Dear editorial board,

We want to thank both reviewer once again, for the detailed and constructive criticism on our study. As suggested, we substantially revised the manuscript, and partly changed the focus of the paper. We slightly changed the title to “Environmental control on the occurrence of high-coercivity magnetic minerals and formation of iron sulfides in a 640 ka sediment sequence from Lake Ohrid (Balkans)” and extended the author list. The whole paper was largely re-written.

To adequately address the points raised by the reviewers, the discussion was entirely restructured and rewritten. We excluded thermomagnetic data which were presented in the original version, because, in the end, they were not conclusive for the revised picture drawn in the manuscript. Instead, we performed additional analyses, e.g., scanning electron microscopy and included Fourier Transformed Infrared Spectroscopy data of siderite abundances that are now discussed in concert with the rock-magnetic data.

In our opinion, all concerns of the reviewers are sufficiently discussed in the present form of the manuscript. Nevertheless, we would welcome further comments on the manuscript, if the reviewers were willing to check the manuscript again.

Please find enclosed a track-changes version of the revised paper, and the author response to reviewers, as already submitted earlier.

On behalf of the authors

Janna Just

~~Climatic~~Environmental control on the occurrence of high-coercivity magnetic minerals and ~~preservation~~formation of ~~greigite~~iron sulfides in a 640 ka sediment sequence from Lake Ohrid (Balkans)

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Abstract

The bulk magnetic mineral record from Lake Ohrid, spanning the past ~~ca. 640~~637 ka, ~~shows~~reflects large scale shifts in hydrological conditions, and, superimposed, a strong ~~relationship to~~signal of environmental conditions on glacial-interglacial and millennial time scales. ~~During extremely cold glacials, a lower accumulation of organic matter and likely enhanced mixing~~A shift in the formation of ~~the water-column coincides~~early diagenetic ferrimagnetic iron sulfides to siderites is observed around 320 ka. This change is probably associated with variable availability of sulfide in the ~~presence of greigite, whereas greigite is absent in sediments deposited~~pore water. We propose that sulfate concentrations were significantly higher before ~320 ka ago, either due to a higher sulfate flux or to lower dilution of lake sulfate due to a smaller water volume. Diagenetic Fe-minerals appear more abundant during ~~less severe glacials. Those "non-greigite" glacial~~glacials, which are generally characterized by higher Fe/Ca ratios in the sediments.

While in the lower part of the core the ferrimagnetic sulfide signal overprints the primary detrital magnetic signal, the upper part of the core is dominated by variable proportions of high- to low-coercivity iron oxides. Glacial sediments are characterized by high concentration of high-coercivity magnetic minerals~~,~~ (hematite, goethite), which ~~relates~~relate to enhanced erosion of soils that had formed during ~~the ~~preceding interglacials.~~ In contrast, magnetite dominated magnetic mineral assemblages characterize interglacial deposits and most likely originate from detrital particles of physically weathered rocks.~~ Superimposed on the glacial-interglacial behavior are millennial scale oscillations in the magnetic mineral composition that parallel variations in summer insolation. Likewise to the ~~process~~processes on glacial-interglacial time-scales, low summer insolation and a retreat in vegetation resulted in enhanced erosion of soil material. Our study highlights that rock-magnetic studies, in concert with geochemical and sedimentological investigations, provide a multi-level contribution to environmental reconstructions, since the magnetic properties can mirror both~~,~~ environmental conditions on land and intra-~~lacustrine~~lake processes.

1 Introduction

Rock-magnetic properties of sediments can be used to reveal changing input of the lithogenic fraction and can therefore serve as records of past environmental change. Variations in the concentration of magnetic minerals provide information on changing export of terrigenous sediments from land (DeMenocal et al., 1991; Just et al., 2012; Maher, 2011; Reynolds and King, 1995). Furthermore, variations in the composition of the magnetic mineral assemblages can be used for detecting changes in terrestrial climatic conditions, e.g., weathering and soil formation (Hu et al., 2015; Kämpf and Schwertmann, 1983; Larrasoaña et al., 2015; Lyons et al., 2010; Maher and Thompson, 1992). ~~In~~However, in addition to the detrital magnetic inventory, magnetic minerals ~~can~~ form in the course of syn- and post-sedimentary processes. Magnetotactic bacteria living in the oxic-anoxic transition zone in the topmost sediments utilize magnetic minerals, and can either produce magnetite or greigite ~~intra- and extracellularly~~intracellularly (Egli, 2004b; Roberts et al., 2012; Snowball et al., 2002; Vali et al., 1989). Furthermore, iron-reducing bacteria may induce the authigenic precipitation of magnetite (e.g., Bell et al., 1987; Frankel and Bazylinski, 2003). On the other hand, the primary magnetic mineral assemblage of detrital origin is often overprinted by post-depositional alteration (Hounslow and Maher, 1999; Nowaczyk et al., 2013; Roberts et al., 1996). The latter results from changing redox conditions ~~in~~at the lake/sea floor and in subsurface sediments leading to dissolution of iron oxides and formation of ferromagnetic iron sulfides, such as greigite and pyrrothite (Demory et al., 2005; Froelich et al., 1979; Karlin and Levi, 1983; Rowan et al., 2009; Sagnotti, 2007; Vasiliev et al., 2007) or paramagnetic minerals, such as pyrite, siderite, and vivianite (Dong et al., 2000; Karlin and Levi, 1983).

~~Besides~~In addition to the vast number of studies on magnetic minerals in marine sediments,~~ also~~ lake sediments can provide valuable information on terrestrial and lacustrine environmental conditions (e.g., Frank et al., 2002; Nowaczyk et al., 2002; Peck et al., 2004; Peck et al., 1994; Roberts et al., 1996; Snowball, 1993; Snowball et al., 1999; Wang et al., 2008). Depending on the trophic state of the lake, water depth, and stratification, oxygen supply is often limited and may lead to excessive dissolution of iron oxides (e.g., Demory et al., 2005; Frank et al., 2013; Nowaczyk et al., 2013; Snowball et al., 1999). In the course of early diagenesis ~~H_2S species can react with accessible iron and form iron sulfides. Among them, pyrrothite and greigite are of huge importance for rock and paleo-magnetic studies~~ (Roberts et al., 2011a; Sagnotti, 2007)~~. Because they~~sulfate is reduced during the process of organic matter degradation in the sulfidic zone (Froelich et al., 1979). H_2S species can react with accessible iron and form iron sulfides. Among them, pyrrhotite and greigite are particularly important for rock and paleo-magnetic studies (Roberts et al., 2011a; Sagnotti, 2007). As theses secondary magnetic iron minerals acquire a remanent magnetization these secondary magnetic iron sulfides can bias the primary magnetic signals (Ron et al., 2007), in general carried by detrital (titano-) magnetite. Although ~~pyrrothite~~pyrrhotite and greigite may form as early diagenetic metastable phases during the chemical reaction pathway to pyrite, studies ~~in the last decades~~ have shown that they may be preserved if the concentration of organic matter, and consequently organic-bound sulfur, is low and pyritization is ~~buffered~~hampered by Fe-excess ~~availability~~ (Blanchet et al., 2009; Kao et al., 2004; Roberts et al., 1996; Skinner et al., 1964). Cyclic preservation of greigite in a Pliocene lacustrine sequence from Lake Qinghai (China) was recently linked to periods of high lake levels and humid climate that resulted in oxygen depletion of the bottom water (Fu et al., 2015).

Compared to the ocean, lakes generally contain lower sulfate concentrations, and therefore sulfate may be exhausted at shallow depths in the sediment or even in the water column. Below the sulfidic zone, methanogenesis is the most important process for the degradation of reactive organic matter (Capone and Kiene, 1988; Roberts, 2015). Here, Fe-species may react to form iron-phosphate (vivianite) or iron-carbonate (siderite) (Berner, 1981; Roberts, 2015). In addition~~, greigite~~ to the "early" diagenetic processes, concurring with organic matter degradation, authigenic Fe-minerals can ~~commonly~~ form at a late diagenetic ~~stage,~~phase. Such precipitation and dissolution processes occur mainly as a result of a variety of different mechanisms associated ~~to~~with the migration of mineralized fluids and ~~to~~with changes in the pore water chemistry, which disrupt the steady-state diagenetic progression ~~(Roberts and Weaver, 2005).~~(Roberts and Weaver, 2005; Sagnotti et al., 2005).

Because of the imprint of these interacting processes, rock-magnetic properties of lake sediments can provide a suite of environmental information~~, ranging~~. These range from ~~changes~~variations in the external supply of magnetic detrital mineral phases~~ over~~, changes in lake water oxygenation and sulfate supply and in conditions favorable for magnetotactic bacteria~~ which, in turn, depend on the redox conditions and organic matter availability.~~

. The sediments from Lake Ohrid on the Balkan Peninsula (Fig. 1) provide an excellent opportunity to study these processes over several glacial-interglacial cycles. Lake Ohrid is the oldest lake in Europe, dating back to > 1.2 Ma (Wagner et al., 2014). ~~Its sediments consist of lacustrine carbonates and biogenic silica, and lithogenic compounds (Francke et al., this issue). Lake Ohrid is an oligotrophic lake, which mixes completely every few years~~Its sediments consist of lacustrine carbonates (mostly calcite), biogenic silica, and lithogenic compounds (Francke et al., 2015). Lake Ohrid is an oligotrophic lake, a complete overturn and deep mixing occurs only every few years, while the upper 200 m of the water column is mixed every year during winter (e.g., Matzinger et al., 2007). Temperature variations probably had a strong influence on ~~the~~shallow and deep mixing of Lake Ohrid during past glacials and interglacials (Vogel et al., 2010a; Wagner et al., 2009), however, to date there is no quantitative estimate of this effect.

Terrestrial element concentrations and gamma ray intensities of Lake Ohrid sediments mirror phases of enhanced erosion in the catchment on glacial-interglacial timescales (Baumgarten et al., 2015; Francke et al., 2015)~~. Vogel et al. ~~(2010b)~~ report on changes in the spatial distribution of element abundances in surface sediments of Lake Ohrid that were linked to the different lithologies exposed in the lake's catchment. Moreover, geochemical variations in a core from north eastern Lake Ohrid (Fig. 1) are indicative of changes in sediment dynamics over the last ~140 ka, bringing Cr-rich sediments from the western flanks of the catchment to the eastern part of Lake Ohrid. Such changes in sediment composition are thought to result from either enhanced erosion of soils or stronger winds inducing changes in surface water circulation ~~(Vogel et al., 2010a)~~ or an intra-lacustrine contourite drift (Wagner et al., 2012).~~. Geochemical variations in a core from north eastern Lake Ohrid (Fig. 1) are indicative for changes in sediment dynamics over the last ~140 ka. Here, the increasing deposition of Cr-rich minerals, most likely originating from the western flanks of Lake Ohrid, are thought to result from either enhanced erosion of soils or stronger wind activity, inducing changes in surface water circulation (Vogel et al., 2010a).

~~Our study on the magnetic record from Lake Ohrid focuses on two major objectives. The first objective is to understand whether the variability in the magnetic mineral inventories can reveal changing environmental conditions in the catchment, beyond the observed general pattern of higher (lower) terrigenous input during glacials (interglacials). The second objective is to investigate proxies for the occurrence of magnetic iron sulfides for their capability to reflect hydrological and environmental conditions in the lake, because their existence as early diagenetic phases is strongly linked to the accumulation and decomposition of organic material. To address these objectives, we~~

~~jointly investigated magnetic and organic proxies as well as XRF-Fe (X-ray fluorescence) intensities~~ (Francke et al., 2015)~~ and performed a cluster analysis in order to disentangle relationships and influencing processes in the proxy variations.~~

This first study on the magnetic properties of the Lake Ohrid composite profile focusses on observations of changing magnetic mineralogy and possible implications for lacustrine and terrestrial environmental conditions. We aim to identify primary detrital magnetic minerals, and evaluate if these reveal changing environmental conditions in the catchment, beyond the observed general pattern of higher (lower) terrigenous input during glacials (interglacials). Secondly, we discuss the occurrence of (early) diagenetic minerals to develop a working-hypothesis concerning changes in redox conditions and shifts in the chemical and hydrological environment in the lake. To address these objectives, we jointly investigated mineral magnetic properties and organic proxies, X-ray fluorescence (XRF) data (Francke et al., 2015) and Fourier Transformed Infrared Spectroscopy (FTIRS, Lacey et al., 2015).

