

Interactive comment on “Thermomagnetic properties of vivianite nodules, Lake El’gygytyn, Northeast Russia” by P. S. Minyuk et al.

M. J. Dekkers (Referee)

m.j.dekkers@uu.nl

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Review of “Thermomagnetic properties of vivianite nodules, Lake El’gygytyn, Northeast Russia” By Minyuk, Subbotnikova, Brown and Murdock Submitted for publication in Climate of the Past General 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

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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. 4990 line 4 weight = mass-specific

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 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? 4991 line 18. With surface temperature you imply ambient temperature? Vivianite is paramagnetic at that temperature. 4991 line 22. Is the room temperature value quoted from Frederichs et al. (2003)? 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? 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

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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.

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? 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? 4992 line 22-23. Vivianite was recognized by low-temperature magnetic measurements. Down to 4K? Be more specific here. 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? Also what is the present study going to add with respect to Minyuk et al. (2007)?

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? 4993 line 23. studs = 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?

Results

4.1 microprobe analyses – sediments and nodules (please, note that the order in the

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text is nodules first followed by sediments) 4994 line 12-16. The compositional variability of the vivianite nodules is described here. How do these compare to other nodules reported in the literature? 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? 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? 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? 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.

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

4.3 Magnetic susceptibility of vivianite nodules 4996 line 2-12. Can this information better be put in a table (or below 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 m³/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? 4996 line 14. This minimum value relates to vivianite being a paramagnet with a distinct, positive low-field susceptibility.

4.4 Field variation of susceptibility 4996 line 19. Change mA to A/m since that is the field range of the MFK1 instrument. Paramagnets should show no field dependence

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which concurs with measurements. Combine sections 4.3 and 4.4? Leave out figure 6 or move it to a supplementary information section?

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. 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. 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. 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. 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. 4998 line 14. Make certain that you infer slope-corrected parameters and ratios here. 4.5.3 4998 line 18. How was the percentage calculated? Phrase something on it in the methods section? 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. 4998 line 26. I am not that sure of the MD claim. $J_r/J_s(\text{corrected})$ 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

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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.

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.

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. 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

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decomposition. 5000 line 4. Do we recall what the 'first type k-T non-reversible curves' imply? 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. 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? 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? 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. 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.

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

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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.

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? 5002 lines 10-19. This is the motivation for this study. Transfer to introduction? 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). 5002 line 25. MS acronym used throughout manuscript? 5003 lines 11-13. Close up with previous paragraph. 5003 lines 19-20. What do you wish to convey with this sentence? 5003 lines 23-25. What do you wish to convey with this sentence? 5003 line 26. Insert a subsection here? 5004 lines 1-7. Largely result-like. How can vivianite show a saturation magnetization, it is a paramagnetic material? I've mentioned this before. 5004 lines 8-17. Information from literature to frame the interpretation. 5004 lines 18-25. Relatively descriptive information. 5004 line 26-30. The linkage with goethite is made very rapidly here. It probably would benefit from some more introduction. 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. 5005 lines 4-8. The J_r/J_s (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 J_s (corrected). I would tone down the SD claim. It is indeed logical that grains grow (slightly) larger during further temperature cycling. 5005 lines 9-11. This statement is correct but is only loosely linked with the foregoing text. 5005 line 12. Insert a subsection here? 5005 lines 19-24. Indeed

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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? 5006 lines 7-9. I wonder how a phosphate phase would be able to suppress the dehydroxylation of goethite. The low-field susceptibility of goethite 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?

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.

Table 1. Analyze = analysis. 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?). Apparently some manganese has been substituted for iron, well possible in an anoxic natural environment. Do measured compositions match with $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$? Or are the analyses expressed as P_2O_5 , Fe_2O_3 and MnO forced 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 B_c and B_{cr} 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 ($0.1 \text{ mT} = 79.57 \text{ A/m}$) and some conversion error has crept in. $J_r/J_i(\text{uncorrected})$ is meaningless because the J_i value depends on the maximum field applied. Only the sloped-corrected J_i value is meaningful. Change the table accordingly. The same applies to H_c (B_c) only

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after slope correction it is meaningful. EV687 in figure 7 is not tabulated in table 4. EV621 in figure 7 is not tabulated in table 4.

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.

Figure 8. Units along the ordinate are mA m^2 not mA/m^2 .

Figure 9. Panel 9d. AS = As. In panel f only heating curves are shown why there are no cooling curves of those experiments?

Best regards, Mark J. Dekkers

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