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Climatic control on the occurrence of high-coercivity magnetic minerals and preservation of greigite 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 ka, shows a strong relationship to environmental conditions on glacial–interglacial and millennial time scales. During extremely cold glacials, a lower accumulation of organic matter and likely enhanced mixing of the water-column coincides with the presence of greigite, whereas greigite is absent in sediments deposited during less severe glacials. Those "non-greigite" glacial sediments are characterized by high concentration of high-coercivity magnetic minerals, which relates 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 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 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 addition to the detrital magnetic inventory, magnetic minerals can form syn- and post-sedimentary. 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 (Egli, 2004b; Roberts et al., 2012; Snowball et al., 2002; Vali et al., 1989). 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 the subsurface leading to dissolution of iron oxides and formation of ferromagnetic iron sulfides, such as greigite and pyrrothite (Demory et al., 2005; Karlin and Levi, 1983; Rowan et al., 2009; Sagnotti, 2007) or paramagnetic minerals, such as pyrite, siderite, and vivianite (Dong et al., 2000; Karlin and Levi, 1983).

Besides the vast 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., 1994, 2004; 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., 2011b; Sagnotti, 2007). Because they 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 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 by Fe-excess availability (Kao et al., 2004; Roberts et al., 1996; Skinner et al., 1964). Cyclic preservation of greigite in

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a Pliocene lacustrine sequence from Lake Qinghai (China) was recently linked to high lake levels and humid climate that resulted in oxygen depletion of the bottom water (Fu et al., 2015). In addition, greigite can commonly form at a late diagenetic stage, as a result of a variety of different mechanisms associated to migration of mineralized fluids and to changes in the pore water chemistry, which disrupt the steady-state diagenetic progression (Roberts and Weaver, 2005).

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

The sediments from Lake Ohrid (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., 2015). Lake Ohrid is an oligotrophic lake, which mixes completely every few years during winter (e.g., Matzinger et al., 2007). Temperature variations probably had a strong influence on the mixing of Lake Ohrid during past glacials and interglacials (Vogel et al., 2010b; 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. (2010a) 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 ero-

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sion of soils or stronger winds inducing changes in surface water circulation (Vogel et al., 2010b) or an intra-lacustrine contourite drift (Wagner et al., 2012).

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.

2 Study area and materials

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

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 the lake through the River Crn Drim (accounting for 60 %) and evaporation (~ 40 %) is balanced by river inflow (25 %), direct precipitation (25 %) and karst aquifers (50 %). The karst aquifers are fed by mountain range precipitation and the neighboring higher altitude (849 m a.s.l.) Lake Prespa (Matzinger et al., 2006a, b; Wagner et al., 2014).

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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, 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) in summer 2013 with a maximum sediment penetration of 569 m. The recovered sedimentary sequence covers probably 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 (100–247 m) 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 was measured using an AGICO MFK-1 susceptometer. Natural and artificial remanence parameters were measured using a 2G Enterprises 755 superconducting 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 Magnetization (ARM), a proxy for fine-grained, mostly single domain magnetite (King et al., 1982), was imparted with a single-axis 2G 600 AF demagnetizer by using 100 mT AF and 50 µT DC field. Isothermal Remanent Magnetization (IRM), which depends on the magnetic mineral mixture in the samples, was induced using a 2G 660 pulse magnetizer applying a 1500 mT DC peak field and a 200 mT reversed field. The ratio of ARM to Saturation IRM (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

$$\mathrm{HIRM} = 0.5(\mathrm{SIRM} + \mathrm{IRM}_{(-200\,\mathrm{mT})}) \quad (1)$$

Additionally, the S-Ratio, calculated as

$$S = 0.5(1 - (\mathrm{IRM}_{-200\,\mathrm{mT}}/\mathrm{SIRM}) \quad (2)$$

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

Moreover, we calculated SIRM/κ which is often used as a proxy for the presence of greigite (e.g., 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),

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

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 magnetic minerals by carbonate we calculated SIRM and HIRM on a carbonate-free basis

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

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

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The concentration of carbonate (c_{carb}) was calculated by multiplying TIC contents (Francke et al., 2015) with the molar mass of $CaCO_3$.

