

***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.***

Jan-Peter Duda et al.

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Comment from referee: “This is innovative, thorough and significant work addressing the biogenicity of the oldest known well preserved organic matter in the geological record and the biological affinities of its precursor organisms. The techniques involved have been applied rigorously but the interpretations are only as good as those techniques allow; I lack the expertise to judge them carefully so it is essential that this be done by well informed experts such as Roger Summons, Simon George and Jochen Brocks.

Comment from referee: “There is a need to discuss the possibility that there could have been contamination by organic compounds derived from the 2.7-2.8 Ga Fortescue Group that overlies the Dresser Fm in the studied area. It is conceivable that a “hydrothermal pump” could have circulated fluids downwards into the older succession. There is a significant literature on the organic geochemistry of the Fortescue Group by George, Coffey, Summons and others. The same applies to the Strelley Pool Fm where there are abundant stromatolites and microfossils”.

Author’s response: The depositional age of the Dresser Formation is constrained to ca. 3481 ± 3.6 Ma (Van Kranendonk et al., 2008). An emplacement of organic material into the Dresser hydrothermal chert vein by fluids circulating during the deposition of stratigraphically younger units as e.g. the Strelley Pool Formation (ca. 3.43–3.35 Ga; Hickman, 2008) and Fortescue Group (ca. 2.7–2.6, see reviewer comment) is unlikely. Firstly, there is no petrographic evidence that the analysed Dresser hydrothermal chert vein has been affected by fluid-flow events that post-date the initial formation (e.g. brecciation textures, etc.). The kerogen exclusively occurs in form of fluffy aggregates and clots embedded within a very dense chert matrix which is, once solidified, highly impermeable to fluids. It does furthermore not occur along grain boundaries, cracks etc. which could indicate possible transport by later fluids. This has also been described for other hydrothermal chert veins of the Dresser Formation, where the kerogen has been interpreted as being syngeneic (i.e. formed prior to host rock lithification; Morag et al., 2016). A later transport of kerogen without fluids, as alternative scenario, can also be excluded as macromolecular organic matter is not mobile in solid, impermeable materials.

Author’s changes in manuscript: We tried to make this clearer (first paragraph of chapter 4.2 Syngeneity of the Dresser kerogen-derived compounds), now: “The kerogen of the Dresser Formation exclusively occurs in form of fluffy aggregates and clots embedded within a very dense chert matrix that is, once solidified, highly

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impermeable to fluids. The depositional age of the formation is constrained to 3481 ± 3.6 Ma (Van Kranendonk et al., 2008), and the investigated chert vein shows no evidence for disruption by post-depositional hydrothermal fluids. This has also been described for other hydrothermal chert veins of the Dresser Formation, where the kerogen has been interpreted as being syngenetic (i.e. formed prior to host rock lithification; Ueno et al., 2001, 2004; Morag et al., 2016). Furthermore, the maturity of the embedded kerogen is in good accordance with the thermal history of the host rock. An introduction of solid macromolecular organic matter from stratigraphically younger units in this region during later fluid flow phases, as proposed for the younger Apex chert (Olcott-Marshall et al., 2014), can therefore be excluded”.

Comment from referee: “The manuscript would be enhanced by adding a paragraph outlining the evidence that indicates that the 3.5Ga environment was anoxic”.

Author’s response & changes in manuscript: We now provide information on existing evidence for reducing conditions during deposition of the Dresser Formation (widespread presence of pyrite, Fe-rich carbonates, trace element signatures) and cite the relevant studies (Van Kranendonk et al., 2003, 2008) (chapter 4.3 Origin of the Dresser kerogen: hydrothermal vs. biological origin).

Comment from referee: “It seems to me that the evidence from the Apex Chert needs to be at least briefly reviewed here as it would add significantly to the context of this new work”.

Author’s response & changes in manuscript: In contrast to the Dresser hydrothermal chert vein analyzed in our study, the younger Apex chert has been affected by multiple fluid flow events. Some of these events significantly post-date the initial formation time and also led to an emplacement of younger organic materials (Olcott-Marshall et al., 2014). Our hypothesis may be relevant for the Apex chert in that it explains the

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possible presence of organic matter during its initial formation. It cannot, however, help to pinpoint the formation pathways of distinct carbonaceous structures (e.g. Schopf, 1993, 2002; Brasier et al., 2002, 2005). We now explicitly state this problem in the manuscript (last paragraph of chapter 4.4 The “hydrothermal pump hypothesis”).

Comment from referee: “The manuscript is well written and almost free of errors. P.11 l. 19 change to instantaneously”.

Author’s response & changes in manuscript: Done.

Comment from referee: “References to the published geological maps of the North Pole area should be added. There may be other publications by Hickman that should be cited”. Author’s response & changes in manuscript: We now provide information on published geological maps by Hickman (1983), Van Kranendonk (1999) and Hickman and Van Kranendonk (2012) (chapter 2.1). We also cite further publications by Hickman (1973, 1975, 2012) (chapters 1 Introduction and 4.1 Maturity of the kerogen).

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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

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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, chemolithoautotrophs), 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

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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.

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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 Precambrian cherts”.

Author's response & changes in manuscript: The D5 peaks were fitted in the Lab-Spec™ 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

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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).

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

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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: Archaeal kerogens are easily contaminated. HyPy of Archaeal kerogens therefore requires the addition of a thermal desorption step (~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).

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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”).

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Ideas and perspectives: Hydrothermally driven redistribution and sequestration of early Archaean biomass—the ‘hydrothermal pump hypothesis’

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20 **Abstract.** Archaean hydrothermal chert veins commonly contain abundant organic carbon of uncertain origin (abiotic vs. biotic). In this study, we analysed kerogen contained in a hydrothermal chert vein from the ca. 3.5 Ga-old Dresser Formation (Pilbara Craton, Western Australia). Catalytic hydrolysis (HyPy) of this kerogen yielded *n*-alkanes up to *n*-C₂₂, with a sharp decrease in abundance beyond *n*-C₁₈. ~~A very similar~~ This distribution ($\leq n\text{-C}_{18}$) ~~was~~ is very similar to that observed in HyPy products of ~~pre-extracted~~ Recent bacterial biomass, ~~while~~ which was used as reference material, whereas it differs markedly from the unimodal distribution of abiotic compounds ~~synthesised~~ experimentally formed via Fischer-Tropsch-type synthesis ~~exhibited a modal distribution.~~ We therefore propose that the ~~original~~ organic matter in the Archaean chert veins has a primarily microbial origin. ~~We hypothesise that~~ The microbially-derived organic matter may have accumulated in ~~different~~ anoxic aquatic (surface and/or subsurface ~~Dresser~~) environments, and was then assimilated, redistributed and sequestered by the hydrothermal fluids (‘hydrothermal pump hypothesis’).

1 Introduction

30 Extensive hydrothermal chert vein systems containing abundant organic carbon are a unique phenomenon of early Archaean successions worldwide (Lindsay et al., 2005; Van Kranendonk, 2006; Hofmann, 2011). A dense stockwork of several

hundred kerogen-rich hydrothermal chert veins [that penetrate footwall pillowed komatiitic basalts](#) of the ca. 3.5 Ga Dresser Formation (Pilbara Craton, Western Australia; Fig. 1) are up to 2 km deep by 25 m wide ~~and penetrate footwall pillowed komatiitic basalts~~ [\(Hickman, 1973, 1983; Nijman et al., 1999; Van Kranendonk and Pirajno, 2004; Lindsay et al., 2005; Van Kranendonk, 2006; Van Kranendonk et al., 2008\)](#) (Fig. S1). Depleted stable carbon isotope signatures ($\delta^{13}\text{C}$) of bulk kerogens (−38.1 ‰ to −24.3 ‰) and of organic microstructures (−33.6 ‰ to −25.7 ‰) in these hydrothermal chert veins, [as well as remnants of what appear to be microbial remains](#), are consistent with a biological origin of the organic matter (Ueno et al., 2001, 2004; Glikson et al., 2008; Pinti et al., 2009; Morag et al., 2016). Problematically, however, similarly depleted $\delta^{13}\text{C}$ values (partly down to ca. −36 ‰ relative to the initial substrate) can also be formed through abiotic processes, for instance via Fischer-Tropsch-type synthesis (McCollom et al., 1999; McCollom and Seewald, 2006), [and putative microbial remains are not always reliable](#) (Schopf, 1993; Schopf et al., 2002; Brasier et al., 2002, 2005; Bower et al., 2016).

