Interactive comment on "Thermomagnetic properties of vivianite nodules, Lake El'gygytgyn, Northeast Russia" by P. S. Minyuk et al.

Anonymous Referee #1

B. Specific comments (Page numbers refer to PDF version of the mnsucript)
Please add the term "high-temperature" to the title of the manuscript such that it will be read as 'High-temperature thermomagnetic. . ...'. Otherwise the reader would expect, at least I would, that the study is about low-temperature measurements since vivianite acts as a remanence carrying mineral only at very low temperature as the authors correctly mention.

We change title as:
High-temperature thermomagnetic properties of vivianite nodules, Lake El'gygytgyn, Northeast Russia

Page 4999, line 4: To me, the 'slight increase' in magnetization is rather a change in slope than a real increase, only for sample EV294 there is a very minor increase in Js.
Please explain this a bit more precise.

Yes, it is really like change in slope of curve. We change sentence as:
"The initial heating curve for each sample shows a small but distinctive "hump" marked by change in slope or a slight increase in J_i at 180–200°C and a decrease at 320–340°C."

9 - 14: Which curves of susceptibility are meant, 1st, 2nd or 3rd; to which curves of Js are they compared? This needs to be expressed more precise.
We edit sentence:
"In comparing the high-temperatures curves of magnetic susceptibility of first heating run (Fig. 7a, c, e) to the saturation magnetization of first heating (Fig. 8a, b, c), several differences are noted."

Page 5002, 19: I did not really get the point: I cannot recognize significantly increased susceptibilities in core interval 7.05-7.26m from Fig. 3 ; also for interval 9.13-9.33 m MS is not distinctly increased, it might be slightly higher than the lowest values throughout the core but are much lower than MS during, e.g., sub-stage 6.5. How does your findings correlate with the, at least from my perspective, significantly increased MS during cold stage 8.2 at about 12.75-13.00 m core depth? In this interval neither P2O5 nor MnO show increased values. Consequently vivianite is not present. Does this mean that the increased MS in this interval reflects a true paleoclimatic signal? But why is it almost as high as for warm intervals? Compared to this effect, the presence of vivianite seems to affect MS to only a minor extent. The argumentation needs to be clarified here.
Please explain how a SIGNIFICANT increase of MS (caused by the presence of viviante in contrast to a true climatically induced increase) is defined. Perhaps cross-plots of MS vs. P205 and MS vs. MnO could also strengthen your findings. Nevertheless: in general, I agree to your conclusion that the presence of vivianite aggregates may affect the reliability of rock magnetic parameters in terms of environmental proxies and thus has to be evaluated.

On large scale oscillation of MS it is really not significantly increase in this intervals (if compare MS of sediment of cold stages and MS of sediments of warm stages). But we study distribution of MS in cold intervals also. And we saw that inside of some cold intervals (where MS is very low) the variations of MS are also. Some intervals with "high MS" correlated with enriched in P_2O_5, MnO intervals and we suppose that in this levels could be present vivianite nodules and reflect some environmental or climate signal. We will compare our data with pollen that will help with interpretation.
In general variation of MS in Lake El'gygytgyn is complicated. There are plenty thin intervals of high and low of MS along the core profile. It in not mean that they reflect of shot cold and warm climate events. In this paper we don't try to explain all variations of MS. Some spikes of MS possible are due greigite (we found this minerals at few levels), some due to pieces of rocks.

C. Technical corrections (Page numbers refer to PDF version)

Page 4990, line 4: Please replace 'weight' by 'mass-specific'

Corrected

5: add hyphen to 'field-dependent'

Corrected

6: omit 'the' before 'saturation magnetization'

Corrected

12: replace 'product' by 'the respective products'

Corrected

13: add hyphen to 'high-temperature'

Corrected

14: replace #dependence' by 'dependent'

Corrected

17: replace 'mixture' by 'mixtures'

Corrected

19: replace 'produces' by 'lead to'

Corrected

24: insert 'a' between 'in' and 'variety'

Corrected

26: replace 'phosphorous' by 'phosphorus'

Corrected

Page 4991, lines 24-27: Give a more detailed motivation for the outcome of your study

We change text

"In this paper we investigate the magnetic properties, especially those at high temperature (up to 700°C), for vivianite nodules found in the sediments of Lake El'gygytgyn in northeast Siberia. Magnetic behavior of vivianite particles and nodules is important to overall the interpretation of magnetic properties of lacustrine sediments that are used as environmental proxies. At room temperature the susceptibility of El'gygytgyn Lake nodules is close to 1×10^{-6} m^3/kg; this is higher than MS of cold stage sediment, but lower than MS of warm stage sediment. Sediment of high and low magnetic parameters shows different curves of temperature dependence magnetic susceptibility. Cooling curves plot above heating curves for samples from cold climate intervals indicating formation of new higher susceptibility phases and possibly as the result of vivianite alteration."

Page 4992, line 2: turn 'El'gygytgyn Lake' into 'Lake El'gygytgyn '

Corrected

Page 4993, line 7: Please replace 'weight' by 'mass-specific'

Corrected

8: replace 'field dependent and frequency dependent' by 'field-dependent and frequency-dependent'

Corrected

10: omit 'the' before 'magnetization'

Corrected

13: omit 'the' before 'saturation'

Corrected

14: replace 'in field 500 mT' by 'in a field of 500 mT'

Corrected

15: is it really 100_/min?

Yes

21: add the term 'microprobe' after 'CAMEBAX' if this is correct

Corrected

Page 4994, line 6: Please replace 'Surface of nodules is' by 'Surfaces of nodules are'

Corrected

22: replace 'phosphorous' by 'phosphorus'

Corrected

22/23: replace 'coefficient correlation' by 'correlation coefficient'

Corrected

23: is it really 0.55 in both cases

It is correct

24: replace 'phosphorous' by 'phosphorus'
Corrected
Page 4995, line 1: Interval is 24.31 – 24.73 not very prominent
8: replace 'polish' by 'polished'
Corrected
13: 'attracted to a magnet in hand samples' ? Is this meant? Please reword this.
We change sentence as:
"Some of the studied vivianite nodules were attracted to a hand magnet."

