# Preliminary observations on hydrocarbon biomarker patterns of the Barney Creek Formation in the well GR-10

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## 1. Introduction

Initial interest in the Proterozoic basins of Northern Australia concerned the thermal maturation and petroleum potential of black shales of the Roper and McArthur Groups (Crick et al., 1988; Powell et al., 1987; Summons et al., 1988; Summons et al., 1994). Subsequently interest expanded to include the biogeochemical processes that took place during their deposition with special interest in the redox conditions prevailing at the time of their deposition (Johnston et al., 2008) and the preservation of organic molecules that were informative about biological communities that were responsible for the formation of organic matter that is well-preserved in these settings (Brocks et al., 2009; Brocks et al., 2005; Brocks and Schaeffer, 2008; Summons et al., 1988).

The present work is aimed to critically re-examine the terpane and carotenoid patterns in the Barney Creek Formation to evaluate down-core trends of redox-sensitive and maturity-sensitive biomarker proxies. We stress that these results are very preliminary and presented to justify further sampling of this well down to the point (~300m) where the compounds of interest disappear due to the increased levels of thermal maturation. Should the re-sampling be approved, our next step will be to expand this data set as well as to measure the C-isotopic compositions of amenable molecules.

## 2. Samples

Barney Creek Formation samples from the well Glyde River-10 (aka GR-10) were from an earlier collection made by GA. These were initially analysed for their bulk carbon and sulfur isotopic compositions prior to being evaluated for hydrocarbon biomarkers of paleo-environmental interest:

Isotope data for the McArthur Group, McArthur Basin, Australia

| Barney Creek Fm GR-10 | Depth (m) | $\delta^{13}C_{org}$ | $\delta^{33}S$ | $\delta^{34}S$ | $\delta^{36}S$ | $\Delta^{33}S$ | $\Delta^{36}S$ |
|---|---|---|---|---|---|---|---|
| | 51.8 | -33.12 | 11.74 | 22.96 | 44.18 | -0.015 | 0.11 |
| | 80.2 | -31.79 | 12.53 | 24.50 | 47.30 | -0.016 | 0.23 |
| | 89.2 | -33.04 | 12.38 | 24.19 | 46.69 | -0.008 | 0.23 |
| | 133.8 | -32.11 | 12.45 | 24.39 | 47.11 | -0.035 | 0.26 |
| | 141.9 | -31.95 | 12.75 | 24.95 | 48.27 | -0.024 | 0.32 |
| | 182.0 | -32.22 | 13.48 | 26.40 | 51.05 | -0.033 | 0.30 |
| | 232.0 | -32.02 | 10.07 | 19.71 | 38.08 | -0.027 | 0.30 |
| | 252.0 | -31.23 | 14.98 | 29.39 | 57.08 | -0.055 | 0.50 |
| | 305.5 | -32.24 | 17.93 | 35.22 | 68.54 | -0.054 | 0.57 |

## 2. Sample preparation

Core samples were cleaned by removal of the outer edges using a fine rock saw before being broken into chips. These were further separated into 'inside' and 'outside' components using the abrasion method developed by Jarrett et al. (Jarrett et al., 2013). Dried and crushed rock samples were ground to <200 mesh grain size in a puck mill prior to being extracted by sonication with a mixture of DCM;methanol 1:1. The extracts were reduced to ~ 500 μl under a stream of purified nitrogen gas and separated into saturated, aromatic and polar fractions using column chromatography over 12 g activated and dry-packed silica gel Saturated hydrocarbons were eluted with 1.5 dead volumes (DV) hexane, aromatic hydrocarbons with 2 DV hexane : DCM (1:1 v/v) and polars with 2 DV DCM : methanol (1:1 v/v). An internal standard comprising $D_4$ ($d_4$-$C_{29}$-ααα-ethylcholestane; Chiron Laboratories AS) was added to the saturated hydrocarbon fraction. For selected samples, the aromatic fraction was further separated into monoaromatics, diaromatics and

triaromatics by column chromatography on activated (120°C, 12 h) alumina powder using DCM as eluent.

*Gas chromatography-mass spectroscopy (GC-MS)*. Recombined saturated and aromatic fractions were analyzed on an Agilent gas chromatograph (GC, 7890C) coupled to an Agilent triple quadrupole MS (QQQ, 7010B) operated in multiple reaction monitoring (MRM) mode (Fig. S1). A multi-mode injector was with an initial injection temperature of 45℃ was ramped at a rate of 720ºC /min to 340ºC. A DB-5MS column (60m×250μm×0.25μm) was used with the GC oven temperature held isothermal at 40 ºC for 2 mins, ramped to 320ºC at a rate 4ºC /min, and the held at this temperature for 22mins. The transfer line and source temperatures were set at 300ºC and 250ºC, respectively. The electron energy was set at 50eV to ensure a stronger signal for the Precursor-Product transitions. All biomarker data were processed using MassHunter QQQ quantitative software. Each compound was identified and integrated under MRM mode within a narrow retention time window (0.5min).