Organic biomarkers can help to trace life and biological processes through deep time and add important information on the origin of the organic matter, even in very old sedimentary rocks (Brocks and Summons, 2003; Summons and Hallmann, 2014). In Archaean rocks, however, molecular fingerprints in the conventionally analysed bitumen (i.e. the extractable portion of organic matter) are commonly blurred by thermal maturation and/or [ancient or modern](#) contamination (Brocks et al., 2008; [Gérard et al., 2009](#); Brocks, 2011; French et al., 2015). In contrast, the non-extractable portion of organic matter, known as kerogen, tends to be less affected by thermal maturation and contamination and is considered to be syngenetic with the host rock (Love et al., 1995; Brocks et al., 2003b; Marshall et al., 2007; Lockhart et al., 2008). Catalytic hydrolysis (HyPy) is a powerful tool for sensitively releasing kerogen-bound hydrocarbon moieties with little structural alteration (Love et al., 1995). HyPy has been successfully applied to Archaean kerogens in rocks from the Pilbara Craton, liberating syngenetic organic compounds consistent with a biogenic origin (Brocks et al., 2003b; Marshall et al., 2007). However, this technique has not [yet](#) been used on kerogens contained in hydrothermal chert veins of this age ~~yet~~.

Here, we present the results of analyses of kerogen embedded in a freshly exposed hydrothermal chert vein of the ca. 3.5 Ga Dresser Formation. Our analyses include field and petrographic observations, Raman spectroscopy, and organic geochemistry ($\delta^{13}\text{C}_{\text{TOC}}$; kerogen-bound molecules via HyPy followed by gas chromatography-mass spectrometry (GC-MS) and gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS)). To further constrain potential sources of the Dresser kerogen, we additionally applied HyPy on (i) excessively pre-extracted cyanobacterial biomass and (ii) produced abiotic organic matter via Fischer-Tropsch-type synthesis using a hydrothermal reactor. Results of these investigations suggest that the Dresser kerogen has a primarily microbial origin. We hypothesise that biomass-derived organic compounds accumulated in [different Dresser anoxic aquatic](#) environments and [werewas](#) then redistributed and sequestered by subsurface hydrothermal fluids ('hydrothermal pump hypothesis').

2 Material & methods

2.1 Sample preparation

5 A fresh decimetre-sized sample of a Dresser chert vein was obtained from a recent cut wall of the abandoned Dresser Mine in the Pilbara Craton, Western Australia (~~Figs. 1, S1d~~-GPS: 21°09'04.13" S; 119°26'15.21" E; [Figs. 1, S1d: for geological maps see Hickman, 1983; Van Kranendonk, 1999; Hickman and Van Kranendonk, 2012](#)). External surfaces (ca. 1–2 cm) of the sample block were removed using an acetone-cleaned rock saw and then used for the preparation of thin sections. The surfaces of the resulting inner block were extensively rinsed with acetone and then removed (ca. 1–2 cm) with an acetone-cleaned high precision saw (Buehler; Isomet 1000, Germany). The surfaces of the resulting sample were again rinsed with acetone, and then crushed and powdered using a carefully acetone-cleaned pebble mill (Retsch MM 301, Germany).

10

2.2 Petrography and Raman spectroscopy

Petrographic analysis was conducted using a Zeiss SteREO Discovery.V8 stereomicroscope (transmitted and reflected light) linked to an AxioCam MRc5 5-megapixel camera.

15 Raman spectra were recorded using a Horiba Jobin Yvon LabRam-HR 800 UV spectrometer (focal length of 800 mm) attached to an Olympus BX41 microscope. For excitation an Argon ion laser (Melles Griot IMA 106020B0S) with a laser strength of 20 mW was used. The laser beam was focused onto the sample using an Olympus MPlane 100 x objective with a numerical aperture of 0.9 and dispersed by a 600 l mm⁻¹ grating on a CCD detector with 1024 x 256 pixels. This yielded a spectral resolution of <2 cm⁻¹ per pixel. Data were acquired over 10 to 30 s for a spectral range of 100–4000 cm⁻¹. The spectrometer was calibrated by using a silicon standard with a major peak at 520.4 cm⁻¹. All spectra were recorded and
20 processed using the LabSpecTM database (version 5.19.17; Jobin-Yvon, Villeneuve d'Ascq, France).

2.3 Raman-derived H/C data

H/C values were calculated based on integrated peak intensities of Raman spectra using the formula $H/C = 0.871 * I_{D5}/(I_{G+D2}) - 0.0508$ (Ferralis et al., 2016). [The peaks were fitted in the LabSpecTM software \(see 2.2\) using the Gauss/Lorentz function.](#)

2.4 Molecular analysis of the Dresser kerogen

25 All materials used for preparation were heated to 500°C for 3h and/or extensively rinsed with acetone prior to sample contact. A laboratory blank was prepared and analysed in parallel to monitor laboratory contaminations.

We applied catalytic hydrolysis (HyPy) to release molecules from the Dresser kerogen and pre-extracted biomass of the heterocystous cyanobacterium *Anabaena cylindrica* [SAG 1403-2](#) following [existing previously published](#) protocols (Snape et al., 1989; Love et al., 1995; Love et al., 2005). HyPy allows the breaking of covalent bonds by progressive heating under
30 high hydrogen pressure (150 bar). The released products are immediately removed from the hot zone by a constant hydrogen

flow, and trapped downstream on clean, combusted silica powder cooled with dry ice (Meredith et al., 2004). All hydropyrolysates were eluted from the silica trap with high-purity dichloromethane (DCM), desulfurised overnight using activated copper, and subjected to gas chromatography-mass spectrometry (GC-MS). Before all experiments, the empty HyPy system was heated (ambient temperature to 520°C, held for 30min) to remove any residual molecules.

5 Isolation of the Dresser kerogen followed standard procedures (cf. Brocks et al., 2003b). 57 g of powdered sample was first demineralised with hydrochloric acid (24h) and then hydrofluoric acid (11 days). The purified organic matter was then exhaustively extracted using 3 excess volumes of DCM and *n*-hexane, respectively (x3), ultrasonic swelling in pyridine (2 x 20 min at 80°C), and ultrasonic extraction with [methanol](#), DCM (x3) and DCM/methanol (1/1; v/v). The kerogen was subsequently extracted with *n*-hexane until no more compounds were detected via GC-MS. The pure kerogen was used for
10 HyPy: [following an experimental protocol optimised for the analysis of Archaean kerogens \(Brocks et al., 2003b; Marshall et al., 2007\)](#).

In order to monitor potential contamination, we applied HyPy to blanks before and after the kerogen run. The Dresser kerogen (131.06 mg) and blanks were sequentially heated in the presence of a sulphided molybdenum catalyst (10 wt%) and under a constant hydrogen flow (5 dm³ min⁻¹) using a two-step approach (cf. Brocks et al., 2003b; Marshall et al., 2007; Fig.
15 S2). The low-temperature step included heating from ambient temperature to 250°C (300°C min⁻¹) and then to 330°C (8°C min⁻¹) to release any molecules that were strongly adsorbed to the kerogen and not accessible to solvent extraction. The silica powder was subsequently recovered from the product trap, and the trap was refilled with clean, combusted silica powder for the following high-temperature step. This step included heating from ambient temperature to 520°C (8°C min⁻¹) to release molecules covalently bound to the kerogen.

20 2.5 Molecular analysis of pre-extracted cyanobacterial biomass (*Anabaena cylindrica*)

We used cell material of the heterocystous cyanobacterium *Anabaena cylindrica* strain SAG 1403-2 as it fulfils all criteria for reference material (availability, well characterized, etc.). The material was obtained from the Culture Collection of Algae at the Georg-August-University Göttingen, (Germany) and [grown at the Christian-Albrechts-University Kiel \(Germany\)](#).

