high TOC/TS ratios correspond to minima in the Fe intensities (cf. Fig. 2), which suggests that Fe-sulfide formation was limited by iron and/or sulfate availability limited the pyrite formation (cf. also Holmer and Storkholm, 2001). Sulfide formation in the sediments is consistent with temperature dependent magnetic susceptibility measurement on selected samples that indicate minor contents of Lake Ohrid is restricted to deposits where Fe availability (i.e. lithotype 2 and 3 sediments) is high (cf. pyrite throughout the sedimentary sequence (Just et al., 2015). Furthermore, this issue). Urban et al. (1999) have shown that early diagenetic sulfur enrichment in OM is low in oligotrophic lakes, as up to 90% of the produced sulfides can be re-oxidized seasonally or episodically, which affects the sulfur storage over several years. At Lake Ohrid, re-oxidation of sulfides may

1 occur during the mixing season, or under present climate conditions during the irregular

complete overturn of the entire water column every few years. If re-oxidation has biased the

TOC/TS ratio as an indicator for restricted mixing conditions, the lower ratios in lithotype 2

and 3 sediments are rather a result of the overall low TOC concentrations, which is confirmed

5 by the good correspondence between the TOC/TS ratio and the TOC content.

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Elemental intensities of the clastic matter, as—obtained from high resolution XRF scanning, can provide information about the sedimentological composition of the deposits, and about erosional processes in the catchment. Variations in the potassium intensities (K, Fig. 2) and in the clastic matter content of DEEP site sequence sediments could primarily, as inferred from the potassium intensities (K, Fig. 2), can be a result of changing erosion in the catchment, such as it has also been reported from other lakes on the Balkan Peninsula (e.g. Francke et al., 2013). This implies that increased denudation and soil erosion could be inferred for lithotype 2 and 3 sediments, while less clastic matter supply occurs during deposition of a lithotype 1 sediments deposits. However, mutual dilution with authigenic components such as calcite, OM and diatom frustules can bias the potassium record as indicator for denudation and clastic matter supply.

Potassium K intensities can occur in K-feldspars, micas, and clay minerals and. Potassium is mobilized particularly during chemical weathering and pedogenesis, and the residual soils in the catchment become depleted in potassium (Chen et al., 1999). In contrast to K, Zirconium (Zr) Zircon mostly occurs in the mineral zirconzirconium, which has a high density and a high resistance against physical and chemical weathering and is therefore commonly enriched in coarse-grained (aeolian) sediments. However, in lithotype 1 and 2 sediments, low Zr/K ratios match low percentages of the <4 µm fraction (cf. -Fig. 2). This implies that coarse-grained sediments (low <4 \mu m percentages) are depleted in Zr and enriched in K at the DEEP site. Thus, the Zr/K ratio rather provides insights into the intensity of the chemical weathering, which affected the clastic matter in the catchment than being dependent on the physical grain size. As chemically altered minerals may be stored for hundreds and thousands of years in the catchment before they are eroded, transported, and finally deposited (cf. Dosseto et al., 2010), Thereby, the Zr/K ratio does not provide information about weathering processes during the time of deposition at as chemically altered minerals may be stored for long time periods in the DEEP site. The match of loweatchment before they are eroded and transported to a sedimentary basin (cf. also Dosseto et al., 2010). Low Zr/K ratios and in lithotype 1 and 2 sediments match with low percentages of the <4 \mu fraction in lithotype 1 and 2 sediments and imply that more coarse detrital matter, predominately consisting of K-rich clastic material from young and <u>lessmoderately</u> chemically weathered soils, were deposited at the DEEP site. In contrast, high Zr/K ratios in lithotype 3 sediments match with high percentages of the < 4µm fraction and suggest that more fine grained, chemically weathered, and K-depleted <u>siliciclasticselastics</u> from <u>matureold</u> soils were supplied to the lake. <u>Deviations from the correspondence between Zr/K and the <4µm grain size fraction can be explained by additional processes that affect the deposition of clastic matter at the DEEP site, such as the transportation energy in the inlet streams, lake level fluctuations and the shoreline distance, and the strength of lake-internal current systems, respectively (cf. also Vogel et al., 2010b).</u>

