Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2017-516-AC2, 2018

Biogeosciences Discussions

Interactive comment on "Ideas and perspectives: Hydrothermally driven redistribution and sequestration of early Archaean biomass – the "hydrothermal pump hypothesis"" *by* Jan-Peter Duda et al.

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Received and published: 5 February 2018

Comment from referee: "This is a very interesting paper showing a potential key characteristic of kerogen in chert veins of the early Archean Dresser Fm. The origin of the kerogen in this chert vein (and other early Archean chert veins in the Pilbara) still remains debated. It could represent sedimentary biomass that was recirculated by hydrothermal fluids, or represent the abiogenic product of FTT synthesis that was generated during hydrothermal serpentinization of ultramafic crust. This paper therefore addresses a very relevant scientific question. Based

on HyPy extraction, GC-MS and compound-specific isotope analysis, the authors showed that the kerogen phase releases n-alkanes with a specific carbon-number distribution. The sharp decrease in n-alkane abundance above n-C18, is similar to the distribution of n-alkanes released during HyPy of cyanobacteria. This distribution is not observed, however, in n-alkane products of FTT synthesis. Based on these observations, the authors conclude that the kerogen in the chert vein of the Dresser Fm is derived from biomass (such as e.g. phototrophs, chemolithoautrophs), and not from FTT synthesis associated with hydrothermal circulation. In order to explain the presence of kerogen in deep feeder chert veins, the authors propose a 'hydrothermal pump' hypothesis, in which redistribution and sequestration of microbial biomass occurs through hydrothermal circulation. This is a very nice explanation, and would confirm that microbial life was abundantly present in the ancient oceans. The paper is very well written, and experimental results support the conclusions. I have 3 issues that should be worked out better in this paper, which are listed below".

Comment from referee: "The conclusion of this paper strongly depends on the drop in >C18 n-alkanes in biologic materials. It should then be explained in detail why this happens. Is this drop observed in all biologic materials? Is it related to specific compounds that are present in cell membranes? There is now only a very short description about this (P10, line 10-11), stating that bacteria commonly (though not exclusively) form linear carbon chains <C18 (cf. Kaneda, 1991). I think it is important that this discussion is expanded here. Is there a chemical reason for this drop in abundance of n-alkanes beyond C18?

Author's response: Bacteria form acetyl-based hydrocarbon moieties such as fatty acids (the potential precursors of the kerogen-derived n-alkanes) as membrane- or storage lipids. Different biosynthetic pathways exist for the production of these lipids, which control carbon chain-lengths, number and positions of double bonds etc. These biosynthetic mechanisms typically result in the formation of lipids with chain-lengths $\leq$

n-C18.

Author's changes in manuscript: We now provide this information in the discussion (chapter 4.3 Origin of the Dresser kerogen: hydrothermal vs. biological origin), now: "[. . .] Straight-chain (acetyl-based) hydrocarbon moieties such as fatty acids – the potential precursors of the kerogen-derived n-alkanes – are to the current knowledge being formed only by Bacteria and Eukarya, where they typically function as constituents of membranes or storage lipids (cf. Kaneda, 1991; Erwin, 2012). The formation of these lipids is tightly controlled by different biosynthetic pathways resulting in characteristic chain-length distributions. In bacterial lipids, carbon chain-lengths typically do not extend above n-C18 (cf. Kaneda, 1991). [. . .]".

Comment from referee: "The HyPy products of kerogen of the Dresser Fm are compared with HyPy products of cyanobacteria, but – if I understand correctly – not with the HyPy products of FTT synthesized carbonaceous solids. Only the direct gaseous FTT synthesis products are compared. Were there any solid phases produced during FTT synthesis? It would have been important to see what kind of HyPy products this would have generated, in comparison with that of HyPy products of cyanobacteria and Dresser Fm kerogen. I think the authors should discuss this better, in order to make clear that a comparison with a true abiogenic carbonaceous solid has not been made here".