The axenic batch culture was [grown/maintained](#) in 250 ml of BG11₀ medium free of combined nitrogen sources (Rippka et al.,
25 1979) at 29°C. A light/dark regime of 14 h:10 h with a photon flux density of 135 μmol photons m⁻²s⁻¹ was provided by a white fluorescent light bulb. At the end of the logarithmic growth phase, cells were harvested by centrifugation and they were lyophilised thereafter. Subsequently, an aliquot of the freeze-dried biomass was exhaustively extracted following the methodology described by [ref.](#) (Bauersachs et al., (2014)).

HyPy ~~on the extraction residue~~ was performed ~~according to~~ [following an experimental protocol optimised for biomass applications \(Love et al., 2005\)](#). [Briefly](#), the material was heated in the presence of a sulphided molybdenum catalyst (1.5 times weight of the bacterial extraction residue) and under a constant hydrogen flow (6 dm³ min⁻¹). The HyPy program included heating from ambient temperature to 260°C (300°C min⁻¹) and then to 500°C (8°C min⁻¹).

2.6 Fischer-Tropsch-type synthesis of organic matter under hydrothermal conditions

Fischer-Tropsch-type reactions were carried out based on McCollom et al. (1999). A mixture of 2.5 g oxalic acid (dihydrate, suprapur®, Merck KGaA), 1 g montmorillonite (K10, Sigma Aldrich; pre-extracted with DCM; x4) and ca. 11 ml ultrapure water was heated to 175°C for 66 to 74 h in a sealed Morey-type stainless steel autoclave. The autoclave was rapidly (≤ 15 min) cooled to room temperature with compressed air.

Fluid- and solid phases were collected and extracted with DCM (x4). The montmorillonite was removed by centrifugation and filtration with silica powder and sea sand (combusted, respectively). The obtained extracts were then concentrated by rotary evaporation (40°C, 670 mbar) and subjected to GC-MS analysis. Analytical blank experiments were carried out with all reactants to keep track of contamination.

10 2.7 Gas chromatography-mass spectrometry (GC-MS)

GC-MS analysis of HyPy products was carried out with a Thermo Scientific Trace ~~1300-Series~~1310 GC coupled to a Thermo Scientific Quantum XLS Ultra MS. The GC instrument was equipped with a capillary column (Phenomenex Zebron ZB-5, 30 m, 0.25 μm film thickness, 0.25 mm inner diameter). Fractions were injected into a splitless injector and transferred to the GC column at 270°C. He was used as carrier gas with a constant flow rate of 1.5 ml min⁻¹. The GC oven temperature was held isothermal at 80°C for 1 min and then ramped to 310°C at 5°C min⁻¹, at which it was kept for 20 min. Electron ionization mass spectra were recorded in full scan mode at an electron energy of 70 eV with a mass range of m/z 50–600 and scan time of 0.42 s.

2.8 Polyaromatic hydrocarbon (PAH) ~~ratio definitions~~ratios

20 Polyaromatic hydrocarbons (PAH) are organic compounds consisting of multiple fused benzene rings. Methylation- and isomerization characteristics of various GC-amenable PAH are altered during maturation and thus provide a measure for assessing the thermal maturity of organic matter (Peters et al., 2005; Killops and Killops 2005). The following PAH maturity parameters were used in this study:

1. Methylnaphthalene ratio (MNR) = 2-MN/1-MN (Radke et al., 1984)
2. Methylphenanthrene index (MPI-I) = 1.5 * (2-MP + 3-MP)/(P + 1-MP + 9-MP) (Radke and Welte, 1983)
- 25 3. Computed vitrinite reflectance [Rc (MPI-I)] = 0.7 * MPI-I + 0.22 (according to P/MP >1; Boreham et al., 1988)

MN = Methylnaphthalene; P = Phenanthrene; MP = Methylphenanthrene.

2.9 Total organic carbon (TOC) and $\delta^{13}\text{C}$ analyses (TOC and compound specific)

30 TOC, $\delta^{13}\text{C}_{\text{TOC}}$, and compound specific $\delta^{13}\text{C}$ analyses were conducted at the Centre for Stable Isotope Research and Analysis (KOSI) at the Georg-August-University Göttingen, Germany. Stable carbon isotope data are expressed as delta values relative to the Vienna Pee Dee Belemnite (VPDB) reference standard.

The TOC content and $\delta^{13}\text{C}_{\text{TOC}}$ values were determined in duplicate using an elemental analyser (NA-2500 CE-Instruments) coupled to an isotope ratio mass spectrometer (Finnigan MAT Delta plus). Ca. 100 mg of powdered and homogenised whole rock material were analysed in each run. For internal calibration an acetanilide standard was used ($\delta^{13}\text{C} = -29.6 \text{ ‰}$; SD = 0.1). TOC content measurements showed a mean deviation of 0.1. The average $\delta^{13}\text{C}_{\text{TOC}}$ value had a standard deviation of 0.3.

5 Compound specific $\delta^{13}\text{C}$ analyses were conducted with a Trace GC coupled to a Delta Plus isotope ratio mass spectrometer (IRMS) via a combustion-interface (all Thermo Scientific). The combustion reactor contained CuO, Ni and Pt and was operated at 940°C. The GC was equipped with two [serially coupled](#) capillary columns (Agilent DB-5 and DB-1; each 30 m, 0.25 μm film thickness, 0.250 μm inner diameter). Fractions were injected into a splitless injector and transferred to the GC column at 290°C. The carrier gas was He at a flow rate of 1.2 ml min^{-1} . The GC oven temperature program was identical to

10 the one used for GC-MS analysis (see above). CO_2 with known $\delta^{13}\text{C}$ value was used for internal calibration. Instrument precision was checked using [a mixture of *n*-alkanes with known isotopic composition laboratory standards](#). Standard deviations of duplicate measurements were better than 1.7.

3 Results

15 The [studied](#) hydrothermal chert vein [studied \(GPS: 021°09'04.13" S; 119°26'15.21" E; Fig. 1\)](#) is hosted in komatiitic pillow [basalts](#) [basalt](#) that [have](#) [has](#) undergone severe hydrothermal acid-sulphate alteration, producing a kaolinite-illite-quartz mineral assemblage (Van Kranendonk, 2006; Van Kranendonk and Pirajno, 2004) (Fig. S1). The sampled vein crops out in a recent cut wall of the abandoned Dresser Mine (Fig. S1) and consists of a dense chert (microquartz) matrix of deep black colour that contains [kerogen and](#) local concentrations of fresh (unweathered) pyrite crystals (Fig. 2a, b). [There is no field- and/or petrographic evidence for fluid-flow events that post-date the initial vein formation \(e.g. brecciation textures, etc.\)](#).

20 Petrographic analysis and Raman-spectroscopy revealed that kerogen (D bands at 1353 cm^{-1} , G bands at 1602 cm^{-1}) is embedded in the chert matrix (SiO_2 band at 464 cm^{-1}) (see Fig. 2c for a representative Raman spectrum). The organic matter occurs as small clots (<50 μm) of variable shape. Raman spectra of the organic matter exhibit relatively wide D and G bands (82 and 55 cm^{-1} width, respectively) (Fig. 2c). The total organic carbon (TOC) content is 0.2 wt%, and the $\delta^{13}\text{C}_{\text{TOC}}$ value is $-32.8 \pm 0.3 \text{ ‰}$ ([Tab. Table](#) 1). Raman-derived H/C ratios ([calculated after Ferralis et al., 2016](#)) range between 0.03 and 0.14.

25 HyPy was applied to the isolated Dresser kerogen, as well as to preceding and subsequent analytical blanks (combusted sea sand). Hydropyrolysates of the preceding blank contained a series of *n*-alkanes $\leq n\text{-C}_{24}$, with maximum abundances at *n*-C₁₅ (Figs. 3, S2–S4). [Furthermore, Present also were](#) sulphur (only after low-temperature HyPy), traces of siloxanes, and a phenol (Figs. 3, S2, S4) [were present](#). The blank runs also contained traces of aromatic hydrocarbons (Fig. S5).

30 Low-temperature HyPy of the Dresser kerogen produced traces of C_{14–18} *n*-alkanes, with a maximum at *n*-C₁₅ (Fig. S3). However, these compounds were significantly less abundant than those released during high-temperature HyPy (see below). Other compounds observed in the low-temperature step pyrolysate were elemental sulphur, phenols, phthalic acid, siloxanes and traces of aromatic hydrocarbons (Figs. S2, S4–S5).