4.2.2 Event Layers

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Probable trigger mechanismsmechanism for MMDs have widely been discussed and encompass earthquakes, delta collapses, flooding events, over steepening of slopes, rock falls, and lake-level fluctuations (e.g. Cohen, 2003; Schnellmann et al., 2006; Girardclos et al., 2007; Sauerbrey et al., 2013). At Lake Ohrid, MMDs in front of the Lini Peninsula (Fig. 1) and in the southwestern part of the lakeLake Ohrid were likely triggered by earthquakes (Lindhorst et al., 2012; Wagner et al., 2012; Lindhorst et al., 2015). AnA strong earthquake might have also triggered the deposition of the MMD in core 1F-4H-3 (cf. Fig. 3M,2,3), which is composed of a turbidite succession and an underlying, poorly sorted debrite (after the classification of Mulder and Alexander, 2001). The disturbance generated by a debris flow can cause co-genetic turbidity currents of fine-grained material in front and above the mass movement (Schnellmann et al., 2005; Sauerbrey et al., 2013). As the debrite-turbidite succession occurs at 7.87 mcd in hole 5045-1F, it likely corresponds to a massive slide complex north of the DEEP site (cf. hydro acoustic profile of Fig. 2 in Wagner et al., 2014). Density flows that enter the central part of the Lake Ohrid basin close to the DEEP site from eastern or southern directions have not been observed in upper parts of hydro-acoustic profiles (cf. Fig. 2 and 3 in Wagner et al., 2014). The three massive MMDs that occur in front of the Lini Peninsula to the west of the DEEP site (cf. Wagner et al., 2012) are likely not related to the debrite-turbidite succession in core 1F-4H-3Fig. 3M. The underlying debrite does not occur in overlapping segments of holes 5045-1B, 5045-1C, and 5045-1D. Holes 5045-1B, 50455054-1C, and 5045-1D form a N-S transect, (40 m distance between each hole), whereas hole 5045-1F is located approximately 70 m to the east. Due to the absence of the debrite deposits in most drill holes, and the relatively low thickness in hole 5045-1F, and 1F, erosional processes at the DEEP site are likely low. In addition, hydroplaning that generates a basal water layer below athe debris flows, which causes high flow velocities with

little basal erosion (Mohrig et al., 1998; Mulder and Alexander, 2001), erosional processes at the DEEP site are likely low.

The sand lenses and normal graded MMDs (cf. Fig. 2, 3) can be classified as grain-flow deposits (after the classification of Mulder and Alexander, 2001; Sauerbrey et al., 2013) and are composed of reworked lacustrine sediments from shallow water depths or subaquatic slopes close to riverine inflows. Grain flows that enter the deep parts of the Lake Ohrid basin via the steep slopes might transform into a mesopycnal flow at the boundary of the hypolimmion (cf. also Mulder and Alexander, 2001; Juschus et al., 2009), which would have prevented prevents erosion of the underlying sediments.

5 Core chronology

The chronologyehronostratigraphy for the sediments of the DEEP site sequence down to 247.8 mcd was established by using tephrochronological information from 11 out of 13radiometric ages from nine tephra layers (cf. Tabletable 2 and Leicher et al., 2015), and by cross-correlation to orbital parameters. The tephra layers were correlated (Laskar et al., 2004) and to the global benthic isotope stack LR04 (Lisiecki and Raymo, 2005, Fig. 5, 6). Correlation of the tephra layers to well-known eruptions from Italian volcanoes or central Mediterranean marker tephra by geochemical and morphological fingerprint analyses of glass shards. Radiocarbon and 40 Ar/ 39 Ar ages were transferred from the reference records to the DEEP site sequence (tephrostratigraphic results of the DEEP site are provided by Leicher et al. (2015)). a re-calibration of 40 Ar/39 Ar ages from the literature were re-calculated by using the same flux standard in order to obtain a homogenous set of ages (see Leicher et al., 2015). The stratigraphic position and chronology of the OH-DP-0499/P-11 tephra layer at 49.947 mcd in different records from the vicinity of Lake Ohrid is discussed in detail by Zanchetta et al. (2015). Their results imply that the P-11 tephra layer has an age of 133±2 ka, which was incorporated into the age-depth modeling. As the 11 tephra layers provide provided a robust basis for the age depth model of the DEEP site sequence, the tephrostratigraphic information was (Leicher et al., this issue). Thus, the nine tephra layers were used as 1st order tie points.

The chronological information from the <u>11nine</u> tephra layers was also used to define cross correlation points to orbital parameters, which were included into the age depth <u>model</u> as 2nd order tie points. The tephra layers Y-5, X-6, <u>P-11P11</u>, and A11/12 were deposited when <u>there</u> are minima in the TOC content and in the TOC/TN ratio can be observed (cf. Fig. 5), and when there is <u>ana</u> inflection point (<u>blue dots, black vertical line in insolation and winter season length plots, Fig. Fig. 5) of increasing local summer insolation (<u>21st21</u>. June, 41°N).</u>

Thereby, the inflection points coincide with an increasing) and winter season length (21st21. September to 21st21. March, Fig. 5). Summer insolation and winter season length have a direct impact on the OM content and the TOC/TN ratio, as they may trigger primary productivity and decomposition. Low insolation and colder temperatures during summer reduce the primary productivity in the lake, but simultaneously, a shorter winter season would have reduced mixing in the lake, which reduces the decomposition of OM and increases TOC and the TOC/TN ratios (cf. Fig 5, insolation and winter season length minima). A longer winter season improves the mixing, but a strong insolation during summer promotes the primary productivity in the lake, which also results in higher TOC and TOC/TN (cf. Fig. 5, insolation and winter season length maxima). Thus, low OM preservation and low TOC and TOC/TN in the sediments may occur when summer insolation strength and winter season length are balanced. In addition, the inflection points coincide with the perihelion passage in March. As the highest proportion of the annual radiation gets lost through surface albedo during spring (Berger et al., 1981), the time period of the perihelion passage in March is characterized by cold and dry conditions in the central Mediterranean region (Magri and Tzedakis, 2000; Tzedakis et al., 2003; Tzedakis et al., 2006). Cold conditions at Lake Ohrid promote mixing during winter and restrict the primary productivity during summer. Thus, minima in TOC and TOC/TN are tuned to increasing insolation and winter season length. 5 i.e. when both summer insolation and winter season length are at their inflection points. Hence, minima in the TOC content and the TOC/TN ratio were tuned to increasing insolation and winter season lengths. 3rd-order tie points were obtained by tuning the LR04 δ¹⁸O record to the TIC content, as maxima in the TIC record have a good correspondence with minima in the LR04 8¹⁸O record (cf. Fig. 5), when the stratigraphic positions of the 1st and 2nd order tie points are considered. This is supported by the P11 tephra layer, which has an age of 129 ka. Its position below a TIC peak at ca. 48 mcd (cf. Fig. 5) implies that this TIC peak likely corresponds to peak interglacial conditions at 123 ka (MIS 5.5), which is confirmed by results of former sediment core studies (Belmecheri et al., 2009; Vogel et al., 2010a). Potential explanations for a strong correlation between global benthic 8¹⁸O variability and the TIC content in the DEEP site sediments could be a synchronous timing of marine and terrestrial events, or a teleconnection between ice sheet variability and the environmental settings in the Mediterranean Region. Minimum ice sheet expansion (minima in LR04 8¹⁸O) in the Northern Hemisphere and a northern location of the atmospheric circulation patterns and of the Inter-Tropical Convergence Zone (ITCZ), such as it occurs today, could have