2 Study area and materials

Lake Ohrid (45°54 N, 38°20 E, Fig. 1~~),~~) is located at the boundary between Albania and the Former Yugoslav Republic of Macedonia at an altitude of 690 meters above sea level~~,~~. It is ~30 km long and ~15 km wide, and has a maximum water depth of ~~289~~293 m. It is flanked by high mountain ranges in the West (~~ultramafic extrusive rocks~~Jurassic ophiolites and Triassic carbonates) and East (Triassic carbonates), and an alluvial plain in the North (Fig. 1, Vogel et al., 2010b)~~. Vegetation at present~~(Fig. 1, Hoffmann et al., 2010 and references therein; Vogel et al., 2010b). Modern vegetation is dominated by deciduous forest~~.~~ (Lézine et al., 2010).

At present, there are two major rivers draining into Lake Ohrid, the Sateska in the North and Cerava in the South, ~~and~~ bringing detrital sediments to the lake. ~~Loss of freshwater in~~Fresh-water is supplied to the lake ~~through the River Crn Drim (accounting for 60%) and evaporation (~40%) is balanced~~ by ~~river inflow~~rivers (25%), direct precipitation (25%) and karst aquifers (50%). The karst aquifers are fed by mountain range precipitation and from the neighboring higher altitude (849 -m above sea level) Lake Prespa. The gain in fresh water is balanced by the drainage through the River Crn Drim (accounting for 60% of water loss) and evaporation (~40%) of lake water (Matzinger et al., 2006a; Matzinger et al., 2006b; Wagner et al., 2014).

Maximum precipitation occurs during winter, and air temperatures at present range between -5~~.1~~° and 31°C (Popovska and Bonacci, 2007). Ohrid is an oligotrophic lake with maximum productivity during summer (Matzinger et al., 2007; Wagner et al., 2010)~~ however~~. However, at present, it shows indications for the onset of eutrophication (e.g., Matzinger et al., 2007).

Six holes were drilled at the “DEEP” site (ICDP Site 5045-1) within the SCOPSCO project (Scientific Collaboration on Past Speciation Conditions in Lake Ohrid) in summer 2013 ~~with~~down to a maximum sediment penetration ~~of~~was 569 m~~.~~ (Fig. 1b). The recovered sedimentary sequence ~~covers probably~~is thought to cover more than 1.2 Ma (Wagner et al., 2014)~~. For this study we analyzed the upper 247 m of the composite profile. The age model was developed by Francke et al.~~ (2015)~~ and is based on tephrostratigraphy ~~(Leicher et al., 2015)~~ and correlating proxies to climate records. The age model reveals that the analyzed interval spans the past 640 ka. We sampled the core at 50 cm (0-100 m) and 48 cm (100 - 247m) intervals – in total 500 samples - using 6.2 cm^3 oriented plastic boxes. Furthermore, we included total organic carbon and total sulfur data, and XRF-Fe intensities provided by Francke et al. ~~(2015)~~ in our statistical analyses.~~

~~3 Methods~~

~~3.1 Rock -magnetic measurements~~

~~Magnetic susceptibility κ~~. A composite profile was constructed and an age model was developed by Francke et al. (2015) which is based on 11 tephrostratigraphic tie points (Leicher et al., 2015) and correlating geochemical proxies to orbital parameters (using an age uncertainty of ± 2000 years). Here, we analyzed the upper 247 m of the composite profile. The age model reveals that the analyzed interval spans the past 637 ka.

3 Methods

3.1 Rock -magnetic measurements

We sampled the composite profile at 50 cm (0-100 m) and 48 cm (100 - 247m) intervals – in total 500 samples - using 6.2 cm^3 oriented plastic boxes. Magnetic susceptibility χ was measured using an AGICO MFK-1 susceptometer. Natural and artificial remanence parameters were measured using a 2G Enterprises 755 superconducting long-core rock magnetometer with an in-line tri-axial alternating field (AF) demagnetizer. The Natural Remanent Magnetization (NRM) was demagnetized in 10 incremental steps of up to 100 mT AF peak amplitude. Anhysteretic ~~Remanenent~~Remanent Magnetization (ARM), a proxy for fine-grained, mostly single domain (SD) and pseudosingle domain (PSD) magnetite (King et al., 1982), was imparted with a single-axis 2G

600 AF demagnetizer by using 100mT AF and 50µT DC field. Subsequently ARM was AF demagnetized at fields of 10, 20, 30, 40, 50, 65 mT. The median destructive field ($\mathrm{MDF}_{\mathrm{ARM}}$), defined as the field required to decrease ARM by 50% was calculated. This parameter is indicative of the coercivity within the fine ferrimagnetic mineral fraction.

Isothermal Remanent Magnetization (IRM), which depends on the magnetic mineral mixture in the samples, was induced using a 2G 660 pulse magnetizer applying a 1500mT DC peak field and a 200mT reversed field. The ratio of ~~ARM~~χ_{ARM} to Saturation IRM (~~ARM~~χ_{ARM}/SIRM) serves as a proxy for the magnetic grain size. Furthermore, hard IRM (HIRM), reflecting the contribution of high-coercivity magnetic minerals to SIRM, was calculated using the equation

$$HIRM = 0.5(SIRM + IRM_{(-200mT)}) \qquad (1)$$

Additionally, the S-Ratio, calculated as

$$S = 0.5(1 - (IRM_{-200mT} / SIRM) \qquad (2)$$

serves as a proxy for the proportion of high- (e.g., hematite + goethite, 0<S<<1) to low-coercivity (magnetite, greigite) magnetic minerals (0<<S<=1).

Moreover, we calculated SIRM/~~κ~~χ which is often ~~used as a proxy for~~observed to be elevated in the presence of greigite (e.g., Maher and Thompson, 1999; Nowaczyk et al., 2012; Snowball and Thompson, 1990). Another characteristic behavior of greigite is that it acquires a so-called Gyro-Remanent Magnetization (GRM). To further quantify the possible imprint of greigite, we calculated the ratio between the differences of Final Remanent Magnetization (FRM) at 100 mT AF peak amplitude and minimum magnetization (MRM) during NRM demagnetization, and the difference of NRM and MRM according to (Fu et al., 2008),

$$\Delta\mathrm{GRM}/\Delta\mathrm{NRM} = (FRM - MRM)/(NRM - MRM) \qquad (3)$$

~~On selected samples high temperature susceptibility measurements (~~~~κ_T~~~~) were performed using the temperature unit of the MFK-1 device. For this purpose, dried sediments were inserted into glass vials and heated in argon atmosphere from room temperature to 700°C and subsequently cooled back to room temperature.~~

To account for ~~the dilution of~~down-core increasing sediment compaction, magnetic ~~minerals by carbonate we calculated SIRM and HIRM on a carbonate-free basis~~

~~$\mathrm{SIRM}_{\mathrm{cfb}} = 100(SIRM/(100 - c_{carb}))$ (4)~~

~~$\mathrm{HIRM}_{\mathrm{cfb}} = 100(HIRM/(100 - c_{carb}))$ (5)~~

~~The ~~concentration ~~of carbonate (c_{carb}) was calculated by multiplying TIC contents ~~(Francke et al., 2015)~~ with the molar ~~parameters were mass~~ of $CaCO_3$~~-normalized using the dry bulk density. The latter data were available at 4 cm intervals and interpolated to the depths of magnetic samples.

3.2 Cluster Analysis

We performed *fuzzy-c-means* cluster analysis for a suite of data that ~~can basically be~~are indicative for the magnetic mineralogy and ~~impact the formation and preservation of greigite. Thus, SIRM/κ, ΔGRM/ΔNRM, ARM/SIRM, TOC, TS and XRF Fe-intensities served as input variables.~~magnetic granulometry. To achieve ~~more ~~symmetric distributions of the suite of data, we performed data *ln* (natural ~~logaritm~~logarithm) transformations, except for ΔGRM/ΔNRM~~.~~ and the S-Ratio. The latter ~~values~~parameters show a J-shaped distribution that cannot be transformed into a normal distribution. All datasets were standardized before clustering.

~~4~~3.3 ~~Rock-~~Scanning electron microscopy of magnetic ~~results~~extracts

~~A major change in the magnetic properties can be observed at the MIS 9/MIS 8 boundary and we therefore divided the record into two magnetic units (Fig. 2). Proxies for the whole record are shown in Fig. 2, whereas additional rock-magnetic properties of the upper unit are displayed in Fig. 3. SIRM and HIRM in Fig. 3 were corrected for the dilution of carbonate and are shown on a carbonate-free basis (cfb).~~

Six samples that are characterized by divergent magnetic properties were selected for scanning electron microscopy (SEM) analyses. Magnetic extracts were prepared following the protocol of Nowaczyk (2011). 2 cm^3 of sediment were dispersed in 60 ml alcohol and Na-Solution was added. The solutions was put in an ultrasonic-bath for 10 minutes. A rare-earth magnet inside a plastic hose was submerged into the solution. Minerals attracted to the hose were washed into a fresh vial. The procedure was repeated twice to obtain a clean extract. Particles in the alcohol solution were then concentrated and a drop of the solute was placed on SEM stub and sputtered with carbon.

Magnetic extracts were analyzed using a Carl Zeiss SMT Ultra 55 Plus SEM. Images were obtained using the secondary and back scatter electron beams of single particles. To obtain the chemical composition of the analyzed particles, energy dispersive spectroscopy was performed at energy levels of 20 keV.

3.4 Geochemical and mineralogical data

Total organic carbon (TOC), total inorganic carbon (TIC) and X-ray Fluorescence (XRF) data, measured by Francke et al. (2015), are used for discussion of rock-magnetic data. XRF scanning was carried out at 2.5 mm resolution and with an integration time of 10 s using an ITRAX core scanner equipped with a chromium X-Ray source. Total carbon (TC) and total TIC were analyzed at 16 cm resolution. For TIC, homogenized and dispersed sediments were treated with phosphoric acid. TC and TIC was measured in the form of released CO_2 after combustion at 900 °C and 160°C, respectively, using a DIMATOC 100. Total organic carbon (TOC) content was calculated from the mass difference between TC and TIC In addition, we show relative changes in siderite ($FeCO_3$) concentration determined from infrared (IR) spectra. IR spectra were measured on a Bruker Vertex 70 Fourier Transform infrared (FTIR) spectrometer at the Institute of Geological Sciences at the University of Bern. Details on measurement set up and data evaluation procedures are outlined in Lacey et al. (2015).

4 Results

4.1 Rock magnetism

In the magnetic properties, a major change is visible around ca. 320 ka corresponding to the transition between Marine Isotope Stage (MIS) 9/MIS 8. Below this transition S-Ratio is rather constant, but SIRM shows large amplitudinal change, while above, SIRM is relatively constant, but compositional magnetic proxies, e.g. the S-Ratio, show interglacial-glacial variability. We therefore divided the record into two magnetic units (Fig. 2).

~~4.1~~ MIS 16-MIS 9 (unit 2)

~~Generally~~Except for a stable S-Ratio (Fig. 2 e), this unit is characterized by high amplitude variations on glacial-interglacial timescales. Susceptibility (Fig. ~~2d) and SIRM (Fig. 2e) are elevated and ARM/SIRM (Fig. 2f) is low during glacials compared to interglacials. The ΔGRM/ΔNRM (Fig. 2g) and SIRM/κ parameters (Fig. 2h) show large variations, indicating the presence of large amounts of greigite. Maxima in the latter parameters appear to occur at eccentricity minima (Fig. 2a).~~2b) and SIRM (Fig. 2c) and HIRM (Fig. 2d) are elevated during glacials, while χ_{ARM}/SIRM (Fig. 2g) and χ_{ARM}/χ (Fig. 2h) decrease and the MDF_{ARM} (Fig. 2f) rises to fields of up to 50 mT. Increasing ΔGRM/ΔNRM (Fig. 2j) is often associated with interglacial-glacial transitions, and early glacials. Moreover, short-lasting spikes of GRM acquisition during interglacials are accompanied by brief increases in Fe/Ca ratios (Fig. 2 k, e.g., during MIS 15, 13, 11). In contrast, SIRM/χ (Fig. 2i) shows maximum values at the end of the glacials (MIS10, MIS12), when GRM acquisition is mostly low.

