GEOCHEMICAL MEASUREMENT OF THERMAL MATURITY IN NEOPROTEROZOIC AND CAMBRIAN SEDIMENTS, EASTERN OFFICER BASIN

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INTRODUCTION

As part of the South Australian Exploration Initiative, a study of the burial history of the sediments comprising the eastern Officer Basin is being undertaken by R. Moussavi-Harami (Department of Geology and Geophysics, University of Adelaide) and D.I. Gravestock (MESA). A logical extension of this work is to model the thermal history of the Ediacaran (Late Neoproterozoic) and Early Cambrian sequences that are host to oil shows and potential source and reservoir rocks (McKirdy, 1993; Kamali et al., 1993; McKirdy et al., 1994). An essential prerequisite of any such thermal modelling exercise is reliable maturity data. Measurement of the present-day maturation levels of the target formations in strategically located drillholes across the basin makes possible determination of the timing of oil and gas generation in relation to trap formation.

Previous studies of the Offficer Basin by McKirdy (1987), McKirdy et al. (1987, 1991) and Kamali et al. (1993) exploited the capability of triaromatic hydrocarbon distributions (Radke and Welte, 1983; Radke et al., 1984; Radke, 1987) to provide thermal maturity data on pre-Devonian sediments devoid of vitrinite phytoclasts (Summons et al., 1994).

The aim of the present investigation was to augment the existing aromatic maturity database for the Officer Basin (Table 1) by undertaking measurements of methylphenanthrene index (MPI), methylphenanthrene ratio (MPR) and calculated vitrinite reflectance (VR_{calc}) on the triaromatic hydrocarbons extracted from another ten mudstone samples. The samples were selected from drillcore to provide data on specific stratigraphic units and structural provinces, as follows:

| Province | Well | Formation | No. of Samples |
|-------------------|---------------------------------|---------------------|----------------|
| Tallaringa Trough | Duvall KD-2A | Ouldburra Formation | 2 |
| Manya Trough | Marla-9 | Mena Mudstone | 2 |
| Murnaroo Platform | Murnaroo-1 | Karlaya Limestone | 2 |
| | Karlaya-1 | Dey Dey Mudstone | 2 |
| | SMD 5001 (Lake Maurice West) | Dey Dey Mudstone | 2 |

EXPERIMENTAL

The rock samples (lengths of quarter core) were scraped and brushed clean to remove surficial contamination before crushing in a Siebtechnik mill. Powdered rock (~50 g) was extracted in Soxhlet apparatus for 72 hours using an azeotropic solvent mixture (CH₂Cl₂:CH₃OH; 93:7). The extract was fractionated by open column liquid chromatography on activated silica into saturated hydrocarbons, aromatic hydrocarbons and nonhydrocarbons (NSO compounds and asphaltenes).

GC-MS analyses of the aromatic hydrocarbons were undertaken using a Varian 3400 gas chromatograph interfaced with a Finnigan TSQ 70 mass spectrometer. The gas chromatograph was fitted with a 30 m x 0.25 mm i.d. fused silica column (DB-5, 0.25 µm film thickness; J&W Scientific). Helium was used as the carrier gas at an inlet pressure of approximately 10 psi. The temperature program of the oven was as follows: 50°C for 2 min, 50°C to 120°C at 8°C min-1, 120°C to 300°C at 4°C min-1 and then held at 300°C for 35 min. Mass spectrometer operating parameters included an ionization voltage of 70 eV, a filament current of 200 µA and a photomultiplier voltage of 1100 V. Aromatic fractions in CH₂Cl₂ were injected on-column. The injector was held at 50°C for 10 seconds then ramped to 300°C at 180°C min-1, and held at 300°C for 5 minutes. The mass spectrometer was programmed (MID mode) to monitor m/z 128 (naphthalene), m/z 141+142 (methylnaphthalenes), m/z 156 (dimethylnaphthalenes), m/z 170 (trimethylnaphthalenes), m/z 178 (phenanthrene), m/z 192 (methylphenanthrenes), m/z 206 (dimethylphenanthrenes), m/z 219 (retene), m/z 231+245 (triaromatic steranes) and m/z 253 (monoaromatic steranes).

