Ref: 608387

Title: **Ultrafine Magnetic Particles: A DIET-Proxy in Organic Rich Sediments?**
Journal: Frontiers in Earth Sciences

Answer to reviewers:

The authors would like to thank the reviewers for the contributions to this manuscript with their careful review. We believe that this manuscript was much improved after this revision round. In this document we address the questions and comments raised by the reviewers, making alterations in the manuscript main body when necessary. We hope to have clarified all questions about this work. All significant changes to the text are in red in the revised manuscript.

Reviewer 1

2. Please highlight the limitations and strengths.
Although the authors use valid and sensitive magnetic measurements for identification of superparamagnetic magnetite, their conclusions are difficult to follow and link to the exact environmental settings at study site. This weakness of the manuscript makes the analysis and data interpretation lacking solid proves for their hypothesis. The strength of the manuscript is in its approach combining experimental and modelling data.

Author's response: Thank you. We provided further information about the study site hopping intending to make easier the association between magnetic properties and occurrences of methane pockets. We hope the revised version shows more clearly the links between the different experimental data (magnetic analysis) and previous data (microbiological and gas composition analysis) that lead us to build our hypothesis.

3. Please comment on the methods, results and data interpretation. If there are any objective errors, or if the conclusions are not supported, you should detail your concerns.
Methodology is appropriate for the defined aims and scope of the study. however, there are some important weaknesses in data presentation and interpretation which need to be addressed. Interpretation of thermal demagnetization of magnetic susceptibility during cooling as reflecting goethite presence is wrong, as far as this mineral is formed at ambient conditions and transforms upon heating to hematite. Another weakness of the manuscript relates to the examples shown in the figures in support of the hypothesis for the microbially assisted formation of the superparamagnetic fraction – the authors show examples from the uppermost 2.5m of the sediment core, which, however are not considered by the authors to be of the same origin.

Author's response: Thank you for this critical analysis. Please see the answers to thermomagnetic analysis below. Regarding the reviewer's second concern, related to the hypothesis for the microbial assisted formation of the superparamagnetic fraction, we hope the revised manuscript is more explicit in presenting procedures to identify these specific magnetic signatures. We evaluate the presented methodology is adequate to identify these fingerprints and therefore this specific magnetic grains size range. However, the DIET magnetic signature is a possibility not proven at this stage. It is crucial that it's clear to the reader that even though DIET is a hypothesis, its association with magnetic properties is compatible with the model proposed for the DIET mechanism.

5. **Please provide your detailed review report to the editor and authors (including any comments on the Q4 Check List):**

1) Lines 29 – 31 from the abstract "The distribution of SP particles correlates well with the detected methanogens, suggesting that the microbial activity producing methane generates these ultra fine particles…." – this statement is not supported by the data, at least in the way they are presented.

Author's response: Thanks for pointing to this misleading statement. We actually mean that the higher SP particles content correlates well with the detected biogas, suggesting that the methanogens activity produces these ultrafine particles.

Changes: Page 2, line 30: "…The higher SP particles content correlates well with the detected biogas, suggesting that the methanogens activity produces these ultrafine particles, different from the magnetic particles at other depth levels."

2) It is not possible to locate the samples in the sediment column and assign them to organogenic sediments. I found in one of the cited papers (Mendonca et al., 2015b) site and sediments description, which is totally missing in the present manuscript. However, from this description it appears that at least half of the examples given come from the upper 0 – 2.5m anthropogenic sediments from the unsaturated zone, for which authors explicitly mention that are not included in their analysis (lines 323 – 325).

Author's response: We agree with the reviewer that site and samples descriptions were too short. Samples were cored every 0.5 m, from 0.5 to 10.5 m deep.

Changes: Page 9, line 189 "…magnetic properties within and in the vicinity of the methane pockets 21 sediment samples from direct pushing coring (every 0.5 m, from 0.5 to 10.5 m deep)were analysed with focus…"

3) Again in the Abstract authors speak about 'magnetization decay" experiments. In mineral magnetic studies this term applies to monitoring changes in magnetic remanence with elapsed time or temperature, or other demagnetizing agent. From experimental data in the manuscript it is not clear to me what exactly experiment is referred to by this expression.

Author's response: By magnetization decay, we mean time-dependent IRM, as proposed by Worn (1999). In the revised version, we adopted the expression "time-dependent IRM".

4) Lines 99 – 106 The paragraph explaining the properties and occurrence of magnetotactic bacteria and biogenic intracellular magnetite is not related to the subject and can be omitted.

Author's response: The sentence has been removed from the text.

5) Line 123 – Research site – please, add information on the type of sediments along the sediment column. Describe depth intervals with different rock types and mark those ones with supposed methanogenesis.

