Organic geochemistry and petroleum potential of Permian outcrop and core samples from the southern Sydney Basin

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SUMMARY

Permian sediments occur throughout the southern Sydney Basin, exposed on the coastline south of Wollongong, and penetrated by various boreholes. This study uses outcrop samples and samples from three boreholes held by NSW Resources and Energy at the core library at Londonderry (Department of Mines Callala DDH1 [Callala-1] from near Callala Bay, Elecom Clyde River DDH07 [ECR-7] from near Nowra, and Elecom Clyde River DDH01 [ECR-1] from near Wingello). Formations analysed include the Berry Siltstone, Nowra Sandstone, Wandrawandian Siltstone, the Snapper Point Formation, the Pebbley Beach Formation and the Yarrunga Coal Measures. The objectives are to determine the depositional environment, organic matter inputs, thermal maturity and petroleum generation potential of these formations, which were deposited when Australia was close to the South Pole. The rocks at outcrop and in ECR-1 are in the early oil window, while rocks from near Jervis Bay (Callala-1, ECR-7) are in the gas window. Total organic carbon content is heterogeneous and varies from 0.2–6.7%. The rocks were deposited in oxic to suboxic depositional environments. The Wandrawandian Siltstone contains biomarkers dominated by very high amounts of diahopanes and diasteranes, whereas these biomarkers are of lower relative abundance in the other formations. This is suggestive of a clay-rich sediment in an oxic, acid-catalysed depositional environment, with enhanced diagenetic alteration of the biomarkers, or alternatively an unusual organic input. The Pebbley Beach and Snapper Point formations are characterised by biomarker distributions dominated by terrigenously sourced terpanes (e.g. C_{24} tetracyclic terpane and C_{19} tricyclic terpane), corroborating their deltaic and shallow marine depositional environments, respectively. In contrast, the Wandrawandian Siltstone contains dominantly C_{21}, C_{23}, and C_{24} tricyclic terpanes. The Pebbley Beach Formation contains high amounts of C_{29} relative to C_{28} and C_{27} steranes, also consistent with a dominant terrigenous input.

Key words: Biomarkers, Permian, Sydney Basin, depositional environment, maturity.

INTRODUCTION

Early to late Permian sediments deposited during the Gondwanan ice age are exposed on the coast between Nowra and Batemans Bay in the southern part of the Sydney Basin, NSW, Australia (Herbert and Helby, 1980). The formations are part of the Shoalhaven Group and include the Berry Siltstone, the Nowra Sandstone, the Wandrawandian Siltstone, the Snapper Point Formation, the Pebbley Beach Formation, and the Yarrunga Coal Measures (Fig. 1). There are many varying and at times controversial opinions about the depositional environments and climatic conditions in which these formations were deposited (Carey, 1978; Tye et al., 1996; Eyles et al., 1998; Bann et al., 2004; Fielding et al., 2006; Thomas et al., 2007; Bann et al., 2008; Fielding et al., 2008). The Pebbley Beach and Snapper Point formations were deposited in shallow marine to coastal environments, whereas the Wandrawandian Siltstone was deposited during a marine transgression in deeper waters (Eyles et al., 1998; Fielding et al., 2006; Thomas et al., 2007). Some have suggested that the Pebbley Beach Formation was deposited in coastal and near-shore marine environments (Tye et al., 1996; Bann et al., 2004), while others support the idea of its deposition in a marine inner to outer shelf environment (Eyles et al., 1998). Fielding et al. (2006) argued that the unit comprises two parts that preserve quite different facies assemblages. The lower part has been related to glacial and inter-glacial cycles in a shallow marine environment, while the upper part has channel-like structures, which seem to be coastal estuarine channels (Fielding et al., 2006). Little has been published on the younger Berry Siltstone and Nowra Sandstone or the older Yarrunga Coal Measures. Furthermore, nothing is known of the organic geochemistry, organic inputs or petroleum prospectivity of these units, and no studies have been published on the thermal maturity of the southern part of the Sydney Basin. The objectives of this study are to determine the depositional environment, organic matter inputs, thermal maturity and petroleum generation potential of these formations, which were deposited when Australia was close to the South Pole.