3.2 Cluster analysis

We performed fuzzy-c-means cluster analysis for a suite of data that can basically be indicative 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. To achieve more symmetric distributions of the suite of data, we performed data ln (natural logaritm) transformations, except for ΔGRM/ΔNRM. The latter values show a J-shaped distribution that cannot be transformed into a normal distribution. All datasets were standardized before clustering.

4 Rock-magnetic results

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).

4.1 MIS 16-MIS 9 (unit 2)

Generally 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).

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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 (Figs. 2f and 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 Figs. 2e, 3d and e). Superimposed on long-term patterns are higher frequency variations that are most expressed in the S-Ratio and ARM/SIRM (Fig. 3c and f). In contrast, low SIRM/κ and ΔGRM/ΔNRM of mostly zero (Fig. 2g and h) indicate that greigite is mostly absent.

5 Discussion

5.1 Identification of changing magnetic mineral assemblages

Many samples from unit 2 have high ΔGRM/ΔNRM and SIRM/κ (Fig. 2g and h), indicating the occurrence of greigite (Fu et al., 2008; Nowaczyk et al., 2012; Roberts and Turner, 1993; Ron et al., 2007; Snowball and Thompson, 1990). It is important to note that the greigite proxies provide sometimes ambiguous results; high SIRM/κ is not always accompanied by high ΔGRM/ΔNRM. On the other hand, if samples acquire a GRM, SIRM/κ always shows elevated values. Missing GRM acquisition of greigite bearing samples have been 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., 2011b). 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 and 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., 2011b 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 Sect. 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 and 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 (Fig. 3d and e; carbonate concentrations vary between 0.5–45 %, see Francke et al., 2015). $SIRM_{cfb}$ 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 re-

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ductive 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 Sect. 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 and 3). This argues for a change in the composition of the magnetic mineral assemblage. An increased input in lithogenic magnetic minerals relative to carbonates can be ruled out since TOC and TIC is high (see also Francke et al., 2015). κ_T of two samples from this part of the record (Fig. 4a and 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.

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). 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., 2011a; 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). 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). 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 anal-

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yses, we cannot infer if this occurrence is triggered by high TOC and/or nutrient inputs, or it just results from an not-yet completed dissolution of magnetosomes (Snowball, 1994).

5.2 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., 2011b). 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 Supplement Fig. S1. 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).

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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".

5.3 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., 2011b; 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., 2015). 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 mix-

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ing 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. 2b) 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.

5.4 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 Sect. 5.1), we propose that the composition of terrigenous input changed over glacial–interglacial timescales.

The catchment of Lake Ohrid comprises different lithologies (cf. Sect. 1) that are mirrored by the distribution of element concentrations in surface sediments (Vogel et al., 2010a). Vogel et al. (2010b) 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. (2010b) 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 δ^{18}O stack (Lisiecki and Raymo, 2005) and the S-Ratio from Lake Ohrid (Fig. 3b and 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. (2010b), 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 and 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).

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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 magnetic properties of sediments deposited during the past 350 ka 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 rich vegetation during interglacials limited the erosion of soil material and only detrital magnetite originating from physically weathered rocks was transported into Lake Ohrid. Millennial scale variations in rock-magnetic properties, which concur with changes in summer insolation, suggest that also on those time-scales the proposed mechanism influenced the erosion of soil materials. All together, our findings demonstrate the valuable contribution of rock-magnetic methods to environmental studies, because they provide information about a suite of different processes, comprising studies on terrestrial environmental conditions, sediment dynamics and internal lake processes.

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Table 1. Cluster center properties obtained from fuzzy-c-means clustering.