16: replace 'phosphorous' by 'phosphorus'
Corrected
23: replace 'included' by 'include' and 'content' by 'contents'
Corrected
24: Suggestion: 'show' or 'appear in' instead of 'take on'
Corrected
Page 4996, line 7: replace 'low MS intervals' by 'intervals of low MS'
Corrected
8: replace 'low magnetic' by 'low-magnetic'
Corrected
9: replace 'high magnetic' by 'high-magnetic'
Corrected
12: omit 'the' before' magnetic'
Corrected
14: replace 'susceptibility' by 'susceptibilities'
Corrected
19: replace 'mA' by 'A/m'
Corrected
21: omit 'the' before 'very'
Corrected
Page 4997, line 1: replace 'High temperature' by 'High-temperature'
Corrected
5: Suggestion 'split' instead of 'broken down'
Corrected
9: omit 'the' before 'heating'
Corrected
15/16: replace ' curves' by 'curve'
Corrected
20: insert 'the' between 'have' and 'same', insert 'the' before 'cooling'
Corrected
21: replace 'curves' by 'curve', insert 'the' before 'second', insert 'the' before 'sharp'
Corrected
23: Omit 'the' before 'samples'; replace 'mA' by 'A/m'
24: replace 'mA' by 'A/m'
We insert mT
25: is it really 'higher temperature'? Or was meant 'higher-coercive'?
Sentence was changed:

"Coercive force decreases from 50.3 to 20 mT and coercivity of remanence decreases from 91 to 56 mT after heating runs suggesting the formation of a lower coercivity magnetic phase".
Page 4998, line 1: replace 'Non reversible' by 'Non-reversible'
Corrected
2: omit 'the' before 'heating'
Corrected
3: replace 'shows' by 'show'
Corrected
4: replace 'a presence' by 'the presence', replace 'curves' by 'curve'
Corrected

5: replace 'after' by 'below'
Corrected
6: omit 'the' before 'susceptibility'
Corrected
7: replace 'curves of the second run are similar as for 1st type curve and display' by 'curve of the 2nd run is similar to that of the 1st run and displays'
Corrected
10: omit 'the' before 'susceptibility'
Corrected
16: replace 'In the samples shown In Fig. 7e the initial heating and cooling curves ' by 'For the sample shown In Fig. 7e the initial heating and cooling curves of the 1st run'
Corrected
25/26: There is no data of sample EV621 listed in Table 4. Even if this is just a typo (EV622 in Table 4) there is no Hcr/Hc for the first run. Thus it's hard to assess, which kind of particles have formed. Please clarify that.

Number Sample 621 must be sample 622 (our mistake). Impossible to determine Bc and Bcr (paramagnetic, see loops)

26: insert 'a' after 'of'
Corrected
Page 4999, 7: omit 'the'
Corrected
9: delete 's' in 'temperatures'
Corrected
12: replace 'hump' by 'humps'
Corrected
15: replace 'High temperature' by 'High-temperature'
Corrected
17: replace 'High temperature' by 'High-temperature'
Corrected
We move part of paragraph to **Materials and Method.**
We add more explanation why we use these additives:

"Crushed vivianite nodules were heated in air. Powder from several vivianite nodules were mixed with sucrose (organic carbon), carbamide (nitrogen compound $(NH_2)_2CO$), metallic powders of arsenic, and elemental sulfur, with the additives never being more then 5% of the total material. Samples were then heated continuously from room temperature to 700°C and cooled back to room temperature. Additives were used to simulate some chemical conditions in bottom sediments. Melles et al. (2007) show that El'gygytgyn Lake sediment, accumulated during cold climates, is enriched in total organic carbon, total sulfur, and total nitrogen. We found framboidal pyrite and fine grained greigite in the sediment. Some sulfides grains included in vivianite nodules and as heating products of decomposition of pyrite and greigite can affect on high temperature property of vivianite. Chalcopyrite (FeAsS) and impurity of arsenic in some pyrite framboids were determined by energy dispersive spectroscopy. Although arsenic was not found in El'gygytgyn vivianite nodules it could potentially be adsorbed onto vivianite (Thinnappan et al., 2008)."

23: omit 'and cooling' since cooling curve of sample EVSM+C (Fig. 9b) is different from those of samples EVSM and EVSM+N as is described on page 5000 lines 1 and 2
Corrected
27: replace 'as the temperature decrease' by 'as temperature decreases'
Corrected
Page 5000, line 3: replace 'greater' by 'higher'
Corrected
7: omit 'there' after 'although'
Corrected
7/8: replace 'temperature' by 'temperatures'
Corrected

8: omit 'the' before 'arsenic'
Corrected
10: suggestion: replace to 'sample does form magnetite' to 'sample indicates the formation of magnetite'
Corrected
28: please turn it around '580_C and 685_C' instead of '685_C and 580_C'
Corrected
Page 5001, line 22-24: Suggestion: reword sentence into 'On the cooling curves on both runs, no visible increase in susceptibility at the Curie temperature of monoclinic pyrrhotite is visible.'
Corrected
Page 5002, line 1: replace 'El'gygytgyn Lake' by 'Lake El'gygytgyn'
Corrected
4/5: Suggestion: Reword sentence into 'The nodules and concretions of vivianite amount to a few grams per sample along the core profile (..'
Corrected
8: insert 'the' before 'center'
Corrected
12: replace 'proxies' by 'archives'
Corrected
13: suggestion: change into 'core description, correlation and dating'
Corrected
15: replace 'antiferromagnetic' by 'anti-ferromagnetic'
Corrected
16: replace 'susceptibility' by 'susceptibilities'
Corrected
17: suggestion: replace 'lake sediments' by 'bulk sediments'
Corrected
18: omit 'the' before 'cold intervals'
Corrected
24: replace 'fine grained' by 'fine-grained'
Corrected
Page 5003, line 1: omit 'the' before vivianite
Corrected
6: suggestion: replace 'indicates' by 'reports'
Corrected
8: suggestion: replace 'indicate' by 'mention'
Corrected
14: replace 'low field' by 'low-field'
15: replace 'antiferromagnetic' by 'anti-ferromagnetic'
Corrected
20: Shouldn't it be the other way around: magnetic susceptibility is increased and, thus, the attraction to a magnet is increased
Corrected
24: replace 'low magnetic' by 'low-magnetic'
Corrected
26: insert 'the' before 'behavior', omit 'the' before 'mineralogical'
Corrected
26-29: This happens during heating experiments in the lab, but will it occur also under natural conditions. Please comment on this.
We add:
Such conditions occur in nature during peat deposit fires where vivianite often occur (Matukhina et al., 1986).
29: change into 'heated and cooled between room temperature and 700_C'
Corrected
Page 5004, line 7: insert 'of' before 'Fe2+'
Corrected
10/11: change 'temperature' into 'temperatures of'
Corrected
11: replace 'marks' by 'mark'
Corrected