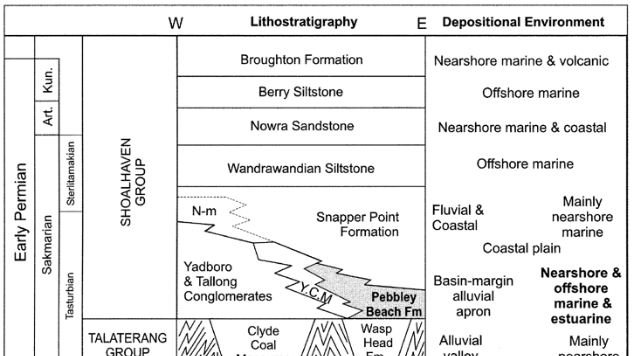

Figure 1: Revised stratigraphy of the Shoalhaven and Talaterang Groups. The Nowra-Jervis Bay-Bateman's Bay region is located slightly east of the centre. YCM = Yarrunga Coal Measures, N-m = non-marine. From Bann et al., 2004.

SAMPLES AND METHODS

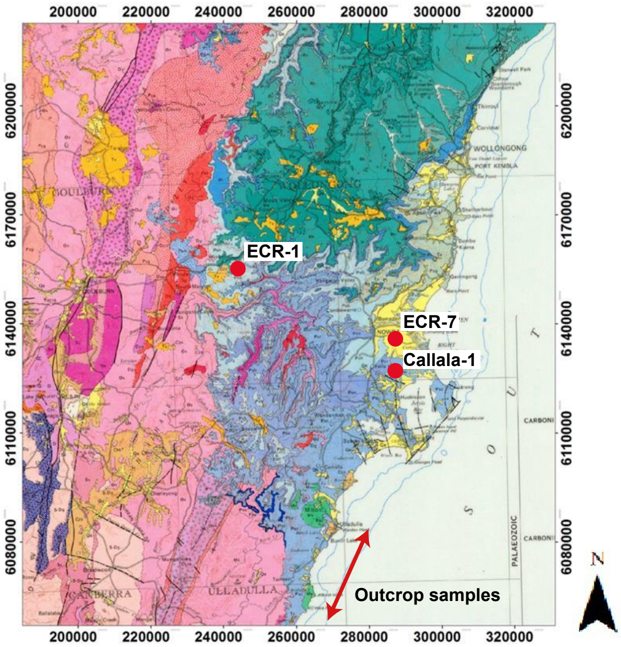

Figure 2: Geological map of the southern Sydney Basin area, showing sampled borehole locations at Department of Mines Callala DDH1 [Callala-1], Elecom Clyde River DDH07 [ECR-7], and Elecom Clyde River DDH01 [ECR-1], and the area where outcrop samples were collected between Ulladulla and Batemans Bay.

This study uses 16 outcrop samples of the Wandrawandian Siltstone, the Snapper Point Formation and the Pebbley Beach Formation from Ulladulla (Warden Head), Dolphin Point, Snapper Point to the SE of Merry Beach, the N side of Pebbly Beach, and between Depot Beach and Point Upright (Figure 2). The Permian sediments in the southern Sydney Basin have also been penetrated by various boreholes. This study uses samples from three boreholes held by NSW Resources and Energy at the core library at Londonderry: Callala-1 from Callala Bay, near Jervis Bay (30 samples); ECR-7 from near Nowra (12 samples); and ECR-1 from near Wingello (8 samples).