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resulted in maximum summer temperatures at Lake Ohrid. Warm temperatures promote calcite precipitation in the epilimnion. During glacial periods, the northern ice sheet expansion caused a southward shift of the atmospheric circulation patterns (LR04 δ^{18} O maxima), which could have triggered lower temperatures at Lake Ohrid, and less calcite precipitation in the epilimnion.

The <u>11nine</u> tephra layers and <u>3145</u> cross correlation points of 2nd and 3rd—order (<u>supplementsupplementary</u> 1) were used for the establishment of an age-depth model. An uncertainty of ± <u>20001000</u> years was applied for each 2nd order tie point-of 2nd and 3rd order in order to account for inaccuracies in the tuning process. For the age depth modeling using the Bacon 2.2 software package (Blaauw and Christen, 2011), overall stable sedimentation rates at the DEEP site (mem.strength = <u>604</u>, mem.meanshape = 0.97, thick = <u>8040</u> cm) and expected sedimentation rates (acc.shape = 1.5, acc.mean = 20) from first age estimations for the DEEP site sequence by Wagner et al. (2014) were considered (cf. Fig. 6). Finally, the age model was evaluated and refined by a detailed comparison with the age-depth model for the downhole logging depth scale (<u>Baumgarten et al., 2015, cf. Fig. 7</u>) by tuning Potassium counts (K) obtained from high-resolution XRF scanning to the spectral gamma radiation (SGR) of potassium (cf. <u>supplementsupplementary</u> 2) in hole 5045-1D (<u>for more details see</u> Baumgarten et al., 2015, <u>cf. Fig. 6</u>). The obtained age model reveals that the upper 247.8 mcd of the DEEP site sequence <u>compriseseomprise</u> the last ca. <u>637 kyrs. 640 ka (MIS16)</u>.

On the basis of the established core chronology for the DEEP site sequence, glacial-interglacial environmental variability at Lake Ohrid inferred from the TOC record is in agreement with other paleoclimate records from the Mediterranean region such as the Tenaghi Philippon (Tzedakis et al., 2006) and the Soreq cave records (Grant et al., 2012 cf. Fig. 6). This supports the quality of the chronology for the DEEP site sediments. Whereas the chronology of the Tenaghi Philippon record is, similar to the DEEP site sequence, based on tuning against orbital parameters, the Soreq Cave speleothem record is the longest absolute dated (U-Th) paleoclimate record currently available for the Mediterranean region.

6 Overview about the Paleoenvironmental History of Lake Ohrid

Variations in the TIC, bSi, TOC, K, and Zr/K records of the DEEP site sequence correspond to global and regional climatic variability on glacial-interglacial time scales, such as indicated by a comparison to the global benthic isotope stack LR04 (Lisiecki and Raymo, 2005), to North Greenland isotope record (NGRIP-members, 2004; Barker et al., 2011), and to variations in the arboreal pollen percentage of the Tenaghi Philippon record from

- northernNorthern Greece (Tzedakis et al., 2006, cf. Fig. 7). In addition to the <u>close match of</u> climatic variability on orbital time scales <u>between those records and the Lake Ohrid record</u>, a
- 3 comparison of the individual interglacial and glacial stages allows a first discrimination of the
- 4 intensity of these stages at Lake Ohrid.