15: replace 'a-FePO4' by 'alpha-FePO4'
Corrected
24: reword into 'monoclinic or hexagonal pyrrhotite is produced'
Corrected
Page 5005, line 2: reword into 'On the third run the temperature has increased to 650_C.'
Corrected
3: replace 'then' by 'than that of hematite and closer to that of maghemite'
Corrected
4: omit 'the' before 'single'
Corrected
16:/17: reword into '..at higher temperatures is of the same amount as that which had formed . . .'
Corrected
25: replace 'indicates' by 'indicate'
Corrected
28: reword into '. . .at a temperature of 320_C, is formed'
Corrected
Page 5006, line3: replace 'diagnostic' by 'diagnose'
Corrected
11: replace 'mixture' by 'mixture
Corrected
23: omit 'the' before 'cold'; replace 'can then' by 'may'
Corrected
26: please rephrase 'due to the respective products of oxidation'
Corrected
Page 5007, line 1: add hyphen to 'high temperature'
Corrected
3: replace 'act' by 'acts'
Corrected
7: replace 'shows' by 'show'
Corrected
Tables and Figures:
Table 1: replace 'El'gygytgyn Lake' by 'Lake El'gygytgyn'
Corrected
Table 2: Why are Mn and Fe not both normalized by P?
Corrected.
Mn and Fe both are normalized by P now.
Table 4: Please add units for hysteresis parameters; EV-622-1 is EV-621-1 in Fig. 7f, please check
Corrected, we add units. In fig.7 EV-621 is wrong number
Fig. 3: From my perspective, this diagram is too small to see much from it. Omit all depth scales or at least tick labels except the left most one. Caption: replace 'sediments samples' by 'sediment samples'. Why is the topmost 5 m sediment missing? Thus it is not 28 m of core material but 23 m.

Capture is corrected. We enlarge Figure 3.
Because of drilling problem we lost upper 5 m sediments.
Fig. 4: The diagrams, not the photographs, are much too small
We think that figure 4 in printed variant will be bigger but in any way we enlarge font and line width.

Fig. 5: It seems that there is only a poor linear correlation. Thus R2 may be not much meaningful. Please add how R2 was calculated (Pearson's r?)

On figures R^2 is not Pearson correlation coefficient. It is linear regression coefficient or linear trend. In text coefficient correlation of Pearson market as r.

Fig. 6: What does 'representative' means? Please explain.
This is typical samples from groups. Sentence was changed as:
"Susceptibility versus temperature (in air) curves (a,c,e) of representative vivianite samples of groups…."

Fig. 7: Run 2 is missing in Fig. 7d).
Yes, we lost sample, no data
Please add an explanation for the dashed lines.
We add: where dash line – hysteresis loops of samples before heating
Caption: replace 'cursive number shows' by 'cursive numbers show'
Caption is corrected
Fig. 8: 'mA/m2' is not a unit for 'magnetization', please correct. Caption: replace 'cursive number shows' by 'cursive numbers show'
mA/m^2 was replace by Am^2/kg
Caption is corrected also
Fig. 10: Caption: Replace 'indicates' by 'indicate'
Corrected

Interactive comment on "Thermomagnetic properties of vivianite nodules, Lake El'gygytgyn, Northeast Russia" by P. S. Minyuk et al.

M.J. Dekkers (Referee)

This manuscript reports an analysis of the temperature dependence of the susceptibility and magnetization of vivianite nodules in lake sediments in NE Russia in an attempt to further explore the paleoclimate information that potentially can be retrieved from them. While the material discussed is worthwhile, the present version is rather tedious to read. The linkage between the experiments and their potential climate implications is only loosely returned to in the discussion which leaves readers rather 'open-ended'. I recommend revision of the material according to the lines set out in my review below taking into consideration the specific points raised. The discussion section would benefit from a number of thematic subsections (3?) to create more structure. One of those could be used to emphasize the paleoclimate implications of the vivianite nodules in this setting.
Specific
Abstract
Presumably susceptibility and hysteresis data were acquired at room temperature. This makes me wondering whether vivianite properties are reported since it is paramagnetic above _12 Kelvin. How can it show magnetic hysteresis at room temperature? Are included iron oxide impurities being measured? Saturation magnetization should be zero. Later on (line 12-13) this can be read in between the lines. Apparently the vivianite prominence is associated with warm climate episodes. The abstract would benefit from a concise mentioning of the (presumed) relation between vivianite and climate. The final part of the abstract is not that clear, is the hematite and goethite present as well in the sediments? These are anoxic? Why would a vivianite-sulfur mixture be heated? What is the potential environmental relevance? Also why arsenic is added (to kill ongoing microbial action that potentially biases environmental interpretation?) should be explained at some point in the paper. Heating experimental(?) vivianite-pyrite mixtures could have bearing on interpretation of anoxic sediments. Be aware that pyrite is relatively uncommon in freshwater lake sediments where vivianite is often reported. All in all the second half of the abstract reads detailed.

We response on this suggestions in text and see our corrections below

4990 line 4 weight = mass-specific
Corrected

1 Introduction
Next to dissolution of iron oxides also desorption of ferrous iron from silicates is an important source of iron.
4990 line 25. ferric = ferrous
We replace ferric with ferrous and change sentence as "This authigenic mineral forms when anoxic environments provide readily available ferrous iron, usually dissolution products of iron oxides, desorption of iron-bearing silicates, and inorganic phosphorous"

4991 lines 13- 16. I read that vivianite is often(?) partially oxidized as Fe2+ becomes Fe3+, how can it act as reductor in such cases?