	SIRM/κ	ΔGRM/ΔNRM	TOC %	TS %	Fe (cts/kcts)	ARM/SIRM
Cluster 1	9.45	0.028	1.63	0.099	1.02	19.99
Cluster 2	4.05	0.028	1.11	0.101	2.44	11.61
Cluster 3	13.18	0.096	0.99	0.115	2.44	5.94

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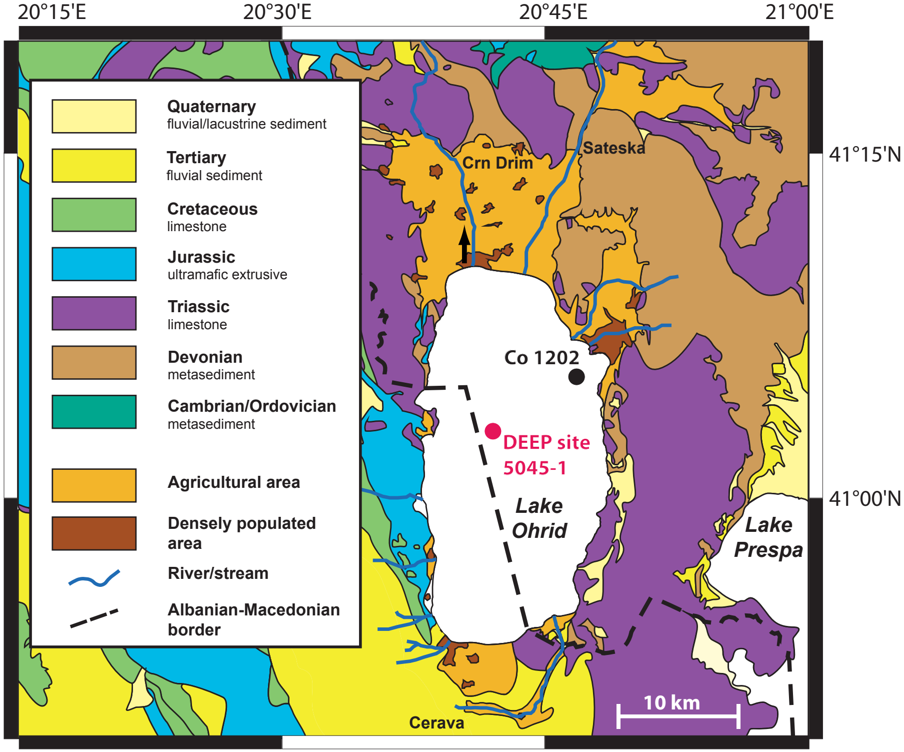

Figure 1. Geological map of the Lake Ohrid region and coring locations of the DEEP site (5045-1) and Co1202 (Vogel et al., 2010). Modified after Vogel et al. (2010).

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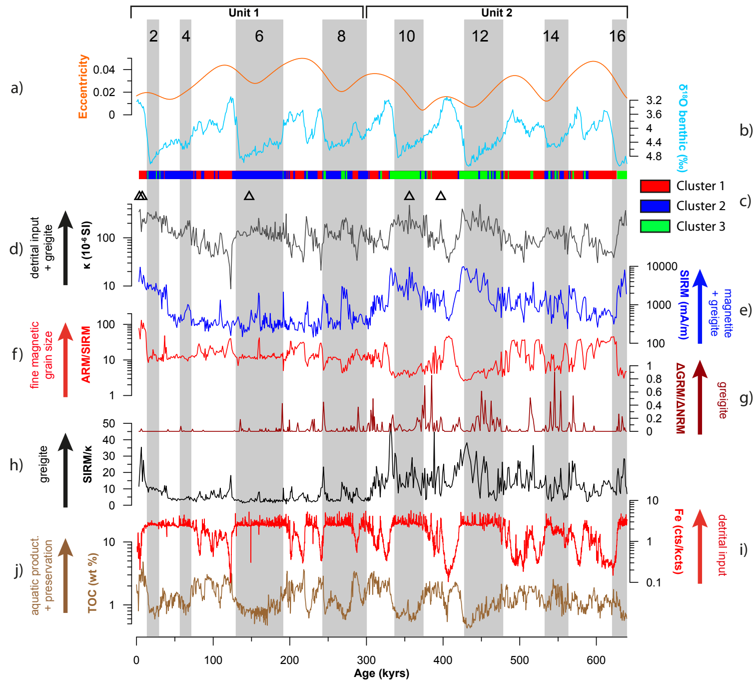