6.1 Interglacials

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Between 637640 ka and present day, the DEEP site sediments deposited during the interglacial periods (MIS boundaries after Lisiecki and Raymo, 2005, see Fig. 7)sediments of the DEEP site sequence mainly consist of lithotype 1 and 2 sediments. Moderate to high TIC, TOC, and bSi contents in lithotype 1 and 2 sediments imply a moderate to strong primary productivity, and thus, moderate to high temperatures during spring and summer. The overall high temperatures during spring and summer and a longer summer season during interglacial periods likely resulted in an incomplete and restricted mixing of the water column during winter, such as it also persists today. Poor mixing hampers the oxidative mineralization decomposition of OM and thus, promotes the preservation of TOC and restricts the bacterial CO₂ release at the sediment surface. A reduction in the H₂CO₃ formation and a higher pH hampers the acidification in the hypolimnion and consequently bottom waters improve the calcite preservation. In addition, interglacial climate conditions likely promoted high Ca2+ and HCO3 concentrations and a high pH also in the epilimnion, as warm temperatures increased chemical weathering of the limestones in the catchment. In addition and evaporation of lake water. The good correspondence between high TIC during interglacials, which also exhibit overall high δ^{18} O-calcitelake water (δ^{18} O_{lw}) values indicatingand indicate a low Precipitation/Evaporation (P/E) ratio (Lacey et al., 2015b2015), suggest that evaporation may also contribute to high Ca²⁺ and HCO₃⁻ concentrations in the lake water (cf. Fig. 7). Supply from the catchment and increased. Increased evaporation could have also increased the concentration of Si ions in the epilimnion, which could have promoted diatom productivity. The sensitivity of diatom productivity to increasing, as it is indicated by a correspondence between high $\delta^{18}O_{1w}$ and high bSi concentrations. Similar fertilization processes can be observed after the deposition of tephras, when leaching of these tephras results in higher Si concentrations in the lake-water column is impressively shown in leaching experiments of tephras (D'Addabbo et al., 2015), and trigger diatom growth in high resolution studies of diatom changes after the deposition of the Y-5 tephra (epilimnion (cf. Jovanovska et al., <u>2015</u>this issue).

Low supply of clastic matter from Despite intensive chemical weathering and pedogenesis in the catchment can be inferred forduring interglacials, low K intensities in lithotype 1 and 2 sediments, where K intensities and along with the stable-sedimentation rates are low ($\sim <0.04$ cm/yr). Low supply of clastic matterdespite high accumulation of calcite, bSi, and OM, indicates that the clastic matter supply to the lake basin was low. This is likely a result of low denudationerosion rates despite intensive chemical weathering and pedogenesis during interglacial periods in the catchment. Relatively high pollen concentrations in the interglacial sediments of the DEEP site core imply a dense vegetation cover (cf. Fig. 7 and Sadori et al., 2015this issue), which likely reduces restricted erosion in the catchment of Lake Ohrid. In addition, the low Zr/K ratios and the low proportion of the <4 µm grain size fraction in lithotype 1 and 2 sediments imply that in particular K-rich minerals and the products of young soils were transported to the lake. This hypothesis is supported by high S-ratios in interglacial deposits, which indicate a high proportion of primary magnetic minerals (i.e. (titano-) magnetite) from the bedrock in the sediments, whereas the amount of secondary minerals (hematite + goethite) as products of chemical weathering is low (cf. Fig 7 and Just et al., this issue).

Lithotype 3 deposits with negligible TIC contents only occur at the onsets and terminations of interglacial periods, and during MIS7 and 3 (cf. Fig. 7). The low TIC, TOC, and bSi contents of these sediments correspond to colder periods with a restricted primary productivity. In addition, low temperatures during winter would have improved the mixing, which could promote decomposition of OM in the surface sediments and led to lower TOC₂ and to lower TIC by dissolution of calcite.

Variations of interglacial conditions since 637640 ka

Differing OM, bSi, and TIC contents in the interglacial sediments of the DEEP site sequence corresponding to interglacial time periods imply different intensities of interglacials at Lake Ohrid. Comparable conditions can be inferred for MIS15 and 13, with high TIC and bSi, and low OM, which indicate are characterized by strong primary productivity and high temperatures during spring and summer, and decomposition of OM during the mixing season. However, although MIS15 and 13 are regarded as relatively weak interglacials based on the synthetic modeled Greenland isotope record (Barker et al., 2011) and the global benthic isotope stack LR04 (Lisiecki and Raymo, 2005 cf. also Fig. 7). Possible explanations On possible explanation could be that the inferred high intensity of these interglacials at Lake Ohrid is due to a strong seasonality or a lower water volume, which promotes a high ion

concentration (high TIC, bSi)restricted inflow and high $\delta^{18}O_{calcite}$ values in the lake waterprecipitation, and high evaporation, as it is suggested by high $\delta^{18}O_{lw}$ concentrations (Lacey et al., 2015b), and decomposition of OM (low TOC) during the mixing season. A lower water volume can be explained by the ongoing subsidence in the lake basin, which persist until today (Lindhorst et al., 2015). In addition, the high TIC and bSi concentrations could also be a result of the lower TOC contents and of mutual dilution with OM.

During the first part of MIS11, between 420 <u>ka</u> and 400 ka, highest TIC concentrations along with moderate and high bSi and TOC <u>concentration</u> imply highest productivity (high TOC) and highest temperatures (highest TIC), <u>wherebywhile biogenic silica preservation in the moderate bSi concentrations can be explained by mutual dilution with calcitesediments is restricted</u>. This is consistent with other records, where strongest interglacial conditions and highest temperatures since <u>637640</u> ka are reported for the onset of MIS11 (Lang and Wolff, 2011).

