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Interactive comment on "Climatic control on the occurrence of high-coercivity magnetic minerals and preservation of greigite in a 640 ka sediment sequence from Lake Ohrid (Balkans)" *by* J. Just et al.

Anonymous Referee #2

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Part A: General comment for the Lake Ohrid group of manuscripts (including Just et al.)

The Just et al. manuscript relies on four other manuscripts that are currently also in review in *Biogeosciences* (Baumgarten et al., 2015; Francke et al., 2015; Leicher et al., 2015; Sadori et al., 2015). Consequently, in order to evaluate the manuscript in terms of scientific content, I have read through many manuscripts. This was time consuming, but I applaud the fact that all Lake Ohrid manuscripts are available to read in an open access review process and it was exciting to read about all the data being produced by

the Lake Ohrid project. The Just et al. manuscript I am reviewing uses the age model developed in the Francke et al. manuscript (Fig 5 therein), yet there also exists the Baumgarten et al. manuscript entitled *"Age depth-model for the past 630 ka in Lake Ohrid (Macedonia/Albania) based on cyclostratigraphic analysis of downhole gamma ray data."* Perhaps the Lake Ohrid group could briefly explain, for the benefit of the readers, the difference between the two age models?

The Francke et al. age model used by Just et al. is constructed by wiggle matching TOC, TIC and TOC/TN in the Lake Ohrid record to the LR04 benthic stack (Lisiecki and Raymo, 2004), local insolation and winter season days, thereby transferring the LR04 and insolation based chronology to Lake Ohrid. This 640 ka age model is strengthened by the identification of eight independently dated tephra layers. I am concerned that Just et al. (and perhaps other Lake Ohrid manuscripts) compare the trends in their magnetic data, plotted against age inferred from LR04, to the trends in δ18O in the LR04 benthic stack to understand the influence of global climate upon the Lake Ohrid magnetic record. This could be considered circular reasoning.

The Lake Ohrid group could furthermore consult a recent publication by Stern and Lisiecke (2014; doi:10.1002/2014PA002700), which promotes the use of regional stacks instead of global stacks.

Part B: Review of Just et al. manuscript

It was very interesting to read the manuscript by Just et al., as it is very exciting to find a magnetic record from such a long, continuous sediment record in Europe. Clearly, the authors have carried out a lot of painstaking subsampling and diligent measurement work, for which they should be congratulated.

I review the manuscript by evaluating it against the two major research objectives set out by the authors in their introduction section. These objectives are quite broad and perhaps a bit too ambitious. Consequently, the manuscript attempts to explain a great deal of processes at once, which has disrupted the flow of the manuscript and, at times, clouded the analysis of fundamental mineral magnetism. Most notably, the manuscript makes somewhat simple assumptions about magnetic susceptibility (MS) as a terrigenous input proxy, and also uses greigite as an indicator for lake palaeoconditions, but fails to identify the type(s) of greigite encountered. Consequently, the mechanism between climate and greigite is not well explained.

Perhaps a more focussed hypothesis would help the authors answer a fundamental question and describe processes at a more basic level, which could eventually result in a publication suited to *Biogeosciences*. The extensive record produced by the authors does offer such potential, so the authors should be optimistic, but very major alterations and additions are required to make the manuscript acceptable, so a resubmission is perhaps required. In any case, I make suggestions for improvements and look forward to seeing the finished product. My expanded review based on the the two major research objectives can be found below:

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.

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.

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. Seeing that the authors seek to use greigite as an indicator for lake/sediment palaeoconditions, 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 post-depositional 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).

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.

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.

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.

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.

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.

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

(3) The corresponding values of all the magnetic parameters from Fig 2 should be displayed for each sample in Figure 4.

(4) The correct mass specific unit notation that should be used:

- Magnetic susceptibility should be reported as χ (m$^3/kg)$

- SIRM should be reported as $\sigma_{SIRM}(Am^2/kg)$

- ARM should be reported as $\chi_{ARM}(m^3/kg)$

- SRIM/k should be reported as σ_{SIRM}/χ (A/m)

- ARM/SIRM should be reported as $\chi_{ARM}/\sigma_{SIRM}(m/A)$

(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.

Interactive comment on Biogeosciences Discuss., 12, 14215, 2015.