RESULTS

Analytical data are summarised and presented herein as follows:

| | <u>Table</u> | <u>Figure</u> |
|-------------------------------|--------------|---------------|
| Extract yield and composition | 2 | |
| Triaromatic maturity data | 3 | 1–10 |

Although the alkylnáphthalene distributions of the sediment extacts were recorded, only the nominated maturity parameters based on the relative abundances of phenanthrene and the isomeric methylphenanthrenes are considered in this report.

DISCUSSION

Extract Yield and Composition

The concentration of extractable organic matter (EOM: Table 2) in these mudstones ranges from poor (<500 ppm) to very good (>2000 ppm). The highest yields were obtained from the Ouldburra Formation in Duvall KD-2A (1082–2540 ppm) and the Dey Dey Mudstone in SMD 5001 (1260–1815 ppm). A similarly high yield (1899 ppm) characterises the Dey Dey Mudstone at 2094 metres depth in Karlaya-1, although a second sample from about 250 metres deeper in the same well and formation is almost twenty times leaner (Table 2). The low EOM yield in the latter sample may reflect highly efficient drainage or expulsion of hydrocarbons into an adjacent porous carrier bed during primary migration. This process might also explain the unusually low proportion of hydrocarbons in the residual source rock bitumen (6.2% of EOM: Table 2).

The total hydrocarbon content (saturates + aromatics) of the EOM increases systematically with increasing thermal maturity as follows:

| Well | Formation | Hydrocarbons (% EOM) |
|--------------|---------------------|----------------------|
| SMD 5001 | Dey Dey Mudstone | 13 |
| Duvall KD-2A | Ouldburra Formation | 28 |
| Murnaroo-1 | Karlaya Limestone | 22–28 |
| Karlaya-1 | Dey Dey Mudstone | 68 |
| Marla-9 | Mena Mudstone | 60–73 |

Aromatic hydrocarbons comprise between 2% (least mature) and 21% (most mature) of the EOM in these mudstones. For all but the least mature samples, the ratio of saturated to aromatic hydrocarbons is reasonably uniform (sat/arom = 0.7–3.3: Table 2).

Thermal Maturity

For each of the targetted structural provinces – Tallaringa Trough, Murnaroo Platform and Manya Trough – the new maturity measurements (Table 3) are broadly congruent with existing data (Table 1). The lack of internal consistency in the VR_{calc} values obtained for the sample pairs from Duvall KD-2A and Karlaya-1 (viz. deeper sample significantly less mature than shallower sample: Table 3) is difficult to explain. It may be due to a mineral or organic matrix effect which inhibited the catagenic methylation of phenanthrene. Such problems are commonly encountered when working with sediments containing non-humic organic matter (Type I or Type II kerogen) (Radke, 1987).

Another feature of the new data set is that, for a given sample, the MPI-derived VR_{calc} is consistently lower than that based on MPR. For most samples the difference between the two VR_{calc} values is slight. The greatest discrepancy (0.17–0.19% VR) is evident in the least mature sample pair (Dey Dey Mudstone from SMD 5001: Table 3). In this case, which of the two parameters, MPI and MPR, provides the most accurate measure of maturation level? The answer seems to be MPI. Lamalginite reflectance data presented by McKirdy *et al.* (1992) (see Table 4) corroborate the MPI-based VR_{calc} value here obtained for the Dey Dey Mudstone in SMD 5001 (Lake Maurice West).