We guess that may be phosphor is reductor

4991 line 18. With surface temperature you imply ambient temperature? Vivianite is paramagnetic at that temperature.

Corrected to "The magnetic properties of vivianite are well-known (Meijer et al., 1967), and although it is paramagnetic in natural environments and ambient temperature, it becomes antiferromagnetic at exceedingly low temperature with a Néel temperature of ~12K (Meijer et al., 1967; Frederichs et al., 2003)".

4991 line 22. Is the room temperature value quoted from Frederichs et al. (2003)?

Room temperature values of MS are our data.
We remove "*at room temperature the susceptibility of El'gygytgyn Lake nodules is close to 1 × 10^{-6} m^3/kg.*" to the next paragraph.

4991 line 23. What temperature range you infer with 'high temperature'? Up to 700_C? Be specific. Presumably the vivianite nodules alter on heating; (most of) this study will pertain to a magnetic analysis of these alteration products? What about the heating atmosphere?

We change text from these lines as:
"In this paper we investigate the magnetic properties, especially those at high temperature (up to 700°C), for vivianite nodules found in the sediments of Lake El'gygytgyn in northeast Siberia. Magnetic behavior of vivianite particles and nodules is important to overall the interpretation of magnetic properties of lacustrine sediments that are used as environmental proxies. At room temperature the susceptibility of El'gygytgyn Lake nodules is close to 1×10^{-6} m^3/kg; this is higher than MS of cold stage sediment, but lower than MS of warm stage sediment. Sediment of high and low magnetic parameters shows different curves of temperature dependence magnetic susceptibility. Cooling curves plot above heating curves for samples from cold climate intervals indicating formation of new higher susceptibility phases possibly as the result of vivianite alteration. "

4991 line 24-27. Finally it is made clear that magnetic properties of vivianite are largely dependent on the presence of magnetite inclusions. I bet that all room temperature magnetic hysteresis, remanence and saturation magnetization are due to these inclusions. For the sake of environmental interpretation it would be neat to know whether the vivianite nodules contain more, less or a similar amount of magnetite grains as 'normal' sediment.

Yes. We agree that magnetic properties of vivianite are largely dependent on the presence of magnetite inclusions but depend on oxidation product also. "Oxidation" was added in text. We change "magnetite" inclusion to magnetic inclusion because in vivianite we found different magnetic minerals (titanomagnetite, greigite, iron).
We can't to determine amount of magnetic grains in vivianite nodules and in sediment including of nodules. But because of MS of sediment including of nodules is higher then MS of nodules (we show this in table 3) we suppose that sediment are more enriched with magnetic grains.

2 Geologic setting
4992 line 16. I read that the age model for the core was established elsewhere (Nowaczyk et al., 2012). However, for the sake being informative it would be good to provide the essential outcome of that study. Was the lake site covered with glacier ice during the Quaternary glaciations so essentially no sedimentation took place during those times?

We add more information to this section:

"Geomorphological data indicates that the crater has never been glaciated (Glushkova, 2001) and no hiastus in sedimentation is observed (Melles et al., 2011).
Chronology of the entire package has been established using paleomagnetic time scale with detailed tuning to the marine oxygen isotope record and insolation variations (Melles et al., 2012; Nowaczyk et al., this issue).). Biological, physical and chemical proxies reflect glacial/interglacial climatic conditions (Melles et al., 2012). During cold climatic stages

conditions included perennial lake ice, oxygen-depleted bottom waters, absence of bioturbation and enhanced preservation of organic matter (Melles et al., 2007), resulting in the dissolution of magnetic minerals (Nowaczyk et al., 2002). A perennial ice cover on the lake obviously restricted the transport of coarse-grained sediments but enabled finer particles to be transported to central part of lake basin through cracks or moats around the shore in during summer (Asikainen et al., 2007).
Sediment from cold climate stages are enriched in Al_2O_3, MgO, TiO_2, Fe_2O_3, Ni, Cr, and have high MS (Minyuk et al., 2007; Minyuk et al., this issue). During warm climate periods conditions include seasonal ice cover, decomposition of organic matter in bottom waters, oxic conditions, high level of bioturbation, low dissolution of magnetic minerals, and input of less chemical altered material. The resulting sediment is characterized by high content of CaO, NaO, SiO_2, K_2O, Sr, and low values of organic carbon, sulfar, nitrogen."

What is the age range of the sediments and from which age range the sample for this study were taken? Are you investigating glacial-interglacial climate expression on vivianite nodules for example?

We studied vivianite nodules from depth interval 5.67–28 m with ages 125.1–682.5 ky. This information we put in section **Materials and method**:

"Vivianite nodules and pieces were collected down continuous core (Core 1A, 1B of ICDP site 5011) from 5.67 to 28 meters in composite depth with ages 125.1–682.5 ky (Melles et al., 2012)".

4992 line 22-23. Vivianite was recognized by low-temperature magnetic measurements. Down to 4K? Be more specific here.
We add:
"Fine-grained dispersed vivianite has been recognized using low-temperature magnetic measurements down to 10 K (Murdock et al, this issue)".

4992 line 23-26. The phrasing reads somehow confusing to me. These claimed diagenetic microenvironments probably bear some relation with prevailing climatic conditions? E.g. more organic matter during warmer climate, more detrital material during glacial climate?

"Due to the ubiquitous occurrence of vivianite in cold (anoxic) and warm (oxic) stage sediments, Minyuk et al. (2007) conclude its formation is controlled by diagenetic microenvironments and not influenced by large-scale climate conditions."

Also what is the present study going to add with respect to Minyuk et al. (2007)?

In paper Minyuk et al. (2007) there are no any magnetic and thermomagnetic data of vivianite nodules.

3 Materials and methods
Provide typical sample masses, typical signal-to-noise ratios for all instruments used. The heating rate of 100_/min in the Curie balance is very rapid. What about potential thermal lagging of the sample? Can you cool that fast as well? Can you compare the magnetization behaviour with the thermal behaviour of the magnetic susceptibility that was warmed an order of magnitude slower?