The external surfaces of samples were removed using a rock saw, and the internal pieces were cleaned by ultrasonication in solvent (dichloromethane: methanol, 9:1v/v). The samples were milled to a fine powder and extracted using an accelerator solvent extractor (ASE300). Elemental sulphur was removed by treatment of the extractable organic matter (EOM) with activated copper, and then an aliquot of the EOM was weighed. The EOM (10-20 mg) was firstly fractionated into total hydrocarbons (THC) and polar compounds, and then the THC was fractionated into aliphatic and aromatic hydrocarbons (HC). The two HC fractions were analysed by gas chromatography-mass spectrometry (GC-MS) with a DB-5MS fused silica column (length: 60m, diameter: 0.25µm, phase thickness: 0.25µm). For further details of the methodologies, see Flannery and George (2014) and Aharonovich and George (2016).

RESULTS AND DISCUSSION

Thermal maturity parameters show that the least mature location is ECR-1 from near Wingello, and that the most mature are the ECR-7 and Callala-1 holes near Jervis Bay. The outcrop samples from the coastline are mostly closer in maturity to the ECR-1 borehole, but this varies somewhat with parameter. The alkylnaphthalene ratios TMNr and TeMNr (Figure 3) for ECR-1 show a correlation with depth, with the deeper Pebbley Beach Formation being more mature than the shallower Berry Siltstone. Values for TMNr are <0.4 and for TeMNr are ≤0.3, consistent with the early oil window (van Aarssen et al., 1999; George and Ahmed, 2002). The methylphenanthrene index (MPI) for ECR-1 varies from 0.54–0.7 and the methylphenanthrene distribution fraction (MPDF) from 0.43–0.48 (Figure 4), which suggests calculated reflectance values of 0.73–0.82% in the early oil window. Based on the methylnaphthalene ratio (MNR), MPI and MPDF, the outcrop samples have a similar thermal maturity as the samples from ECR-1 (Figure 4). However the outcrop samples have widely varying TMNr and TeMNr ratios, with the younger Wandrawandian Siltstone having higher values than the older units (Figure 3). This distribution is hard to explain just based on thermal maturity, and suggests that these ratios are exhibiting a significant source control.

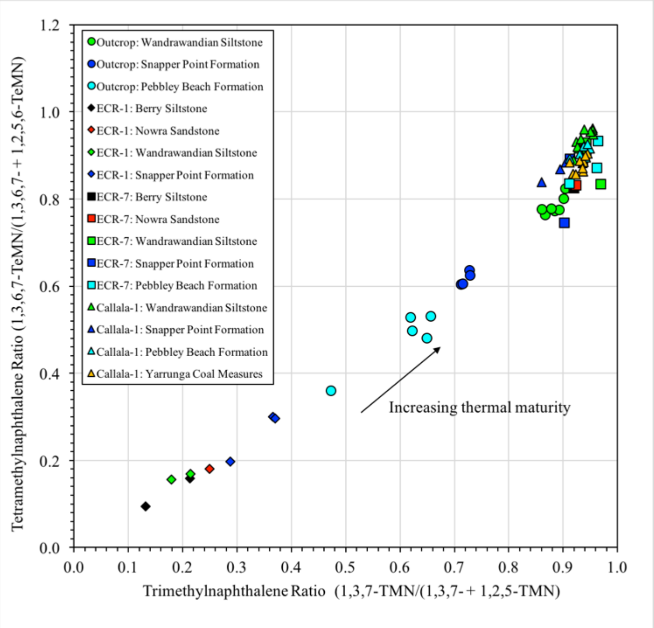

Figure 3: Cross plot of trimethylnaphthalene ratio (TMNr) versus tetramethylnaphthalene ratio (TeMNr) for Permian samples from ECR-1, ECR-7, Callala-1 and outcrop samples from between Ulladulla and Batemans Bay.