~~4.2~~ MIS 8-MIS 1 (unit 1)

~~Glacial-interglacial variations in this unit are expressed differently by the magnetic proxies. ARM/SIRM is generally low during MIS 8, 6, 4-2, and higher during interglacials. MIS 1 is characterized by the highest ARM/SIRM values (Fig. 2f, 3f). The S-Ratio shows low values during MIS 6, MIS 4 and MIS 3, up to ~40 ka, where it starts to increase sharply (Fig. 3c). Also HIRM and SIRM rise strongly at 40 ka (note the log-scales in Fig. 2e, Fig 3d, e). Superimposed on long-term patterns are higher frequency variations that are most expressed in the S-Ratio and ARM/SIRM (Fig. 3c, f). In contrast, low SIRM/κ and ΔGRM/ΔNRM of mostly zero (Fig. 2g, h) indicate that greigite is mostly absent.~~

Compared to unit 2, glacial-interglacial variations are expressed through different proxies. SIRM/χ (Fig. 2i) is low and ΔGRM/ΔNRM (Fig. 2j) is mostly zero. SIRM (Fig. 2c) and the MDF$_{ARM}$ (Fig. 2f) are relatively stable, while susceptibility (Fig. 2b) and HIRM (Fig. 2d) show glacial-interglacial cyclicity. χ_{ARM}/SIRM (Fig. 2g), χ_{ARM} /χ (Fig. 2h) and the S-Ratio (Fig. 2e) is lower during glacials, in concert with higher TOC (Fig 2l) and lower Fe/Ca ratios (Fig. 2k). An exception to this glacial-interglacial behavior is observed in the uppermost part of unit 1, where TOC increases and Fe/Ca decreases. In contrast to the relationship observed for the rest of the unit, the intensity of the magnetic concentration parameters (χ, SIRM, Fig. 2b, c) increase, and the S-Ratio rises to high values. Also the MDF$_{ARM}$ and χ_{ARM}/SIRM, and χ_{ARM} /χ and SIRM/χ rise to maximum values.

4.2 SEM observations

We analyzed samples that are characterized by diverging magnetic properties (c.f., Table 1). Detrital titanomagnetites and Cr-Fe Oxides are present in almost all analyzed samples (Fig. 3a, b, d). Magnetic extracts from the upper unit contain relatively high proportions of siderite (Fig. 3g), whereas Fe-sulfides are abundant in samples from the lower unit (Fig. 3c-f, h).

All analyzed samples in unit 2 are characterized by a high MDF$_{ARM}$ (>45 mT). Of those, two samples did acquire a significant GRM (>68%), but had lower SIRM/χ compared to two samples which have the most extreme SIRM/χ values, but GRM acquisition is insignificant (Table 1). The high GRM samples contain mixtures of Ti-magnetites and fine grained and microcrystalline Fe-sulfides, which most likely correspond to greigite (Fig. 3 c, d). Also the low GRM-samples, contained fine-grained Fe-sulfides and idiomorphic greigite crystals, but additionally large Fe-sulfide nodules (Fig 3e, f, h) that apparently have a higher Fe:S ratio, compared to the finer grained greigite (data not shown). Although the number of investigated SEM samples is relatively low the results suggest, that a high MDF_{ARM} appears closely related to or at least accompanied by the general presence of Fe-sulfides, while maximum SIRM/χ is associated with the coarse-grained sulfide nodules. GRM is rather strong when microcrystalline or individual greigite crystals occur.

5 Discussion

~~5.1 Identification of changing magnetic mineral assemblages~~

5.1 Magnetic proxy evaluation

Many samples from unit 2 have high values in MDF_{ARM}, SIRM/χ and ΔGRM/ΔNRM ~~and SIRM/κ~~ (Fig. 2 ~~g, h), indicating~~f, i, j), which are often associated with the ~~occurrence~~presence of greigite (e.g., Fu et al., 2008; Peters and Dekkers, 2003; Rowan et al., 2009). It is important to note that ~~the greigite proxies provide~~ these parameters can sometimes provide ambiguous results; high SIRM/~~κ~~χ is not always accompanied by high ΔGRM/ΔNRM~~. On the other hand,~~, however, MDFs are high if ~~samples acquire a GRM, SIRM/κ always shows~~any of the former proxies are elevated ~~values~~. Missing GRM acquisition of greigite bearing samples ~~have been~~hasbeen reported from other studies (Roberts et al., 1998; Sagnotti et al., 2005)~~. Therefore it is useful to combine different proxies for greigite~~ (Roberts et al., 2011a)~~. SIRM/κ appears to be a more reliable proxy for greigite in the Lake Ohrid sediments.~~

~~Greigite bearing samples have lower ARM/SIRM (Fig. 2f) values compared to the rest of unit 2. Low ARM/SIRM values suggest an enhanced dissolution of fine-grained detrital magnetite. Accordingly,~~ ~~κ_T~~ ~~of those samples (Fig. 4d, e, sample positions are indicated in Fig. 2) show a strong increase of susceptibility at 400°C and have higher susceptibilities in the cooling curve, indicating that reduced iron is oxidized to magnetite~~ (Passier et al., 2001; Roberts et al., 2011a and references therein; Sagnotti et al., 2010)~~. The samples containing greigite are associated to glacials concurring with phases of low eccentricity (Fig. 2a). The occurrence of greigite during specific climatic conditions suggests that it rather formed as an early diagenetic phase than being a late diagenetic product and it can be therefore considered as an almost syn-sedimentary mineral whose growth was climatically controlled, as it will be further discussed in section 5.3.~~

~~In unit 1 SIRM/κ is relatively constant and only few samples acquire GRM, implying that greigite is virtually not present. Susceptibility is higher during glacials, while SIRM peaks are only weakly expressed (Fig. 2). At the same time ARM/SIRM exhibits minima, indicating coarsening of the magnetic fraction. Moreover, samples from glacial times have a low S-Ratio (Fig. 3c, e), signifying an enhanced contribution of high-coercivity mineral relative to low-coercivity minerals.~~

~~For a sample corresponding to 147 ka (Fig. 4c), magnetic susceptibility rises above 400 °C and heating and cooling curves are not reversible. This indicates that iron sulfides are transformed into magnetite and suggests that magnetite was reduced into pyrite during early diagenesis. To address this issue we calculated magnetic concentration parameters on a carbonate-free basis (Figs. 3d, e; carbonate concentrations vary between 0.5-45%, see Francke et al. this issue). SIRM$_{cfb}$ indicates that the magnetite concentrations within the bulk terrigenous sediment fraction are relatively constant throughout unit 1, while the variations in HIRM$_{cfb}$, i.e., concentration of hematite and goethite, is higher during glacials compared to interglacials. Moreover, if reductive diagenesis occurred and resulted in the dissolution of magnetite, it would be linked to high TOC concentrations and restricted mixing of lake water, i.e., during interglacials~~ (cf., Francke et al., 2015)~~. The trend in the magnetic proxies, however, shows the opposite of what would be expected. The S-Ratio, indicates even higher magnetite vs. hematite + goethite proportions during interglacials. We therefore assume that if reductive diagenesis had occurred it affected the whole unit equally. Accordingly, trends in ARM/SIRM ratio are not due to dissolution of magnetite, but rather signify changing composition in terrigenous sediment supply. These temporal variations are further discussed in section 5.4.~~

~~In the uppermost section, covering the Holocene, ARM/SIRM and SIRM and SIRM/κ reach the highest values at the same time when TOC is very high (Figs. 2, 3). This argues for a change in the composition of the magnetic mineral assemblage. An~~, and could be related to grain-size effects, because only fine grained (SD) greigite acquires GRM. As observed in the images of the magnetic extracts, coarse grained Fe-sulfides are abundant in samples with low GRM and high SIRM/χ and we therefore hypothesize that greigite either grew to too coarse grain-size for GRM acquisition or was transformed into other Fe-sulfides, e.g., pyrrhotite, which is also characterized by high SIRM/χ (Maher and Thompson, 1999). The second significant feature in the rock magnetic record are variations on interglacial-glacial time scales within the upper unit. The variations could stem from compositional changes in the magnetic mineral supply to the lake, but could also result from selective dissolution of low-coercivity magnetic minerals. To further evaluate the rock magnetic properties, we show cross plots of selected parameters (Fig. 4). As ΔGRM/ΔNRM is a robust indicator for the presence of greigite, the cross plot is color coded according to GRM acquisition.

The χ_{ARM}/SIRM ratio (Fig. 2g) is often utilized as a proxy for magnetic grain size, but can be biased if SIRM is dominated by high-coercivity magnetic minerals (HIRM). However, HIRM is more than two orders of magnitude smaller than SIRM (Fig. 2), and thus SIRM can be applied as a proxy for the concentration of the low-coercivity fractions (e.g., magnetite and greigite).

For non-GRM samples, low S-Ratios are associated with low χ_{ARM}/SIRM (Fig. 4a) implying that a shift towards high-coercivity minerals is accompanied by a coarsening of the low-coercivity fraction. In contrast, GRM samples have high S-Ratios but low χ_{ARM}/SIRM values, indicating that in combination these parameters are valuable indicators for the presence of greigite. The low χ_{ARM}/SIRM (0.06-0.2 10^{-3} mA^{-1}) values of the latter samples lie close to the range of authigenic inorganically precipitated greigite which is characterized by 0.058-0.084 10^{-3} mA^{-1} (Snowball, 1997a), in contrast to high values observed for sediments containing bacterial magnetite (Snowball, 1994) and greigite (Reinholdsson et al., 2013, Fig. 3b). Only a few samples that did not acquire GRM lie in these latter areas, i.e., samples from the uppermost part of the core (cf. Fig. 2 g, h). These results suggest that except for the latter samples, a significant contribution of magnetite and greigite magnetosomes can be ruled out as a source for rock-magnetic signals. Furthermore, we propose that greigite, within the GRM acquiring samples, formed out of a chemical process. However, this process was likely induced by biological activity (iron reducing bacteria).

There appears a strong positive correlation between SIRM/χ and χ_{ARM}/χ (Fig. 4c). The latter parameter is often used as a magnetic grain size indicator for low-coercivity minerals, especially magnetite, while SIRM/χ can be influenced by different mechanisms, ranging from changes in magnetic grain size (Peters and Dekkers, 2003) and magnetic mineralogy, including the presence of greigite (Frank et al., 2007; Fu et al., 2008; Nowaczyk et al., 2012; Reinholdsson et al., 2013; Snowball, 1997b). Although paramagnetic minerals may contribute to the susceptibility, this bias would be expressed in both ratios, and a cross plot of those two parameters is valid to compare ferrimagnetic mineralogic properties between samples. The linear behavior of the two parameters indicates that SIRM/χ is influenced by magnetic grain-size effects. However, the bigger gradient for GRM samples implies that the presence of greigite is shifting SIRM to higher levels.

The MDF_{ARM} is indicative of the hardness of magnetic minerals within the low-coercivity magnetic fraction (i.e. SD and PSD magnetite), and is therefore also affected by a preferential dissolution of fine magnetic particles. As outlined above, the S-Ratio signifies the relative concentration of high vs. low-coercivity minerals and is influenced by relative increases of high-coercivity particles, or decreases of magnetite, the latter could also be induced by dissolution. From the MDF and S-Ratio plot, two clusters can be distinguished (Fig. 4d). Non-GRM samples have MDFs between 25 and 33 mT and a broad range of S-Ratios, whereas the MDF for GRM samples is higher than 30 mT and are mainly confined by S-Ratios higher than 0.96. The co-occurrence of high MDFs and GRM acquisition strongly suggests that increasing coercivity results from the presence of greigite. Moreover, the high S-Ratios reveal that greigite mostly contributes to the low-coercivity component of magnetization. For the non-GRM samples the pattern implies that relative increases of the high-coercivity fraction are not accompanied by changes within the low-coercivity mineral assemblage. A preferential dissolution of ferrimagnetic minerals, expressed as a drop in the S-Ratio, would be expected to be accompanied by changing coercivity also within low-coercivity assemblage (i.e., changing MDF). This is not observed for our samples. Moreover, the constant SIRM throughout unit 1, whereby HIRM shows variations (c.f. Fig. 2c, d), rather indicates the addition of high-coercivity minerals, instead of a decrease in low-coercivity minerals. Further support for this hypothesis comes from the low TOC concentrations, accompanying the low S-Ratio intervals. Enhanced magnetite dissolution is typically observed, when TOC concentrations are elevated. The trend in the magnetic proxies, however, shows the opposite of what would be expected in the case of enhanced dissolution. The S-Ratio indicates even higher contents of low vs. high-coercivity minerals during interglacials with elevated TOC content. We therefore assume that if reductive diagenesis had occurred it affected the whole unit equally, and variation in the S-Ratio is indicative for increasing high-coercivity minerals within the detrital magnetic mineral fraction.

