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PETROLEUM GEOCHEMISTRY

INTRODUCTORY NOTE

A geochemical investigation has been conducted to assess hydrocarbon prospectivity of the Mallabah Dolostone in the LMDH3 well located in the Birrindudu Basin, Northern Territories, Australia. Four (4) core chip samples from this well were analyzed by a variety of geochemical techniques, including total organic carbon (TOC, LECO®) and programmed pyrolysis (SRA). The complete results of these analyses are documented in this report along with an integrated geochemical interpretation that is summarized in the following table.

<table>
<thead>
<tr>
<th>Well Name</th>
<th>Formation</th>
<th>Main Product</th>
<th>Thermal Maturity</th>
<th>Source Rock Richness</th>
<th>Organic Matter Type</th>
<th>Shale Oil Risk</th>
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</thead>
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<tr>
<td>LMDH3</td>
<td>Mallabah Dolostone</td>
<td>Estimated Original</td>
<td>Good</td>
<td>Oil-prone Type I/II</td>
<td>Moderate</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Measured Currently</td>
<td>Oil</td>
<td>Peak Oil Window</td>
<td>Mixed Type II/III</td>
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</tr>
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</table>

Table 1. Geochemical Summary

MALLABAH DOLOSTONE

Four (4) samples from the Mallabah Dolostone Formation were analyzed for LECO TOC content and programmed pyrolysis (Fig. 1). TOC contents ranged from 1.06 to 1.85 wt.% and averaged 1.37 wt.% (good). All of these samples have TOC content above the minimum requirement of 1 wt.% for effective petroleum source rocks, while none have TOC content above the minimum requirement of 2 wt.% for economic petroleum source rocks. Highest TOC content was found near the top of the designated Mallabah Dolostone interval (194 m depth) (Fig. 1) and TOC shows a progressive decreasing trend toward the base of the interval based upon the sparse sampling available (Fig. 1).

The S1 values of the Mallabah Dolostone source rock samples average 0.30 mg HC/g rock (6 bbl oil/acre-ft) and the S2 values average 3.49 mg HC/g rock (76 bbl oil/acre-ft). The S1 and S2 values imply poor in-situ hydrocarbon saturation and fair remaining generative potential (Fig. 1). The normalized oil contents (NOC) in the Mallabah Dolostone samples, (S1/TOC) x 100, average 22 (Fig. 1). NOC values of 20 to 50 are typical of low maturity source rocks, whereas values of 50 to 100 indicate possible oil staining or shows in thermally mature, tight petroleum source rocks. NOC > 100 are often associated with conventional oil reservoirs and indicate good prospectivity in unconventional shale oil plays. Very low NOC values < 20 are most likely related to post-mature source rocks that have likely generated and expelled most of their in-situ hydrocarbon saturation. Jarvis (2012) has utilized a depth comparison of TOC versus programmed pyrolysis S1 yields as a potential indicator of producible hydrocarbon saturation in unconventional source rocks. When the S1 yields (reported as mg HC/g rock) exceed or “cross-over” the measured TOC content (reported as wt.%), this would be interpreted to represent zones with good potential for containing producible hydrocarbon saturation (or zones of possible contamination). In the present study, there is no S1 cross over TOC in any of the Mallabah Dolostone samples analyzed in this well (Fig. 1).
Figure 1. Geochemical depth plots for the LMDH3 well.
The measured Hydrogen Index (HI) values in the Mallabah Dolostone average 246 mg HC/g TOC, indicating mixed oil/gas-prone Type II/III kerogen quality in these source rocks at present day. Original HI of these samples are estimated to average 579 mg HC/g rock, which indicate oil-prone Type I/II kerogen. Transformation Ratios (TR) based upon HI are 72%, which suggest a peak to late oil window thermal maturity. The T_{max} values in the Mallabah Dolostone samples average is 440°C. T_{max} between 435 and 445°C typically indicate peak oil window, while samples in the late oil window usually have values between 445 and 450°C (Type II kerogen). On the basis of these guidelines, the average Mallabah Dolostone T_{max} values in this well would be interpreted to be in the peak oil window. Using the formula published by Jarvie et al. (2007) for Type II kerogen (Calculated R_o = (0.0180)(T_{max}) – 7.16), the measured T_{max} value of 440°C is equivalent to a Calc. %R_o value of 0.76%. It is important to note that T_{max} is only a crude measure of thermal maturation (Peters, 1986) and it can be compromised by a variety of pyrolysis artifacts and caveats.