Tallaringa Trough

- In Duvall KD-1 and 2, located on the southern edge of the trough, the *Ouldburra Formation* is early mature (VR_{calc} = 0.58-0.68%).
- Some 65 km to the northwest, in Wilkinson-1, the same formation is somewhat more mature $(VR_{calc} = 0.90\%)$ and actively expelling hydrocarbons, as indicated by common oil staining of drillcore from this locality.
- The regional maturation level of this formation appears to increase towards the southwest (cf. $VR_{calc} = 0.99\%$ in Hughes-2 on the Nullarbor Platform: Table 1).

Murnaroo Platform

- The *Karlaya Limestone* in Murnaroo-1 is mature ($VR_{calc} = 0.78-0.82\%$). The maturity of this unit increases northwards into the Munyarai Trough ($VR_{calc} = 1.40\%$ at 2612 metres depth in Munyarai-1).
- The *Dey Dey Mudstone* is early mature in SMD 5001 (418 metres depth, $VR_{calc} = 0.57\%$) and mature in Karlaya-1 (2094–2345 metres depth, $VR_{calc} = 0.79$ –(?)0.86%).

Manya Trough

- Here the *Ouldburra Formation* attains its highest known degree of thermal alteration (VR_{calc} = 1.00–1.68%: late mature to overmature) and therefore is essentially gas-generative.
- The *Observatry Hill Formation* at Byilkaoora-1 is at or just beyond peak maturity (VR_{calc} = 0.99-1.09%) for oil generation from Type I kerogen.
- The *Mena Mudstone* in Marla-9 has a maturity (VR_{calc} = 0.78–0.82%) which seems to be anomalously low with respect to the maturation levels exhibited by younger units in nearby wells (Table 1).

SUMMARY

Ten mudstones analysed in this study provide new maturity data on the Early Cambrian Ouldburra Formation in the Tallaringa Trough (Duvall KD-2A); and the Neoproterozoic Mena Mudstone, Karlaya Limestone and Dey Dey Mudstone on the Murnaroo Platform (SMD 5001, Murnaroo-1, Karlaya-1) and in the Manya Trough (Marla-9).

Calculated vitrinite reflectance values based on the original Radke and Welte (1983) calibration of the methylphenanthrene index (MPI-1) indicate that the sediments in question ($VR_{calc} = 0.57-0.83\%$) all lie within the conventional oil window.

The new results, except perhaps those from Marla-9, are consistent with existing maturity data from the same or adjacent drillholes.

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TABLE 1: Existing aromatic maturity database, Officer Basin