TIC concentration during the second phase of MIS11MIS-11, between 400 ka and 374 ka, and during MIS9 and 7 are generally lower and mostly restricted to confined distinct peaks, which—This implies overall less calcite precipitation, less primary productivity, and lower temperatures at Lake Ohrid. This is consistent with the low bSi concentrations, but not with the high TOC contents, and with relatively stronger interglacials subsequent to the MBE (Mid-Brunhes Event) inferred from the synthetic modeled North Greenland isotope record (Barker et al., 2011) and the LR04 stack (Lisiecki and Raymo, 2005). The temperatures during the second phase of MIS11 and during MIS9 and 7 were likely lower compared to the first phase of MIS11 as indicated by the TIC record (cf. Fig 7). In), and in addition, the somewhat lower TIC and bSi contents also correspond to lower $\delta^{18}O_{calcite}\delta^{18}O_{tw}$ concentrations in the Lake Ohrid sediments, which implies imply that this interglacial periods were are isotopically fresher and less evaporated than the previous interglacial periods (Lacey et al., 2015b). Between, 235 ka and 220 ka (MIS7), restricted primary productivity and improved mixing are indicated by negligible TIC and low TOC and bSi concentrations 2015).

Overall high TIC, TOC, and bSi concentrations during MIS5 imply a strong primary productivity in the <u>epilimnioneplimnion</u> and high temperatures during spring and summer. $\delta^{18}O_{\text{calcite}}\delta^{18}O_{\text{lw}}$ during MIS5 is notably higher compared to the two previous interglacial periods (Lacey et al., 2015b2015) and indicates a low P/E ratio. In particular the onset of MIS5 is reported to be <u>one of</u> the <u>warmeststrongest</u> interglacial period <u>during</u> the last 640 ka in marine records (Lang and Wolff, 2011), which is also indicated in the North Greenland

- 1 temperature variations (NGRIP-members, 2004; Barker et al., 2011), and in the global
- benthic isotope stack LR04 (Lisiecki and Raymo, 2005).), and correspond to high TIC, TOC,
- 3 and bSi concentrations in the DEEP site sequence.

6.2 Glacials

- 5 | Glacial periods between 637640 ka and today are characterized by predominant deposition of
- 6 lithotype 3 sediments, with rare occurrence of lithotype 1 and 2 sediments in MIS14 and 8,
- 7 when TIC contents are higher. Low TOC and bSi and negligible TIC contents in lithotype 3
- 8 sediments imply low primary productivity and overall low temperatures during glacial
- 9 periods. Some minor fluctuations in productivity and temperature are indicated by TOC and
- 10 bSi. They are not documented in TIC, because restricted ion supply from the catchment and as
- 11 oxidation of OM at the sediment surface due to intensified and prolonged mixing, which is
- 12 indicated by TOC/TN ratios <4, may have led to a slight decrease of the bottom water pH and
- dissolution of calcite precipitated from the epilimnion. Dissolution of calcite and the existence
- of a threshold can also explain the delayed increase of TIC compared to TOC and bSi at the
- transitions of MIS16, MIS12, MIS10, MIS8, MIS6, and MIS2 into the following interglacials.
- 16 High K, a high proportion of the fine fraction <4 μm, and highstable sedimentation rates
- 17 (~>0.04 cm/yr) despite low calcite, OM and bSi content in the glacial sediments, indicate high
- input of clastic terrigenous matter and increased erosion in the catchment. Furthermore, the
- 19 high Zr/K ratios suggest the supply of K-depleted, intensively weathered siliciclastics soils
- 20 from the catchment, which is also supported by a higher hematite + goethite to magnetite ratio
- 21 (low S-ratio) in glacial deposits of the DEEP site sequence (cf. Fig. 7 and Just et al., 2015this
- 22 issue). The enhanced erosion of intensively weathered siliciclasticelastic material can be
- explained by less dense vegetation cover in the catchment, such as implied by low pollen
- 24 | concentrations in the DEEP site sequence in most of the glacial periods (cf. Fig. 7 and Sadori
- et al., 2015), and by the existence of local ice caps in the surrounding mountains of Lake
- Ohrid. The existence of ice caps is, as indicated by moraines in the catchment, which are
- 27 thoughthough to have formed during the last glacial cycle (Ribolini et al., 2011).
- Variations of glacial conditions since 637640 ka
- 29 As TIC is affected by dissolution and indicate negligible calcite concentrations, information
- 30 about the severity of the individual glacials at Lake Ohrid can only be inferred from TOC and
- 31 bSi. Minima in the TOC and bSi imply that most severe glacial conditions at Lake Ohrid
- occurred at the end of MIS16, and during MIS12, 10, and 6. Somewhat higher bSi and TOC

in parts of MIS14 and 8, and in MIS6, 4, and 2 imply less severe glacial conditions. This suggestsimplies that the finding of glacial moraines from MIS2 (Ribolini et al., 2011) is probably only due to better preservation of these glacial features compared to the older glacials. Interglacial-like conditions with higher primary productivity and reduced oxidation of OM in the surface sediments prevailed at the occurrence of lithotype 1 and 2 sedimentation, i.e. between 563 ka and 540 ka during MIS14, and between 292 ka and 282 ka during MIS8. Interglacial-like conditions along with a forest expansion and more warm conditions between 292 ka and 282 ka can also be seen in the pollen records of Lake Ohrid (cf. Fig 7 and Sadori et al., 2015) and Tenaghi Philippon (Fletcher et al., 2013). MIS-8.