The Production Index (PI) values in the Mallabah Dolostone samples average 0.08. These low PI values would normally indicate immature source rocks, which typically have PI values < 0.1. Alternatively, the low PI values in these Mallabah Dolostone samples are a consequence of low S1 yields and could suggest significant expulsion/migration of hydrocarbons out of these potential source rocks.

The thermal maturity of the Mallabah Dolostone source was also evaluated by measured Kübler Index values from XRD, which are based upon illite crystallinity. These values can be used as maturity indicator when samples contain sufficient high quality clays (Abad, 2008). A single sample (207.01 m) from the Mallabah Dolostone (avg. 30% clays) has a measured Kübler Index of 0.159, which is equivalent to a measured vitrinite reflectance of > 4% (late stage metagenesis). This interpretation is inconsistent with other geochemical maturity ratios evaluated in this study and suggests the Kübler Index should be used with caution to evaluate thermal maturity in Palaeoproterozoic aged source rocks.

ORIGINAL GENERATIVE POTENTIAL AND HYDROCARBON YIELD CALCULATIONS

Petroleum generative capacity depends on the original quantity of organic matter (TOC_o) and the original type of organic matter (HI_o) (Peters et al., 2005, p. 97). The petroleum generation process has likely decreased the remaining generative potential as measured by TOC_{pd} and HI_{pd} in the Mallabah Dolostone source rocks examined in this study. We can estimate the extent of the petroleum generation process, the volume of expelled oil and the expulsion efficiency by making some reasonable assumptions based on the core geochemical data and published regional information (Jarvie et al., 2007; Peters et al., 2005).

HI_o values can be computed from visual kerogen assessments and assigned kerogen-type HI_o average values using the following equation (Jarvie et al., 2007):

$$HI_o = \left( \frac{\% \text{Type I}}{100} \times 750 \right) + \left( \frac{\% \text{Type II}}{100} \times 450 \right) + \left( \frac{\% \text{ Type III}}{100} \times 125 \right) + \left( \frac{\% \text{Type IV}}{100} \times 50 \right)$$

(1)

This equation requires the input of maceral percentages from visual kerogen assessment of a source rock. For the present study, only limited kerogen data were available. Where available, these kerogen data sets were used. In the absence of other measured kerogen data original kerogen type were interpreted in the context of measured present day TOC, HI and OI values to arrive at an appropriate kerogen mix for each sample examined in this investigation. All samples were modeled using appropriate kerogen mix to maintain an appropriate transformation ratio consistent with the interpreted thermal maturity. The average maceral percentage in the various formations evaluated in the current study are shown in Table 2, along with the resultant average original HI_o values calculated using equation (1) above. The kerogen estimations used in this study are generally in agreement with other published sedimentological information regarding this formation. Stromatolites are common throughout the succession, which was deposited in low- to medium-energy, shallow- to deep-marine conditions (Munson, 2014).
Table 2. Average Kerogen Estimations for LMDH3 well.

The extent of the petroleum-generation process, or transformation ratio (TR) which is also called fractional conversion, is calculated as follows (Jarvie et al., 2007, p. 497):

\[
TR_{III} = 1 - \frac{H_{II_p}d[1200 - H_{II}d(1 - P_{II})]}{H_{II}d[1200 - H_{II_p}d(1 - P_{II_p})]}
\]  

(2)

H_{II_p}d and P_{II_p}d are the measured HI and PI values for the various source rock samples in this well. The average H_{II_p}d and P_{II_p}d for the formations evaluated in the current study are shown in Table 3. H_{II_o} and P_{II_o} are the original HI and PI values for immature organic matter in the rocks. For this calculation using the assumptions described previously results in an average H_{II_o} values of 579 mg HC/g TOC (Table 2). We assume a P_{II_o} of 0.02 (see Peters et al., 2005). Using these values in equation 2, the extent of fractional conversion of H_{II_o} to petroleum is 0.76 (Table 3), i.e., on average an estimated 76% of the petroleum generation process has been completed.