Author's response: In Mendonça et al (2015a), Fig 5 shows analytical results for the Well (gas composition; total organic carbon, sand grain, fraction in cored sediments and other parameters). The shallower horizon corresponds to the vadose zone, but two gas horizons are found below the water table (2.5 m), both of them embedded in an organic-rich layer of the Quaternary São Paulo Basin.

Changes:

Pg 6, line 140 "The area contains a series of anthropogenic deposits (~4 m) that overlies Quaternary fluvial sediments (~6 m) and Neogene sandstones…."

Pg7, line 145 "…Two main methane pockets were sampled along …"

6) Please, give also the age of the deposits, is there a soil on top of the section, which may be responsible for the observed higher magnetic susceptibility in the uppermost 2.5m?

Author's response: We don't have the age of the deposits. Nevertheless, it is difficult to interpret the site magnetic properties as natural sediments or soils (in term of their horizons development), due to the extent of anthropogenic sources. We interpret the higher susceptibility in the uppermost 2.5 m as characteristic of the unsaturated sediments.

Changes:
Pg 6, line 140 "The area contains a series of anthropogenic deposits (~4 m) that overlies Quaternary fluvial sediments (~6 m) and Neogene sandstones…."

Page 16, 352: "The high MS in the uppermost 2.5 m is attributed to the unsaturated sediments magnetic properties."

7) Lines 286 – 287 "The formation of new magnetite (and sometimes goethite, with an increase in magnetic susceptibility around 120oC) is supported by the irreversible behavior in the cooling curves, which exhibit higher values of magnetic susceptibility." Goethite presence on the cooling curve cannot be claimed as I explained at the beginning. Moreover, heating goethite in organic rich sediment most probably will result in magnetite formation due to reducing atmosphere from burning organic matter after 300oC.

Author's response: We now see that this sentence is misleading and we have removed the mention of goethite from the text.

8) Ferrihydrite presence is assumed without any experimental evidences or reference to previous studies.

Author's response: Ferrihydrite presence is assumed because the thermomagnetic curves show magnetic susceptibility changes during heating, between 250^o and 350^{o}C, indicating transformations of iron (hydr)oxides under a reducing atmosphere. Our measurements are compatible with some of the thermomagnetic curves presented by Hanesch et al. (2006) which show transformations of goethite at about 450^{o}C (see also Ponomar, 2018) and of ferrihydrite between 200^o and 350^{o}C. According with Hanesch et al. (2006), the exact temperature depends upon the crystallinity of the sample, the amount of organic carbonand the heating rate.

Ponomar, V. P. 2018. Thermomagnetic properties of the goethite transformation during high-temperature treatment, Minerals Engineering, 127, 143-152. https://doi.org/10.1016/j.mineng.2018.08.016.
Hanesch, H., Stanjek, H., Petersen, N. 2006. Thermomagnetic measurements of soil iron minerals: The role of organic carbon. Geophysical Journal International, 165, 53–61. https://doi.org/10.1111/j.1365-246X.2006.02933.x.

Changes: Pg 14, line 312 "All heating curves captured the magnetic susceptibility increase above 250 – 300 ^{o}C, indicating transformations of iron (hydr)oxides under a reducing atmosphere (Hanesch et al., 2006)"

9) Fig. 1 – a) and b) indexes are missing

Author's response: Thank you. Figure 1 doesn´t have a) and b). The text has been correct.

10) Fig. 2 – please, indicate the type of sediment for each example, what is the heating rate utilized and the atmosphere (air or Ar).

Author's response: Samples were heated at a 0.2^{o}C/second, in Ar atmosphere. The type of sediment of each sample were included in the figure captions. Thanks for this suggestion.

Changes:
Pg 10, line 213: "The measurements presented in this work were taken with Kappabridge KLY-4S at USPMAG (University of São Paulo), at the heating rate of 0.2^{o}C/second, under inert Ar atmosphere."
Pg 28-30:
Figure 2: … The samples are representative of the anthropogenic deposits (a-c) and the Quaternary sediments (organic (d-e).
Figure 3: FORC distribution of sample collected at (a) 2.5 m (anthropogenic deposit sediments) and at (b) 6.0 m (Quaternary sediments).

Figure 4: Hysteresis cycles at distinct temperatures: (a) 2.5 m and (b) 8 m. The samples are representative of the anthropogenic deposits (a) and Quaternary sediments ….

11) Fig. 3 – FORC diagram - why example from the upper depth interval (2.5m) is presented, while emphasis of the study is on the lower depths? At least you may present additionally example from deeper horizon with SP behavior.