High-temperature HyPy of the Dresser kerogen yielded *n*-alkanes ranging from *n*-C₁₁ to *n*-C₂₂ with a notable decrease ('step') in the abundance of homologues above *n*-C₁₈ (Figs. 3b, S2, S3), which remained virtually unaffected by blank subtraction ('step' in Fig. 3c). Apart from that 'step', no carbon number preference is evident. The *n*-alkanes have δ¹³C values ranging from -29.4 ‰ to -33.3 ‰ (mean -31.4±1.2 ‰; Fig. 3b; [Tab. Table 1](#)). The hydropyrolysate also contained isomeric mixtures of C₁₂₋₁₈ monomethylalkanes (Fig. S3) and a variety of aromatic hydrocarbons, including (dimethyl-, methyl-)naphthalene(s), (methyl-)biphenyl(s), (methyl-)acenaphthene(s), dibenzofuran, and (methyl-)phenanthrene(s) (Figs. 3b, c, S4-S6). Biologically-diagnostic hydrocarbons such as hopanoids or steroids were absent.

HyPy-treatment of excessively pre-extracted biomass of the heterocystous cyanobacterium *Anabaena cylindrica* SAG 1403-2 yielded a variety of organic compounds, but also included *n*-alkanes with a clear restriction in carbon number to homologues ≤ *n*-C₁₈ (Fig. 3d). In contrast, our experimental synthesis of abiotic *n*-alkanes through Fischer-Tropsch-type reactions under hydrothermal conditions produced a modal/unimodal distribution of homologues ranging from *n*-C₁₂ to *n*-C₄₁ without any carbon number preference (Fig. 3e).

4 Discussion

4.1 Maturity of the Dresser kerogen

The organic record of Archaean rocks is commonly affected by thermal maturation (Brocks et al., 2008; Brocks, 2011; French et al., 2015). ~~The vein chert studied here was obtained from a fresh outcrop and shows no evidence for weathering (e.g., re-oxidation of pyrite; Fig. 2b). The kerogen within the~~The kerogen within the analysed Dresser sample is thermally mature and structurally disordered, as evidenced by relatively wide D and G bands in the Raman spectra (see Fig. 2c for a representative Raman spectrum). This is further also supported by the absence of ~~a-S1~~ bandbands at 2450 cm⁻¹, high RI ratios (0.98-1.05), and low FWHM-D1 values (68.64-76.12), consistent with prehnite-pumpellyite ~~and to~~ lower greenschist metamorphism at a temperature of ca. 300°C (cf. Yui et al., 1996). ~~Both; Delarue et al., 2016). All of these~~ observations are well in line with published Raman spectra of Archaean organic matter from the same region (Ueno et al., 2001; Marshall et al., 2007; [Delarue et al., 2016](#)) and the general thermal history of the host rock (regional prehnite-pumpellyite to lower greenschist metamorphism; Hickman, 1983; Terabayashi et al., 2003). ~~The kerogen is embedded in a very dense and relatively impermeable chert matrix, similar to indigenous and syngenetic organic matter in other hydrothermal chert veins of the Dresser Formation (Morag et al., 2016). An introduction of younger solid macromolecular organic matter during later fluid flow phases, as proposed for the younger Apex chert (Olcott-Marshall et al., 2014), therefore appears highly unlikely. (1975, 1983, 2012; Terabayashi et al., 2003).~~

~~The observed spread in~~Fitting of D5-peaks can be difficult for Raman spectra of highly mature organic matter (Ferralis et al., 2016). Therefore, the ~~Raman-derived~~ H/C ratios calculated herein (0.03-0.14) ~~is due to uncertainties in peak integration should be treated with caution.~~ However, ~~both~~ the Raman-based H/C ratios and the methylphenanthrene/phenanthrene value (MP/P = 0.33; [Tab. Table 2](#)) of the Dresser kerogen are in good accordance with

data reported from more mature [kerogens from the same region \(ca. 3.4 Ga Strelley Pool kerogens \(Formation: 0.08–0.14 and 0.37–0.24, respectively; Marshall et al., 2007\)](#). The low methylphenanthrene index (MPI-I = 0.23) and high phenanthrene/methylphenanthrene index (P/MP = 3.01) result in a computed vitrinite reflectance (R_c (MPI-I)) of 2.87 ([Tab. Table 2](#)), indicating a thermal maturity far beyond the oil generative stage (Radke and Welte, 1983; Boreham et al., 1988). However, it has to be considered that the MPI-I is potentially affected by (de-)methylation reactions (Brocks et al., 2003a). The calculated methylnaphthalene ratio (MNR = 2.52) corresponds to a somewhat lower mean vitrinite reflectance of ca. 1.5 ([Tab. Table 2](#)), which is again in line with a post oil window maturity (cf. Radke et al., 1984). The mismatches between single aromatic maturity parameters are negligible, as these indices have limited application for highly mature Archaean organic matter (Brocks et al., 2003a). The putative offset between the indices and the metamorphic overprint indicated by Raman data is most likely due to the protection of kerogen-bound moieties even under elevated thermal stress (Love et al., 1995; Lockhart et al., 2008). Furthermore, it has been shown that kerogen isolated from the [ca. 3.4 Ga Strelley Pool Formation of the Pilbara Craton](#) also contains larger PAH clusters which are not GC-amenable (>10-15 rings; Marshall et al., 2007). Consequently, it can be anticipated that the compounds detected in the HyPy pyrolysate of the Dresser kerogen represent only a small fraction of the bulk macromolecular organic matter.

The distribution of monomethylalkanes $\leq n-C_{18}$ (Figs. S3, S4) released from the Dresser kerogen resembles high-temperature HyPy products from the Strelley Pool kerogen (Marshall et al., 2007; their Fig. 15). Such isomeric mixtures are typically formed during thermal cracking of alkyl moieties (Kissin, 1987) and are in good agreement with the estimated maturity range. Methylated aromatics such as methylnaphthalenes and -phenanthrenes have also been observed in other hydropyrolysates from Archaean kerogens that experienced low-[regional-grade](#) metamorphism ([French et al., 2015](#); Brocks et al., 2003b; Marshall et al., 2007; [French et al., 2015](#)). In all of these cases, the degree of alkylation varied with the exact thermal alteration of the respective kerogens ([French et al., 2015](#); Marshall et al., 2007; [French et al., 2015](#)).

4.2 Syngeneity of the Dresser kerogen-derived compounds

[The kerogen of the Dresser Formation exclusively occurs in form of fluffy aggregates and clots embedded within a very dense chert matrix that is, once solidified, highly impermeable to fluids. The depositional age of the formation is constrained to \$3481 \pm 3.6\$ Ma \(Van Kranendonk et al., 2008\), and the investigated chert vein shows no evidence for disruption by post-depositional hydrothermal fluids. This has also been described for other hydrothermal chert veins of the Dresser Formation, where the kerogen has been interpreted as being syngenetic \(i.e. formed prior to host rock lithification; Ueno et al., 2001, 2004; Morag et al., 2016\). Furthermore, the maturity of the embedded kerogen is in good accordance with the thermal history of the host rock. An introduction of solid macromolecular organic matter from stratigraphically younger units in this region during later fluid flow phases, as proposed for the younger Apex chert \(Olcott-Marshall et al., 2014\), can therefore be excluded.](#)

As the bitumen fractions of Precambrian rocks are easily biased by the incorporation of contaminants during later stages of rock history (Brocks et al., 2008; Brocks, 2011; French et al., 2015), studies have increasingly focussed on kerogen-bound

compounds that are more likely to be syngenetic to the host rock (Love et al., 1995; Brocks et al., 2003b; Marshall et al., 2007; French et al., 2015). Potential volatile organic contaminants adhering to the kerogen are removed through excessive extraction and a thermal desorption step (~350°C) prior to high-temperature HyPy (550°C; cf. Brocks et al., 2003b; Marshall et al., 2007). The recurrence of few *n*-alkanes in the range of *n*-C₁₄ to *n*-C₂₄ (maximum at *n*-C₁₅) in high-temperature HyPy blank runs obtained immediately before and after the actual sample run (Figs. 3a, S2, S3) indicates minor background contamination during pyrolysis, with a source most likely within the HyPy system. However, these contaminants do not significantly affect the *n*-alkane pattern yielded by high-temperature HyPy of the Dresser kerogen, as evidenced by blank subtraction (Fig. 3c).

