Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2018-513-AC1, 2019

Biogeosciences Discussions
Open Access
EGU

Interactive comment on "Organic signatures in Pleistocene cherts from Lake Magadi (Kenya), analogs for early Earth hydrothermal deposits" *by* Manuel Reinhardt et al.

Manuel Reinhardt et al.

mreinha@gwdg.de

Received and published: 9 March 2019

Comment from referee: "The title suggests more than the contents of the full article, since: 1) Cyanobacteria, Algae, Higher plants, ciliates, fungi and many bacteria and Archaea present in the Pleistocene setting were not present during the "early Earth", i.e. the (early) Archean. . .,

Author's response: We agree in that the organic matter sources of modern and Archean organic matter were certainly not identical. We therefore will use a more cautious wording of the title, avoiding the term 'analog' in respect to organic matter.

Printer-friendly version

Discussion paper

Planned changes in manuscript: The title will be reworded.

. . .2) most, if not all, hydrothermal vents in the early Archean were at the bottom of the oceans, a setting very different from the Pleistocene setting investigated. The analogy is therefore limited to the syngeneity of immature and mature organic matter as a result of the hydrothermal pump hypothesis".

Author's response: We do not agree with the referee here. Recent works demonstrated that a variety of early Archean facies in Barberton and Pilbara areas reflect shallow marine hydrothermal (Allwood et al., 2006; Hickman-Lewis et al., 2018) or even terrestrial hot spring environments (Djokic et al., 2017), and several authors have pointed at the similarities of the Magadi cherts and Archean cherts with respect to their formation and lithology (Brenna, 2016; Eugster and Jones, 1968).

Comment from referee: "The authors have analysed the extracts as such by GC/MS. High molecular weight compounds such as Intact GDGTs or their lipid cores, polyesters, etc. (compounds expected to be present in these immature sediments in relative high concentrations), have been missed since the extraction method was not sufficient for extracting such compounds and/or they cannot be analysed by GC/MS. A more polar extraction method in combination with base- and/or acid hydrolysis of extracts and LC/MS analysis would have opened the analytical window very considerably".

Author's response: We agree that the use of further analytical techniques may have led to the identification of additional compounds. However, our methodology was not designed as being comprehensive with respect to all (polar) compounds present. As we regard our Pleistocene (10–100 ka old) thermally altered samples essentially as 'fossil', we focused more on the GC-amenable alkyl moieties and adhered as much as possible to the techniques typically used on ancient (incl. Archaean) organic matter, i.e., Raman, GC–MS, HyPy, and microscopy. It should nonetheless be noted that we did use acidic hydrolysis on the TOEs to cleave ester-bound compounds (TMCS/MeOH), so

Printer-friendly version

Discussion paper

that GC-amenable ester-bound moieties have been covered in the bitumen fractions.

Planned changes in manuscript: We will clarify that high molecular weight compounds like GDGTs and polymers were not analyzed in this study (introduction; chapter 3.2.1) and limit our conclusions on archaeal lipid preservation in the Magadi chert kerogens to low/medium molecular weight compounds.

Comment from referee: “The kerogens obtained have not been hydrolysed either, so that non-extracted moderate polar, partly high molecular weight, compounds were not removed and analysed by GC/MS or LC/MS. This implies that the HyPy results of the non-hydrolysed kerogens may be biased by pyrolysis products of relatively polar, high molecular weight immature organic matter which is not the result of hydrothermal maturation”.

Author’s response:

(i) As outlined above we intentionally used the techniques generally applied to study ancient organic matter, hence for kerogen preparation we strictly adhered to the established and commonly used method of Durand (1980), i.e., sequential extraction with different solvents, HCl-treatment, HF-treatment, and repeated extractions of the resulting residue.

(ii) A potential bias by non-extracted low-molecular weight moieties in the kerogen pyrolysis products (‘bitumen II’) can be excluded, because these compounds were removed during the pre-heating step (330 °C) in the HyPy runs. Notably, this step yielded only minor products (thus excluded from discussion).

(iii) DCM/MeOH-based solvent combinations similar to those used in our study were reported to successfully extract lipids of higher molecular weight such as GDGTs (e.g., Pancost et al., 2008). We feel that most lipid-like material including GDGT lipids should have been removed from the kerogen during the sequential extraction and acid dissolution steps. However, the possibility that some biomarkers may partly originate from

Printer-friendly version

Discussion paper

residual compounds trapped in the ‘kerogen’ and missed by the extensive kerogen extraction procedure can hardly be fully excluded (and could hardly be ever excluded in kerogen studies).

Planned changes in manuscript: We will mention the possibility that biphytane may partly derive from incomplete removal of GDGTs during extraction and tone down the implications on archaeal lipid preservation in the kerogens accordingly (see author’s response to the previous referee comment).

Comment from referee: “It’s also possible that the "kerogen" contains high molecular weight compounds produced through sulfurization of immature functionalized low molecular compounds. I understand very well that the authors have limited themselves analytically. That’s OK as long as the consequences of such a narrow analytical window is considered in the results and discussion paragraphs”.