"Temperature-dependent susceptibility (k-T) of crushed nodules was measured continuously from room temperature up to 700°C and back to room temperature using a kappabridge MFK1-FA equipped with a CS-3 high-temperature furnace (AGICO Ltd., Brno, Czech Republic) with sensitivity 1×10^{-7} SI and maximum specimen volume 0.25 cm^3. The heating and cooling rates were 10-12°C/min. Software CUREVAL ver.8.0.1. (http://www.agico.com/) was used for resolution of susceptibility into ferromagnetic and paramagnetic components based on Curie-Weiss law (Hrouda, 1994) and for Curie temperatures estimation using two-tangent method (Petrovský and Kapička, 2006).

Crushed vivianite nodules were heated in air. Powders from several vivianite nodules were mixed with sucrose (organic carbon), carbamide (nitrogen compound $(NH_2)_2CO$), metallic powders of arsenic, and elemental sulfur, with the additives never being more then 5% of the total material. Samples were then heated continuously from room temperature to 700°C and cooled back to room temperature. Additives were used to simulate some chemical conditions in bottom sediments. Melles et al. (2007) show that El'gygytgyn Lake sediment, accumulated during cold climates, is enriched in total organic carbon, total sulfur, and total nitrogen. We found framboidal pyrite and fine grained greigite in the sediment. Some sulfides grains included in vivianite nodules and as heating products of decomposition of pyrite and greigite can affect on high temperature property of vivianite. Chalcopyrite (FeAsS) and impurity of arsenic in some pyrite framboids were determined by energy dispersive spectroscopy. Although arsenic was not found in El'gygytgyn vivianite nodules it could potentially be adsorbed onto vivianite (Thinnappan et al., 2008). To study affect vivianite on other minerals during heating selected vivianite samples were heated with hematite and goethite, both of which were also detected in the sediments.
Electron-microprobe (EMP) analyses of polished nodules mounted in epoxy resin were performed using "Camebax" microprobe (manufactured by Cameca Instruments in France) under an accelerating voltage of 25 kV and electron-beam spot-size of 4 μm. Crystal LIF for FeK_α and MnK_α-lines, and crystal PET for PK_α-lines were used. The standards used were hematite (Fe), apatite (P) and $MnTiO_3$ (Mn)."
4993 line 23. studs = stubs

Corrected to stubs

4993 line 27-29. Apparently the sediment and vivianite nodules were separated and the sediment was analysed chemically with XRF. What is the relation with the magnetic properties of the vivianite nodules?

Not all nodules were separated – only the large (>250 μm) nodules. We add this to text.

***Results 4.1 microprobe analyses** – sediments and nodules (please, note that the order in the text is nodules first followed by sediments)*

Corrected: **Microprobe analyses – nodules and sediments**

4994 line12-16. The compositional variability of the vivianite nodules is described here. How do these compare to other nodules reported in the literature?

We add some literature data on nodules composition.

"This composition is very close to the composition of vivianite nodules from lacustrine sediment in Greece (Stamatakis and Koukouzas, 2001): Fe_2O_3 – (36.67–38.04%), MnO – (2.53–2.66%), P_2O_5 – (21.92–24.81%). On the other hand, nodules from Baikal Lake sediment are enriched in MnO but depleted in P_2O_5 (Fagel et al., 2006). Except for MnO, trace Mg and Zn were detected in vivianite nodules from Bolivia (Rodgers et al., 1993)."

4994 line 17ff. The sediments have only been measured for Fe, P and Mn as well? No Si, Al, Mg, Ca etc. data are available?

We cited papers where distribution of major and rare elements is available:
"Major elements determination was performed on sediment samples from which vivianite nodules were removed (Minyuk et al., 2007, 2012)"

In figure 3 the P2O5 contents seem to have a base level of _0.1%. Yet there are spikes with higher P2O5, is that due to incomplete nodule removal?

Yes, due to incomplete nodules removal

The only reasonable phosphate mineral is apatite and I do not see a reason why that would vary so much with time given the catchment size of the lake. Visually Mn and P seem to correlate indicating a common source, i.e. the vivianite?

Yes, we don't think that apatite is responsible for phosphor spikes. On phosphor spike levels there are no any correlation between P_2O_5 and CaO (main element of apatite).
"The phosphate mineral apatite is not responsible for phosphorus spikes because of the absence of correlation between phosphorus and calcium, the main elements of apatite."
Can you correct the Fe2O3 trends for remaining vivianite? Perhaps it is nice to show scatter plots of Mn vs P and Fe vs P.

New Figure - Fe vs P and Fe vs Mn was added

4.2 Scanning electron microscopy and energy dispersive spectroscopy
4995 line 8. polish = polished

Corrected

4995 line 15. Greigite is a very plausible option but pyrrhotite should not be excluded beforehand. Both have distinct thermomagnetic properties that can be utilized for their discrimination.

Greigite was fond at some level, so we left greigite

4995 line 20-22.
This reads as suggesting metallic iron in traces (how much, one per mil, seen twice?). Apparently this instrument can measure O, are those Fe-rich patches really not ferrihydrite, goethite, hydrohematite? How can you get metallic iron? Or is it a left-over of the impact?

We found iron in one nodule only. Yes, QuemScan can measure oxygen. Grain of iron is without oxygen. At backscattered electron image this grain is very bright and differs from magnetite-titanomagnetite grains. We don't discuss here origin of iron. It is possible a volcanic or impact origin. But we sure it is not chips of metal from drilling pipe and bits which are plenty.

4.3 Magnetic susceptibility of vivianite nodules
4996 line 2-12. Can this information better be put in a table (or below table 3)?

Because of in table 3 there are different columns we left this information as is. But we hope in printed variant this data will locate close to table 3.

