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

**Anonymous Referee #3**

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This is a detailed study of organic matter in cherts from Lake Magadi. These cherts of Pleistocene age are very well preserved, which makes them an interesting analogue for hydrothermally influenced and metamorphosed cherts of Archean age. These ancient silica deposits are ubiquitous in the ancient rock record, and are often found in relation with seafloor hydrothermal activity. The organic fractions in these ancient cherts have been subject to heated debate; do they represent altered remains of ancient life or are they the result of abiologic reactions (such as e.g. Fischer-Tropsch Type synthesis)? As the authors state in the beginning of their paper, in order to interpret this potential archive of ancient life, a sound understanding is necessary of organic matter preservation and alteration in hydrothermal systems. This can be achieved by studying rare modern analogs of this type of silica deposit. Many of such studies have focused on preserved life in silica sinters that surround hot springs and geysers. The current study, in contrast, focuses on silica deposits in a pure evaporative setting.

The authors used a suite of analytical techniques to characterize the bitumen and kerogen fractions in these rocks, including a detailed description of molecular biomarkers. Several types of prokaryotes could be identified, including thermophilic organisms that typically thrive in hydrothermal settings. Although the majority of the organic fraction is thermally immature, a range of maturities was found that includes highly altered carbonaceous phases. The authors argue that this is evidence for syndepositional hydrothermal alteration and redistribution within the depositional environment. This conclusion has important implications for the interpretation of heterogeneous carbonaceous fractions in Archean cherts. It shows that a range of maturities can occur in the same rock. Also, it shows that certain biomarker molecules can apparently survive hydrothermal circulation, by sequestration into kerogen. Based on this result they hypothesize that preservation of kerogen-bound molecular biosignatures in early Archean hydrothermal cherts may be possible.

Evaluation:

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.

Comments:

1) A laser power of 1 mW was used during Raman spectroscopy. 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).

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.

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 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 Raman-based 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 Raman-based 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).

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 Sforna et al. (2014, GCA, 124, 18-33), it is suggested that variation in kerogen maturity is linked to multiple episodes of hydrothermal fluid





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Discussion paper

flow. The authors should better describe this process, and refer to these papers.

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.

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