Figure 2. Compilation of parameters measured on samples from the DEEP site compared to **(a)** eccentricity (after Laskar et al., 2004) benthic δ^{18}O stack (Lisiecki and Raymo, 2005). **(c)** Color bar indicates cluster-membership of the sediments, see also Supplement Fig. S1 and Table 1. **(d–h)** 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).

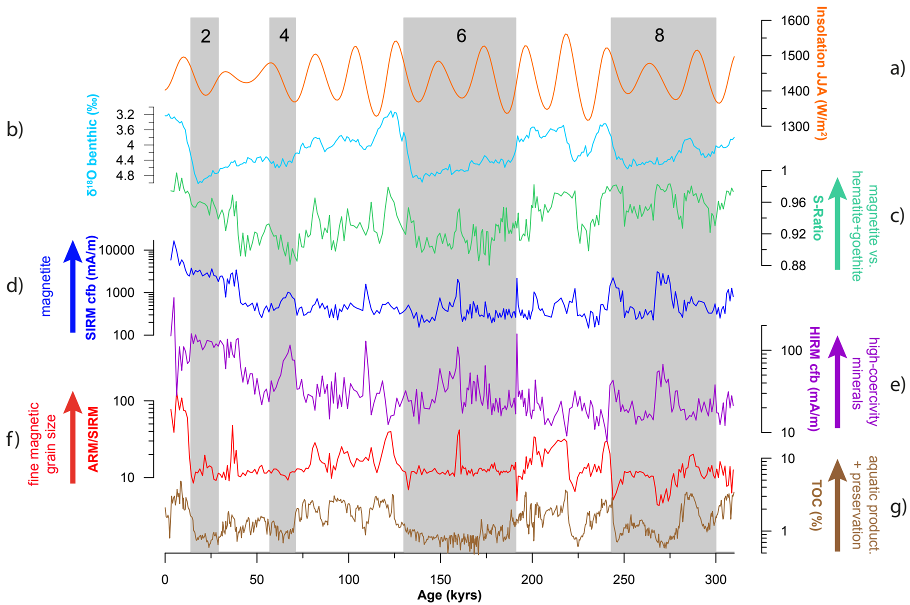

Figure 3. Rock-magnetic properties **(c–f)** and TOC concentration **(g)** for Unit 1 compared to **(a)** summer insolation at Lake Ohrid (after Laskar et al., 2004) **(b)** benthic δ^{18}O stack (Lisiecki and Raymo, 2005).

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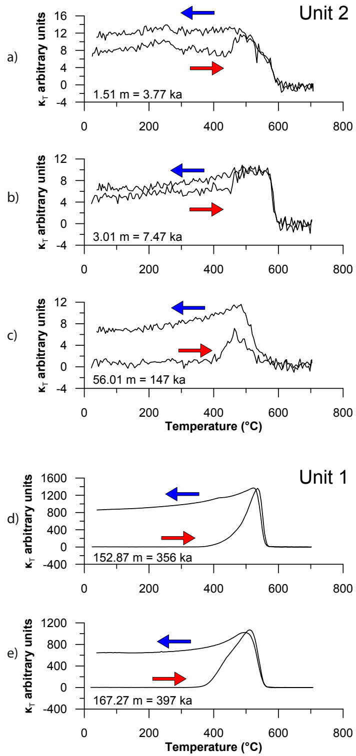

Figure 4. High-temperature susceptibility measurements on selected samples from Unit 1 **(a–c)** and Unit 2 **(d–e)**. Positions of samples are indicated as triangles in Fig. 2.