Author's response: Thanks for this question. The authors agree this is not clear in the text. The FORC analyses show that at 2.5 m we have magnetite, as expected. In this revised manuscript we present a FORC image from a sample collected at 6.0 m, which shows a SP feature, in agreement with the occurrence of SP content detected by the SPCDM.

Pg 15, line 333: "Figure 3 (b) shows the FORC diagram from the sample collected at 6m (Quaternary sediments). A maximum coercivity peak close to the origin at around 5mT indicates a prevalent reversible component of magnetization (Sagnotti and Winkler, 2012), with open contours diverging asymmetrically on the *Bu* axis, showing resemblance to SP dominated population of grains (Roberts et al., 2014)."

Reviewer 2

5. **Please provide your detailed review report to the editor and authors (including any comments on the Q4 Check List):**

(1)
1.1. The authors should provide more discussion on the mechanism of magnetic enhancements of samples collected near the Tietê River.

Author's response: Thank you for this suggestion. Your comments, together with the first reviewer´s comments have helped us to enrich the discussion of this work.

1.2. Figure 5 shows that high magnetic susceptibility values can be found at depths of 1-2.5 m, 3.5-4 m, and 6-7 m. In contrast, the concentrations of superparamagnetic ferrimagnetic particles (SP) suggested by the parameter of η show high values at depths of 2-2.5 m, 5-6 m, and 10-10.5 m. These characteristics demonstrate that increasing content of SP ferrimagnetic particles alone cannot account for the variations of magnetic susceptibility of the samples. Thus, the authors should provide more evidence and discussion for this hypothesis.

Author's response: Thanks for raising this crucial observation that is not well discussed in the manuscript. This apparent contradiction results from the limitations of both the Frequency Dependent Susceptibility (FDS) and the Superparamagnetic Particles Concentration and Dipole Moment (SPCDM) methods. The FDS method captures a relaxation from magnetic particles within the SP-SSD threshold, in the 976-15616 Hz AC field frequency range. On the other hand, the SPCDM captures faster relaxations, which are produced by finer particles.

Figure 1 below illustrates the wide variation of relaxation frequencies and relaxation times from minor changes in diameter that would be expected from spherical particles of magnetite (mineral specific saturation magnetization σ*S*= 480 kAm−1, *K* = 2.31 × 104 Jm−3). The FDS with the Kappabridge frequenciesis able to capture relaxation signatures of coarser particles, when compared to the relaxations captured by the SPCDM, well suited for fast relaxations.

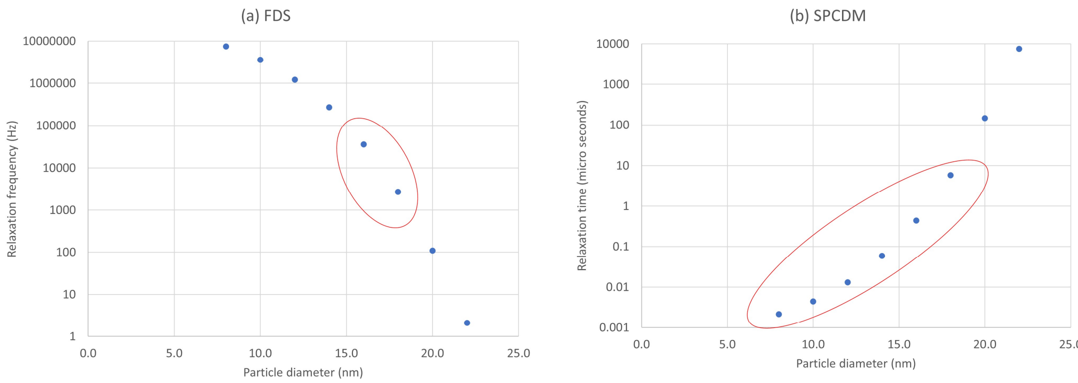

Figure 1: Variations of relaxation timesand frequencies (1/2πτ) with diameter of spherical magnetite-like minerals. (a) FDS and (b) SPCDM. The red ellipses show the particle sizes detectable with the instrumentation/parameters used in this work.

In the present study, both methods were complementary, delimiting a zone of increasing the abundance SP-SSD particles (high Ft-1 and low η) and a zone of mostly SP particles (low Ft-1 and high η). We agree with the reviewer that the SP increase cannot alone account for the variations of MS, and we attribute these complexes signals to the complex contamination history of the site. This is a challenge for brown field geophysical studies.

Changes: Pg 16, line 365: …The high MS values are not always in agreement with high SP particles shown by *η*, demonstrating that that increasing content of SP ferrimagnetic particles alone cannot account for the variations of magnetic susceptibility of the samples.…

1.3. In addition, it is better to conduct a correlation analysis between the magnetic susceptibility and the concentrations of SP ferrimagnetic particles.

