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Biogeosciences Discussions

Interactive comment on "Miniaturized biosignature analysis reveals implications for the formation of cold seep carbonates at Hydrate Ridge (off Oregon, USA)" *by* T. Leefmann et al.

T. Leefmann et al.

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"General Comments: The work submitted by Leefmann an co-authors is introducing a novel approach to extract lipid biomarkers of micro-drilled carbonate phases from a cold seep carbonate by using a miniaturized extraction protocol. The method enables to measure lipid biomarkers in mg-sized samples. This is the first time that a miniaturization approach was applied to sub-recent seep carbonates to further elucidate the biomarker inventory of specific carbonate phases. In their study they are able to show that specific carbonate precipitates (here: whitish aragonite) were formed by biofilms of a former active Anaerobic Oxidation of Methane (AOM) consortium, whereas the formation of other carbonate phases seems not to be or only poorly related to AOM. Overall the manuscript is well written and consistent, and should be published after

minor revision."
The authors would like to thank the referee for the constructive remarks. Below we will answer the specific comments.

"Specific Comments: The inventory of lipid biomarkers as revealed by the miniaturized approach are consistent with findings from earlier studies from Hydrate Ridge (e. g. Elvert et al., 2005). The signatures found in the whitish aragonite clearly report AOM as responsible process forming this carbonate phase. For the other phases, especially the gray micrite, AOM cannot be excluded or was at least partially responsible for the formation of this phase. It would be very interesting to see differences in stable carbon isotopes of specific compounds, but I can imagine that it is not possible to measure miniaturized samples on the GC-IRMS. Therefore I suggest to include the bulk stable carbon isotope values of the drilled samples in Table 1. These results will at least provide additional data whether the carbonates are showing AOM signatures or not."
Considered. Stable carbon isotope data are included in the revised manuscript. The δ^{13}C-values of the carbonate phases (-40.17 $‰$ PDB to -46.98$‰$ PDB) are well in the range for methane-derived carbonates.

"The second comment is dealing with the presence of lipid biomarkers from sulfatereducingbacteria (SRB) in the carbonates. Since the SRB thriving at seeps in the consortia have never been found to synthesize DAGEs it is still not as clear-cut if DAGEs are sourced by SRBs living in the AOM consortium or if they were sourced from other, unknown SRBs, or other unknown bacteria. I am aware that most authors use DAGEs as SRB markers, but I would prefer to see distribution patterns of typical SRB fatty acids as well. It appears to be from the results presented here, that no specific SRB fatty acids (for example terminally branched fatty acids) were preserved. Maybe this is because the samples were not saponified prior extraction? Fatty acids which have been part of the AOM consortium may still be ester-bond or stored within the carbonate lattice and cannot be released by extraction only. The fatty acids presented in this study are most likely sourced only by autochthonous organisms. Therefore I reckon

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that it may be beneficial to saponify at least samples 7r1 and 9 (those with the highest concentrations) to test whether SRB fatty acids can be released or not after saponification. Since SRB-specific fatty acids could have been traced back to the Oligocene (see Peckmann and Thiel, 2004; Lincoln Creek site), I would expect at least terminally branched fatty acids to have the potential to be excellently preserved in the studied Hydrate Ridge samples."

Considered. Samples 7r1 and 9 were carefully saponified using 200 μl TMCS-MeOH 1:10 for 60 min at 70°C. Only the previously observed *n*-fatty acids but no SRB-specific terminally branched fatty acids were detected.

"The last comment is dealing with a) the presence and stability of hydroxyarchaeol and b) the using of the hydroxyarchaeol/archaeol ratio to discriminate ANME-1 from ANME-2: a) Starting from page 4449, line 27 the authors pointed out that hydroxyarchaeol is rarely present in the fossil record and explained this fact by preferential degradation of this compound. It is true that Peckmann and Thiel (2004) only were able to report hydroxyarchaeol in trace amounts from the Oligocene Lincoln Creek, but not in the other Neogene and Mesozoic sites. However, in a recently published article in Organic Geochemistry hydroxyarchaeol was detected in three different ancient locations with strong 13C-depletions (see Birgel et al., in press). Although no hydroxyarchaeol/archaeol ratios have been shown in their article, at least hydroxyarchaeol was still present in Neogene samples. I suggest that the statement should be modified."

These new findings are now mentioned in the discussion. However, we still consider the preferred degradation of hydroxyarchaeol as a likely option to explain the differences in hydroxyarchaeol/archaeol ratios between our fossil samples and recent materials, e.g. microbial mats.

"b) Though the concentrations of hydroxyarchaeol are as high or even higher than those of archaeol and the ratio in the whitish aragonite are in 5 out of 8 samples >1 and might indicate that ANME-2 were the major consortium precipitating whitish aragonite, ANME-1 cannot be excluded as further candidates participating in carbonate

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formation, since no data of GDGTs are available. In Blumenberg et al. (2004) mixed ANME-1 and ANME-2 consortia provided hydroxyarchaeol/archaeol ratios varying from 0.6-1.4. Three out of the eight analysed whitish aragonite samples showed similar ratios. The authors discussed that preferential degradation lead to these ratios, but still the presence of ANME-1 cannot be excluded entirely. I am aware that it is unlikely or even impossible to measure GDGTs in miniaturized samples, but I would suggest to weaken the argument that the whitish aragonite is almost only precipitated by ANME-2."

Considered. The occurrence of crocetane coinciding with *sn*-2-hydroxyarchaeol/archaeol ratios >1 indicate an involvement of ANME-2 in the precipitation of the whitish aragonite, but cannot exclude the presence of ANME-1. The text section was reworded accordingly.

Interactive comment on Biogeosciences Discuss., 4, 4443, 2007.