Supplementary information for:

A very unconventional hydrocarbon play: the Mesoproterozoic Velkerri Formation of Northern Australia.

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New samples

New samples acquired for this study were obtained from the petroleum wells Tarlee S3, Altree 2, Amungee NW1, Tanumbirini 1, and Marmbulligan 1 housed in the Northern Territory Geological Surveys core facility in Darwin, N.T. Details of these wells can be found at http://www.geoscience.nt.gov.au/gemis/. Samples obtained from these wells were broken into ~2cm^3 fragments and the resulting chips where milled in a tungsten carbide mill until the powder could pass through a 75 μm mesh resulting in a homogenous sample powder.

Major and trace element analyses

Bulk elemental analysis where analysed by Bureau Veritas. Major elements where analysed by X-ray fluorescence (XRF) using a Panalytical Axios 1™ spectrometer. XRF analysis where conducted on 40mm diameter fused beads prepared from a 1:10 sample/lithium tetraborate mixture (12:22 tetraborate/metaborate) from calcined powder. Calibration regression lines were prepared using between Spec Pure oxides and certified reference materials. Corrections for mass absorption effects were applied on concentration values using a combination of alpha coefficients and/or Compton scatter. The accuracy for silica is within 0.5% absolute and is within 1% for other majors and within 5% for trace elements.

Trace elements were analysed on an Agilent 7900 ICP-MS. Analysis was performed on ~0.15g of rock powder which underwent mixed acid digestion (HNO$_3$, HClO$_4$ and HF) and made up to 10ml analytical volume. Rh and Ir were used as an internal standard for drift correction. The generation of oxides and doubly charged species was monitored using the mass ratios Th/ThO with on-line interference correction and internal standard correction carried out. To assess accuracy of the digestion process and analysis,) certified reference materials (CRMs) Rmad25, Rmad 500 (A set), Rref25, Rref500 (B set) where run. Analytical reproducibility was assessed by repeat analysis of these CRMs throughout the run and repeat analysis of a random selection of solutions at the end of the run.

Carbon stable isotope analyses

One to two grams of sample powder were treated with excess 3N HCl to remove trace carbonate minerals. The insoluble residual was centrifuged and rinsed with deionized water. Isotopic analyses for nitrogen and carbon were performed using a Euro EA Elemental Analyzer coupled to a Nu Horizons continuous-flow stable isotope mass spectrometer. Analyses were performed in the stable isotope laboratory at the University of Adelaide. Powdered, decarbonated samples were weighed and sealed in tin capsules for isotopic analysis and were combusted at 1050ºC. Data are reported using delta notation relative to the Vienna Pee Dee

Belemnite International Standard (V-PDB) for carbon. $\delta^{13}C$ was calibrated to IAEA CH-6 and CH-7; USGS 24, 40, and 41; and NBS-22. Standard deviation for bulk samples is 0.15 for $\delta^{13}C$ and 0.1. Results for $\delta^{13}C$ analysis were combined with previously published data from Cox et. al. (2018) and all data are available as an electronic supplement.

Carbon and sulfur analyses

Samples were analysed by elemental analysis (EA) using a Perkin Elmer 2400 series II CHNS/O Elemental Analyzer in CHNS configuration at the University of Adelaide Biogeochemistry Lab Facilities. The combined combustion/reduction tube was packed using Perkin Elmer EA6000 and Perkin Elmer 'Hi-Purity' copper with a reaction temperature was 975°C. Results were calibrated to 2mg of Perkin Elmer Organic Analytical Standard Cystine $((SCH_2CH(NH_2)CO_2H)_2)$ with known abundances of carbon (29.99%), hydrogen (5.07%), nitrogen (11.67%) and sulfur (26.69%). The accepted error range between standards was ±0.3 % for carbon, hydrogen and nitrogen and ±0.4 % for sulphur calculated against 12 replicates.

Bulk rock pyrolysis data

Pyrolysis measurements were undertaken using a Weatherford's Source Rock Analyser™. Crucibles were loaded into the carousel and heated under inert Helium in both the pyrolysis (to obtain S1, S2, Tmax and S3 peaks) and oxidation modes (to obtain the S4 peak). The pyrolysis oven was first held at 300°C for 5 minutes and ramped at 25°C per minute from 300°C to 650°C. Subsequently the oven was reduced to 220°C and held for 5 minutes with the carrier gas converted to inert air (CO & CO_2 free) and purged, ramped at maximum heating to 580°C and held for 20 minutes. The flame ionisation detector (FID) was calibrated by running Weatherford Laboratories Instruments Division Standard 533. The IR Analysers were calibrated against standard gas with known concentration of CO_2 and CO. An analysis blank was run as 'blank' mode with the sample batch and the blank data were automatically subtracted from all analyses. An external check standard was also run first with each batch to ensure the instrument status with additional check standards every 10 samples. The results were processed where peak areas and geochemical indices including Total organic carbon (TOC), Oxygen Index (OI), Hydrogen Index (HI) and Production Index (PI) are automatically calculated. SRA pyrolysis data was screened using quality control criteria defined in Hall et al. (2016).

These results were combined with previously published data from Cox et al. (2016) and Data Information Package 14 (Revie and Normington, 2018) available from the Northern Territory Geological Survey at https://geoscience.nt.gov.au/gemis/ntgsjspui/handle/1/82595. The complete data file is available as an electronic supplement.