| | Depth | Formation | Sample | MPI | MPR | VR _{calc} | VR _{calc} | VR _{calc} | Reference |
|------------|-------------|---------------------|----------|--------------|--------------|--------------------|--------------------|--------------------|--|
| | m | | type | | | % (a) | % (a') | % (b) | |
| 1 | Byilkaoora- | -1 | | | | | | | |
| | 262.95 | Observatory Hill Fm | extract | 0.98 | 1.15 | 0.99 | 0.91 | 1.00 | McKirdy and Cox (1986) |
| | 285.00 | Observatory Hill Fm | extract | 1.16 | 0.87 | 1.09 | 1.03 | 0.88 | McKirdy and Cox (1986) |
| | 293.17 | Observatory Hill Fm | oil | 0.38 | 0.25 | 0.63 | 0.49 | 0.34 | McKirdy (1985) |
| | Duvall KD- | | | | | | | | • |
| | 263.35 | Ouldburra Fm | extract | 0.38 | 0.46 | 0.63 | 0.49 | 0.60 | Michaelsen et al. (1994) |
| | Duvall KD- | ·2A | | | | | | | |
| | 298.13 | Ouldburra Fm | extract* | 0.34 | 0.38 | 0.60 | 0.46 | 0.52 | McKirdy (1986) |
| | Hughes-2 | | | | | | | | |
| | 242.92 | Ouldburra Fm | extract | 0.99 | | 0.99 | 0.91 | | O'Leary (1987) |
| | | (Lake Maurice West) | | | | | | | |
| | 534.14 | Murnaroo Fm | oil | 1.03 | | 1.02 | 0.94 | | McKirdy and Watson (1989) |
| | | (Lake Maurice East) | | | | | 4.00 | | 7 TT 1 1 1 TT 1 (1000) |
| | 540.83 | Murnaroo Fm | oil | 1.40 | | 1.24 | 1.20 | | McKirdy and Watson (1989) |
| | Munyarai- | | | | | | 1.00 | 0.00 | N TT 1 10 (1000) |
| | 633.00 | E-M Devonian | extract | 1.43 | 2.78 | 1.26 | 1.22 | 0.98 | McKirdy and Cox (1986) |
| Tancina Fm | | -Leemurra-Mdst | extract | 1.63 | | 1.38 | 1.36 | | McKirdy and Cox (1986) |
| | 2611.83 | Karlaya Lst | extract | 1.67 | | 1.40 | 1.39 | | McKirdy and Cox (1986) |
| | Observatory | | | 0.00 | 0.00 | 0.04 | 0.05 | 0.00 | M-771-1 - 4 1 (1007) |
| | 34.14 | Observatory Hill Fm | extract | 0.90 | 0.88 | 0.94 | 0.85 | 0.89 | McKirdy et al. (1986) |
| | 155.35 | Relief Sandstone | oil | 1.32 | 1.46 | 1.19 | 1.15 | 1.10 | McKirdy and Watson (1989) |
| | Wilkinson- | | t at* | 0.50 | 0.64 | 0.75 | 0.62 | 0.75 | MaVirdy and Car (1096) |
| | 333.07 | Ouldburra Fm | extract* | 0.58 | 0.64 | 0.75 | 0.63 0.80 | 0.75 0.60 | McKirdy and Cox (1986) McKirdy and Cox (1986) |
| | 390.08 | Ouldburra Fm | extract* | 0.83 0.52 | 0.45 0.55 | 0.90 0.71 | 0.58 | 0.68 | McKirdy and Cox (1986) |
| | 461.87 | Ouldburra Fm | extract* | 0.32 | 0.33 | 0.71 | 0,38 | 0.00 | MCKII dy alld Cox (1980) |
| | | | | | at Out | 1 1 13 | | • | |

* Stained by oil

TABLE 1: Existing aromatic maturity database, Officer Basin (continued)

| Depth m | Formation | Sample type | MPI | MPR | VR _{calc} % (a) | VR _{calc} % (a') | VR _{calc} % (b) | Reference |
|------------|--|----------------|------|------|--------------------------|---------------------------|--------------------------|------------------------------|
| Marla-3 | | | | | | | | |
| 619.60 | Ouldburra Fm | extract | 1.00 | 1.24 | 1.00 | 0.92 | 1.03 | Kamali <i>et al</i> . (1993) |
| Marla-6 | | | | | | | | |
| 416.00 | Ouldburra Fm | extract | 1.43 | 1.76 | 1.26 | 1.22 | 1.18 | Michaelsen et al. (1994) |
| 671.25 | Ouldburra Fm | extract | 2.13 | 4.98 | 1.68 | 1.71 | 1.63 | Kamali <i>et al</i> . (1993) |
| Marla-7 | | | | | | | | |
| 392.85 | Ouldburra Fm | extract | 1.30 | 1.92 | 1.18 | 1.13 | 1.22 | Michaelsen et al. (1994) |
| Marla-9 | | | | | | | | |
| 234.83 | Mena Mudstone | extract | 0.68 | 0.73 | 0.81 | 0.70 | 0.81 | Michaelsen et al. (1994) |
| Manya-6 | | | | | | | | , , |
| 698.60 | Ouldburra Fm | extract | 1.11 | 2.34 | 1.07 | 1.00 | 1.31 | Kamali et al. (1993) |
| 1279.15 | Ouldburra Fm | extract* | 0.85 | 1.33 | 0.91 | 0.82 | 1.06 | Kamali <i>et al</i> . (1993) |
| Giles-1 | ~ ~~~ ~~ ~~ ~~ ~~ ~~ ~~ ~~ ~~ ~~ ~~ ~~ | | | | | | | |
| 5341.00 | Alinya Fm | extract | 0.43 | 1.27 | 0.66 | 0.52 | 1.04 | Zang and McKirdy (1993) |
| 6m 12650 | 5m | | | | | | | |