We also conducted high-temperature susceptibility measurements, in order to discriminate the Fe-sulfides. The susceptibility of all samples increased sharply above 400 °C and decreased above 500° (data not shown). The cooling curve has higher susceptibilities. This behavior is typical if reduced iron is oxidized to magnetite upon heating. This iron, however, can be derived from different mineral phases, e.g., from clay minerals (Bell et al., 1987) or iron sulfides and siderites.

5.2 Cluster Analysis

To further evaluate temporal changes in the magnetic mineraology of Lake Ohrid sediments we performed a cluster analysis. Based on the evaluation of the magnetic parameters, we included χ_{ARM}/χ, χ_{ARM}/SIRM, S-Ratio, MDF and ΔGRM/ΔNRM which are indicative of magnetic grain-size, magnetic coercivity, and the occurrence of greigite.

Cluster center 3 is characterized by the lowest χ_{ARM}/SIRM value, high S-Ratio, a high MDF of 40 mT and a high GRM (Table 2). The association of these parameters was also suggested by the cross plots (Fig. 4), and are often observed for chemically produced greigite and thus, we infer that cluster 3 is related to greigite and other ferrimagnetic Fe-sulfides, e.g., pyrrhotite.

Cluster centers 1 and 2 have similarly low GRM and MDF, indicating the absence of greigite and undistinguishable different coercivities within the magnetically soft fraction. However, χ_{ARM} /χ, χ_{ARM} /SIRM and the S-Ratio are lower in cluster 1 compared to cluster 2. As discussed above, the differences are due to the higher contribution of high-coercivity minerals, concurrent with a coarsening of the ferrimagnetic fraction.

The variations in cluster membership coefficients (Fig. 2 a) captures the variability in magnetic proxies (Fig. 2b-j). Cluster 1 mainly relates to interglacial samples, whereas cluster 2 corresponds mainly to glacial samples in the upper part of the core (Fig 5f). Glacials samples from the lower part of the core are associated to cluster 3.

5.3 Iron-sulfides in Lake Ohrid sediments

The concentration of magnetic minerals, approximated by remanence intensities (and susceptibilities), are relatively low in Lake Ohrid sediments in the upper unit. This gives a strong indication that the magnetic fraction was subject to reductive diagenesis. In unit 2 remanence intensities are enhanced, due to the presence of ferrimagnetic Fe-sulfides (Fig. 2). Concerning the occurrence of greigite and Fe-sulfides, the cluster analysis reveals two different patterns that modulate each other (Fig. 5f). First, the absence of Fe-sulfides in unit 1, and secondly, a cyclic occurrences of Fe-sulfides on glacial-interglacial timescales in unit 2. Besides Fe-sulfides, siderite, which also forms during (early) diagenesis, is contained in the sediments. When discussing the mechanism for diagenetic Fe-mineral formation, it is worthwhile to also consider the occurrence of paramagnetic siderites.

5.3.1 Early versus late diagenetic formation

For Fe-sulfides to precipitate, accessible Fe and S have to be available. In the course of early diagenesis sulfate is reduced during organic matter degradation. Typically, Fe-sulfides such as greigite and pyrite form in the sulfidic pore water zone, associated with the upward migrating sulfate methane transition zone (SMTZ), where H_2S accumulates (Kasten et al., 1998).

In contrast, siderite mainly forms in the methanogenic zone, if pore waters have high $CaCO_3$ concentrations (e.g., Berner, 1981; Roberts, 2015). However, siderite and greigite (Fe-sulfides) can form at the same time if the rate of iron reduction is higher than the rate of sulfate reduction (e.g. Pye 1981, 1990). Sulfate concentrations are much lower in lakes (10-500µM), compared to the ocean (28 mM, Holmer & Storkholm, 2001) and sulfate is depleted within the uppermost cm of the sediments. Thus, methanogenesis plays a more important role for organic matter degradation compared to marine environments (Capone and Kiene, 1988).

During late diagenesis, Fe-sulfides may precipitate from mineralized fluids (Sagnotti et al., 2010), if pore-water chemistry changes, i.e., by up- or downward migrating dissolved H_2S species. Newly formed Fe-sulfides have been observed to overgrow earlier diagenetic Fe-minerals, such as siderite (Roberts and Weaver, 2005; Sagnotti et al., 2005).

From SEM observations, we find no indication that sulfides formed at a later stage than siderites. Sulfide nodules are much coarser than the apparently well preserved siderite crystals (Fig. 3g). The shape of Fe-sulfide nodules rather appear to fill cavities of former organic compounds (Fig. 3c).

Siderite abundances are higher in the upper part of the core (Fig. 5e), where the ferrimagnetic Fe-sulfide proxies are low. In the older glacials of unit 2, siderite concentrations decrease when GRM, MDF_{ARM} and/or SIRM/χ increases (Fig. 5 b-d). This rather suggests that during early diagenesis one over the other, Fe-sulfide or siderite formation dominated.

Finally, this assumption is supported by unpublished relative paleointensity (RPI) data that will be presented elsewhere. If the ferrimagnetic Fe-sulfides formed later during diagenesis, a disruption of the match between the RPI trend from Lake Ohrid and global RPI stacks would be expected. However, the good quality of the RPI correlation suggests that the Fe-sulfide nodules, associated with elevated SIRM/χ, grew during early diagenesis.

5.3.2 Large scale shifts in redox conditions

The most prominent feature of the magnetic record is the transition from a dominance of Fe-sulfides in unit 2 (> 320 ka) and siderite in unit 1 (<320 ka), suggesting a change in pore-water chemistry. Other proxy data sets from the Ohrid composite profile also indicate that lacustrine conditions changed at this boundary. As outlined above, siderite abundances are distinctly higher in the upper part of the core (Fig. 5e). Furthermore, interglacial TIC concentrations are generally lower in the upper unit 1 (up to 6%) compared to unit 2 (up to 10%, Fig. 5h), while interglacial TOC concentrations are relatively low in unit 2 (Fig. 2l). The higher TIC, relative to TOC concentrations were tentatively discussed to be dependent on higher ion concentrations in lake water due to increased evaporation (Lacey et al., 2015) during the deposition of the lower unit, but could also relate to enhanced organic matter degradation (Francke et al., 2015).

As outlined above, siderite typically forms during methanogenesis (Berner, 1981), which is the only process for organic matter degradation after sulfate is consumed. The shift of siderite to sulfide formation implies a shift in the redox conditions between unit 1 and 2. We propose that during the deposition of Unit 1, SO_4 was rapidly consumed in the shallow sediments, or even within the bottom water. Magnetic iron oxides were readily reduced, but due to the lack of sufficient H_2S, siderite precipitated out of $CaCO_3$ supersaturated waters (Coleman et al., 1985), as was also observed in the sister lake Prespa (Leng et al., 2013). In contrast, the sulfidic zone apparently penetrated deeper into the sediments during the deposition of unit 2. Pyrite formation (Canfield and Berner, 1987) and, thus, precursors of pyrite, as greigite, requires sulfate concentrations > 1mM. These prerequisites were apparently met, however sulfate concentrations were probably still low, and not sufficient to transform metastable Fe-sulfides into pyrite.

The depth of the sulfidic zone is influenced by a number of different process which can modulate each other. First of all, the input of sulfate or sulfide could differ. Generally, sulfate is mainly derived from sulfur-bearing weathered rocks in the catchment (Holmer and Storkholm, 2001). Enhanced erosion or a stronger chemical weathering could thus increase the sulfate supply to the lake. Sulfides may also derive from upward migrating fluids in active tectonic settings. Secondly, even if sulfate fluxes are stable, sulfate concentrations increase when evaporation is enhanced. Another process of sulfate consumption in the sediments is linked to O_2 concentrations in the bottom water and to the accumulation and degradation of organic matter. Enhanced degradation of organic matter within the oxic zone, e.g., due to better ventilation of bottom water would modify the oxidation state of bottom water, and shift the sulfidic zone to a deeper depth.

At this point we cannot infer which process, or combination of processes, are responsible for the observed pattern. Given that Lake Ohrid is a subsiding basin, the water volume of the lake may have been smaller during deposition of unit 2. This could have led to a more regular deep mixing of Lake Ohrid and a slower sulfate consumption, both resulting in the sulfidic zone migrating deeper in to the underlying sediments. This scenario is in-line with higher TIC concentrations in the lower part of the core most likely due to higher ion concentrations and to comparably low TOC concentrations, linked to organic matter degradation. In addition, the glacials in the lower part of the core correspond to phases of low eccentricity, i.e., weaker seasonality (Fig. 5a). The annual temperature distribution may have had an additional effect on deep convection and lacustrine productivity of Lake Ohrid, which might have contributed to a change in mixing processes and the production and degradation of organic material.

5.3.3 Glacial-interglacial variability of Fe-Sulfide formation

Ferrimagnetic Fe-sulfides (paramagnetic siderites) are contained within glacial sediments in the lower (upper) unit. Moreover, diagenetic Fe-minerals, represented by the Fe-sulfide cluster (Fig. 5f) and siderite abundances (Fig. 5e) occur at peak Fe/Ca ratios and minimum TIC concentrations (Fig. 5) within interglacials.

In the older glacials (unit 2), siderite concentrations are high, when GRM acquisition and SIRM/χ is relatively low, and vice versa. SIRM/χ rises in turn to maximum values when GRM and siderite content are reduced. Again, this highlights the importance of sulfate concentrations and Fe-availability for the early diagenetic formation of Fe-minerals.

A further characterization of Fe-mineral genesis in the course of redox conditions, however, needs to be further investigated by performing geochemical and mineralogical classification. Sulfur isotopes could further improve the understanding of the sulfur source, and a discrimination of the chemical composition of the Fe-sulfide nodules will help to understand the processes responsible for their formation and preservation.

5.4 High-coercivity minerals in Lake Ohrid sediments

Since the magnetic signal in unit 2 is dominated by the presence of diagenetic ferrimagnetic Fe-sulfides, we only investigated unit 1 (MIS 1 – MIS 8) for changing lithogenic sediment supply (Fig. 5). Terrigenous input vs. limnic productivity is high during glacials, indicated by higher Fe/Ca ratio, and higher susceptibility (integrating ferri- and paramagnetic minerals) and low TIC concentrations. At the same time, the concentration of high-coercivity magnetic minerals increases within the magnetic fraction. Since this pattern is not due to preferential dissolution of magnetite (cf., section 5.1), we propose that the composition of terrigenous input changed over glacial-interglacial timescales.

The catchment of Lake Ohrid comprises different lithologies (c.f. section 1) that are mirrored by the distribution of element concentrations in surface sediments (Vogel et al., 2010b). Vogel et al. (2010a) assumed that changes in Cr/Ti ratios on glacial-interglacial timescales result from either increased aeolian activity or a stronger erosion of soil material from sparsely vegetated soils. The detrital Fe-oxides in the magnetic extracts often contain Cr, which is a typical element for mantle rocks. The ophiolite belt, located west of the basin, is therefore a possible source for the magnetic minerals in Lake Ohrid. The magnetic mineralogy of the ophiolites (oceanic core complexes) in the Albanides consists mainly of magnetite (Maffione et al., 2014).

We observe a large similarity between the benthic δ^{18}O stack (Lisiecki and Raymo, 2005) and the S-Ratio from Lake Ohrid (Fig. 3b, c). This suggests compositional changes in the magnetic mineralogy reflect changing environmental conditions. During warm (and humid) interglacials, chemical weathering was enhanced and accumulation of soils and pedogenetic formation of (magnetic) minerals was promoted. However, as already proposed by Vogel et al. (2010a), vegetation cover prevented the erosion of the soil materials, and terrigenous magnetic minerals were diluted by biogenic sedimentary components. In the following glacials, vegetation cover decreased, as is indicated by arboreal pollen abundances from Lake Ohrid (Sadori et al., 2015) and soils were exposed and more susceptible to erosion. As a result, increased input of high-coercivity minerals, e.g., hematite and/or goethite can be observed, the latter being the most widespread pedogenetic magnetic minerals (Cornell and Schwertmann, 2006; Vodyanitskii, 2010).