The samples from the ECR-7 and Callala-1 boreholes near Jervis Bay have significantly higher thermal maturities, based on TMNr, TeMNr, MNR, MPI, and MPDF (Figures 3 and 4). These values are in the gas window, based on comparison to previous data sets (George and Ahmed, 2002) and calibrations to calculated reflectance. For example, the methylphenanthrene ratio (2-MP/1-MP; 1.6–4.4) gives a calculated vitrinite reflectance range of 1.2–1.6% (Radke et al., 1984), and the MPI gives a very similar calculated vitrinite reflectance range (1.3–1.7%), based on the gas

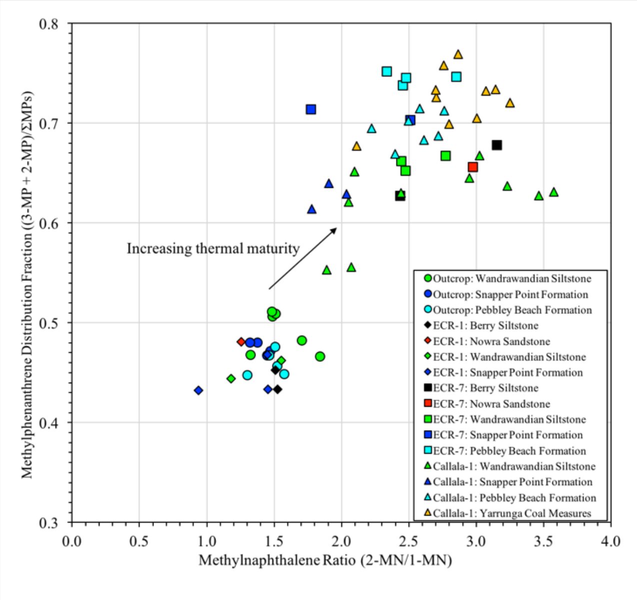

Figure 4: Cross plot of methylnaphthalene ratio (MNR) versus methylphenanthrene distribution fraction (MPDF) for Permian samples from ECR-1, ECR-7, Callala-1 and outcrop samples from between Ulladulla and Batemans Bay.

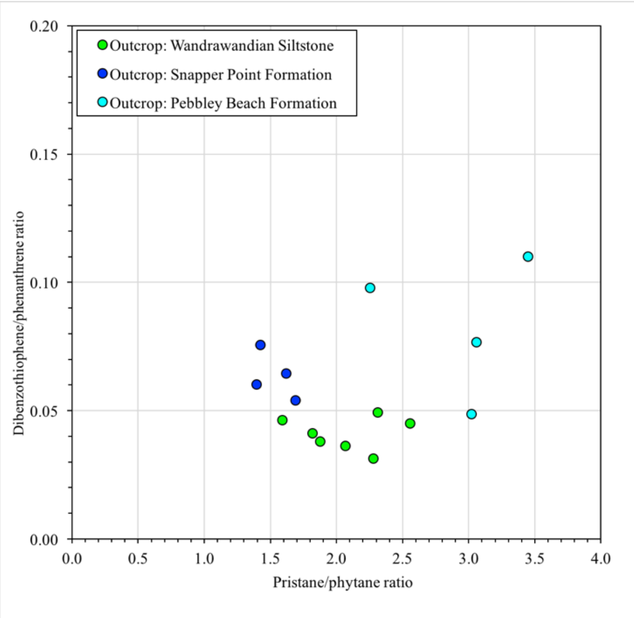

Figure 6: Organic matter type and oxicity of the depositional environment, based on the Pr/Ph and the DBT/P ratios for outcrop samples from the Wandrawandian Siltstone, the Snapper Point Formation and the Pebbley Beach Formation.

window calibration (Radke and Welte, 1983). The reason for the greater thermal maturity in the Jervis Bay region may partly relate to igneous intrusions, but mainly reflects greater palaeo burial depth towards the centre of the Sydney Basin. It would be expected that the Permian strata would be even more mature underneath Sydney. From a petroleum prospectivity viewpoint, these deeply buried Permian rocks might be a significant shale gas resource, as their thermal maturity is similar to the highly producible Barnett Shale in Texas, USA (Jarvie et al., 2007).