Data analysis

Estimates of means and their corresponding 95% confidence intervals were conducted using Monte Carlo Bootstrap Simulation. These calculations were conducted in Mathlab™ using the "bootstrp" and "bootci" commands. Details of Mathlab's implementation of Monte Carlo Bootstrap Simulation can be found at: https://au.mathworks.com/help/stats/bootstrp.html Details on the theoretical basis of this analysis can be found in Davison and Hinkley (1997).

Kernel density calculations where performed in Mathlab™ using the code implementation of Botev et. al. (2010).

Estimates of organic carbon burial where calculated using a simple carbon isotope mass balance approach for the calculation of f_{org} (i.e. Equation 1 - (Kump et al., 2010)).

$$f_{org} = \frac{\left[\left(\delta^{13}C_{org} + \Delta_{org-carb}\right) + \delta^{13}C_{in}\right]}{\Delta_{org-carb}} \quad Equation\ 1$$

Using modern parameterization of marine carbon cycle (i.e., carbon isotope composition of volcanic input of ~-5‰ to ~-8‰, Javoy et al., 1986), and fractionation factor between inorganic and organic carbon of ~ 27‰ to ~33‰ (Hayes et al., 1999). To account for variability of in both $\delta^{13}C_{in}$ and $\Delta_{org-carb}$, a Monte Carlo simulation approach was used to simulate the variability of these parameters (Fig. 1A/B). The code implementation of this is shown below.
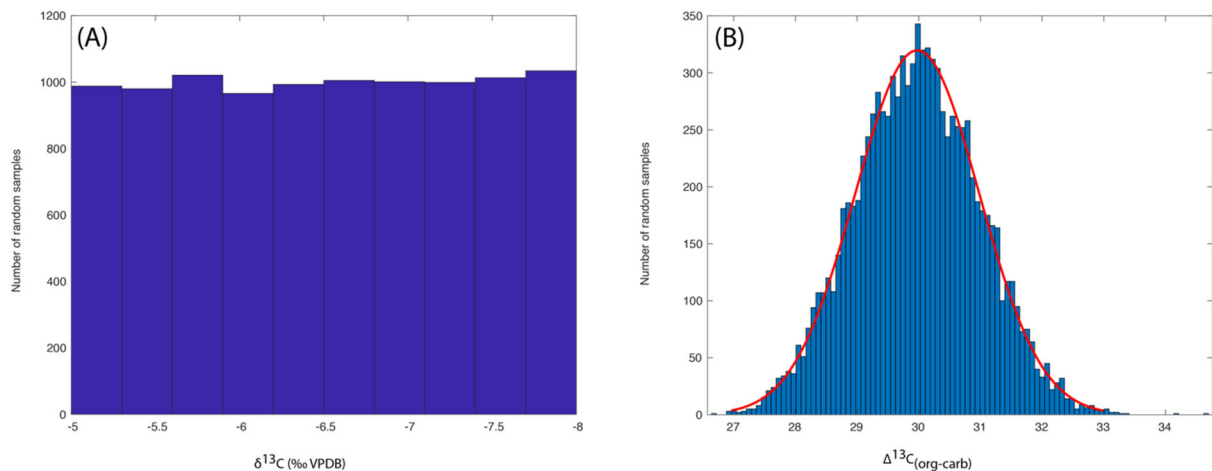

Figure 1. Example of the range of values used for (A) $\delta^{13}C_{in}$ and (B) $\Delta_{org-carb}$. These 10000 randomly generated values where used to calculate 10000 values for f_{org}. From this simulated data an average and standard deviation for f_{org} was calculated.

```matlab
% Isotopic mass balance calculation based on Monte Carlo simulation with
% variable input parameters.
function [fboot,std_forg] = Org_Model(d13Corg)

% Number of Monte Carlo simulations
nsamples = 10000;
%d13Cin is allowed to randomly vary (uniform distribution) between
%-5 and -8 per mil
mantle = 5 + 3*rand(nsamples,1);
%Organic-carbonate fractionation factor is allowed to randomly vary
%(guassian distribution) around 30 per mil (Hayes et al 1998).
fract = 30 + 1*randn(nsamples,1);

for i = 1:length(d13Corg)
% Final calculation of 10000 forg calculations
    forg = (d13Corg(i) + fract + mantle)/30;
% bootstrap resampling of forg calculations
    fboot(:,i) = bootci(10000,@nanmean,forg);
    std_forg(:,i) = std(forg);
end

return
```

Reconstructing initial total organic carbon (TOC$_i$)

Using filtered source rock data, we reconstructed TOC$_i$ using the following approach.

1. Transformation Ratio (TR) was estimated based on Equation 3 (Espitalie et al., 1987) and assumed Type 1 organic matter with an initial Hydrogen Index = 750.

$$TR = \frac{1200 \times (H_i - H_o)}{H_o \times (1200 - H_i)} \; Equation \; 3$$

where:
H_i = Initial hydrogen index (assumed to be 750)
H_o = Measured hydrogen index

2. Original TOC was the calculated using Equation 4 (Modica and Scott, 2012).

$$TOC_i = \frac{TOC_o}{1 - \alpha(TR)} \; Equation \; 4$$

where:
TOC_i = Initial TOC
TOC_o = Measured TOC

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