Author’s response: We agree that the sulfurization of immature compounds may contribute, with or without hydrothermal influence, to the formation of early kerogen-like macromolecules. However, the Magadi cherts have extremely low sulfur contents (Table 1) and these tiny amounts of sulfur are mostly hosted in inorganic oxidized species, mostly gypsum. Therefore we do not consider sulfurization as an important process in this setting. Yet the biomarker inventory revealed evidence for lipid inputs from sulfate reducers, and it may be possible that sulfurization could occur in microscale environments where sulfate reduction was active. Unfortunately this possibility could not be further explored using our analytical setup.

Planned changes in manuscript: The occurrence of sulfates will be specified and the possibility of sulfurization will be discussed.

Comment from referee: “Table 4. Sample LM-1694 seems to have highly deviating isotope values. Why is that? A HyPy m/z 85 trace might be added to Figs 4 and 6”.

Author’s response: Magadi is an evaporitic environment showing varying salinities,

Printer-friendly version

Discussion paper

so the 13C enrichment in compounds from LM-1694 may be explained by a higher salinity/evaporation (stronger CO2-limitation) during deposition of that specific chert.

Planned changes in manuscript: As suggested a m/z 85 HyPy trace of LM-1694 will be added to Fig. 6 and the corresponding bitumen TIC to Fig. 3.

Comment from referee: "The authors note the presence of a clear UMC in sample LM-1697. UMCs are often the consequence of bacterial biodegradation. In this case it's not clear when this happened, shortly after deposition or recently due to bacterial infection of the outcrop samples. A UMC is also recognized in some of the other samples. I suggest that the authors discuss this topic in more detail".

Author's response and planned changes in manuscript: We agree and will discuss biodegradation in the manuscript. However, UCMs may also appear in non-biodegraded low-maturity oils (Peters et al., 2005, p. 106) and the Ph/n-C18 value of LM-1697 is not elevated as compared to other Magadi chert bitumens without pronounced UCMs (see Table 2).

Comment from referee: "For future work related to "kerogen" analysis I suggest that the authors consider to apply Thermally assisted hydrolysis (TMH) in combination with GC/MS (see for example K.G.J. Nierop et al., J. of Anal. and Appl. Pyrolysis, 83, pp 227-231 (2008) instead of HyPy. I'm convinced that by applying this TMH method much more info will be obtained due to the release of functionalized compounds also indicating the mode of chemical binding to the macromolecular matrix, since it can be expected that in this particular case the so called kerogen may partly consist of GDGTs and many other bio(macro)molecules".

Author's response: We thank the referee for his suggestion. While we are still convinced that our analytical setup appropriately supports the conclusions drawn in this manuscript, we will certainly consider the TMH method for the design of our future experiments!

References cited in the reply:

Allwood, A. C., Walter, M. R., and Marshall, C. P.: Raman spectroscopy reveals thermal palaeoenvironments of c.3.5 billion-year-old organic matter, Vib. Spectrosc., 41, 190–197, 10.1016/j.vibspec.2006.02.006, 2006.

Brenna, B. L.: The Chemical, Physical, and Microbial Origins of Pleistocene Cherts at Lake Magadi, Kenya Rift Valley, M.Sc. thesis, Department of Geological Sciences, University of Saskatchewan, Saskatoon, 158 pp., 2016.

Durand, B.: Sedimentary organic matter and kerogen. Definition and quantitative importance of kerogen, in: Kerogen: Insoluble Organic Matter from Sedimentary Rocks, edited by: Durand, B., Editions Technip., Paris, 13–34, 1980.

Djokic, T., Van Kranendonk, M. J., Campbell, K. A., Walter, M. R., and Ward, C. R.: Earliest signs of life on land preserved in ca. 3.5 Ga hot spring deposits, Nat. Commun., 8, e15263, 10.1038/ncomms15263, 2017.

Eugster, H. P., and Jones, B. F.: Gels Composed of Sodium-Aluminium Silicate, Lake Magadi, Kenya, Science, 161, 160–163, 10.1126/science.161.3837.160, 1968.

Hickman-Lewis, K., Cavalazzi, B., Foucher, F., and Westall, F.: Most ancient evidence for life in the Barberton greenstone belt: Microbial mats and biofabrics of the ~3.47âĂŕGa Middle Marker horizon, Precambrian Res., 312, 45–67, 10.1016/j.precamres.2018.04.007, 2018.

Pancost, R. D., Coleman, J. M., Love, G. D., Chatzi, A., Bouloubassi, I., and Snape, C. E.: Kerogen-bound glycerol dialkyl tetraether lipids released by hydropyrolysis of marine sediments: A bias against incorporation of sedimentary organisms?, Org. Geochem., 39, 1359–1371, 10.1016/j.orggeochem.2008.05.002, 2008.

Peters, K. E., Walters, C. C., and Moldowan, J. M.: The Biomarker Guide: I. Biomarkers and Isotopes in the Environment and Human History, 2nd ed., Cambridge University Press., Cambridge, 471 pp., 2005.

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-513, 2019.

Printer-friendly version

Discussion paper