The original TOC_o in the source rocks before burial and thermal maturation is constrained by mass balance considerations as follows (corrected from Jarvie et al., 2007):

\[
TOC_o = \frac{H_{II_p}d \left( \frac{TOC_{II_p}d}{1+k} \right) (83.33)}{H_{II}(1-TR_{III}) \left( 83.33 - \frac{TOC_{II_p}d}{1+k} \right) + \left[ \frac{H_{II_p}d \left( \frac{TOC_{II_p}d}{1+k} \right)}{1+k} \right]}
\]  

(3)

In this equation k is a correction factor based on residual organic carbon being enriched in carbon over original values at high maturity (Jarvie et al., 2007, p. 497). For Type II kerogen the increase in residual carbon C_R at high maturity is assigned a value of 15% (whereas for Type I, it is 50%, and for Type III, it is 0%) and the correction factor k is then TR_{III} × C_R. The kerogen mix for each individual sample was used in this calculation.

Using equation 3, the estimated original TOC_o for the Mallabah Dolostone source rock samples in this well before petroleum generation average 1.71 wt.% (Table 3).

The original generation potential S_2_o can be calculated using the following equation:

\[
S_2_o = \left( \frac{H_{II_o} \times TOC_o}{100} \right)
\]  

(4)

For the Mallabah Dolostone source rocks examined in the LMDH3 well, the average S_2_o values are 9.9 mg HC/g rock or approximately 217 bbl/acre-ft (multiply S_2_o by 21.89 to calculate barrels/acre-ft, Jarvie and Tobey, 1999) (Table 3).

Knowing the measured remaining generation potential S_2 from programmed pyrolysis and using the calculated original generation potential S_2_o enables a determination of the amounts of hydrocarbons generated. A VR_o algorithm can then be applied to estimate fractional oil cracking thereby converting yields to estimated oil and cracked gas (reported as Mcf/acre-ft or thousand cubic feet/acre-ft).
Using this methodology for the Mallabah Dolostone samples analyzed in the current study, the estimated generated oil yields average 140 bbl/acre-ft (Table 3).

For shale oil systems, the amount of hydrocarbons (oil + gas) expelled from the rocks can be estimated as the difference between the amount of residual oil measured via programmed pyrolysis (S1) and the amount of estimated generated hydrocarbon yields determined above (equation 5). The expulsion efficiency (ExEf) can then be calculated as a direct proportion of the measured retained oil saturations and the average generated hydrocarbon yields. Thus, the resulting expulsion efficiency for the Mallabah Dolostone interval is 95%, which is more consistent with a source rock in the late oil to early wet gas/condensate window.

The Mallabah Dolostone source rock interval in the LMDH3 well is interpreted to be in the peak oil window and hydrocarbon yield calculations suggest significant amounts of generation have occurred (predominantly oil with some associated gas). From an exploration risk perspective, this is generally favorable. However, it is useful to relate these hydrocarbon yields to other productive unconventional US Shale plays (Table 4). In doing so, the potential critical value is not necessarily the generated oil and gas yields, but also the original (S2o) generation potential of the source rocks. These values related to the ultimate volumes of hydrocarbon that could be generated at depth in the basin. For the Mallabah Dolostone, original generation potential (S2o) averages 217 bbl oil/acre-ft, this is below all of the other formations on the list of unconventional US Shale plays shown below.