The total organic carbon (TOC) is highest in the outcrop samples from the Pebbley Beach Formation (Figure 5). The highest value (6.7%) is for a sample of fossilised wood, but the mudstones have an average TOC of 3.7%. The Wandrawandian Siltstone and the Snapper Point Formation have lower average TOCs (0.92%, 1.3%). The ECR-1 core samples have TOC values from 1.1–1.6, except for the Snapper Point Formation which is significantly leaner that at outcrop (0.46%). The ECR-1 core samples, despite being much more thermally mature, also have a similar TOC range (0.7–1.9%), except that the Snapper Point Formation is also the leanest formation.

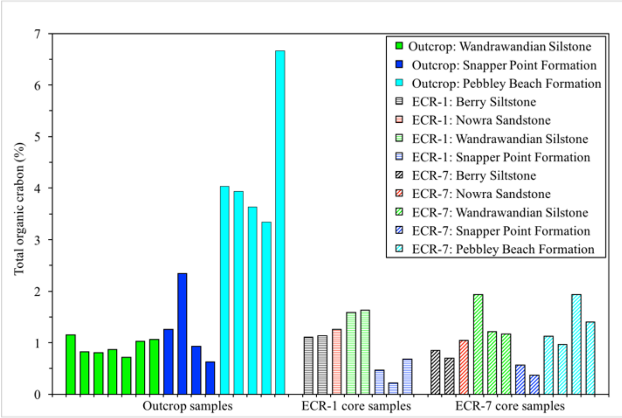

Figure 5: Distribution of total organic carbon (TOC, %) values for Permian samples from ECR-1, ECR-7 and outcrop samples from between Ulladulla and Batemans Bay.

Depositional environment and organic matter inputs are best determined using less thermally mature rocks, as the biomarkers are better preserved. In this study the outcrop samples are used to assess the Wandrawandian Siltstone, the Snapper Point Formation, and the Pebbley Beach Formation. The rocks were deposited in oxic to suboxic depositional environments that were mostly low in organic sulphur, based on the pristane/phytane and the dibenzothiophene/phenanthrene ratios (Figure 6). The Snapper Point Formation samples were deposited in somewhat more reducing conditions than the other formations, with Pr/Ph ratios slightly lower (1.4–1.7) than for the Wandrawandian Siltstone (1.6–2.3) and the Pebbley Beach Formation (2.3–3.5).

The Wandrawandian Siltstone contains biomarkers dominated by very high amounts of diahopanes, rearranged hopanes such as Ts, and diasteranes, whereas these biomarkers are of lower relative abundance in the other formations (Figure 7). This is suggestive of a clay-rich sediment in an oxic, acid-catalysed depositional environment, with enhanced diagenetic alteration of the biomarkers, or alternatively an unusual organic input.

The Pebbley Beach and Snapper Point formations are characterised by biomarker distributions dominated by terrigenously sourced terpanes (e.g. C_{24} tetracyclic terpane; C_{19} tricyclic terpane), corroborating their deltaic and shallow marine depositional environments, respectively (Figure 8). In contrast, the Wandrawandian Siltstone contains dominantly C_{21}, C_{23}, and C_{24} tricyclic terpanes. The Pebbley Beach Formation contains high amounts of C_{29} relative to C_{28} and C_{27} steranes, also consistent with a dominant terrigenous input.

