

## ***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

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This is a very nice and detailed study of organic matter in recent, relatively unaltered cherts. Indeed, a good case is made for variable maturity as a result of localized hydrothermal circulation. I have some points of criticism (mostly focusing on the interpretation of the Raman spectral analyses), but these are not critical. There are some issues (as described below) that need to be clarified better, and some references to literature on these issues should be made. Overall, this manuscript can be published after only minor revisions.

Comment from referee: 1) A laser power of 1 mW was used during Raman spec-

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troscopy. These kerogen fractions are very immature, with derived temperatures as low as 40 C. For such unaltered, fragile material, a laser power of 1mW is quite high. Did the authors test if the laser actually affects the kerogen during analysis? For instance causing alteration, or worse, cause combustion?. This should be demonstrated, by a comparison analysis using lower laser power (e.g. 0.1 mW).

Author's response: We agree, and we are fully aware of this problem. In our study, laser energy and exposure time were optimized on representative organic-bearing test spots prior to analyzing the actual spots selected for presentation in the manuscript. With the resulting protocol the degradation of organics (during laser irradiation) was found to be minor.

Changes planned: We will describe the laser power test in the “Materials and Methods” section (2.6 Raman Spectroscopy).

Comment from referee: 2) The very low temperature of alteration (as low as 40C), and the presence of biomarkers for specific groups of prokaryotes, suggests that the Raman spectra of the organic fractions do not only reflect degree of alteration, but also could reflect the type of biologic precursor. For instance, this is suggested by Qu et al. (2015, *Astrobiology*, 15, 825-841) for carbonaceous fractions found in e.g. the Rhynie chert and the Bitter Springs chert. This should at least be expressed as a possibility, that the Raman-based geothermometer (I don't know if Schito et al., 2017, actually address this issue) is influenced by the type of biomass.

Author's response: We agree, this is certainly an important point.

Changes planned: We will refer to the study by Qu et al. (2015) and include the information that the obtained low temperature Raman data possibly reflect both, thermal maturity and the specific type of biological precursor.

Comment from referee: 3) The Raman spectra that are presented in Fig.2 are not of high quality. There is a very low signal to noise ratio. The presented peak-fitting

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protocol, however, is quite sophisticated and requires a high-quality spectrum. It should be explained in detail then, what the uncertainties actually are of fitting these peaks to the range of Raman spectra that were obtained. Also, in general, the calibration of low-temperature Ramanbased geothermometers is quite difficult. The geothermometer of Schito et al. (2017) is quite new. There are other, well-known geothermometers, that should also be applied to check if similar temperatures are obtained. The most important ones are the Ramanbased determination of H/C-ratio by Ferralis et al. (2016, Carbon, 108, 440-449) and the D1-peak-based geothermometer of Kouketsu et al. (2014, Island Arc, 23, 33-50).

Author's response: Most Raman geothermometers, including those mentioned in this referee comment, focus on temperatures above 150°C, so we feel that they cannot be usefully applied here. Schito et al. (2017) appear to be the only authors attempting Raman thermometry below 100 °C.

Changes planned: CoD-values (R2) for the fittings and a word of caution (see point 2 above) will be added to the manuscript. The signal-to-noise ratio has been addressed under point 1 (see above).

Comment from referee: 4) In the Discussion, on page 14 line 1-5, it is said that hydrothermal processes can cause syndepositional variation in kerogen maturity. This is not new, and has particularly been suggested for carbonaceous fractions in the hydrothermal feeder part of the 3.5 Ga Apex Chert, Pilbara, Western Australia. In the papers Olcott et al. (2012, Astrobiology, 12, 160-166) and Sforza et al. (2014, GCA, 124, 18-33), it is suggested that variation in kerogen maturity is linked to multiple episodes of hydrothermal fluid flow. The authors should better describe this process, and refer to these papers.

Author's response: We agree.

Changes planned: We will rephrase the respective part (p. 14) and include these papers into our discussion.

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Comment from referee: 5) The last part of the discussion, and end of the conclusions, is quite positive about the prospect of finding biomarkers in kerogen in Archean cherts. The authors argue that this is possible because they find good biomarkers in these hydrothermally influenced cherts at Lake Magadi. However, they should mention that most (if not all) cherts of Archean age have experienced greenschist-facies metamorphism, and that they thus have been buried and heated under pressure for millions of years. That's a very different thermal history than the Pleistocene cherts that are studied here. Time is an important factor. Biomarkers are extremely rare in Archean cherts, and the small fractions that have been described are highly controversial. The authors can work that issue out a bit better, and refer to e.g. French et al. (2015, PNAS, 112, 5915-5920) that described these issues. Nevertheless, the authors have proven an important point, that syndepositional hydrothermal circulation would indeed have created a range of maturities, and possibly have caused preservation of kerogen-bound biomarker molecules. That such biomarkers could be found in the Archean, however, remains to be seen.

Author's response: We agree. The post-depositional thermal history of the Magadi cherts is not comparable with Archean hydrothermal deposits. Nevertheless, our data indicate that not all molecular fingerprints, such as lipid biomarkers, are lost during initial hydrothermal heating and mild diagenesis in hydrothermal environments.

Changes planned: We will tone down our positive view and implement the work by French and colleagues.

References cited in the reply:

French, K. L., Hallmann, C., Hope, J. M., Schoon, P. L., Zumberge, J. A., Hoshino, Y., Peters, C. A., George, S. C., Love, G. D., Brocks, J. J., Buick, R., Summons, R. E.: Reappraisal of hydrocarbon biomarkers in Archean rocks, PNAS, 112, 5915–5920, 10.1073/pnas.1419563112, 2015.

Qu, Y., Engdahl, A., Zhu, S., Vajda, V., McLoughlin, N.: Ultrastructural Heterogeneity

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of Carbonaceous Material in Ancient Cherts: Investigating Biosignature Origin and Preservation, *Astrobiol.*, 15, 10.1089/ast.2015.1298, 2015.

Schito, A., Romano, C., Corrado, S., Grigo, D., and Poe, B.: Diagenetic thermal evolution of organic matter by Raman spectroscopy, *Org. Geochem.*, 106, 57–67, 0.1016/j.orggeochem.2016.12.006, 2017.

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