Contamination of the sample can be further deciphered by the presence of polar additives or hydrocarbons that are not consistent with the thermal history of the host rock. Plastic-derived branched alkanes with quaternary carbon centres (BAQCs), a common contaminant in Precambrian rock samples (Brocks et al., 2008), have not been detected (Fig. S7). Traces of functionalized plasticizers (phenols and phthalic acid; Figs. S2, S6, S8) are unlikely to survive (or result from) HyPy-treatment. These compounds are therefore considered as background contamination introduced during sample preparation and analysis after HyPy. The observed siloxanes (Fig. 3, S2) probably originate from the GC column or septum bleeding and are unlikely to be contained in the sample. All of these compounds occur only in low or trace abundances and can be clearly distinguished from the ancient aliphatic and aromatic hydrocarbons contained in the Dresser kerogen.

Contamination by (sub-)recent endoliths can be excluded as sample surfaces have been carefully removed and there is no petrographic indication for borings or fissures containing recent organic material (Fig. 2). HyPy of untreated or extracted biomass would yield a variety of acyclic and cyclic biomarkers (cf. Love et al., 2005). However, high-temperature HyPy of the Dresser kerogen almost exclusively yielded *n*-alkanes, minor amounts of monomethylalkanes, and various aromatic hydrocarbons (Figs. 3b, c, S2–S6), while hopanoids or steroids were absent (Figs. S8, S9). This is also in good agreement with the maturity of the Dresser kerogen and previous HyPy studies of Archaean rocks (French et al., 2015; Brocks et al., 2003b; Marshall et al., 2007).

Accidental contamination of the kerogen by mono-, di- and triglycerides (e.g., dust, skin surface lipids) can also be ruled out as HyPy-treatment of these compounds typically results in *n*-alkane distributions with a distinct predominance of *n*-C₁₆ and *n*-C₁₈ homologues, corresponding to the *n*-C₁₆ and *n*-C₁₈ fatty acid precursors (Love et al., 2005; Craig et al., 2004; unpublished data from our own observations). At the same time, the observed distribution of kerogen-derived *n*-alkanes, with a distinct decrease beyond *n*-C₁₈ (Fig. 3b, c) is notably similar to high-temperature HyPy products of kerogens isolated from the ca. 3.4 Ga Strelley Pool Formation of the Pilbara Craton (Marshall et al., 2007; their Fig. 14). Marshall and co-workers considered these *n*-alkanes unlikely to be contaminants as they were released only in the high-temperature HyPy step. Furthermore, the stable carbon isotopic composition of *n*-alkanes in the Dresser high-temperature pyrolysate (–29.4 ‰ to –33.3 ‰; mean –31.4±1.2 ‰) is very similar to the δ¹³C_{TOC} signature of the sample (–32.8±0.3 ‰; Figs. 3, S10; Tab-Table 1), indicating that these compounds were generated from the kerogen. Hence, we consider the compounds released from the Dresser kerogen during high-temperature HyPy (Fig. 3b, c) as syngenetic.

High-temperature HyPy of the Dresser kerogen yielded a variety of aromatic hydrocarbons, which are orders of magnitudes lower or absent in all other pyrolysates (Figs. 3, S2, S4–S6). It also produced significantly higher amounts of *n*-alkanes than the low-temperature step, and these further showed a distinct distribution pattern (i.e. a step $\leq n\text{-C}_{18}$; Figs. 3, S2, S3). The lack of even low quantities of *n*-alkenes that typically accompany bond cleavage in kerogen pyrolysis was also observed by Marshall et al. (2007) in their HyPy analysis of cherts from the Strelley Pool Formation. As a possible explanation for the lack of *n*-alkenes, these authors suggested that the *n*-alkanes were not cracked from the kerogen but were rather trapped in closed micropores until the organic host matrix was pyrolytically disrupted. Alternatively, however, unsaturated cleavage-products may have been immediately reduced during HyPy by the steadily available hydrogen and catalysts. Indeed, it has been demonstrated that double bonds in linear alkyl chains are efficiently hydrogenated during HyPy, even in case of pre-extracted microbial biomass (e.g. Love et al., 2005, our Fig. 3d). We consider both as plausible scenarios to explain the absence of *n*-alkenes in the Dresser chert hydropyrolysate.

4.3 Origin of the Dresser kerogen: hydrothermal vs. biological origin

The $\delta^{13}\text{C}_{\text{TOC}}$ value of -32.8 ± 0.3 ‰ is consistent with carbon fixation by photo- or chemoautotrophs (cf. Schidlowski, 2001). However, organic compounds exhibiting similar ^{13}C depletions (partly down to ca. -36 ‰ relative to the initial substrate) could also be formed abiotically during serpentinisation of ultramafic rocks (Fischer-Tropsch-type synthesis; McCollom et al., 1999; McCollom and Seewald, 2006; Proskurowski et al., 2008). A further constraint on the origin of the Dresser kerogen is provided by the distinct decrease in *n*-alkane abundance beyond $n\text{-C}_{18}$ observed in the high-temperature HyPy pyrolysate (Fig. 3b, c). This distribution resembles HyPy products of pre-extracted Recent cyanobacterial biomass, which also shows a very pronounced restriction in carbon number to homologues $\leq n\text{-C}_{18}$ (Fig. 3d).

The pre-extracted cyanobacterial [biomasscell material](#) and the abiotically produced *n*-alkanes studied as reference samples experienced no thermal maturation. It can nevertheless be expected that burial, and thus heating, of *Anabaena* biomass (Fig. 3d) would initially liberate lower *n*-alkane homologues from their predominant *n*-alkyl moieties while, up to a certain point, retaining the distinct step at $n\text{-C}_{18}$. Experimental maturation of an immature kerogen revealed the preservation of distinct alkyl-chain length preferences even after 100 days at 300°C (Mißbach et al., 2016; e.g. step beyond $n\text{-C}_{31}$ in their Fig. 2). Further maturation would ultimately lead to a [modaunimodal](#) distribution of short-chain *n*-alkanes and erase the biologically inherited pattern (cf. Mißbach et al., 2016). In contrast, abiotically synthesised [extractable organic matter shows compounds show a modaunimodal](#) 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.](#) Consequently, the distinctive distribution of *n*-alkanes released from the Dresser kerogen (i.e. the step $\leq n\text{-C}_{18}$; Figs. 3b, c) can be regarded as a molecular fingerprint relating to a biosynthetic origin of the organic matter.

Highly ^{13}C depleted methane in primary fluid inclusions in hydrothermal chert veins of the Dresser Formation ($\delta^{13}\text{C} < -56$ ‰) was taken as evidence for biological methanogenesis and thus the presence of Archaea (Ueno et al., 2006). Our $\delta^{13}\text{C}_{\text{TOC}}$

value (-32.8 ± 0.3 ‰; [Tab. Table 1](#); Fig. S10) would generally be consistent with both bacterial and archaeal sources (cf. Schidlowski, 2001). [Archaea only synthesize isoprene-based compounds](#) (Koga and Morii, 2007; Matsumi et al., 2011). Straight-chain (acetyl-based) hydrocarbon moieties [—such as fatty acids—](#) the potential precursors of the kerogen-derived *n*-alkanes [— are currently to the current knowledge being formed only by Bacteria and Eukarya, whereas Archaea synthesize isoprene-based compounds](#) (Koga and Morii, 2007; Matsumi et al., 2011). [Moreover, Bacteria commonly \(though not exclusively\) form linear 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 chains ≤ chain-lengths typically do not extend above *n*-C₁₈](#) (cf. Kaneda, 1991). [Hence Consequently](#), given the lack of convincing evidence for the presence of Eukarya as early as 3.5 Ga (cf. French et al., 2015; Parfrey et al., 2011; Knoll, 2014), the most plausible source of kerogen-occluded *n*-alkanes in the Dresser hydrothermal chert is Bacteria. [Given the largely anoxic Strongly reducing conditions during deposition of the Dresser Formation are indicated by widespread pyrite, Fe-rich carbonates, and trace element signatures](#) (Van Kranendonk et al., 2003; Li et al., 2013), [potential biological, 2008](#)). [Potential microbial sources for the Dresser kerogen could include therefore may have included](#) anoxygenic photoautotrophic, chemoautotrophic, and heterotrophic microorganisms.