*Identification of arylisoprenoids and carotenoids:* The 2,3,4- and 2,3,6-trimethylarylisoprenoids and their precursor carotenoids, okenane, chlorobactane, isorenieratane, renieratane and renierapurpurane were identified by their diagnostic mass spectral precursor-product transitions and relative retention times. β-carotane was identified similarly.

*Identification of steranes and triterpanes:* These identifications were made on the basis precursor-product transitions and relative retention times and by comparisons with authentic compounds in the AGSO-1 standard oil (Grosjean et al., 2009).

**Results**

Molecular ratios of biogeochemical interest include the proportions of hopanes that preserve information about bacterial processes including oxygenic photosynthesis by cyanobacteria (2-MHI) and methanotrophy (3-MHI). Carotenoids are of particular interest here because they represent the oldest known preserved records of anoxygenic phototrophs

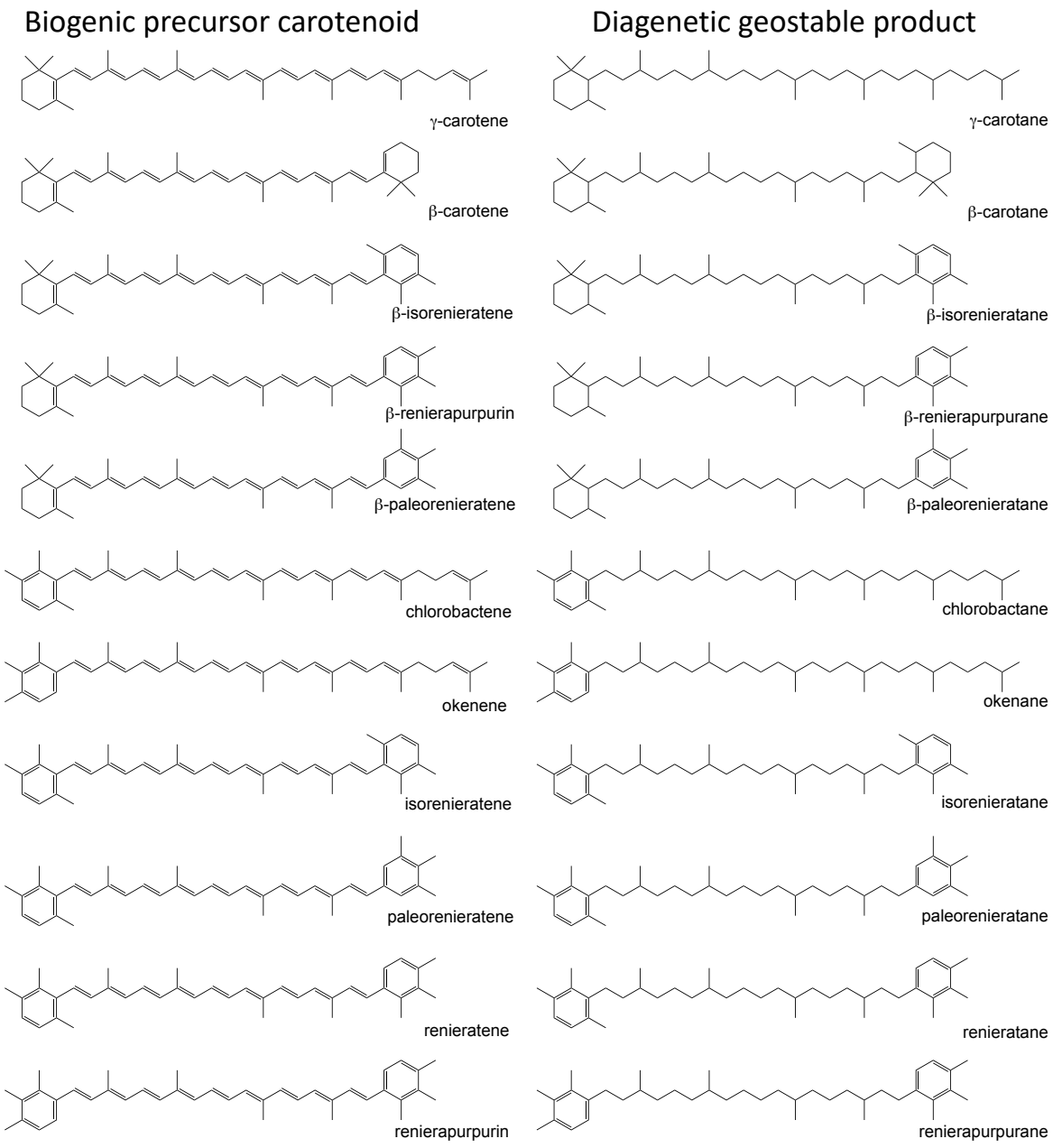
(Brocks et al., 2005). The structures of carotenoid-derived molecules investigated here are shown in Figure 1 while the results of the carotenoid and terpane hydrocarbon analyses are presented in Table 1.