^{*} Stained by oil

KEY TO AROMATIC MATURITY PARAMETERS

Methylphenanthrene index (MPI), methylphenanthrene ratio (MPR) and VR_{CalC} are defined by Radke and Welte (1983), Radke *et al.* (1984), Radke (1987) and Boreham *et al.* (1988) as follows:

MPI-1 =
$$\frac{1.5 [2-MP + 3-MP]}{P + 1-MP + 9-MP}$$

MPR = $\frac{2-MP}{1-MP}$
 $VR_{calc}(a) = 0.60 MPI + 0.40 (for VR in the range 0.65-1.35%; r = 0.96)$
= $-0.60 MPI + 2.30 (for VR > 1.35\%)$
 $VR_{calc}(a') = 0.70 MPI + 0.22 (for VR in the range 0.5-1.7%; r = 0.84)$

 VR_{calc} (b) = 0.99 log 10 MPR + 0.94 (for VR in the range 0.4–1.7%; r = 0.84)

where P = phenanthrene*

1-MP = 1-methylphenanthrene

2-MP = 2-methylphenanthrene

3-MP = 3-methylphenanthrene

9-MP = 9-methylphenanthrene

^{*} Note: a response factor of 0.69 was applied to the area of this peak in Figures 1–10 when calculating MPI

TABLE 2: Extract yield and composition

| Well | Depth m | Formation | Sample size | EOM yield | Saturates | Aromatics | NSO's + Asphaltenes | Sat/Arom |
|--------------|-----------------|--------------|----------------|--------------|-----------|-----------|---------------------|----------|
| | | | g | ppm | % EOM | % EOM | % EOM | |
| Duvall KD-2A | 285.50–285.60 | Ouldburra Fm | 51.13 | 2540 | 13.8 | 14.1 | 72.1 | 0.98 |
| | 297.95–298.05 | Ouldburra Fm | 51.04 | 1082 | 11.2 | 16.7 | 72.1 | 0.67 |
| Marla-9 | 209.72–209.78 | Mena Mdst | 50.26 | 780 | 56.3 | 17.1 | 26.6 | 3.29 |
| | 269.87–269.97 | Mena Mdst | 50.08 | 494 | 39.4 | 21.0 | 39.6 | 1.96 |
| Murnaroo-1 | 183.88–183.90 | Karlaya Lst | 17.61 | 912 | 13.3 | 9.0 | 77.7 | 1.48 |
| | 190.91–191.00 | Karlaya Lst | 52.08 | 332 | 16.9 | 11.5 | 71.6 | 1.47 |
| Karlaya-1 | 2093.67–2093.78 | Dey Dey Mdst | 49.76 | 1899 | 47.1 | 20.4 | 32.5 | 2.30 |
| | 2345.09–2345.22 | Dey Dey Mdst | 48.56 | 101 | 3.5 | 2.7 | 93.8 | 1.31 |
| SMD 5001 | 417.59–417.78 | Dey Dey Mdst | 50.74 | 1815 | 10.9 | 1.7 | 87.4 | 6.58 |
| | 418.15–418.25 | Dey Dey Mdst | 49.77 | 1260 | 11.2 | nd | nd | nd |