15 4.4 The ‘hydrothermal pump hypothesis’

Our results strongly support a biological origin of the kerogen [found](#) in the early Archaean hydrothermal chert veins of the Dresser Formation. We explain this finding by the redistribution and sequestration of microbial organic matter [that may have formed in different a variety of Dresser environments \(see below\)](#) through hydrothermal circulation ([“\(proposed herein as ‘hydrothermal pump hypothesis’; Fig. 4\)](#). Higher geothermal gradients prior to the onset of modern-type plate tectonics [\(≈ at ca 3.2–3.0 Ga— \(Smithies et al., 2005; Shirey and Richardson, 2011\)](#) were possibly important drivers of early Archaean hydrothermal systems. In fact, the Dresser Formation was formed in a volcanic caldera environment affected by strong hydrothermal circulation, where voluminous fluid circulation locally caused intense acid-sulphate alteration of basalts and the formation of a dense hydrothermal vein swarm (Nijman et al., 1999; Van Kranendonk and Pirajno, 2004; Van Kranendonk, 2006; Van Kranendonk et al., 2008; Harris et al., 2009). In addition to the high crustal heat flow, the absence of thick sedimentary [eoverscover](#) may have facilitated the intrusion of sea water into the hydrothermal system. The associated large-scale assimilation of particulate and dissolved organic matter and its transport and alteration by hydrothermal fluids (Fig. 4) therefore appears a plausible mechanism that may, at least partly, explain the high amounts of kerogen in early Archaean hydrothermal veins.

The ‘hydrothermal pump hypothesis’ requires a source of organic matter during the deposition of the Dresser Formation (Fig. 4). Whereas contributions from extra-terrestrial sources, as well as [from Fischer-Tropsch-type synthesis linked to the serpentinisation of ultramafic rocks,](#) cannot be excluded, our results indicate a primarily biological origin for the kerogen contained in the chert veins (Fig. 4). The inferred biogenicity is also in line with the consistent $\delta^{13}\text{C}$ offset between bulk kerogens (ca. -20 to -30 ‰) and carbonate (ca. ± 2 ‰) in Archaean rocks ([Hayes, 1983; Schidlowski, 2001; Hayes, 1983](#)).

Prokaryotic primary producers and heterotrophs may have flourished in microbial mats (Dresser stromatolites; Walter et al., 1980; Van Kranendonk, 2006, 2011; Philippot et al., 2007; Van Kranendonk et al., 2008), the water column (planktic ‘marine snow’, Brasier et al., 2006; Blake et al., 2010), and [hotsprings](#) [seven hot springs](#) on land (Djokic et al., 2017). Another biological source for the ancient organic matter could have been chemoautotrophs and heterotrophs thriving in [more](#) [eryptiesubsurface](#) environments, such as basalts (Banerjee et al., 2007; Furnes et al., 2008) and hydrothermal vent systems (Shen et al., 2001; Ueno et al., 2001, 2004, 2006; Pinti et al., 2009; Morag et al., 2016) (Fig. 4). All of these systems are not mutually exclusive and the largely anoxic conditions would have encouraged a high steady-state abundance of organic matter in the aquatic environment (Fig. 4).

Dissolved organic matter (DOM) in modern seawater may resist decomposition over millennial timescales (Druffel and Griffin, 2015). In recent hydrothermal fields, however, organic matter becomes thermally altered and redistributed (Simoneit, 1993; Delacour et al., 2008; Konn et al., 2009). Laboratory experiments using marine DOM indicate that thermal alteration already occurs at temperatures >68–100°C, and efficient removal of organic molecules at 212–401°C (Hawkes et al., 2015, 2016). It has been argued, however, that such DOM removal may also be due to transformation into immiscible material through, for example, condensation (Castello et al., 2014) and/or defunctionalisation reactions (Hawkes et al., 2016). These processes, however, are as yet poorly understood. In the Dresser Formation, hydrothermal temperatures ranged from ca. 300°C at depth to 120°C near the palaeosurface, causing propylitic (ca. 250–350°C) and argillic [alterations](#) ~~(including advanced argillic: ca. 100–200°C) alteration~~ of the host rocks (Van Kranendonk and Pirajno, 2004; Van Kranendonk et al., 2008; Harris et al., 2009). Given this variety of thermal regimes, and the generally anoxic nature of early Archaean sea water, [\(e.g., Van Kranendonk et al., 2003, 2008; Li et al., 2013\)](#), it is likely that some of the organic substances underwent *in situ* alteration, but ~~not~~ complete oxidation, during ~~fast~~ hydrothermal circulation. The entrained organics would have been trapped in the chert that ~~instantaneous~~ [instantaneously](#) precipitated from the ascending hydrothermal fluids due to sub-surface cooling (cf. Van Kranendonk, 2006).

In summary, the ‘hydrothermal pump hypothesis’ [proposed here](#) (Fig. 4) includes (i) a net build-up of organic matter in different Dresser environments under largely anoxic conditions, (ii) a large-scale assimilation of particulate and dissolved organic matter from various biological sources and its subsurface transport and alteration by hydrothermal fluids, as well as (iii) its sequestration within hydrothermal chert veins as kerogen. This model explains the presence of abundant organic carbon in early Archaean hydrothermal veins, as well as its morphological, structural and isotopic variability observed in the Dresser hydrothermal chert veins (Ueno et al., 2001, 2004; Pinti et al., 2009; Morag et al., 2016). [It does not, however, help to pinpoint the formation pathways of distinct carbonaceous structures, as for instance those preserved in the Dresser Formation \(Glikson et al., 2008\) or the younger Apex chert \(e.g. Schopf, 1993; Schopf et al., 2002; Brasier et al., 2002, 2005; Bower et al., 2016\). Further work is necessary to test whether consistent molecular and compound-specific isotopic patterns can be generated from a larger set of Archaean kerogens.](#)

45 Conclusions

Kerogen embedded in a hydrothermal chert vein from the ca. 3.5 Ga-~~old~~ Dresser Formation (Pilbara Craton, Western Australia) is syngenetic. A biological origin is inferred from the presence of short-chain *n*-alkanes in high-temperature HyPy pyrolysates, showing a sharp decrease in homologue abundance beyond *n*-C₁₈. HyPy products of pre-extracted Recent bacterial biomass exhibited a similar restriction to carbon chain-lengths $\leq n$ -C₁₈, ~~while abiotically synthesised~~ whereas abiotic compounds experimentally formed via Fischer-Tropsch-type synthesis exhibited a ~~modal~~ unimodal distribution. ~~This~~ A biological interpretation for Dresser organics is further consistent with the $\delta^{13}\text{C}_{\text{TOC}}$ value (-32.8 ± 0.3 ‰) and the stable carbon isotopic composition of *n*-alkanes in the Dresser high-temperature pyrolysate (-29.4 ‰ to -33.3 ‰; mean -31.4 ± 1.2 ‰). Based on these observations, we propose that the original organic matter was primarily biologically synthesised. We hypothesise that microbially-derived organic matter accumulating in ~~the~~ anoxic aquatic (surface and/or subsurface-environment) environments was assimilated, redistributed and sequestered by hydrothermal fluids ('hydrothermal pump hypothesis').

Supplement

Author contributions

15 JPD, JR and MVK conducted the field work and designed the study. JR conducted petrographic analyses. NS performed Raman spectroscopic analyses. MR and JPD conducted pyrolysis experiments. HM conducted Fischer-Tropsch-type synthesis. TB prepared cyanobacterial cell material. JPD, HM, MR and VT performed biomarker analyses. JPD wrote the manuscript. All authors discussed the results and provided input to the manuscript.