Author’s response: Thanks for this suggestion. We included this correlation figure in the manuscript. The correlation works for the vadoze zone, but not for the saturated sediments. A way to interpret this is that in the vadoze zone, SP particles are abundant (even though they seem masked by SD particles in the FORC) and have an important contribution to MS. This is why we don´t see a correlation with frequency effect. In the Quaternary sediments, MS is best correlated with the SP-SSD range, as shown by the frequency effect and therefore Ft). In this zone, there is an SP peak associated with low MS. However, one must keep in mind that the SPCDM shows us the SP signature within that magnetic signal. In this case, the magnetic signal comes mainly from the SP particles, even though the signal is weak. This is why we have high SP particles/volume, but lower MS.

Changes: Pg 17, line 377: …" The linear correlation between MS and η shown in Figure 6 evidence that η follows the same pattern as magnetic susceptibility within this anthropogenic layer, suggesting the magnetic response of this portion is dominated by the superparamagnetic particles. …"

(2)
2.1. The existing experimental data sets are not enough to identify the grain size and type of magnetic minerals for the samples collected near the Tietê River, although it is a basis for further discussion. For example, the rock magnetic parameter of η demonstrates that superparamagnetic ferrimagnetic particles (SP) are enriched in the samples within the gas pockets.

Author's response: This is the main the main point. In this study we should talk about magnetic signatures, instead of grain sizes. Even though magnetic signatures are a result of the magnetic grain sizes, we cannot estimate their sizes with our investigation approach. However, we can apply these quantitative interpretation procedures to highlight these fingerprints, in kind of a simple way.

Changes: Pg 17, line 384: "Even though magnetic signatures are a result of the magnetic grain sizes, this investigation approach does not aim to estimate the magnetic grain sizes and rather seek for these grains fingerprints. Moreover, the complex history of the site reminds us to expect an assemblage of grain sizes. This aspect enhances the usefulness of our quantitative interpretation procedures, which isolates and quantifies the ultrafine content. "

2.2. This observation is in sharp contrast to the results suggested by FORC diagrams, which show a clear SD-like behavior of SD magnetite rather than SP magnetite particles.

Author's response: Even it may seem a contradiction, we must highlight that the samples are actually an assemblage of grain sizes. This in fact, enhances the usefulness of our quantitative interpretation procedures, which isolates the SP and SP-SSD signatures.

Changes: Pg 17, line 386: "Even though magnetic signatures are a result of the magnetic grain sizes…"

2.3. In addition, high temperature curves demonstrate that mineral phase transformations occur during thermal treatment. It is difficult to identify the existence of magnetite in sediment samples at room temperature. Thus, I strongly suggest that additional rock magnetic studies, such as the low-temperature magnetic measurements should be performed.

Author's response: That's true and the reason to show the FORC image.

(3)

3.1. The authors should describe the experimental procedure with sufficient details. For example, the details of thermomagnetic curves should be provided. Are the samples heated under an argon atmosphere to minimize oxidation?

Author's response: Thanks, we have included more details about the measurements.

Changes: Pg 11, line 213: "The measurements presented in this work were taken with Kappabridge KLY-4S at USPMAG (University of São Paulo), at the heating rate of 0.2^{o}C/second, under inert Ar atmosphere."

3.2. For the hysteresis loops analysis, the external applied field and the instrument should be introduced.

Author's response: Thanks for your careful review.

Changes: Page 12, line 236: "We used the Physical Properties Measurement System (PPMS) Quantum Design using vibrating sample magnetometry (VSM) to record hysteresis loops at 300, 25, 10 and 5 K and maximum external field of approximately 5×10^{4}Oe."

(4) Lines 127-128: The authors described that the grain size and total content of organic carbon of continuous samples from the direct-push coring were analyzed. However, the corresponding figures and data cannot be found in the text. It is important to present these records to reveal the controlling factors for the magnetic enhancements of the samples.

Author's response: Thank you. These data were published in a previous publication, Mendonça et al. (2015a) now cited in the text.

(5) The quality of English language and English grammar needs improving, and the manuscript needs a careful language check before re-submission. In the text, it is better to change " ferromagnetic " to " ferrimagnetic ".
Line 304: change " is " to " are "
Line 309 and 325: change " n " to " η "
Line 563: change " Hc " to " Bc "
Line 573: change " syperparamagnetic" to " superparamagnetic "
Line 583: change " upplementary " to " supplementary "

Author's response: We appreciate your careful review. Thanks.

(6) All the figures should be checked carefully. In figure 1, the letters a and b should be added. In figure 4, subpanel fig.4 c cannot be found.

Author's response: Thank you. All figures were revised.