Table 4. Geochemical Properties and Generation Potential for US Shale plays and current study.
UNCONVENTIONAL OIL & GAS RISK ASSESSMENT

The Palaeoproterozoic Mallabah Dolostone Formation source rocks in the LMDH3 well have been evaluated for unconventional oil and gas potential. These source rock samples are presented in a modified geochemical risk assessment diagram (Fig. 2) based upon published results from the Barnett Shale in the Fort Worth Basin. The data illustrated in the star plot represents average values for three of the four of the diagnostic ratios (measured R_0 data unavailable). Also shown are the recommended areas for unconventional oil (in green) and gas (in red). Data that lies above the minimum threshold and within the shaded areas indicates samples with low geochemical risk for either thermogenic oil or gas production. Data that lie below the minimum threshold and fall in the immature region (in gray) indicate a high risk for commercial shale oil or gas production. Transformation ratios (TR) were calculated based upon HI_o estimates using measured and interpreted fractional composition of kerogen macerals.

![Unconventional Gas & Oil Risk Assessment Diagram](image)

**Figure 2. Geochemical Risk Assessment diagram for Palaeoproterozoic Mallabah Dolostone source rocks in the LMDH3 well.**

The Mallabah Dolostone source rock interval in the LMDH3 well is interpreted to represent a moderate geochemical risk for in-situ shale oil production. The average measured TOC content of 1.37 wt.% is above the generally accepted minimum value of 1% TOC to be considered an *effective* source rock for hydrocarbon generation/expulsion (Fig. 2). However, it is below the minimum requirements of 2 wt.% for *economic* petroleum source rocks, which is also the minimum threshold for prospective shale gas. Original organic matter type is interpreted to be predominantly oil-prone Type I/II marine algal kerogen. Thermal maturity parameters from programmed pyrolysis place the Mallabah Dolostone source interval in peak oil window. The average Tmax value of 440°C is above recommended minimum value of 435°C for shale oil and well below the minimum of 455°C for shale gas (Fig. 2). This amount of conversion would likely be sufficient to generate/expel significant amounts of hydrocarbons from this organic rich, oil prone source facies. Transformation Ratios (TR), the least constrained risk parameter, average 72% and fall
above the recommended minimum of 50% for shale oil and below the 80% threshold for shale gas systems (Fig. 2).

In the Mallabah Dolostone source interval, measured in-situ oil saturation determined by programmed pyrolysis S1 yields is poor (avg. 6 bbl oil/acre-ft), which is a significant concern regarding risk assessment for unconventional oil (Fig. 3). Hydrocarbon yield calculations on as-received samples show estimates of average generated oil from the Mallabah Dolostone at 140 bbl oil/acre-ft. As a comparison, a representative example from the core area of Barnett Shale oil production in the Fort Worth Basin has an estimated generated oil yield of 213 bbl/a-ft with a measured in-situ oil saturation of 79 bbl/a-ft (Fig.3). These values are higher compared to the Mallabah Dolostone and are primarily due to differences in organic richness (Barnett Shale oil example has average of 4.70 wt. % TOC). While the generated oil yield of the Mallabah Dolostone is slightly lower compared to the Barnett, the in-situ oil saturation is significantly lower and this is the reason the Mallabah Dolostone is considered a moderate risk for commercial shale oil development. Further investigation is needed to assess the reasons why measured in-situ hydrocarbon saturation is so low within the Mallabah Dolostone interval. It is likely that any in-situ oil saturation has migrated out of this source facies (est. 95% expulsion) as a consequence of uplift/erosion within the basin, since the depth of this sampled interval in the LMDH3 well is only ~194−210 m deep.

It is important to note that the quantity of oil generated from a potential source rock is only one geochemical factor to consider in regard to risk assessment. Equally important is the quality of the oil generated, since this factor can be a critical element in assessing the movability and ultimate recovery. The interpreted thermal maturity of the Mallabah Dolostone source interval in this well is in the peak oil window and hydrocarbon saturation is likely to be fairly light and mobile. However, the presence of solid bitumen could also indicate a source interval with restricted microporosity. Such microporosity is considered necessary for recovery of in-situ oil saturation and can be better assessed using scanning electron microscopy (SEM). Source rock extract fingerprints and bulk fractional compositional analyses from select Mallabah Dolostone samples would also aid in the determination of the quality of the in-situ hydrocarbon saturation and provide a better assessment of their movability and ultimate recovery potential.
GEOCHEMICAL SUMMARY