Competing interests

20 The authors declare that they have no competing financial interests.

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Figures

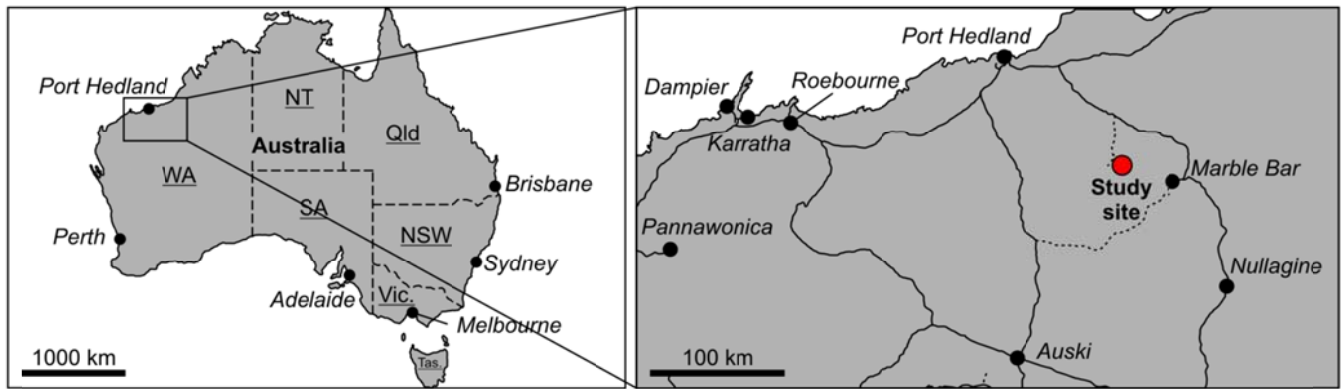


Figure 1. Location of the study site in Western Australia. The hydrothermal chert vein analysed occurs in a recent cut wall of the abandoned Dresser Mine close to Marble Bar.

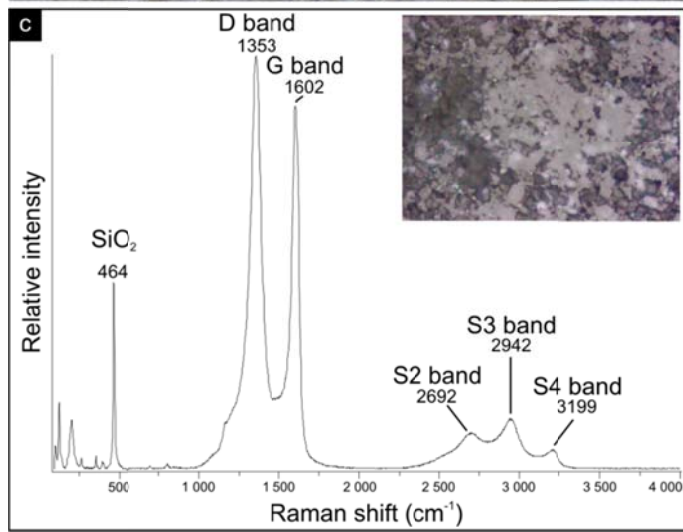
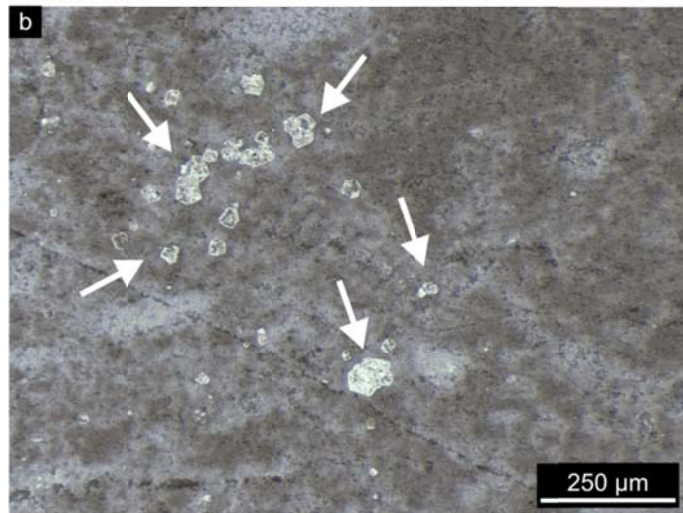
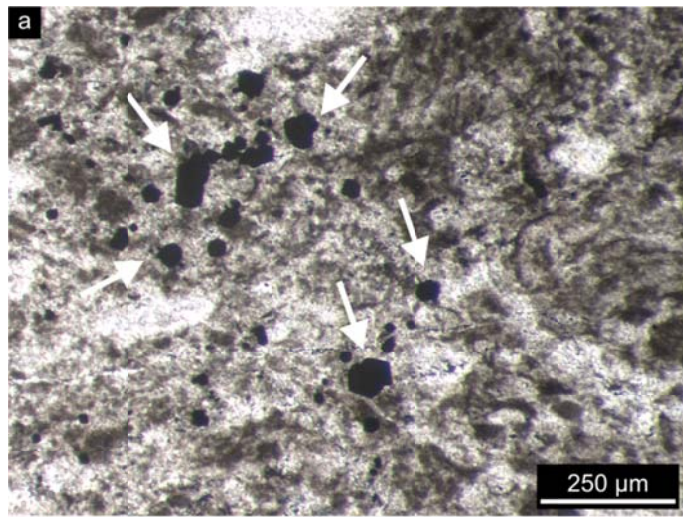


Figure 2. Petrographic observations on the hydrothermal chert vein. **(a,b)** Thin section photographs (**a**: transmitted light; **b**: reflected light) showing kerogen (brownish colours) and pyrite (arrows, black colours in **a**, bright colours in **b**) embedded within a fine grained chert matrix. Note that the pyrite crystals (arrows) are excellently preserved and show no evidence of oxidation. **(c)** Representative Raman spectrum of kerogen (D band at 1353 cm^{-1} and G band at 1602 cm^{-1}) present in the hydrothermal chert vein. Note the wide D and G bands (82 and 55 cm^{-1} width, respectively), pointing to thermally mature and structurally disordered kerogen, and the absence of a S1 band (at 2450 cm^{-1}) being consistent with prehnite-pumpellyite ~~and~~ lower greenschist metamorphosis and a temperature of ca. 300°C (cf. Yui et al., 1996); Delarue et al., 2016.