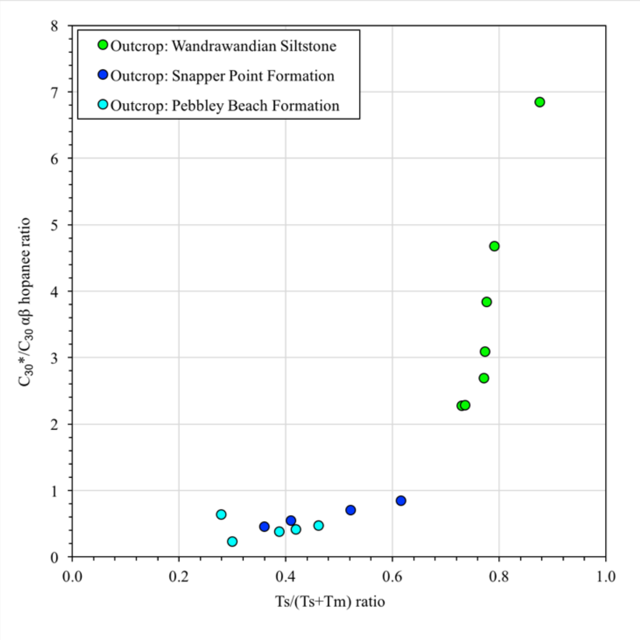

Figure 7: Relative amounts of rearranged hopanes, based on the Ts/(Ts+Tm) and the C_{30}*/C_{30} αβ hopane ratios, for outcrop samples from the Wandrawandian Siltstone, the Snapper Point Formation and the Pebbley Beach Formation.

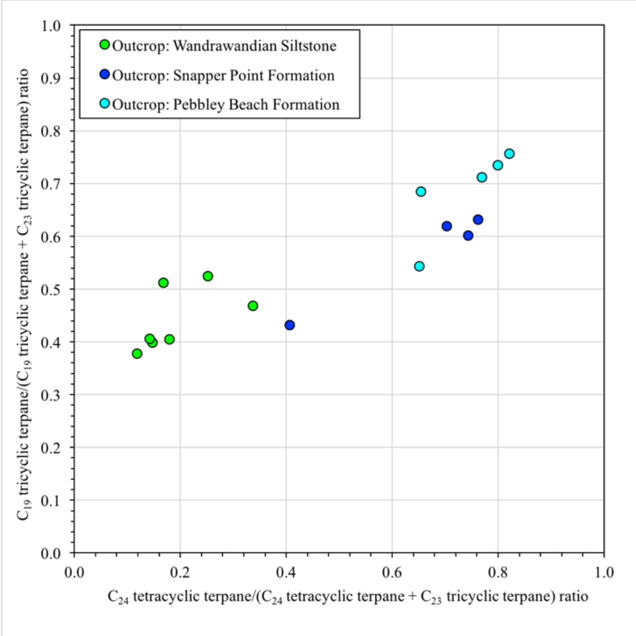

Figure 8: Relative amounts of terpanes as source indicators, based on the C_{24} tetracyclic terpane/(C_{24} tetracyclic terpane + C_{23} tricyclic terpane) and the C_{19} tricyclic terpane/(C_{19} tricyclic terpane + C_{23} tricyclic terpane) ratios, for outcrop samples from the Wandrawandian Siltstone, the Snapper Point Formation and the Pebbley Beach Formation.

CONCLUSIONS

Permian sediments occur throughout the southern Sydney Basin, exposed on the coastline south of Wollongong, and penetrated by various boreholes. The rocks at outcrop and in ECR-1 from near Wingello are in the early oil window, while samples from near Jervis Bay (Callala-1and ECR-7) are in the gas window. Total organic carbon content is heterogeneous and varies from 0.2–6.7%. The rocks were deposited in oxic to suboxic depositional environments. The Wandrawandian Siltstone contains biomarkers dominated by very high amounts of diahopanes and diasteranes, whereas these biomarkers are of lower relative abundance in the other formations. This is suggestive of a clay-rich sediment in an oxic, acid-catalysed depositional environment, with enhanced diagenetic alteration of the biomarkers, or alternatively an unusual organic input. The Pebbley Beach and Snapper Point formations are characterised by biomarker distributions dominated by terrigenously sourced terpanes (e.g. C_{24} tetracyclic terpane; C_{19} tricyclic terpane), corroborating their deltaic and shallow marine depositional environments, respectively.

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REFERENCES

Aharonovich, S. and George, S.C., 2016, A possible shale gas prospect? First results of the organic composition and thermal maturity of the Carboniferous Namoi Formation, northern NSW, Australia. Australian Journal of Earth Sciences, 63, 771-780.