~~input in~~During interglacials, the S-Ratio (Fig. 6d) and χ_{ARM}/SIRM (cf., Fig. 2 g) show higher frequency variations, where low values approximate to local summer insolation minima (Fig. 6 b). Offsets, e.g., during MIS 5, might be related to age uncertainties (±2000 years for the Lake Ohrid record, Francke et al. 2015). Changes in the magnetic mineraolgy in concert with insolation is also mirrored by the cluster membership coefficients (Fig. 6a). Similar to the mechanism proposed above, these low insolation phases correspond to relatively cold conditions and less dense vegetation cover, also visible in pollen abundance patterns (Sadori et al., 2015), thus increasing erosion of soil materials.

5.5 Bacterial magnetite in Lake Ohrid sediments?

In the uppermost 6 m of the core, covering the Holocene, χ_{ARM}/SIRM and SIRM and SIRM/χ reach the highest values of the sequence (Fig. 2). An increased input of lithogenic magnetic minerals relative to carbonates can be ruled out since TOC and TIC ~~is high (see also Francke et al.). κ_T of two samples from this part of the record (Figs. 4 a, b) rises at 400°C and drops after 450 °C, indicating the presence of SD magnetite (Snowball, 1994). However, although dominated by magnetite, the sample from 3.77 ka shows slightly higher values in the cooling compared to the heating branch and indicates that some iron sulfides are present too.~~concentrations are high (Fig. 2 and 4).

One source for magnetic minerals, independent of detrital material supply is the production of bacterial magnetite and greigite. Magnetotactic bacteria utilize dissolved iron that is either available in the water column or at the Fe^{2+}/Fe^{3+} redox boundary in the sediment ~~(Kopp and Kirschvink, 2008).~~(Kopp and Kirschvink, 2008). These bacteria produce magnetite (Blakemore, 1975; Frankel et al., 1979) or greigite (Heywood et al., 1990; Mann et al., 1990) crystals, so-called magnetosomes, within or outside their cells. It was shown that production of bacterial magnetite is linked to increasing organic matter supply (Egli, 2004a; Roberts et al., 2011b; Snowball et al., 2002), at least for oxic lakes (Egli, 2004b). Moreover, the production of bacterial magnetite can be fostered by the input of nutrients (Egli, 2004b). Magnetotactic bacteria producing greigite prefer reducing conditions, and greigite magnetosomes have a higher potential for preservation under sulfidic conditions (Chang et al., 2014; Vasiliev et al., 2008). Fine magnetite crystals have a potential for preservation, if certain environmental conditions, e.g., supply of oxygen and concentration of hydrogen sulfide, are met (Canfield and Berner, 1987). In Fig. 3, the Holocene samples are the only ones that coincide with the area of bacterial magnetite and greigite.~~Magnetotactic bacteria producing greigite prefer reducing conditions, and greigite magnetosomes have a higher potential for preservation under sulfidic conditions (Chang et al., 2014; Vasiliev et al., 2008).~~ The concurrence of elevated TOC together with the fine-grained magnetic phase could therefore indicate the presence of bacterial magnetite~~ or greigite~~. However, ~~based on our performed analyses, ~~we cannot infer if this occurrence is triggered by high TOC and/or nutrient ~~inputs~~input, or it~~ just~~ results from an not-yet completed dissolution of magnetosomes (Snowball, 1994).

~~5.3~~5.6 ~~Cluster Analysis~~

~~To further evaluate the occurrence of greigite in the Lake Ohrid core, we performed a cluster analysis. Greigite often forms as a precursor of pyrite (Benning et al., 2000; Berner, 1970, 1984). Its preservation is limited to environments with high concentration of reactive iron (Kao et al., 2004) and depends on the balance of sulfide and organic carbon availability ~~(Roberts et al., 2011a)~~. We therefore combined magnetic proxies for greigite (ΔGRM/ΔNRM, SIRM/κ) and magnetic grain-size (ARM/ SIRM), the latter carrying important information for dissolution of fine-grained magnetite, with TOC and TS concentration, and XRF-Fe intensities. Based on maximum mean silhouette values, computed by *k-means* clustering, we chose a three cluster solution for the *fuzzy-c-means* clustering.~~

~~The assigned cluster center for each sample is plotted in Fig. 2c. In addition, for each sample the cluster membership coefficients for each cluster are shown in Supplementary Figure 1. The cluster center properties can be found in Table 1.~~

~~The results show that for MIS 16-9 glacial samples are predominantly assigned to Cluster 3 (green), while interglacial samples fall into Cluster 1 (red). In the upper unit comprising MIS 8 to MIS1, the interglacial samples are likewise assigned to Cluster 1, whereas glacial samples belong to Cluster 2~~

~~(blue).~~

~~Cluster 1 is characterized by moderate SIRM/κ values, low ΔGRM/ΔNRM and high ARM/SIRM, high TOC and low XRF-Fe intensities (Table 1). We hereafter refer to this cluster as the ‘interglacial cluster’.~~

~~Clusters 2 and 3 (blue and green, respectively) differ substantially in the magnetic properties with high (low) SIRM/κ and ΔGRM/ΔNRM ratios, and low (high) ARM/SIRM ratios for the Cluster 3 (Cluster 2). TOC is slightly lower and TS is slightly higher for Cluster 3, compared to Cluster 2, while Fe intensities are similar (Table 1).~~

~~High SIRM/κ and ΔGRM/ΔNRM for Cluster 3 signifies a significant contribution of greigite. Low ARM/SIRM ratios probably result from a substantial loss of fine grained magnetite, whereas magnetite appears well preserved in samples assigned to the Cluster 2. Based on these characteristics we interpret Cluster 3 (green) as the ‘glacial-greigite cluster’ and Cluster 2 (blue) as the ‘glacial-cluster’.~~

~~5.4 Control on greigite preservation~~

~~Greigite is a metastable mineral, and often forms as a precursor of pyrite under anoxic and sulphate-reducing conditions~~ (Morse and Wang, 1997; Roberts et al., 2011a; Wang and Morse, 1996; Wilkin and Barnes, 1996)~~. In the presence of H_2S greigite is transformed into pyrite (Berner, 1984). However, pyritization of greigite can be arrested, if the supply of H_2S, e.g., through the accumulation of organic matter is buffered by high concentrations of accessible iron (Blanchet et al., 2009; Kao et al., 2004; Morse and Wang, 1997; Wilkin and Barnes, 1996).~~

~~In the interglacial sediments of Lake Ohrid, greigite is generally not observed, however, iron sulfides (e.g., pyrite) are present. These interglacials correspond to times of high primary production (cf., Fig. 2j) and restricted mixing, comparable to present times (cf., Francke et al, this issue). Incomplete aerobic decomposition in the water column enabled organic matter to enter the sulfidic zone in the sub surface where anaerobic decomposition and sulfate reduction led to an excess of H_2S. Therefore greigite was either not formed or was transformed into pyrite.~~

~~The ‘glacial greigite cluster’ is only dominating in MIS 10, 12, and 16. In MIS 14 and MIS 8 only few samples belong to the glacial-greigite-cluster. Comparing this observation with climate reference data it is conspicuous that these glacials were extremely cold, whereas the other glacials were less pronounced (cf., Fig, 2b). Moreover, these glacials correlate to phases of low eccentricity, i.e., low climatic precession with relatively cold summers (Fig. 2a). The cooler temperatures probably resulted in low primary productivity and a lower TOC accumulation (cf., cluster Center properties in Table 1). Moreover, the lower temperature gradient between summer and winter~~

~~promoted mixing and aerobic decomposition of organic matter inhibited the reduction of lake sulphate into H_2S species, as it is typical for oligotrophic lakes (Holmer and Storkholm, 2001). Because of the high concentration of Fe-minerals, the low amounts of H_2S that was emitted through the decomposition of organic matter was entirely fixed as iron monosulfides and was no longer available for pyritization of greigite (e.g., Kao et al. 2004).~~

~~The glacials MIS 2-4, MIS 6, MIS 8 and MIS 14 are dominated by the ‘glacial cluster’. Compared to greigite-intervals, these glacials were less cold (Fig. 2 b) and summer productivity and, accordingly, organic matter accumulation was higher (cf., Table 1). As already discussed for interglacials, organic matter degradation occurred in the water-column and oxic zone of the surface sediments through aerobic degradation, as well as in the sulfidic zone through anaerobic decomposition. The latter involves sulfate reduction, increasing the emission of H_2S. Therefore, the potential of greigite formation and/or preservation is low.~~

~~5.5 Changing lithogenic sediment supply~~

~~Since the magnetic signal in unit 2 is overprinted by neo-formation of magnetic minerals, we only investigate unit 1 (MIS 1 – MIS 8) for changing lithogenic sediment supply (Fig. 3). Terrigenous input vs. limnic productivity is high during glacials, indicated by higher susceptibility and low TOC as well as low carbonate concentrations~~ (Francke et al., 2015)~~. At the same time, especially the concentration of high-coercivity magnetic minerals increases within the terrigenous fraction. Since this pattern is not due to preferential dissolution of magnetite (see section 5.1), we propose that the composition of terrigenous input changed over glacial-interglacial timescales.~~

~~The catchment of Lake Ohrid comprises different lithologies (c.f. section 1) that are mirrored by the distribution of element concentrations in surface sediments~~ (Vogel et al., 2010b)~~. Vogel et al.~~ (2010a) ~~assumed that changes in Cr/Ti ratios on glacial-interglacial timescales result from either increased aeolian activity, which changed sediment transport within the basin or a stronger erosion of soil material from sparsely vegetated soils. These processes can principally be responsible for the changing magnetic mineral composition during glacials. However, the site for the study of Vogel at al.~~ (2010a) ~~was in the north eastern part of Lake Ohrid (Fig. 1). We assume that increased counterclockwise advection of terrigenous material, as proposed by these authors would not affect the composition of sediments deposited in the center of the lake, where our study site is located.~~

~~We observe a large similarity between the benthic $\delta^{18}O$ stack (Lisiecki and Raymo, 2005) and the S-Ratio from Lake Ohrid (Fig. 3b, c). This suggests that the magnetic properties reflect changing environmental conditions. During humid interglacials, chemical weathering was enhanced and accumulation of soils and pedogenetic formation of (magnetic) minerals was promoted. However,~~

~~as already proposed by Vogel et al.~~ (2010a)~~, vegetation cover prevented the erosion of the soil materials, and terrigenous sediment input mainly consisted of primary magnetic minerals from the bedrocks (e.g., (titano-) magnetite) with a fine magnetic grain size (high ARM/SIRM). In the following glacials, vegetation cover decreased, as it is indicated by arboreal pollen abundances from the Mediterranean region i.e., from Lake Ohrid~~ (Sadori et al., 2015)~~ and from the Tenaghi Phillipon record from Greece (Tzedakis et al., 2006) and soils were exposed for erosion. As a result, increased input of hematite and/or goethite can be observed, the latter being the most widespread pedogenetic magnetic minerals (Cornell and Schwertmann, 2006; Vodyanitskii, 2010).~~

~~During interglacials, the S-Ratio and ARM/SIRM show higher frequency variations, where low S-Ratios and ARM/SIRM appear to occur at summer insolation minima (Fig. 3a, c, f). Likewise to the mechanism proposed above, these low insolation phases correspond to relatively cold conditions and less dense vegetation cover, also visible in pollen abundances~~ (Sadori et al., 2015)~~, thus increasing erosion of soil materials. However, it should be noted, that TOC variations, which largely parallel changes in the S-Ratio, were correlated to the~~ ~~δ^{18}O benthic stack (Lisiecki and Raymo, 2005).~~

6 Conclusions

~~The rock-magnetic record from Lake Ohrid, covering the past 640 ka, signifies changing terrestrial climate conditions, as well as changes in the lacustrine system. Our investigations show that greigite is preserved in sediments having low TOC and high Fe-minerals concentrations. These greigite bearing intervals are associated with extremely cold glacials, where summer productivity was extremely low, and lake mixing during winter was highest. Due to the lower productivity and aerobic conditions at the lake floor, sulfate reduction was low, so that sulfide availability was not sufficient to complete the polysulfide pathway to pyrite. In contrast, during less cold glacials with somewhat warmer summer temperatures and higher productivity and incomplete degradation of organic matter in the oxic zone, anaerobic degradation of organic material resulted in excess of hydrogen sulfide and led to pyritization of greigite.~~

~~Besides this information about internal lake processes, the~~Rock-magnetic data, in conjunction with sedimentological and geochemical data from the Lake Ohrid DEEP site, signify changing terrestrial climate conditions, as well as changes in the lacustrine system over the past 637 ka. Magnetic parameters often associated with greigite are elevated in glacials periods in the lower part of the core (637-320 ka, unit 2). SEM investigations support the presence of greigite and/or other Fe-sulfides. Ferrimagnetic Fe-Sulfides are absent in the upper part of the core (0-320 ka, unit 1), where, instead siderite is abundant in glacial sediments. Since siderite typically forms during methanogenesis after SO_4 is consumed, we propose that a geochemical shift occurred in Lake Ohrid with higher (lower) sulfate availability during the deposition of the lower (upper) unit. Various mechanisms might be responsible for this pattern. However, based on higher TIC concentrations within the interglacial periods of the lower unit, which are probably linked to higher ion concentrations in the lake water, we suggest that sulfate flux was enhanced and/or sulfate was concentrated due to a smaller water volume or enhanced evaporation. Further studies on the Fe-sulfide mineralogy and sulfur isotopes are required to provide a better understanding of the sources of sulfur and processes responsible for differences in Fe-S morphology and chemistry.