The general observation that MIS16 and 12 were more severe glacials is in broad agreement with other records, such as the North Greenland isotope record (Barker et al., 2011), the global benthic stack LR04 (Lisiecki and Raymo, 2005), and the Tenaghi Philippon pollen record (Tzedakis et al., 2006). Thereby, the comparable low sedimentation rates in combination with the negligible TIC, bSi and TOC concentrations between 460 ka and 430 ka (MIS12, cf. Fig. 7) imply low supply of clastic matter and thus, low erosion in the catchment despite an open vegetation cover in the catchment (cf. Fig. 7 and Sadori et al., 2015). One potential explanation for the low clastic matter supply could be dry conditions and associated reductions in terrestrial runoff compared to other glacials.

The frequent occurrence of MMDs between 280 ka and 241 ka and between 160 ka and 130 ka could reflectimplies significant lake level fluctuations during MIS8 and 6. During the first period (MIS8), distinct fluctuations in the pollen concentrations of the DEEP site sediments (cf. Fig. 7 and Sadori et al., 2015) correspond to similar fluctuations in the AP pollen percentages of the Tenaghi Philippon pollen record (Tzedakis et al., 2006) correspond to similar fluctuations in the pollen concentrations in the DEEP site sequence (cf. Fig. 20067, and Sadori et al., this issue) and probably indicate a shift from cold and dry to more warm and humid conditions in northern Greece and at Lake Ohrid. During MIS6, a 60 m lower lakelevel compared to present conditions, and a subsequent lake level rise during late MIS6 or during the transition from MIS6 to MIS5 is reported from hydro-acoustic and sediment core data from the northeastern corner of Lake Ohrid (Lindhorst et al., 2010). In the sediments of the DEEP site, the MIS6 to MIS5 transition occurs at ca. 50 mcd, which could indicate that the water depth might have not changed significantly compared to the present conditions. This can be explained by the ongoing subsidence (Lindhorst et al., 2015). However, the pollen record from the DEEP site also implies a phase of strong aridity during MIS6 (Sadori et al., 2015), which might imply that climate-induced lake level fluctuations at Lake Ohrid were

probably less severe compared for example to Lake Van in Turkey, where a 260 m lower lake level has been reported for the Younger Dryas (e.g. Wick et al., 2003 and references therein; Stockhecke et al., 2014b). Thereby, the extraordinary high sedimentation rates in particular during the first part of MIS6 in combination with high K intensities and low bSi, TIC, and TOC imply intensive erosion analyses from the northeastern corner of Lake Ohrid (Lindhorst et al., 2010). This is in agreement with pollen data (Sadori et al., this issue), which suggest that quite arid conditions took place during MIS6.

The general observation that MIS16 and 12 were the most-severe glacials is in broad agreement with other records, such as the North Greenland isotope record (Barker et al., 2011), the global benthic stack LR04 (Lisiceki and Raymo, 2005), and the Tenaghi Philippon pollen record (Tzedakis et al., 2006). Furthermore, TOC, bSi and greigite in the Lake Ohrid DEEP site sequence support that MIS10 was more severe than MIS6, as syn sedimentary formation of greigite during the older glacial period is likely linked to a combination of low productivity and improved mixing conditions in the lake (Just et al., this issue). However, the idea that MIS10 is more severe than MIS6 differs from the pollen records from the same core (Sadori et al., this issue) and from Tenaghi Philippon (Tzedakis et al., 2006), as both archives suggest more harsh conditions during MIS6. The pollen record from the DEEP site sequence also imply a strong aridity during MIS6 (Sadori et al., this issue), which is consistent with a low lake level of Lake Ohrid as implied by the frequent occurrence of MMDs between 160 and 130 ka, and the results of the sediment core and hydro-acoustic study in the northeastern corner of the lake (Lindhorst et al., 2010). This implies that the dry conditions during MIS6 are probably not mirrored in TOC, bSi, and greigite concentration.

7 Summary and Conclusion

The investigated sediment succession between 247.8 mcd and the sediment surface from the DEEP site in the central part of Lake Ohrid provides a valuable archive of environmental and climatological change for the last 637 kyrs640 ka. An age model was established by using chronological tie points from 11 nine tephra layers, and by tuning biogeochemical proxy data to orbital parameters and to the global benthic isotope stack LR04. The imprint of environmental change on the lithological, sedimentological, and (bio-)geochemistry data can be used to unravel the lake's history including the development of the Lake Ohrid basin, and the climatological variability on the Balkan Peninsula.

The lithological, sedimentological, and geochemical data from the DEEP site sequence imply that Lake Ohrid did not experience major catastrophic events such as extreme lake-level low

stands or desiccation events during the last 637 kyrs640 ka. Hiatuses are absent and the DEEP

site sequence provides an undisturbed and continuous archive of environmental and

3 climatological change.

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Based on the initial core description and the calcite content, the hemipelagic sediments from the DEEP site sequence can be classified into the three different lithotypes. This classification

is supported by variations in the (bio-)geochemistry proxiesdata and matchesfollows climate

variations on glacial/interglacial time scales. Overall, interglacial periods are characterized by

high primary productivity during summer, restricted mixing during winter, and low erosion in

the catchment. During glacial periods, the primary productivity is low, intense mixing of the

water column promotes the decomposition of OM, which may have lowered the water pH and

led to dissolution of calcite_at the sediment surface. Enhanced erosion of chemically altered

siliciclastics and a overallinterglacial soils and higher clastic matter input into the lake during

glacial periods can be a result of explained by a less dense vegetation cover in the catchment

and melt water run-off from due to the existence of local glacierice caps on the surrounding

15 mountains.