*4996 line 8-12. From what I read is that the bulk sediment susceptibility includes the vivianite nodules? Then the mass of the nodules determines in part the variability of the bulk sediment? Vivianite values vary between _0.86 and _1.5*10^-6 m^3/kg. Is this due to changing ferrous and ferric iron (the latter has higher susceptibility in the spin-only paramagnetic model)? Or due to amount of inclusions? Figure 5 suggests the latter. How do numbers compare to other vivianite values?*

We think that MS of vivianite nodules is both due oxidation of vivianite and magnetic inclusions in nodules. Yes, figure 5 (now figure 6) demonstrate then higher MS of sediment then higher MS of nodules. This is evidence of effect on MS of amount of inclusions. On other hand MS of nodules from low magnetic susceptibility sediment is higher then values MS of low magnetic susceptibility sediments. Here we think MS of oxidation product of vivianite dominate.

4996 line 14. This minimum value relates to vivianite being a paramagnet with a distinct, positive low-field susceptibility.

We agree. But MS of sediment from "low magnetic intervals" (cold climate stages) show much lower values of MS. And we emphasize that MS of nodules is higher.

4.4 Field variation of susceptibility
4996 line 19. Change mA to A/m since that is the field range of the MFK1 instrument.

Corrected

Paramagnets should show no field dependence which concurs with measurements. Combine sections 4.3 and 4.4? Leave out figure 6 or move it to a supplementary information section?

Figure 6 is deleted. We combine section 4.3 and 4.4.

4.5 High-temperature dependence of magnetic susceptibility
4997 line 2-4. This information can be transferred to the methods section, at least in my view.

Such information is in **Materials and Methodic**

Why didn't you measure 'incremental' heating runs, e.g. heating to 400_C back to 300_C heating to 500_C back to 400_C, heating to 620_C back to 500_C and only then to 700_C and back to room temperature? In this way a better discrimination between magnetic phenomena and thermochemical alteration can be made. Also please note that unless air is actively pumped into the furnace tube, the heating atmosphere essentially is oxygen-free above 250_C or so since burning organic matter uses up the small volume of oxygen available in the tube.

Almost all heating curves of 1st run are "flat" so it was no sense to heat to and back. But you are right. For second and 3rd runs it will be very useful. We will do this

4.5.1
4997 line 10-12. Also figure 7a. The susceptibility increase in run1 at 500_C suggests the production of a magnetic phase, probably magnetite. Is this because vivianite alters? It is remarkable that with continued cycling the susceptibility maximum drops to lower temperatures.

Because of not all vivianite nodules show increase MS at 500°C it is not vivianite indicator, so we think that some product of vivianite oxidation (or inclusion –sulphides?) response for formation of magnetite formation.

4997 line 12. How was the Curie point determined? The two-tangent method is less applicable to susceptibility vs. temperature runs. See Petrovsky and Kapicka (JGR 2006, vol 111 B12, art# B12S27 DOI: 10.1029/2006JB004507) for an overview.

We explain and put in **Materials and Method:**

"Software CUREVAL ver.8.0.1. (http://www.agico.com/) was used for resolution of susceptibility into ferromagnetic and paramagnetic components based on Curie-Weiss law (Hrouda, 1994) and for Curie temperatures estimation using two-tangent method (Petrovský and Kapička, 2006)."

4.5.2 4998 line 7. You mean similar to the first heating cycle shown in figure 7c? Or do you imply the second heating cycle displayed in figure 7a? Be more specific to avoid potential confusion.

We change sentence:

"The heating curve of the second run is similar to the heating curve of the second run of the 1st curve class (Fig. 7a) and displays an increase in susceptibility at 330–350°C and a sharp drop at 615°C"

4998 line 14. Make certain that you infer slope-corrected parameters and ratios here.

It is correct

4.5.3 4998 line 18. How was the percentage calculated? Phrase something on it in the methods section?

We explain and put in **Materials and Method:**

"Software CUREVAL ver.8.0.1. (http://www.agico.com/) was used for resolution of susceptibility into ferromagnetic and paramagnetic components based on Curie-Weiss law (Hrouda, 1994) and for Curie temperatures estimation using two-tangent method (Petrovský and Kapička, 2006)."

4998 line 20. Hematite is rather difficult to see in general in susceptibility vs. temperature runs because its low-field susceptibility differs not that much for values for typical paramagnetic material. As with antiferromagnets its susceptibility maximum at the Néel temperature is often rather broad making its distinction not straightforward.

We agree that hematite is difficult to see on curves.

4998 line 26. I am not that sure of the MD claim. Jrs/Js(corrected) is 0.1-0.15 which could be as well indicating PSD particles. However, giving its low signal, the slope correction is critical. With low amounts of (presumably) magnetite-like minerals produced it is unlikely that these would form a relatively small number of comparatively large particles (i.e. MD). You have to diffuse the ions that make up the particle over a large distance. I am in favour of interacting nominally SP particles that also plot in that portion of the Day plot.
We agree.

4.6 saturation magnetization vs. temperature
From visual inspection of figure 8 it appears that the magnetization vs. temperature plots show a dominance of the paramagnetic contribution to the total signal. The curves have a distinct hyperbola shape. That paramagnetic part is not saturated for sure. What was the temperature increment of the actually measured data points? The curves have an interpolated/smoothed appearance. It would have been nice to have cooled the first curves (1) from ca. 250_C to provide explicit information on 'humps' that are being formed. The second paragraph of this section involves a comparison with the susceptibility vs. temperature runs. Two aspects:
1) magnetization vs. temperature curves are dominated by the temperature dependence of the (saturation) magnetization. Low-field susceptibility is distinctly less temperature dependent (it pertains to reversible magnetic phenomena), so it may show other phenomena for the same sample.
2) the heating atmosphere may be different. Do you have a suggestion for this observed difference? It is somehow intriguing.

We change text and use induced magnetization instead saturation magnetization. The temperature increment of the actually measured data points was 2° then curves were smoothed (5°).

4.7 High temperature behaviour of vivianite with additive material
The first paragraph of the section should be transferred to the methods section. In my view it is best to have all methods assembled in one section. This gives a reader a good impression what can be expected in the remainder of the paper. What is added here with respect to Minyuk et al. (2011)? It could be read as that the results are being published twice.
I would mention in one sentence the purpose of these 'additives' experiments, why would you add these materials? Why the focus is somehow on the susceptibility vs. temperature experiments? We've just been informed that magnetization vs. temperature can yield different results.