The magnetic properties of sediments deposited during the past ~~350 ka~~320 ka are also observed to signify changes in terrestrial environmental conditions on glacial-and interglacial timescales. During glacials, high-coercivity magnetic minerals (e.g., hematite and goethite) that ~~were ~~formed in the course of pedogenesis in ~~the ~~preceding interglacials were deposited in the lake. In contrast, ~~humid conditions and~~a rich catchment vegetation during interglacials limited the erosion of soil material and only minor detrital magnetite originating from physically weathered rocks was transported into Lake Ohrid. Millennial scale variations in rock-magnetic properties, which ~~concur~~are concurrent with changes in summer insolation, suggest that also on ~~those~~shorter time-scales the proposed mechanism of vegetation expansion influenced the erosion of soil materials. ~~All together~~Magnetic concentration parameters in the Holocene (upper 6 m) are enhanced, while carbonate and TOC concentrations, normally diluting the magnetic signal, are also high. Together with magnetic proxies for magnetic coercivity, these samples are suspected to contain bacterial magnetite. Overall, our findings demonstrate the valuable contribution of rock-magnetic methods to environmental studies, ~~because~~as they provide important information about a suite of different processes, comprising studies on terrestrial environmental conditions, sediment dynamics and internal lake processes.

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Figure Captions:

Fig. 1: (a) Overview map of the Balkan Peninsula. (b) Geological map of the Lake Ohrid region and coring locations of the DEEP site (5045-1) and Co1202 (Vogel et al., 2010). Modified after Vogel et al. (2010).

~~Fig. 2: Compilation of parameters measured on samples from the DEEP site compared to (a) eccentricity (after Laskar et al., 2004) benthic~~ ~~δ^{18}O stack (Lisiecki and Raymo, 2005). (c) Color bar indicates cluster-membership of the sediments, see also Supplementary Figure 1 and Table 1. (d-h) Rock-magnetic proxies, for abbreviations see text, (i) XRF-Fe counts and (j) TOC concentrations are from Francke et al.~~ (2015)~~. Gray bars represent Marine Oxygen Isotope Stages after Lisiecki and Raymo (2005). Triangles indicate samples on which temperature-dependent susceptibility measurements were performed (Fig.4).~~

~~Fig. 3: Rock-magnetic properties (c~~

Fig. 2: Compilation of magnetic and geochemical parameters measured on samples from the DEEP site. (a) Color bar indicates cluster-membership coefficients for each sample corresponding clusters in Table 2, (d-j) Rock-magnetic proxies, for abbreviations see text, (k) XRF scanning Fe/Ca counts (j) TOC concentrations are from Francke et al. (2015). Gray bars represent Marine Oxygen Isotope Stages after Lisiecki and Raymo (2005).

Fig. 3: SEM images of magnetic extracts, see also Table 1. a) 72.53m depth, detrital Cr-Fe-Oxides, titanomagnetite and magnetite with traces of Cr and Ti. b) 10.53 m depth, idomorphic and fragments of magnetites, traces of Ti and Cr. c) 158.83 m depth, microcrystalline and framboidal Fe-sulfides

within organic shell. d) 162.47 m depth, Cr-Fe-Oxides, fine-grained greigite aggregates. e) 153.83 m depth, microcrystalline Fe-sulfide nodule. f) 153.83 m depth, microcrystalline Fe-sulfide aggregates, idiomorphic greigite crystals (arrows). g) 117.83 m depth, coarse Fe-S nodules and fine-grained siderite grains (elongated particles). h) 176.87 m depth, microcrystalline Fe-sulfide nodule.

Fig. 4: Selected cross plots of magnetic proxy evaluation. Samples that acquire GRM (color code) cluster in different regions of the diagrams. a) GRM samples are characterized by high S-Ratios. A linear relationship between χ_{ARM}/SIRM and S-Ratio relate to co-varying ferrimagnetic grain-size fining and increasing low- vs. high coercivity magnetic mineral content. b) GRM samples plot at χ_{ARM}/SIRM levels typical of authigenic, inorganically precipitated greigite. A few samples from the uppermost part of the core plot in the field of bacterial magnetite (dashed circle, Snowball, 1994) and greigite (green shaded area, Reinholdsson et al., 2013). c) GRM samples have a distinctively different gradient compared to non-GRM samples in the SIRM/χ vs. χ_{ARM}/χ plot. d) GRM samples are characterized by high S-Ratios and high $MDF_{(ARM)}$. Non-GRM samples show no relationship between the two parameters.

Fig. 5: Compilation of parameters indicative for early diagenetic Fe-mineral formation, compared to (a) eccentricity (after Laskar et al., 2004). $MDF_{(ARM)}$ (b), SIRM/χ (c) and ΔGRM/ΔNRM (d) are elevated in the lower part, while siderite abundances (e) are higher in the upper part of the core. Cluster-membership coefficients (f) implicate a glacial-interglacial pattern for Fe-sulfides (green). Fe-sulfides and siderites occur also at elevated Fe/Ca (g) ratios during glacials. Geochemical differences between the upper and lower unit are also visible for TIC (h) concentrations during interglacials.

Fig. 6: Cluster-membership coefficients (a), rock-magnetic properties (d-f) and TOC concentration (g) for Unit 1 compared to (a) summer insolation at Lake Ohrid (after Laskar et al., 2004) and (b) benthic $\delta^{18}O$ stack (Lisiecki and Raymo~~,~~ 2005). Changing magnetic mineralogy parallel glacial-intergleacial variability and summer insolation.

~~Fig. 4: High-temperature susceptibility measurements on selected samples from Unit 1 (a-c) and Unit 2 (d-e). Positions of samples are indicated as triangles in Fig. 2.~~

~~Supplementary Figure 1: Membership coefficients of each samples to the three clusters revealed by fuzzy-c-means cluster analysis (see also Fig. 2c and Table 1).~~

Table 1: Magnetic properties of samples used for scanning electron microscopy

Table ~~1:~~

2: Cluster center properties obtained from fuzzy-c-means clustering

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First of all, we are very grateful for the in-depth evaluation and constructive feedback on our manuscript. We appreciate the time and detail that both reviewers took which included screening of the associated manuscripts from the Ohrid group.

We are aware that the Lake Ohrid dataset and interpretation of the proxies is not complete at the present stage but we are convinced that this manuscript will provide a valuable contribution to better understand the terrestrial environmental and lacustrine conditions in Lake Ohrid. The revision is currently underway and will greatly benefit from the suggestions by the reviewers.

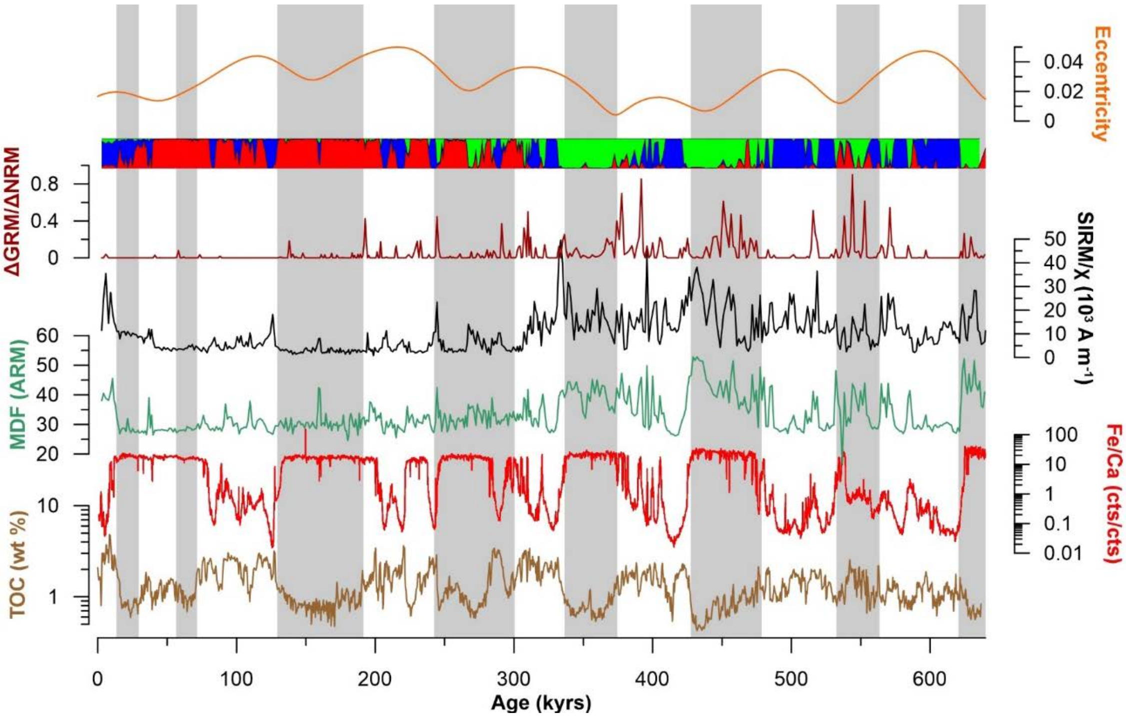
Primary comments: The most obvious feature in the data is the large contrast between Unit 1 and Unit 2. This appears in all proxies, and seems linked to changes in the abundance of greigite (accepting the authors' arguments) and the grain size of magnetite. Despite the prominence of the Unit1/Unit 2 shift, after reading the paper it is not at all clear what causes this transition. Page 14228 line 15 indicates that Unit 2 is "overprinted by neo-formation of magnetic minerals", which would suggest that the authors interpret this transition to reflect down diagenesis. Some of the most prominent features of the Unit 1/Unit 2 boundary are the appearance of greigite in Unit 2, but the interpretation of this as "overprinting" is difficult to reconcile with the interpretation advanced in the paper of syndepositional formation of greigite. Moreover, the transition appears quite sharp, and it is not clear how "overprinting" explains the various changes between the different Units. The authors should present a clear explanation for this transition- could changes in sediment or water sources (via tectonics or similar processes) have altered the supply of sulfur to the lake? Or are there other possibilities to explain the variations?

#1
Thank you for these suggestions, we will clarify the division into the two units more clearly.
We consider it unlikely that this boundary corresponds to a diagenetic front, responsible for the differences in the magnetic properties, because the Fe-sulfides that we observe in the lower unit have formed relatively rapidly after deposition. See also reply #4.