TABLE 4 : Lamalginite random reflectance data, Officer Basin

| Depth | Formation | Lamalginite R ₀ | Equiv Vitrinite Ro | Reference |
|------------|--------------------------------------|----------------------------|--------------------|-----------------------------|
| m | | % | % | |
| Byilkaoore | a-1 | | | |
| 200.30 | Observatory Hill Fm | 0.60 | 1.0 | McKirdy (1985) |
| SMD 500 | 1 (Lake Maurice West) | | | |
| 416.90 | Dey Dey Mudstone | 0.19 | 0.54 | McKirdy et al. (1992) |
| 418.10 | Dey Dey Mudstone | 0.13 | | McKirdy et al. (1992) |
| 431.60 | Dey Dey Mudstone | 0.21 | 0.56 | McKirdy et al. (1992) |
| Observato | ry Hill-1 | | | |
| 261.90 | Dey Dey Mudstone | 0.16 | 0.52 | McKirdy et al. (1992) |
| Munyarai | ;- 1 | | | |
| 2289.7 | Leemurra Mudstone | 1.2 | 1.3 | McKirdy and Kantsler (1980) |
| 2753.4 | Dey Dey Mudstone | 1.1-1.3 | | McKirdy and Kantsler (1980) |
| 2897.3 | Dey Dey Mudstone | 1.3-1.8 | 1.35-1.8 | McKirdy and Kantsler (1980) |

Equivalent vitrinite reflectance estimated from alginite maturation scale of Glikson et al. (1992), Org. Geochem., 18: 881-897.

TABLE 3: Aromatic maturity data

| Well | Depth m | Formation | Sample type | MPI | MPR | VR _{calc} % (a) | VR _{calc} % (b) |
|--------------|-----------------|--------------|----------------|-------|-------|--------------------------|--------------------------|
| Duvall KD-2A | 285.50–285.60 | Ouldburra Fm | extract | 0.462 | 0.598 | 0.68 | 0.72 |
| | 297.95–298.05 | Ouldburra Fm | extract | 0.296 | 0.472 | 0.58 | 0.62 |
| Marla-9 | 209.72–209.78 | Mena Mdst | extract | 0.663 | 0.898 | 0.80 | 0.89 |
| | 269.87–269.97 | Mena Mdst | extract | 0.710 | 0.944 | 0.83 | 0.92 |
| Murnaroo-1 | 183.88–183.90 | Karlaya Lst | extract | 0.637 | 0.847 | 0.78 | 0.87 |
| | 190.91–191.00 | Karlaya Lst | extract | 0.699 | 0.999 | 0.82 | 0.94 |
| Karlaya-1 | 2093.67–2093.78 | Dey Dey Mdst | extract | 0.655 | 0.752 | 0.79 | 0.82 |
| | 2345.09–2345.22 | Dey Dey Mdst | extract | 0.368 | 0.898 | 0.62 | 0.89 |
| SMD 5001 | 417.59–417.78 | Dey Dey Mdst | extract | 0.276 | 0.627 | 0.57 | 0.74 |
| | 418.15–418.25 | Dey Dey Mdst | extract | 0.290 | 0.823 | 0.57 | 0.86 |

FIGURES 1-10

GC-MS RIC chromatograms of triaromatic hydrocarbons in selected mudstones from the eastern Officer Basin

| Figure | Well | Depth (m) | Formation |
|--------|--------------|-----------------|--------------|
| 1 | Duvall KD-2A | 285.50–285.60 | Ouldburra Fm |
| 2 | Duvall KD-2A | 297.95–298.05 | Ouldburra Fm |
| 3 | Marla-9 | 209.72-209.78 | Mena Mdst |
| 4 | Marla-9 | 269.87–269.97 | Mena Mdst |
| 5 | Murnaroo-1 | 183.88-183.90 | Karlaya Lst |
| 6 | Murnaroo-1 | 190.91–191.00 | Karlaya Lst |
| 7 | Karlaya-1 | 2093.67-2093.78 | Dey Dey Mdst |
| 8 | Karlaya-1 | 2345.09-2345.22 | Dey Dey Mdst |
| 9 | SMD 5001 | 417.59–417.78 | Dey Dey Mdst |
| 10 | SMD 5001 | 418.15-418.25 | Dey Dey Mdst |





