We move part of paragraph to **Marerials and Metod.**
We add more explanation why we use these additives:

"Crushed vivianite nodules were heated in air. Powders from several vivianite nodules were mixed with sucrose (organic carbon), carbamide (nitrogen compound $(NH_2)_2CO$), metallic powders of arsenic, and elemental sulfur, with the additives never being more then 5% of the total material. Samples were then heated continuously from room temperature to 700°C and cooled back to room temperature. Additives were used to simulate some chemical conditions in bottom sediments. Melles et al. (2007) show that El'gygytgyn Lake sediment, accumulated during cold climates, is enriched in total organic carbon, total sulfur, and total nitrogen. We found framboidal pyrite and fine grained greigite in the sediment. Some sulfides grains included in vivianite nodules and as heating products of decomposition of pyrite and greigite can affect on high temperature property of vivianite. Chalcopyrite (FeAsS) and impurity of arsenic in some pyrite framboids were determined by energy dispersive spectroscopy. Although arsenic was not found in El'gygytgyn vivianite nodules it could potentially be adsorbed onto vivianite (Thinnappan et al., 2008)."
4999 line 23-24. In figure 9a-c I see notably different cooling curves, i.e. different in the expression of (presumably) a Hopkinson-style peak. What are the decomposition temperature-ranges of sucrose and carbamide? Somewhere in between 100-200_C? Presumably all oxygen is driven out of the furnace tube by their decomposition.

We agree

5000 line 4. Do we recall what the 'first type k-T non-reversible curves' imply?
A vivianite sample representative of first type k-T non-reversible curves with increase MS during heating was heated with arsenic.
5000 line 9-11. Magnetite is not formed at 580_C during the cooling curve: it is formed somewhere between 580 and 700_C and becomes visible by its magnetic ordering only when being cooled through 580_C. Note that the cooling curves are not shown. Curiosity: what happens to the As? It could form compounds with chalcopyrite and suppressing thereby magnetite formation. It is a volatile element that preferentially vaporizes.
Sentence was corrected:
"The cooling curve for the arsenic-added sample indicate the formation magnetite between 580°C and 700°C and shows a steep increase to 450°–500°C as seen in the previous examples".

Yes, arsenic could form compounds. But we didn't study this. You are right, metallic arsenic vaporize we saw that arsenic was condensed on wall of vial after cooling.

5000 line 16-18. Here the incremental heating runs 200-400-600_C are carried out. Why not apply this strategy to other situations as well?
5000 line 21-24. Why are these experiments with goethite and hematite being reported here? The work deals with vivianite nodules? Is there a relation with the susceptibility increase and the amount of sulphur added?

Our plan was to find what product oxidation of vivianite is. It could be hematite or/and goethite. We know and show if hematite and goethite heat with sulfur it will form a lot magnetite and MS significant increase. We heat vivianite and sulfur (sample EVSM fig 9a and 9g) and saw that pyrrhotite was formed no any magnetite.

5000 line 25-26. I bet elemental sulphur has more reducing power than vivianite when expressed on a molar basis. What are the decomposition products of vivianite, can you suggest a mineral reaction? Do the data indicate a complete reaction?

Yes, sulphur has more reducing power, we change sentence:

"Mixtures of vivianite and either hematite or goethite show vivianite to play the reducing role but less that sulfur does"

5001 line 16-25. Pyrrhotite lambda transition discussion. Lambda pyrrhotite has the NA superstructure while monoclinic pyrrhotite has 4C. Hexagonal pyrrhotite (antiferromagnetic) has NC (all Morimoto's nomenclature). Lambda pyrrhotite changes to MC pyrrhotite at 265_C (seems to be antiferromagnetic as well). It remains metastably present when cooled faster than 1_C/minute or so through the lambda transition. So, indeed hexagonal pyrrhotite may form at high temperature, takes the NA structure during cooling but that remains the same all the way back room temperature because the cooling rate is too fast to form NC hexagonal pyrrhotite.

We agree
Monoclinic pyrrhotite is the iron-sulphur phase stable at high temperature. It is formed for example when roasting pyrite-bearing coal; it can be magnetically separated from such coals. This is done industrially to reduce the SO2 output from electrical power plants that burn sulphur-rich coals. Please note that Dekkers (1989b) reported excerpts from the literature, he did not measure lambda transitions thermomagnetically himself in those days.
We agree.
5 Discussion
Insert a few thematic subheading to create structure. Now there are almost 5 pages without any, somewhat tedious for readers. I would reorganize the discussion section. I would first provide an account of the more technical aspects and then of the overall climate implications, the latter under a separate subheading. This distinctly helps the target audience, at least according to me. Most of the audience are probably slightly less interested in the technical aspects of interpretation of the thermomagnetic curves. Nonetheless that should be reported.

We reorganize the discussion section

5002 line 2. Siderite is mentioned here for the first time. It has thermomagnetic implications: it decomposes on heating (fine-grained siderite oxidizes at room temperature in a couple of weeks on exposure to air). The first paragraph can be transferred to the appropriate results section?

We have thermomagnetic and EDS data of siderite, pyrite, greigite as well as magnetite, maghemite, titanomagnetite but we don't publish data yet. We hope it will be separately paper.

5002 lines 10-19. This is the motivation for this study. Transfer to introduction?

We transfer this text to **Introduction:**

"Magnetic behavior of vivianite particles and nodules is important to overall the interpretation of magnetic properties of lacustrine sediments that are used as environmental proxies. At room temperature the susceptibility of El'gygytgyn Lake nodules is close to 1×10^{-6} m^3/kg; this is higher than MS of cold stage sediment, but lower than MS of warm stage sediment."

5002 lines 19-28. This reads result-like with the notable exception of the suggestion the vivianite nodules would form by direct precipitation from the lake water. Has this been suggested before? If so, provide the appropriate reference(s).

We change sentence and add reference:
"Large vivianite nodules are absent in Fe-P-Mn intervals suggesting possible precipitation of vivianite directly from lake water (e.g., Dean, 2002) that can be related to events of climate and environmental change?