16 Following a strong primary productivity during spring and summer, the highest interglacial

temperatures can be inferred for the first part of MIS115 and for MIS5. In contrast, somewhat

lower spring and summer temperatures are observed for MIS15, 13, 9, and 7. The data also

suggestsuggested that high ion and nutrient concentrations in the lake water promote calcite

precipitation and diatom growth in the epilimnion epilmnion during MIS15, 13, and 5,

whereas less evaporated interglacial periods exhibit lower TIC and bSi contents (MIS9 and 7).

22 Most severe glacial conditions at Lake Ohrid occurred during MIS16, 12, 10, and 6,

whereas somewhat warmer temperatures can be inferred for MIS14, 8, 4, and 2.3. A low lake

level implies dry conditions during MIS6. Interglacial-like conditions occurred during parts of

MIS14 and 8, respectively.

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Table 1. The contributions of the different core sections to the <u>composite</u> DEEP site profile.

| I | | | | |
|---------|---------------|-------------------|----------------|-------------------|
| | of core | core runs | of | sections |
| I | runs | | Sections | |
| Co1261 | 2 | <u>2 (1.1%)</u> % | 2 | 2 (0.5%)% |
| 5045-1B | 26 | <u>26 (</u> 14.2 | 50 | <u>50</u> |
| | | <u>%)</u> | | (12.9 <u>%)</u> % |
| 5045-1C | 72 | <u>72</u> | 137 | 137 |
| | | (39.3%)% | | (35.3 <u>%)</u> % |
| 5045-1D | 75 | <u>75</u> | 184 | 184 |
| | | (41.0 <u>%)</u> | | (47.4 <u>%)</u> % |
| 5045-1F | 8 | 8 (4.4%) | 45 | <u>15</u> |
| | | | | (3.9%)% |
| Σ | 183 | | 388 | |

Hole Number Percent of Number Percent of

Table 2: Correlated tephra layer in the DEEP site sequence according to Leicher et al. (2015this issue). ⁴⁰Ar/³⁹Ar ages from the literature were recalculated aton a 2σ confidence levelslevel (Leicher et al., 2015this issue). * Calibrated ¹⁴C age, ⁺ recalculated ⁴⁰Ar/³⁹Ar ages, ° age for P-11 from Zanchetta et al. (2015).

| Ohrid Tephra | Correlated eruption/tephra | Age Recalculated |
|-----------------------------------|----------------------------|--|
| (mcd) | | ⁴⁰ Ar/ ³⁹ Ar age (ka) |
| 2. <u>775</u> 773 | Mercato | 8.540 ± 0.05 * |
| 11.507 | Y-3 | $29.05 \pm 0.37*$ |
| 16.933 | Y-5 | $39.6 \pm 0.1^{\pm}$ |
| 40.486 | POP2 | $102 \pm 2.4^{+}$ |
| 43.513 | X-6 | $109\pm2^{\pm}$ |
| 49.947 | <u>P-11</u> P11 | $133.5 \pm 2^{\circ} 129 \pm$ |
| | | 6 |
| 61.726 | Vico B | $162 \pm 6^{+}$ |
| 181.769 | Pozzolane Rosse | $457\pm2^{\pm}$ |
| <u>195.566</u> 201.049 | SC5Sabatini Fall A | 493.1 ± |
| | | $10.9^{+}496 \pm 3$ |
| 201.782 | A11/A12 | $511 \pm 6^{\pm}$ |
| 206.08 | Tufo di Bagni Albule | $527 \pm 2^+$ |

Figure 1. **A**: Location of lakes Ohrid and Prespa on the Balkan Peninsula at the border of the Former Yugoslav Republic of Macedonia (FYROM) and Albania. TP: Coring location of the Tenaghi Pilippon record. **B**: Map of the area of lakes Ohrid and Prespa and bathymetric map of Lake Ohrid (from Lindhorst et al., 2015). Marked in white are the DEEP site and the short cores Lz1120 (Wagner et al., 2009), Co1202 (Vogel et al., 2010a), and LO2004-1 (Belmecheri et al., 2009). TP: Tenaghi Pilippon pollen record.

Figure 2. Variations of the lithological and (bio-)geochemical proxy data of the DEEP site sequence plotted against meter composite depth (mcd). The core composite profile of the DEEP site sediment sequence consists of core sections from core Co1261 (upper 0.93 mcd),