Moreover, not only the magnetic but also geochemical parameters indicate a shift in lake conditions, i.e., interglacials in unit 2 have much higher TIC concentrations (see Francke et al.). This can be related to water chemistry, leading to a better conservation of carbonate, or to a higher endogenic carbonate precipitation. Since TOC, which is also regarded as a proxy for lacustrine productivity but is also influenced by decomposition, is comparably (to TIC) low, this rather suggests a better ventilation (organic matter degradation) and/or changes in lake water chemistry thus a high production of carbonate. However, the TIC/TOC pattern concerns the interglacials and greigite concentrations concern the glacials, meaning that there is a fundamental shift in lake conditions integrating all over Unit 2.
At the moment we assume that the Lake Ohrid basin was less deep at those times (subsidence is still ongoing). However, it is still puzzling why the boundary is that sharp, and hopefully ongoing work on seismic data will reveal evidence if tectonic movements can be responsible for this. See also reply #4.

The two proxies for greigite abundance, SIRM/K and GRM/NRM, are not entirely consistent during Unit 2, as discussed on page 14223. The authors conclude that SIRM/K is a more reliable proxy for greigite, but do not explain why. Please explain. Related to this, if SIRM/K is in fact the most reliable proxy for greigite, this somewhat weakens the authors' arguments that increased greigite is climatically controlled. GRM/NRM shows very strong glacial/interglacial relationships. SIRM/K shows much weaker signals- values are higher in interglacials MIS 13 and 15 than in MIS 14, for example, and there are strong peaks at the beginning of interglacials MIS 11 and 9. What explains these patterns?

#2
We extended the analyses of the magnetic parameters, and produced various cross-plots and included the MDF into our evaluation. Together with the downcore plots it can be observed that highest SIRM/k values are observed when GRM is low, while MDF is still relatively high (i.e. > 30 mT). We performed SEM on magnetic extracts of samples that either are characterized by high SIRM/k and zero GRM and lower SIRM/k and high GRM. We found that the samples that have zero GRM but a high SIRM/k contain large nodules of Fe-sulfides (up to some tens of microns) while samples that have more moderate SIRM/k and high GRM contain microcrystalline greigite. We therefore assume that the maximum SIRM/k values occur when the authigenically formed Fe-sulfides grew coarser than the SD/MD threshold. In those cases GRM is zero, because only SD greigites acquire significant GRM. The observation that GRM samples are mainly located at glacial transitions (i.e., eccentricity minima) also argues for a climatic control on the greigite formation. We can only hypothesize that in the course of the cooling within a glacial, the nodules grew to bigger size. Additionally, at the transitions mentioned above, SIRM/k drops at the moment were TOC reaches maximum values. See also reply to reviewer 1.



Line 3, p. 14225. The authors interpret Figure 4C to indicate oxidation of reduced Fe minerals such as pyrite) to magnetite during sample heating of a sample of glacial-age sediment in Unit 1. They then use various calculations of the magnetic properties to show that that the magnetic properties are more indicative of oxidizing than reducing conditions. This interpretation seems robust, except that it does not explain the behavior of the sample in Figure 4C. Can the authors provide an interpretation of these data? It would be very helpful to the authors' argument if high-temperature susceptibility measurements were made on sediments in Unit 2 that they infer do NOT have greigite, to show that they changes they observe are in fact due to greigite and not other high coercivity iron phases.

#3
As suggested, we performed additional high-temperature measurements on samples that are inferred to contain or lack greigite. Except the two samples from the uppermost Holocene section, that were already presented in the paper, all samples show an increase in susceptibility above 400°C and higher susceptibilities in the cooling branch. This behavior is not only typical for oxidation of pyrite, but also observed for Fe-bearing clay minerals. The strong contribution of paramagnetic minerals (including clay) is also conveyed by the non-correlating downcore susceptibility and SIRM curves. Consequently, the heating-cooling susceptibility measurements cannot be used to reveal the presence of Fe-sulfides. Accordingly the sentence that pyrite is present all over this section will be modified.

Line 26-28, p. 14227. The authors suggest that low eccentricity in some "stronger" glacials, such as MIS 10, 12, and 16, drove low primary productivity and TOC accumulation via cooler summer conditions. However, the %TOC data are not incredibly clear on this issue- %TOC appears similar in MIS8 to MIS 10. Moreover, all glacials appear to have %TOC values less than 1%, so I question whether a few tenths of a percent difference in TOC contents is strong enough to drive the inferred changes. Are there other possible explanations?

#4
Thank you for this comment. We agree that the slightly lower TOC concentration in those glacials are not solely responsible for the preservation and formation of greigite between those glacials. Based on the two reviewer comments and together with the revision and reviewer comments on related papers from the special issue, we will re-evaluate the interpretation of extremely cold glacials in Unit 2, which contains significant greigite.
We are convinced that a distinct shift in lake conditions occurred. An alternative to the observation that those glacials were extremely cold, a rise in lake level or changes in hydrology and chemistry could be responsible for the observed shift.
1) Tectonics/Subsidence
2) Changes in water exchange between Lake Ohrid and Lake Prespa

3) Changes in water outflow from Lake Ohrid

At the present state, we cannot conclude which of those processes is important, and an evaluation needs additional investigations, including hydroacoustics and biological studies (e.g., shifts in communities), which have at this stage not been carried out down to the corresponding depth.

However, within this lower interval greigite is only present within glacial sediments. For this glacial-interglacial pattern, the process of a better ventilation of Lake Ohrid during glacials, and therefore increased aerobic degradation compared to anaerobic degradation (increase in sulfur reduction) is valid. At least if the greigite formed as an early-diagenetic phase (see also reply to reviewer 2).

Technical comments: Line 18, abstract: delete the comma.
Main text Line 3, p. 14217. It is not just magnetotactic bacteria that do this. Fe-reducing bacteria can induce the formation of extracellular magnetite simply by reducing iron.
Text will be edited

Line 21-30, p. 14218. It is not really clear how the spatial distribution of elemental concentrations links to the downcore variations in elements from these lines. I suggest deleting lines 23-25, which introduces the confusion.
Will be deleted/rephrased.
Line 11, p. 14219. Does XRF-Fe mean X-ray fluorescence intensities of iron? If so, state so. If not, delete the “Fe”.
Will be edited.

Line 4, p. 14222. Delete “basically”
Will be edited if still valid after paper revision.

Line 15, p. 14220. Francke et al. also provide %carbonate data. Please briefly (a few words) state how TIC, TOC, and TS were measured.
Will be included.

Line 15, p. 14227. What is the evidence that Fe sulfides such as pyrite are present in interglacial sediments?
We actually didn´t find any evidence for pyrite. While the magnetic extraction, delivered surprisingly high amounts of paramagnetic siderite and some vivianite, pyrite was not contained. We will revise this part of the text.

Line 10, p. 14229. Fine-grained titano-magnetite is likely a small proportion of the terrigenous inputs, not the “main” component. Rephrase.
Will be rephrased.

Figure 1. I suggest including an inset that shows the location of Lake Ohrid within Europe, for readers not familiar with the location and eastern Mediterranean geography.
Will do.

First of all, we are very grateful for the in-depth evaluation and constructive feedback on our manuscript. We appreciate the time and detail that both reviewers took which included screening of the associated manuscripts from the Ohrid group.
We are aware that the Lake Ohrid dataset and interpretation of the proxies is not complete at the present stage but we are convinced that this manuscript will provide a valuable contribution to better understand the terrestrial environmental and lacustrine conditions in Lake Ohrid. The revision is currently underway and will greatly benefit from the suggestions by the reviewers.

Comment on the age-model by Francke et al.
The course of the revision of the suite of papers in the Ohrid Special Issue, also the age-model for the sediment core has been revised as follows:

- Based on new results from tephrostratigraphy, one tephra age-control point was adjusted.
- age-control by correlating TIC to LR04 was removed
- correlation of TOC minima to increasing local summer insolation and winter-season length can be considered robust, because of the direct influence on lacustrine conditions. Therefore, this age-depth control was retained.

For details please see revision and reply by Francke et al.

Manuscript objective 1 (14219 line 4): “The first objective is to understand whether the variability in the magnetic mineral inventories can reveal changing environmental conditions in the catchment, beyond the observed general pattern of higher (lower) terrigenous input during glacials (interglacials).”

The main problem with this objective is, both in the introduction and throughout the manuscript, that the authors, based on an assumption of magnetic susceptibility (MS) (Fig 2d) being a direct proxy for terrigenous input, have already made an interpretation of higher observed terrigenous input during glacial periods and vice versa. There are two problems with this assumption. Firstly, the assumption that terrigenous input is the main contributor to the MS signal, while a valid hypothesis, needs to be demonstrated. It is possible that the MS signal in the lake environment is at least partly caused by magnetotactic bacteria. There is an interesting literature mini-review in the manuscript about magnetotactic bacteria (14225 lines 14-30). The authors need to use their knowledge of the methods detailed by the sources in this mini-review and apply it to their own data, to analyse if magnetotactic bacteria are generating their MS or not.

#1
Thank you for this valuable comment. The phrasing in the original manuscript was not clear and led to some confusion. We don´t infer an absolute increase in terrigenous materials, but rather a relative increase, compared to bioproductivity. This will be stressed more clearly in the revised version of the manuscript.

Concerning the point of a potential influence of bacterial magnetite on the susceptibility, there is one important observations that was not explicitly discussed in the original paper. When comparing MS and SIRM in our Figure 2 it is well visible that in the upper section of core (MIS2-MIS8) increases in susceptibility are not mirrored by increases in SIRM. In case the susceptibility was carried by magnetosomes, an increase in SIRM would be expected, too.
Secondly, cross-plots of remanence parameters, that are often observed to be indicative for bacterial magnetite, e.g., kARM/SIRM vs. kARM/k and SIRM/k vs. kARM/k fail for the samples from Lake Ohrid (except the few samples from the uppermost Holocene section, that was already suspected to contain magnetosomes, as stated in the original version of the paper).

Moreover, the increases in MS co-varies with potassium and iron XRF intensities and with HIRM, suggesting a detrital source for MS. However, the magnetic extraction that we carried out for the revision of the manuscript provided evidence for a relative high proportion of siderite (see also Lacey et al.). Therefore, the contribution of authigenically formed paramagnetic minerals will be incorporated in the revised version (detrital versus biogenic contribution). See also reply to reviewer 1 #3.

We will work and modify the text and include the discussion about the origin of the susceptibility signal and clarify that we intend talking about relative changes.

Secondly, assuming for the moment that terrigenous input turns out to be the main/sole contributor to the MS signal, one must consider that any MS reduction during interglacial periods could be due to a primary productivity related increase of the contributions of TOC and CaCO3 to the overall sediment accumulation (i.e. a dilution effect) and not directly related to a change in terrigenous input flux. Until the above issues are fully investigated, much of the discussion in the manuscript about changing lithogenic sediment supply and changes in the catchment environment can be considered mostly speculative.

#2
We didn’t mean that the changes were only driven by terrigenous flux, for sure for such a discussion we would have to calculate mass-accumulation rates for biogenic and terrigenous sediments (as outlined above).
However, when we talk about changes in the magnetic properties, we don´t use concentration dependent data.

The most important parameter is the S-Ratio, indicating more high-coercivity minerals compared to low-coercivity minerals. The concentration parameters HIRM and SIRM are shown to evidence that decreases in S-Ratio are not related to a loss in SIRM (which could be an indicator for selective reductive diagenesis of low-coercivity minerals), but to increases in HIRM. Low S-Ratios during the glacials indicate that in those climatic phases the contribution of high-coercivity minerals increased relative to magnetite.

Manuscript objective 2 (14219 line 7): “The second objective is to investigate proxies for the occurrence of magnetic iron sulfides for their capability to reflect hydrological and environmental conditions in the lake, because their existence as early diagenetic phases is strongly linked to the accumulation and decomposition of organic material.” My overall view of the manuscript with regards to Objective 2 is that the various magnetic parameters are interpreted too quickly, with arrows on the figures suggesting too simply that certain magnetic parameters correspond directly with more/less of certain magnetic minerals. The authors need to begin with a more a comprehensive and basic analytical approach whereby elementary mineral magnetic properties (super paramagnetic, single domain, pseudo single domain, multi-domain, hardness, etc.) are first catalogued and considered, long before specific magnetic minerals are named.