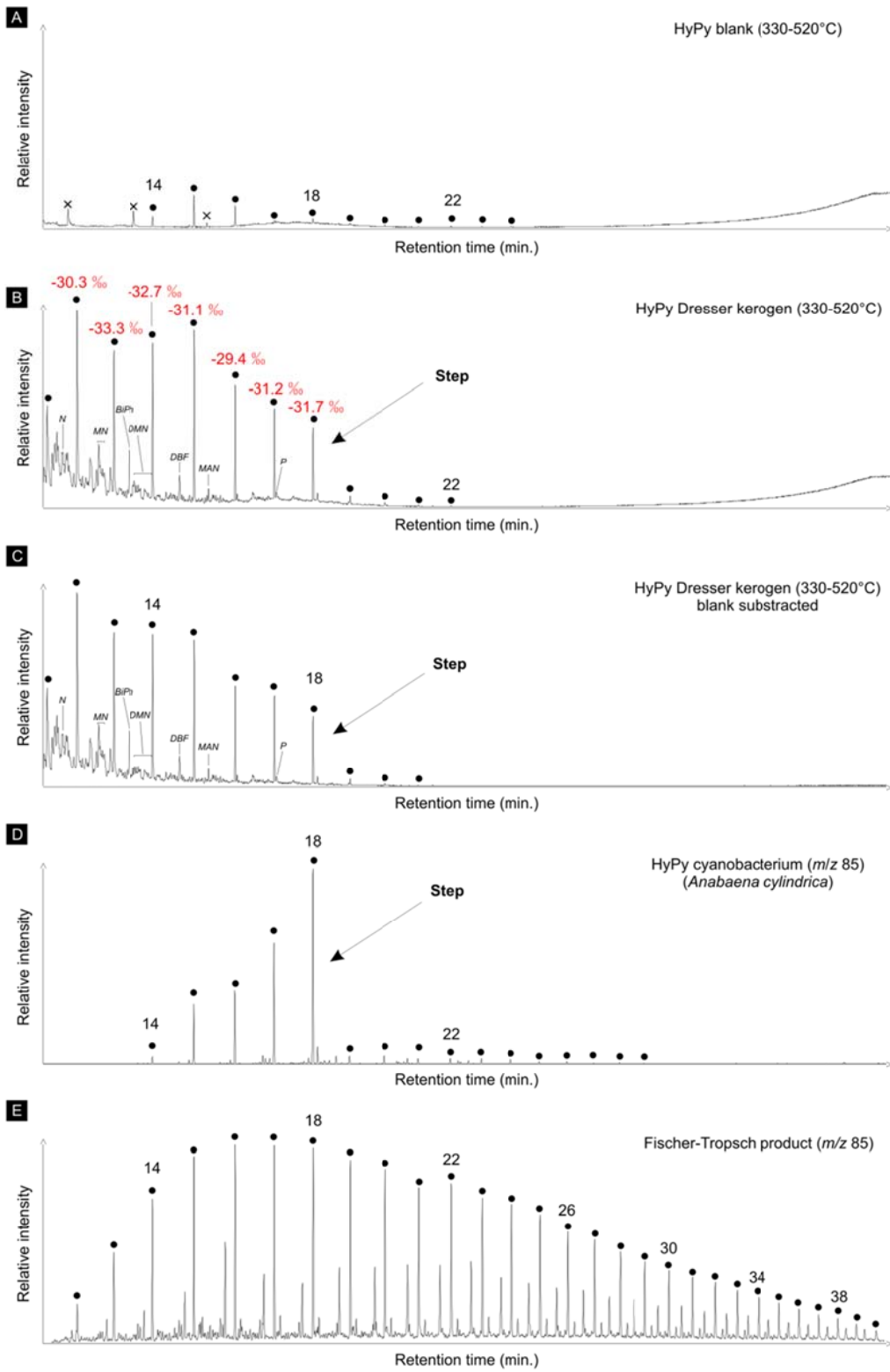


Figure 3. Total ion currents (a–c; in the same scale) and ion chromatograms selective for alkanes (d–f; m/z 85). **(a)** High-temperature HyPy (330–520°C) product of analytical blank (combusted sea sand) obtained prior to HyPy of the Dresser kerogen. *n*-Alkanes in the range of *n*-C₁₄ to *n*-C₂₄ (maxima at *n*-C₁₅) represent HyPy background contamination. **(b)** High-temperature HyPy (330–520°C) product of the Dresser kerogen. Note the sharp decrease in abundance of *n*-alkanes beyond *n*-C₁₈ (see arrows). $\delta^{13}\text{C}$ values of *n*-C₁₂ to *n*-C₂₈ show a high similarity to the $\delta^{13}\text{C}_{\text{TOC}}$ value ($-32.8\pm 0.3\text{‰}$), further confirming syngeneity. **(c)** Blank subtraction (**b** minus **a**) showing that contaminants have no major impact on the *n*-alkane pattern yielded during the high-temperature HyPy step of the Dresser kerogen (**b**). **(d)** HyPy products of cell material of the heterocystous cyanobacterium *Anabaena cylindrica*. Note the sharp decrease in abundance of *n*-alkanes beyond *n*-C₁₈ (see arrows), similar to the *n*-alkane distribution of the Dresser kerogen (**b**). **(e)** Products of experimental Fischer-Tropsch-type synthesis under hydrothermal conditions; abiogenic *n*-alkanes show a ~~modal~~ unimodal distribution that is distinctly different from the Dresser kerogen. Black dots: *n*-alkanes (numbers refer to carbon chain-lengths); N: naphthalene; MN: methylnaphthalenes; BiPh: 1,1'-biphenyl; DMN: dimethylnaphthalenes; DBF: dibenzofuran; MAN: methylacenaphthene; P: phenanthrene; crosses: siloxanes (GC column or septum bleeding).

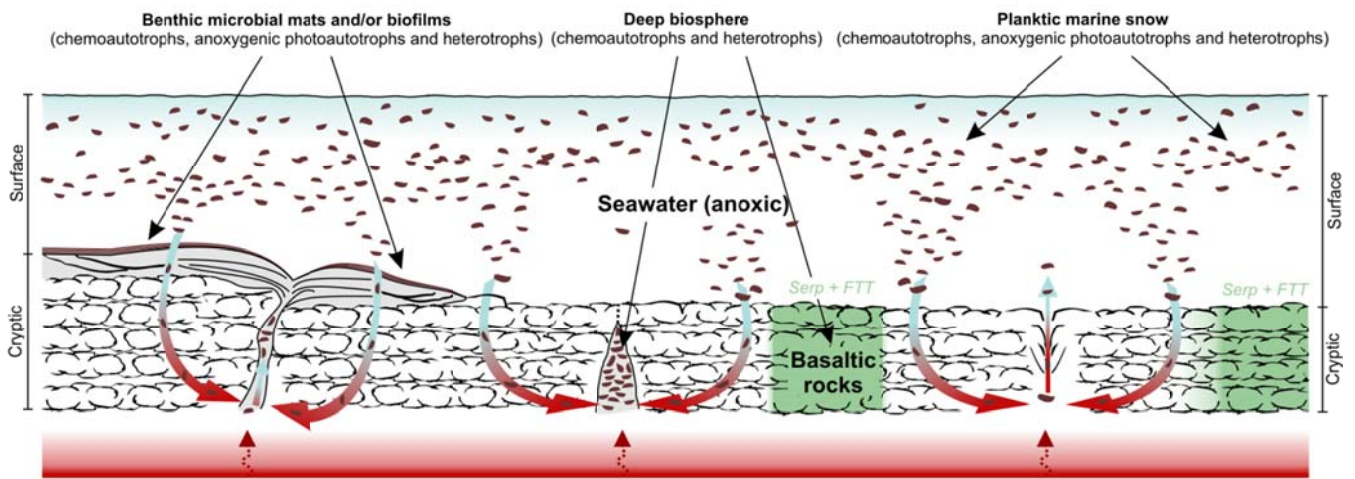


Figure 4. The 'hydrothermal pump hypothesis'. Organic matter was predominantly biologically produced and heterotrophically processed by Bacteria and, possibly, Archaea. Additionally, Fischer-Tropsch-type synthesis of organic matter linked to the serpentinisation of ultramafic rocks (McCollom et al., 1999; McCollom and Seewald, 2006) may have occurred locally. Primary producers (chemoautotrophs, anoxygenic photoautotrophs) and heterotrophs may have flourished in surface waters (planktic 'marine snow'), at the water/rock interface (microbial mats and/or biofilms), and in cryptic environments (e.g., within basalts and hydrothermal vent systems). After accumulating in different Dresser environments, the organic matter was redistributed and sequestered in veins by hydrothermal fluids.

Table 1. Stable carbon isotopic composition ($\delta^{13}\text{C}$) of the total organic carbon (TOC) and *n*-alkanes released from high-temperature HyPy of the Dresser kerogen.

	<i>n</i> -C ₁₂	<i>n</i> -C ₁₃	<i>n</i> -C ₁₄	<i>n</i> -C ₁₅	<i>n</i> -C ₁₆	<i>n</i> -C ₁₇	<i>n</i> -C ₁₈	<i>n</i> -C ₁₂₋₁₈ (mean)	TOC
$\delta^{13}\text{C}$	-30.3	-33.3	-32.7	-31.1	-29.4	-31.2	-31.7	-31.4	-32.8
SD	0.5	1.4	0.2	1.7	0.3	0.8	0.1	1.2	0.3

Table 2. Maturity indices (based on aromatic hydrocarbons) of the Dresser kerogen. MP/P: Methylphenanthrene/phenanthrene ratio; MPI-I: Methylphenanthrene index [$1.5 * (2\text{-MP} + 3\text{-MP}) / (P + 1\text{-MP} + 9\text{-MP})$]; Radke and Welte, 1983]; P/MP: Phenanthrene/methylphenanthrene ratio; R_c (MPI-I): computed vitrinite reflectance ($0.7 * MPI\text{-I} + 0.22$, according to $P/MP > 1$; Boreham et al., 1988); MNR: Methylnaphthalene ratio ($2\text{-MN}/1\text{-MN}$; Radke et al., 1984).

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MP/P	MPI-I	P/MP	R_c (MPI-I)	MNR
0.33	0.23	3.01	2.87	2.52