- and of core sections from holes 5045-1B, 5045-1C, 5045-1D, and 5045-1F (cf. legend
- 2 "Composite"). Marked is also the gap in the composite profile between 204.719 and 204.804
- 3 mcd, where no overlapping core segments are available. The lithological information includes
- 4 the classification of the sediments into the three lithotypes (for color code see legend
- 5 "Lithology"), and information about the water content, TIC, TOC, bSi, TOC/TS, TOC/TN, K,
- 6 | Fe, Zr/K, and grain size variability (<-4μm grain size fraction). High-resolution XRF data was
- 7 filtered by using a lowpass filter (5th order, cut off frequency: 0.064 Hz) in order to remove
- 8 white noise from the data. Red dots mark the results of the conventional XRF analyses. The
- 9 occurrence of siderite <u>layerslayer</u>, tephra layers, and <u>mass movement deposits</u> Mass
- 10 | Movement Deposits (MMD) are indicated on the right column (cf. legend "Lithology).
- 11 Tephra layer and MMDsMass Movement Deposits marked with an asterisk are shown in
- 12 Figure 3: *1: M1F-4H-3, *2: O1D-24H-2, *3: N1C-68-2, *4: P1F-6H-2, *5: H1D-18H-3.
- 13 Figure 3. High-resolution line-scan images showing characteristic core segments from
- deposits of lithotype 1 to 3, and of Mass Movement Deposits (MMD) and tephra layers. The
- vertical scale is in centimeter section depth. For composite depths of the line scan image see
- 16 supplement.
- 17 Figure 4. Siderite layer in core 1F-11H-3 (ca. 60 cm section depth) at 22.56 to 23.57 mcd. The
- 18 yellowish brown siderite layer correlates to enhanced TIC, iron (Fe), and manganese (Mn)
- 19 intensities in the sediments. For SEM images of the siderite, please see Lacey et al. (2015b).
- 20 Figure 5. Left: Comparison between TOC (DEEP site) and arboreal pollen percentages (AP,
- 21 Tenaghi Philippon, Tzedakis et al. (2006)) from 636.69 ka to the present. **Right:** Comparison
- between TOC (DEEP site) and δ^{18} O (Soreg Cave, Grant et al. (2012)) from 160 ka to the
- present. Red dots mark the tephrochonological age control points (1st order tie points), blue
- 24 dots mark the TOC versus orbital parameter tuning points (2nd order tie points). The good
- 25 | correlation of the DEEP site TOC record with both Tenaghi Philippon and the Soreq Cave
- temporal series supports the age model of the DEEP site succession.
- 27 Figure 5. Age modeling of the DEEP site sequence down to 247.8 mcd, with ages and
- 28 occurrence of tephra layers (1st order tie points, red), and tuning of TOC and TOC/TN (2nd
- 29 order tie points, purple) versus local insolation and winter season length (Laskar et al., 2004).
- and TIC (3rd order tie points, green) versus the global benthic isotope stack LR04 and marine
- 31 isotope stages (MIS, grey) 15 to 1 (Lisiecki and Raymo, 2005).
- 32 | Figure 6. Age model of the DEEP site sequence down to 247.8 mcd (637 ka). Ages were
- 33 | calculated 640 ka), using the software package Bacon 2.2 (Blaauw and Christen, 2011).

1 Overall stable sedimentation rates at the DEEP site (mem.strength = 604, mem.meanshape = 2 0.97, thick = 8040 cm) and expected sedimentation rates (acc.shape = 1.5, acc.mean = 20) from first age estimations for the DEEP site sequence by Wagner et al. (2014, cf. Fig. 6) were 3 4 considered. For the ages and errors of the tephra layers (red) see table 2. The cross correlation 5 points (green) include an error of ±2000 years. The age model was re-evaluated 6 and refined by a comparison to the age model of the downhole logging data (purple) by 7 Baumgarten et al. (2015). 8 Figure 7. Proxy data from the DEEP site sediments sequence plotted versus age and compared 9 to the global benthic isotope stack LR04 (Lisiecki and Raymo, 2005), the local (41°N) insolation at June the 21th, the arboreal pollen concentration (AP) in the Tenaghi Philippon 10 record in northern Northern Greece (Tzedakis et al., 2006), the North Greenland temperature 11 derived from the NGRIP δ^{18} O record (% VSMOW, NGRIP-members, 2004) and the 12 GL_T syn $\delta^{18}O$ synthetic isotope record (% VSMOW, Barker et al., 2011). The grey shaded 13 areas indicate interglacial marine isotope stages (MIS; Lisiecki and Raymo (2005). For the 14 15 legend of the mass movement deposits Mass Movement Deposits (MMD) see Fig. 2. Highresolution XRF data was filtered by using a lowpass filter (5th order, cut off frequency: 0.064 16 17 Hz) in order to remove white noise from the data. Note the logarithmic scale for TOC and for 18 the total pollen concentration.- Pollen concentrations are from Sadori et al. (2015this issue), lake water δ^{18} O_{calcite} δ^{18} O_{be} from Lacev et al. (2015b2015), and S-ratios representing hematite 19 + goethite versus magnetite from Just et al. (2015this issue). 20 21

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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 tephrochronologicial 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 δ^{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. 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 3rd order tie points. Together, the 1st and 2nd 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 2nd 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 digenetic 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 is degradation (Leng et al., 1999; Holtvoeth et al., 2015). This process would decrease the organic carbon concentration, which 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 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 $\delta^{13}C_{org}$ data (pers. com. G. Zanchetta).

P.C. Tzedakis pointed out that the 2nd 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 spleothem 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±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 occurred 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 tephras 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 tephrostratigrapic tie points?

The tephra layers were not directly dated in the sediments of Lake Ohrid, but ³⁹Ar/40Ar 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 gammaray 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 μ 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 μ 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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