## Table 1

| GR-10 | terpane ratios | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Depth(m) | Pr/Ph | TAS/$C_{30}$H | 2-MH Index | 3-MH Index | C31,2-MHI | C31,3-MHI | (TNH+28,30 BNH)/C30H | HHI | Gamma Index | βa/αβ Hopane | C31H S/ S+R | C32H S/S+R | Ts/(Ts+Tm) |
| 51.8-51.9 | 1.96 | 15.58 | 0.02 | 0.12 | 0.03 | 0.10 | 0.08 | 0.02 | 0.00 | 0.10 | 0.59 | 0.60 | 0.35 |
| 80.2-80.3 | 1.56 | 10.90 | 0.01 | 0.10 | 0.02 | 0.08 | 0.08 | 0.02 | 0.01 | 0.08 | 0.59 | 0.61 | 0.45 |
| 89.2-89.4 | 0.72 | 1.64 | 0.02 | 0.06 | 0.03 | 0.05 | 0.04 | 0.02 | 0.19 | 0.06 | 0.57 | 0.61 | 0.44 |
| 130.35-130.! | NA | 0.49 | 0.01 | 0.04 | 0.02 | 0.04 | 0.04 | 0.03 | 0.09 | 0.05 | 0.58 | 0.61 | 0.50 |
| 133.8-133.9 | 0.82 | 1.44 | 0.02 | 0.04 | 0.03 | 0.04 | 0.05 | 0.02 | 0.13 | 0.06 | 0.58 | 0.61 | 0.46 |
| 141.9-142.0 | 1.09 | 4.51 | 0.02 | 0.04 | 0.03 | 0.03 | 0.07 | 0.02 | 0.07 | 0.06 | 0.58 | 0.60 | 0.45 |
| 182.8-182.9 | 1.08 | 2.28 | 0.02 | 0.04 | 0.03 | 0.03 | 0.05 | 0.02 | 0.06 | 0.06 | 0.57 | 0.60 | 0.49 |
| 305.5-305.6 | 2.00 | 0.00 | 0.02 | 0.04 | 0.05 | 0.04 | 0.14 | 0.02 | 0.00 | 0.07 | 0.57 | 0.62 | 0.55 |
| 341.5-341.6 | 2.63 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.11 | 0.02 | 0.00 | 0.13 | 0.59 | 0.54 | 0.44 |

| GR-10 | carotenoid ratios | Abr. | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Depth(m) | chlorobactane | chl | ¦chl+oke)/β-carccho+oke)/C30H | iso+ren+rep/β-caro | iso+ren+rep/C30H | iso+ren+rep/chl+oke | β-iso+rep/β-caro | oke/chl | β-caro/C30H | (Iso+β-iso)/chl | -iso+rep/iso+ren+rnso/iso+ren+rnp | | |
| 51.8-51.9 | okenane | oke | 13.24 | 0.08 | 5.72 | 0.04 | 0.43 | 4.92 | 1.79 | 0.01 | 0.71 | 0.86 | 0.21 |
| 80.2-80.3 | isorenieretane | iso | 4.34 | 0.09 | 2.95 | 0.06 | 0.68 | 2.20 | 2.22 | 0.02 | 1.17 | 0.75 | 0.27 |
| 89.2-89.4 | renieratane | ren | 16.19 | 9.53 | 3.22 | 1.89 | 0.20 | 2.87 | 2.54 | 0.59 | 0.16 | 0.89 | 0.08 |
| 130.35-130.! | renierapurpurane | rnp | 4.87 | 3.43 | 0.58 | 0.41 | 0.12 | 0.56 | 4.17 | 0.70 | 0.23 | 0.97 | 0.13 |
| 133.8-133.9 | β-carotane | β-caro | 6.69 | 3.77 | 0.68 | 0.38 | 0.10 | 0.76 | 3.79 | 0.56 | 0.22 | 1.12 | 0.07 |
| 141.9-142.0 | β-isorenieratane | β-iso | 11.35 | 2.49 | 1.45 | 0.32 | 0.13 | 1.49 | 3.71 | 0.22 | 0.21 | 1.02 | 0.07 |
| 182.8-182.9 | | | 8.70 | 1.98 | 0.50 | 0.11 | 0.06 | 0.70 | 4.74 | 0.23 | 0.26 | 1.41 | 0.17 |
| 305.5-305.6 | | | NA | 0.00 | NA | 0.00 | NA | NA | NA | 0.00 | NA | NA | NA |
| 341.5-341.6 | | | NA | 0.14 | NA | 0.00 | 0.00 | NA | 0.00 | 0.00 | NA | NA | NA |

**Figure 1. Structures of relevant biomarkers**



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