Bann, K., Tye, S., MacEachern, J., Fielding, C., and Jones, B., 2008, Ichnological and sedimentological signatures of mixed wave- and storm-dominated deltaic deposits: examples from the Early Permian Sydney Basin, Australia. Recent Advances in Models of Siliciclastic Shallow-Marine Stratigraphy: SEPM, Special Publication, 90, 293-332.

Bann, K.L., Fielding, C.R., MacEachern, J.A., and Tye, S.C., 2004, Differentiation of estuarine and offshore marine deposits using integrated ichnology and sedimentology: Permian Pebbley Beach Formation, Sydney Basin, Australia. Geological Society, London, Special Publications, 228, 179-211.

Carey, J., 1978, Sedimentary environments and trace fossils of the Permian Snapper Point Formation, Southern Sydney Basin. Journal of the Geological Society of Australia, 25, 433-458.

Eyles, C.H., Eyles, N., and Gostin, V.A., 1998, Facies and allostratigraphy of high-latitude, glacially influenced marine strata of the Early Permian southern Sydney Basin, Australia. Sedimentology, 45, 121-162.

Fielding, C.R., Bann, K.L., Maceachern, J.A., Tye, S.C., and Jones, B.G., 2006, Cyclicity in the nearshore marine to coastal, Lower Permian, Pebbley Beach Formation, southern Sydney Basin, Australia: a record of relative sea-level fluctuations at the close of the Late Palaeozoic Gondwanan ice age. Sedimentology, 53, 435-463.

Fielding, C.R., Frank, T.D., Birgenheier, L.P., Rygel, M.C., Jones, A.T., and Roberts, J., 2008, Stratigraphic imprint of the Late Palaeozoic Ice Age in eastern Australia: a record of alternating glacial and nonglacial climate regime. Journal of the Geological Society, 165, 129-140.

Flannery, E.N. and George, S.C., 2014, Assessing the syngeneity and indigeneity of hydrocarbons in the similar to 1.4 Ga Velkerri Formation, McArthur Basin, using slice experiments. Organic Geochemistry, 77, 115-125.

George, S.C. and Ahmed, M., 2002, Use of aromatic compound distributions to evaluate organic maturity of the Proterozoic middle Velkerri Formation, McArthur Basin, Australia. in M. Keep and S. J. Moss (eds.) *West Australian Basins Symposium*, Petrol. Expl. Soc. Aust., 252-270.

Herbert, C. and Helby, R., 1980, A Guide to the Sydney Basin. Geological Survey of NSW Bulletin, 26, 603.

Jarvie, D.M., Hill, R.J., Ruble, T.E., and Pollastro, R.M., 2007, Unconventional shale-gas systems: The Mississippian Barnett Shale of north-central Texas as one model for thermogenic shale-gas assessment. American Association of Petroleum Geologists Bulletin, 91, 475-499.

Radke, M., Leythaeuser, D., and Teichmüller, M., 1984, Relationship between rank and composition of aromatic hydrocarbons for coals of different origins. Organic Geochemistry, 6, 423-430.

Radke, M. and Welte, D.H., 1983, The Methyl Phenanthrene Index (MPI); a maturity parameter based on aromatic hydrocarbons. in M. Bjorøy (ed.) *Advances in Organic Geochemistry 1981*, Wiley, 504-512.

Thomas, S.G., Fielding, C.R., and Frank, T.D., 2007, Lithostratigraphy of the late Early Permian (Kungurian) Wandrawandian Siltstone, New South Wales: record of glaciation? Australian Journal of Earth Sciences, 54, 1057-1071.

Tye, S.C., Fielding, C.R., and Jones, B.G., 1996, Stratigraphy and sedimentology of the Permian Talaterang and Shoalhaven Groups in the southernmost Sydney Basin, New South Wales. Australian Journal of Earth Sciences, 43, 57-69.

van Aarssen, B.G.K., Bastow, T.P., Alexander, R., and Kagi, R.I., 1999, Distributions of methylated naphthalenes in crude oils: indicators of maturity, biodegradation and mixing. Organic Geochemistry, 30, 1213-1227.