5002 line 25. MS acronym used throughout manuscript?
We use

5003 lines 11-13. Close up with previous paragraph.
Corrected

5003 lines 19-020. What do you wish to convey with this sentence?
5003 lines 23-25. What do you wish to convey with this sentence?
Here we explain what is source of MS of nodules. If it will be only included material it was expect that MS nodules from low MS sediment intervals will be lower then MS of sediment because of we see that MS of nodules from high MS sediment interval is lower then MS of sediment.

5003 line 26. Insert a subsection here?
We insert subsection:

5.2 Interpretation of thermomagnetic data

5004 lines 1-7. Largely result-like. How can vivianite show a saturation magnetization, it is a paramagnetic material? I've mentioned this before.
Saturation magnetization was change to induced magnetization

5004 lines 8-17. Information from literature to frame the interpretation.
Yes, we use this information for interpretation TMA and add sentence:
"For interpretation of TMA results we use data from the literature of differential thermal analyses."
5004 lines 18-25. Relatively descriptive information.
Here we would like to show that hump on heating curves is not attributed to pyrite transformation.

5004 line 26-30. The linkage with goethite is made very rapidly here. It probably would benefit from some more introduction.
Yes, it is our suggesting only.

5005 lines 1-4. I wonder whether the phases are formed at these temperatures or whether you can see them because they have magnetic ordering temperature at that temperature. The line of reasoning to explain the maghemite allocation is rapidly developed.

We change sentence as:

"Continued cycling of samples from the first type shows in the second run drop of MS at ~620°C".

To identify this phases we have plan to make Mossbauer analysis in future.

5005 lines 4-8. The Jrs/Js(corrected) value of 0.84 is pretty high, is true saturation reached in the 0.5 Tesla field? The sample is dominated by paramagnetism, introducing a comparatively large uncertainty in Js(corrected). I would tone down the SD claim. It is indeed logical that grains grow (slightly) larger during further temperature cycling.

We agree. It is really large uncertainly in Is (corrected) data before heating. So we show uncorrected data for non heating samples in Table 4.

5005 lines 9-11. This statement is correct but is only loosely linked with the foregoing text.

5005 line 12. Insert a subsection here?

Influence heating media and Fe-bearing minerals on thermomagnetic properties of vivianite nodules

5005 lines 19-24. Indeed the interpretation is ambiguous. Would hexagonal pyrrhotite form on heating at such low temperatures? Note the notion that magnetization vs. temperature plots show the same(?) hump in this temperature range? There it was mentioned that such behaviour was not found in susceptibility vs. temperature runs. Is that contradicted here?

"A plausible explanation is that hump reflects the dehydration of vivianite that was invisible without sulfur."

5006 lines 7-9. I wonder how a phosphate phase would be able to suppress the dehydroxilation of goethite. The low-field susceptibility of goehite and hematite does not differ too much so their transformation is difficult to diagnose based on this information only. Also would it be possible that the susceptibility behaviour is essentially determined by vivianite?

We agree that it is impossible to suppress the dehydroxilation of goethite. We don't know what really is so we change sentence as:

During heating of goethite-vivianite mixture (1:1) the vivianite masks the goethite-hematite transition but stimulates formation of magnetite (Fig. 10f).

It is possible that during goethite-hematite transition is simultaneously reduction of hematite. We don't think that *the susceptibility behaviour is essentially determined by vivianite.* This both minerals that we used had almost same MS. Relative MS of vivianite (without correction on empty furnace) was -158.6, Relative MS of goethite (without correction on empty furnace) was -160.9).

Tables and figures

Figures 7 through 11 are rather small, in particular those figures with three panels next to each other. I am not aware of their final lay-outing, but some enlarging of the lettering and reduction of the number of minor axis ticks is recommended. Also the number of temperature indications along the abscissas could be halved so that the remaining can be enlarged.

We change font size on figures

Table 1. Analyze = analysis.

Corrected

I don't know the microprobe system that was used to acquire the data shown. Is it capable of measuring oxygen? It would be good to know which standards were used to calibrate the instrument (provide that information in the table caption?).

We add more information to section **Materials and method:**
"Electron-microprobe (EMP) analyses of polished nodules mounted in epoxy resin were performed using "Camebax" microprobe (manufactured by Cameca Instruments in France) under an accelerating voltage of 25 kV and electron-beam spot-size of 4 µm. Crystal LIF for FeK_α and MnK_α-lines, and crystal PET for PK_α-lines were used. The standards used were hematite (Fe), apatite (P) and $MnTiO_3$ (Mn)."

It is impossible to measure of oxygen.

Apparently some manganese has been substituted for iron, well possible in an anoxic natural environment. Do measured compositions match with Fe3(PO4)2.8H2O?
Or are the analyses expressed as P2O5, Fe2O3 and MnO forced to 100%?

Chemical composition were measured as oxides (without water) but in table Fe, P and Mn were normalized to 100%.

Table 4. Provide the units of the numeric values shown. I guess they are in mT (not mA as phrased in the main text). In that case it is better to speak of Bc and Bcr because mT pertains to magnetic induction B and not fieldstrength H, units of H are A/m. Important note: if the mA in the text should be A/m then numbers are incredibly small (0.1 mT = 79.57 A/m) and some conversion error has crept in.

We put units in table 4, H was corrected to B in mT

Jrs/Ji(uncorrected) is meaningless because the Ji value depends on the maximum field applied. Only the sloped-corrected Ji value is meaningful. Change the table accordingly. The same applies to Hc (Bc) only after slope correction it is meaningful.

Corrected

EV687 in figure 7 is not tabulated in table 4.

In table 4 are data of EV687 before heating, and after 1st run heating. There are no data after 2nd run heating.

EV621 in figure 7 is not tabulated in table 4.

Thank you. Number in figure 7 must be 622-1. Corrected

Figure 7b,d,f. What are the dashed lines? Do the hysteresis measurements pertain to the samples before the heating run with the number indicated? Probably but be specific to avoid potential confusion.

We change figure capture and add more explanation

Figure 8. Units along the ordinate are mAmˆ2 not mA/mˆ2.

mA/mˆ2 correct to Am^2/kg. We change font size also.

Figure 9. Panel 9d. AS = As.

Corrected

In panel f only heating curves are shown why there are no cooling curves of those experiments?

We add cooling curves