For example, in the introduction and methods it is already assumed that SIRM/k is a proxy for “greigite”, whereby Snowball and Thompson (1990) and Nowaczyk (2012) are cited as sources. The former source uses multiple analyses to identify greigite and simply notes that greigite tends to exhibit elevated SIRM/k values, not that SIRM/k on its own can be used as a general greigite proxy. The latter source doesn’t explicitly mention SIRM/k being used as a greigite proxy. The authors do use GRM as an additional greigite indicator and in section 14223 lines 15-22 it is correctly noted that GRM acquisition can indicate the presence of greigite, coinciding in many cases with high SIRM/k values. However, the authors then conclude that, for intervals where they find high SIRM/k values and no GRM acquisition, that they still have greigite present, but that it simply failed to be recorded by GRM acquisition (which is possible), and that SIRM/k should be used as a general greigite proxy on its own. Such an assertion requires a more rigorous mineral magnetic and sedimentological investigation in order to identify what type of greigite (syn-depositional bacterial or post-depositional chemical) is present in the samples, which in turn can explain genesis and preservation conditions. Options include FORC analysis, TEM+SEM.

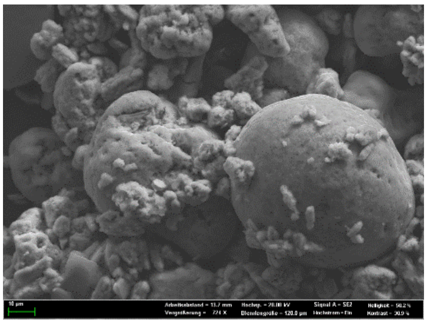
#3
We acknowledge the suggestions for possible biases of the “greigite proxies”. In the revised version, we will also convey a more comprehensive study on the magnetic mineral assemblages. We will produce additional cross-plots indicating relationships between different magnetic parameters (e.g., grain-size dependence and compositional trends). These analyses will also help to evaluate the different proxies for greigite.

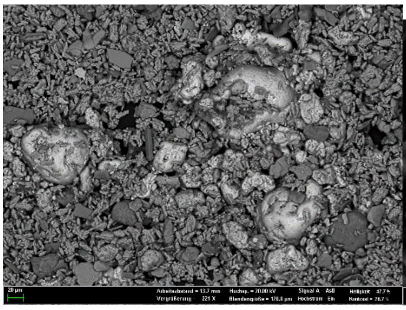
To support these data-based interpretations, as suggested, we performed SEM and edx-analyses on magnetic extracts, that will be used to identify magnetic mineral assemblages and relate those to the magnetic parameters.
The fresh results we obtained from SEM/edx analyses reveal large Fe-S nodules in extracts of samples characterized by high SIRM/k and zero GRM, while microcrystalline greigite is found in samples with significant GRM acquisition. The analytical work is still ongoing, but it seems that the coarse nodules are authigenic and have the same chemical composition as the greigite microcrystals. Thus, we infer that GRM acquisition is related, as it would be expected, to SD greigite minerals, while highest SIRM/k relates to the coarse Fe-S nodules.

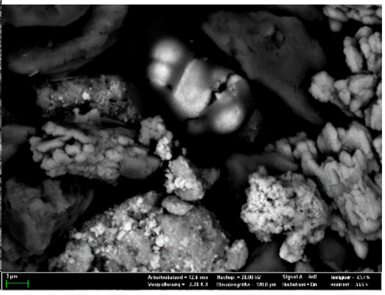
Seeing that the authors seek to use greigite as an indicator for lake/sediment alaeoconditions, it is imperative that they ascertain what types of greigite are present in the various parts of the core, because different types of greigite form and/or are preserved under different circumstances. Post-depositionally formed chemical greigite can form due to the downward migration of isotopically heavy sulphides in the sediment (e.g. Barker Jørgensen et al., 2004; doi:10.1016/j.gca.2003.07.017) and could simply be related to sediment features that trap sulphides (a description/discussion of the sediment features would be helpful).
The authors seek to relate the presence of “greigite” (they do not state what type) in their record to the LR04 global benthic stack (14224 lines 0-10). Any apparent association between post-depositionally formed greigite and syn-depositional climate events cannot be interpreted by way of causality, so it is therefore imperative that the authors conclusively demonstrate where they have postdepositional chemical greigite and where they have syn-depositional bacterial greigite. See the work of Vasiliev et al. (2008, doi:10.1038/ngeo335) and Reinholdsson et al. (2013, doi:10.1016/j.epsl.2013.01.029).

#4
We have found evidence that the greigite is authigenic, and the size of the nodules often exceeds 50 µm, while micro-crystalline greigite is ~ 1 µm. We therefore conclude that the greigite has formed chemically during early diagenesis by processes mediated by Fe-reducing bacteria, which would mean that it would have formed shortly after deposition of the sediments.

Almost syndepositional vs. post-depositional
Besides the Fe-S nodules a lot of siderite is contained in the magnetic extracts. According to Lacey (this issue) who worked on d18O of the siderite, it formed relatively fast after deposition.
Previously different scenarios were discussed for the co-occurring greigite and siderite.
If the Fe-S nodules had formed after siderite, a change in pore-water chemistry with sulfidic pore-waters would be required. We cannot test this, because no pore-water data are available. However, earlier publications from such settings show greigite overgrowth on siderite grains (Sagnotti et al., 2005, Weaver & Roberts 2005). We didn´t observe so in the SEM. Below you can find an example of fine grained siderite together with some coarse Fe-S nodules.
Alternatively, siderite and greigite can form at the same time (e.g. Pye 1981, 1990) in recent environments if the rate of iron reduction is higher than the rate of sulphate reduction, which would be in-line with an inferred higher aerobic compared to anaerobic (sulfate-reducing) degradation. Some of the Fe-Sulfide nodules are perfectly round or within an organic coating. For these specific examples it appears likely that Fe-S crystallized in organic compounds (e.g., a pollen grain) and possibly also more irregular shaped particles could correspond to sulfides formed within microenvironments.







So, to sum up, based on three reasons, we expect greigite formation in the shallow subsurface:

1) Fe-S nodules are not growing on or replace siderite grains
2) Some of these nodules resemble the shape of organic compounds, or are even contained within an organic coating.
3) Relative Paleointensity data (just calculated as NRM/ARM) show a quite good correspondence between the Lake Ohrid core and reference records.

It is stated that "the samples containing greigite are associated to glacials concurring with low phases of eccentricity (Fig 2a)." Once again, the authors do not state what type of greigite. It's difficult to see a significant correlation between the magnetic parameters and LR04 d18O. The authors did carry out a fuzzy cluster analysis of six different magnetic, chemical and physical properties which they say "can basically be indicative of and impact the formation and preservation of greigite". More information is required about what type of greigite is hypothesised as being formed (bacterial, chemical) and how. The rationale behind having (higher) lower TOC associated with (Cluster1)Cluster3 needs to be more clearly explained. It is likely that TOC XRFFe are causing the apparent interglacial/glacial grouping in the cluster analysis, and neither of these parameters is inherently indicative of greigite. TOC is heavily influenced by climate conditions (indeed, it was wiggle matched to LR04 by Francke et al. to produce the age model used in this manuscript). Hence, to use TOC in a cluster analysis to indicate greigite, and then claim that the cluster analysis shows a relationship between LR04 and greigite is not a valid approach. It would be interesting to see how the cluster analysis would look if TOC XRFFe were excluded and only the magnetic parameters were included.

5
We thank the reviewer for this remark on the inclusion of TOC and Fe-intensities into the cluster analyses. We agree that cluster assignment could have been influenced by the strong glacial-interglacial pattern in TOC and Fe intensities.
We repeated the cluster analyses and use now only magnetic properties. Off the same reasons for excluding TOC and Fe, we also excluded concentration magnetic parameters and only used relational proxies. Following this new analysis, the glacial-interglacial clustering in relation to the presence of greigite is still observed.

Concerning the discussion on the type of greigite, see reply #4.

Based on the two reviewer comments and together with the revision and reviewer comments on related papers from the special issue, we will re-evaluate the interpretation of extremely cold glacials in Unit 2, which contains significant greigite.
We are convinced that a distinct shift in lake conditions occurred. An alternative to the observation that those glacials were extremely cold, a rise in lake level or changes in hydrology and chemistry could be responsible for the observed shift.
1) Tectonics/Subsidence
2) Changes in water exchange between Lake Ohrid and Lake Prespa
3) Changes in water outflow from Lake Ohrid

At the present state, we cannot conclude which of those processes is important, and an evaluation needs additional investigations, including hydroacoustics and biological studies (e.g., shifts in communities), which have at this stage not been carried out down to the corresponding depth.

However, within this lower interval greigite is only present within glacial sediments. For this glacial-interglacial pattern, the process of a better ventilation of Lake Ohrid during glacials, and therefore increased aerobic degradation compared to anaerobic degradation (increase in sulfur reduction) is valid. At least if the greigite formed as an early-diagenetic phase (see also reply to reviewer 1).

Additionally, S-ratios can indeed help differentiate between low- and high-coercivity magnetic minerals. But why are only magnetite, goethite and heamatite discussed (and also in Fig. 3c) as the only minerals affecting the magnetic assemblage coercivity? Greigite also contributes to the coercivity.
The magnetic parameters will we discussed in more detail in the revised version. See Answer #3

All magnetic units need to be reported using mass specific standard notation used by mineral magnetists, to allow for easy quantitative comparison with existing publications (see technical comments). Much of the discussion mentions magnetic parameters simply as being "high" or "low", whereas a quantitative description would enable a better comparison to existing mineral magnetic studies. Moreover, dry mass-specific units are important in such a long sediment sequence such as the Lake Ohrid record, where downcore density changes due to sediment compaction can be expected.

6
We agree that corrections for down-core sediment compaction are worthwhile, so, we corrected all data with the wet-bulk density.
Since we are not working with pure magnetic minerals, we don´t think it makes much sense to correct the magnetic parameters by dry-mass. There would still be the bias due to dilution of dia- and paramagnetic minerals, and therefore the comparison to published data would still be difficult (at least for concentration parameters).
When using ratios of magnetic parameters, a comparison is still valid.

Finally, I note that NRM data is not presented in the manuscript, nor are median destructive fields (MDF) of the NRM, which would be very useful for identifying properties of proposed magnetic minerals. The methods detail that NRM was measured with incremental demagnetisation to 100 mT, so these data should exist. Additionally, if the palaeomagnetic cubes have been subsampled with orientation in mind, then palaeomagnetic secular variation (PSV) data such as inclination and declination will also have been measured as part of the NRM measurements. Were the NRM data (and PSV data) judged to be not of sufficient quality for publication, have they been published already or will they be published in a separate manuscript? Elaboration is needed.

#7
We included MDF in our discussion. Moreover, the paleomagnetic data, especially estimates of relative paleointensity appear to be of good quality and will be published elsewhere, when the basic rockmagnetic properties will be groundtruthed.

Brief technical comments
(1) Both SIRM/k and ARM/SIRM can be indicative of magnetic grain size, depending on the number of (ferrimagnetic) magnetic minerals in the assemblage. The authors should look into this more and analyse any possible relationship between SIRM/k and ARM/SIRM

We have produced cross-plots which will show that SIRM/k is negatively correlated with ARM/SIRM, especially for those samples that carry a GRM. This discussion will be added into the revised version, at places where the occurrence of coarse grained Fe-S nodules are being discussed.

(2) There appears to be a minor typo in equation 2.
Ok

(3) The corresponding values of all the magnetic parameters from Fig 2 should be displayed for each sample in Figure 4.
We will revise Fig. 2 and include more and different magnetic parameters. We then will carefully revaluate which parameters will be needed for the discussion of changing magnetic mineral composition in unit 1 (Fig. 4). However, there are some parameters in unit 1 (e.g. MDF , SIRM/kappa) that don´t show variations in unit 1 and therefore we believe it is not necessary to include those parameters again in Fig. 4. Instead, we will show the cluster assignment again in Fig 4, because also there are a few samples that contain greigite (which will be included in the discussion of Fig. 4). By showing this color bar again, it will be easier for the reader to identify those specific intervals and cross-refer to Fig. 2.

(4) The correct mass specific unit notation that should be used:
- Magnetic susceptibility should be reported as (m3=kg)
- SIRM should be reported as SIRM(Am2=kg)
- ARM should be reported as ARM(m3=kg)
- SRIM/k should be reported as SIRM= (A/m)
- ARM/SIRM should be reported as ARM=SIRM(m=A)

Will do.

(5) The division between Unit 1 and Unit 2 appears to be somewhat arbitrary. Perhaps a division based upon sedimentological properties would be more logical.
We will revise the reasoning why these units were divided (see also reply to reviewer 1, #1).