The Mallabah Dolostone source interval in the LMDH3 well is interpreted to represent moderate geochemical risk for unconventional shale oil development. It clearly has elevated organic richness (avg. 1.37 wt.% TOC) and is considered a good source rock with dominantly oil-prone Type I/II kerogen. Thermal maturity parameters indicate that this source interval is in the peak oil window, 0.76% Calc. R_o with a Transformation Ratio of 72%. Although all key risk ratios are above recommended minimum thresholds for shale oil systems, the measured in-situ oil saturations are very low (avg. 6 bbl oil/acre-ft). The Mallabah Dolostone has likely generated moderate to high amounts of oil (140 bbl/acre-ft), but it appears likely that most of this oil has been expelled from the source rock interval. Risk criteria like the S1 versus TOC show no oil cross-over for any of the samples in this interval confirming the elevated risk assessment. Further evaluation of in-situ oil characteristics would be required to fully evaluate potential oil mobility and recovery risk.

Figure 3. Hydrocarbon yield estimates for the Palaeoproterozoic source rocks in the LMDH3 well compared to Barnett Shale in the oil window.
REFERENCES CITED


Appendix I

*Hydrocarbon Yield Calculation*

*Limbunya Group*

*LMDH3*

Northern Territory Geological Survey - Australia
## Hydrocarbon Yield Calculation

### Mallabah Dolomite (Avg)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Top Depth</th>
<th>TOC*</th>
<th>Hº</th>
<th>S1*</th>
<th>S2*</th>
<th>Calc.Ro</th>
<th>Pº</th>
<th>% Type IV 50 HPº</th>
<th>% Type III 125 HPº</th>
<th>% Type II 450 HPº</th>
<th>% Type I 750 HPº</th>
<th>HIº</th>
<th>TR</th>
<th>TOC*</th>
<th>S2º</th>
<th>Remaining Potential</th>
<th>Original Potential</th>
<th>Oil Cracked</th>
<th>S1 Free Oil</th>
<th>Estimated Oil</th>
<th>Cracked Gas</th>
</tr>
</thead>
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### Barnett Shale Oil*<sup>**</sup>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Top Depth</th>
<th>TOC*</th>
<th>Hº</th>
<th>S1*</th>
<th>S2*</th>
<th>Calc.Ro</th>
<th>Pº</th>
<th>% Type IV 50 HPº</th>
<th>% Type III 125 HPº</th>
<th>% Type II 450 HPº</th>
<th>% Type I 750 HPº</th>
<th>HIº</th>
<th>TR</th>
<th>TOC*</th>
<th>S2º</th>
<th>Remaining Potential</th>
<th>Original Potential</th>
<th>Oil Cracked</th>
<th>S1 Free Oil</th>
<th>Estimated Oil</th>
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<td>Barnett Shale</td>
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<td>550</td>
<td>0.87</td>
<td>7</td>
<td>68</td>
<td>2751</td>
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</table>

**Notes:** Calc.Ro values in **bold** are calculated from measured Tmax. Calc.Ro values in red font are interpreted from other geochemical maturity data because Tmax was considered unreliable. All other Calc.Ro values are formation specific averages because Tmax was considered unreliable.

Kerogen Type in **bold** have visual kerogen data for estimates. TR = Transformation Ratio (fractional conversion) (Original Potential - Remaining Potential) = (Estimated Oil + Cracked Gas).

Estimated Oil and Cracked Gas yield data assume complete conversion and no expulsion of hydrocarbon products and the proportion between each is based on empirical Ro calculated % cracking.

Yields do not represent recoverable products and are intended primarily for comparison purposes, yield calculations based on carbon mass balance are likely to be overestimations. **Estimated parameters for productive Barnett Shale in the Ft. Worth Basin.

Hydrocarbon yield calculations and formulas are fully documented in the appendix section of Jarvie et al. (2007).