Author's response: We agree that comparison is not equal. However, the presence of a true 'FTT-kerogen' (i.e. chemically equivalent to a biological kerogen in that it contains GC-amenable organic moieties) has not been observed in our experiments and has also not been reported in the literature. Conceivably, however, initially soluble functionalized FTT-products may evolve into such a 'FTT-kerogen' through diagenetic condensation reactions. It is quite certain that carbon chains released from this material would not show any preferences of distinctive homologues, but rather mirror the unimodal distribution of the initial educts.

Author's changes in manuscript: We included this aspect into the discussion (chapter 4.3 Origin of the Dresser kerogen: hydrothermal vs. biological origin), now: "[. . .]. In contrast, abiotically synthesised extractable organic compounds show a unimodal homologue distribution from the beginning (Fig. 3e) and will retain it, while thermal maturation would gradually shift the n-alkane pattern towards shorter homologues. It can therefore be expected that organic compounds cleaved from an abiotic 'Fischer-Tropsch-kerogen' – whose existence has not been proven yet – would also exhibit a unimodal distribution. [. . .]".

Comment from referee: "The maturity of kerogen in the Dresser Fm is determined using Raman spectroscopy. I have several comments to the methods used here. The H/C ratio of the kerogen fractions is calculated following the method of Ferralis et al. (2016), using a D5-peak in the Raman spectrum. However, based on the example spectrum in Fig.2c I think it is quite difficult to convincingly fit a D5-peak. The authors should at least show how this fit was made. It may well be that the kerogen has reached a degree of alteration where the amount of H is too low to create a significant D5-peak. The other method used here is to check the S1 peak (2450 cm-1) in the second order spectrum. The absence of this peak is consistent with kerogen that has experienced prehnite-pumpellyite to lowergreenschist-facies metamorphism. However, I think there are more precise methods to determine the degree of alteration of the kerogen. For instance, the Raman-based geothermometer of Koketsu et al. (2014) could have been applied to the first-order spectrum. Or even better, the Raman-based indicator of Delarue et al. (2016) can be applied. This indicator has been specifically developed to compare kerogens in Precrambrian cherts".

Author's response & changes in manuscript: The D5 peaks were fitted in the LabSpecTM software (version 5.19.17; Jobin-Yvon, Villeneuve d'Ascq, France) using the Gauss/Lorentz function. We now provide this information (chapter 2 Material & methods) and stress that Raman-based H/C-ratios for highly mature organic

matter should be treated with caution (chapter 4.1 Maturity of the Dresser kerogen). We now also applied further Raman-based maturity proxies and cite the relevant studies (Delarue et al., 2016) (chapter 4.1 Maturity of the Dresser kerogen).

Comment from referee: “P3, Line 27: : : :.(GC-MS). Before: : :.”

Author’s response & changes in manuscript: Done.

Comment from referee: “P4, Line 7 and line 22: Why is the heating program for the cyanobacteria different than for the extracted kerogens?”

Author’s response & changes in manuscript: Archaean kerogens are easily contaminated. HyPy of Archaean kerogens therefore requires the addition of a thermal desorption step ($\sim$350°C) prior to high temperature HyPy (550°C) to remove organic contaminants (cf. Brocks et al., 2003; Marshall et al., 2007). Recent biomass is much more reactive than (highly mature) fossil kerogens and therefore shows a distinctly different behavior during pyrolysis (Love et al. 2005). For this reason, HyPy of recent biomass necessitates a modified experimental protocol that increases reaction efficiencies and minimizes artefact formation. We now provide these information (chapter 2 Material & methods).

Comment from referee: “Section 2.8: It may be good for the reader if a little more information is given here on PAH’s. What are they, and why are these ratios important? And how were these PAH’s measured?”

Author’s response & changes in manuscript: We now provide additional information and references (Killops and Killops, 2005; Peters et al., 2005) on the nature of polyaromatic hydrocarbons (PAH) and the utility of GC-amenable PAHs as maturity indicators (in chapter 2 Material & methods).

Comment from referee: “Section 4.4: The way it is written, it is not clear whether the ‘hydrothermal pump hypothesis’ is an already existing term, or is here proposed for the first time. It should be more clearly stated that this is a new proposed model.”

Author’s response & changes in manuscript: We clarified that we propose the ‘hydrothermal pump hypothesis’ within our study (chapter 4.4 The “hydrothermal pump hypothesis”).

References cited in the reply:

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