

**MATURATION CHARACTERISTICS OF THE NEW ZEALAND COAL BAND:  
PART 2 – KEROGEN RESTRUCTURING AND IMPLICATIONS FOR MODELLING  
PETROLEUM FORMATION**

Richard SYKES<sup>1</sup>, Volker DIECKMANN<sup>2,3</sup>, Brian HORSFIELD<sup>2</sup>, Tiem T.A. VU<sup>2</sup> and  
Per Erling JOHANSEN<sup>4</sup>

*1. GNS Science, PO Box 30368, Lower Hutt 5040, New Zealand*

*2. GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, Germany*

*3. Shell International Exploration and Production, Kessler Park 1, 2288 GS Rijswijk, Netherlands*

*4. Applied Petroleum Technology, Instituttveien 18, PO Box 123, 2027 Kjeller, Norway*

The maturation characteristics of humic (i.e. vitrinite-rich) coals and coaly mudstones are fundamentally different to those of classic marine and lacustrine source rocks and, thus, for basin modelling purposes, require separate study. The unique maturation characteristics of coaly kerogen are well exemplified by the New Zealand Coal Band (Cretaceous–Cenozoic), which displays an unexpected, rank-related increase in HI of up to 150 mg HC/g TOC prior to the onset of oil expulsion (Sykes and Snowdon, 2002). This increase has been attributed primarily to kerogen restructuring (Killops et al., 2002; Sykes and Snowdon, 2002), which is thought to involve mainly aromatisation and polycondensation reactions reincorporating bitumen into the kerogen macromolecular structure and in the process, creating new, higher energy bonds (Schenk and Horsfield, 1998; Dieckmann et al., 2006). In this study, we have used Soxhlet extraction, TLC and open-system pyrolysis techniques to investigate evidence for progressive kerogen restructuring along the NZ Coal Band and to assess its implications for kinetics-based modelling of petroleum formation.

Thirteen well-characterised, rank series coals [Rank( $S_r$ ) 5.4–18.9,  $R_o$  0.39–2.61%] of relatively uniform kerogen type from the NZ Coal Band were Soxhlet-extracted using an azeotropic solvent mixture for 72 hrs. The extracts are dominated by asphaltene and polar compounds. HI values of the extracted coals are up to c. 100 mg HC/g TOC less than those of the non-extracted counterparts (Fig. 1). Indeed, for coals of Rank( $S_r$ ) 12.6 ( $R_o$  0.87%) or less, up to c. 30% of their  $S_2$  hydrocarbon yields is heavy bitumen-derived. Significantly, however, the extracted coals display the same rank-related increase in HI up to the onset of oil expulsion, confirming that the increase is indeed linked to the kerogen fraction.

For both the extracted and non-extracted sample sets, plots of the  $S_2$  hydrocarbon generation rate curves (normalised to mg HC/g initial  $C/^\circ C$ ) against Rock-Eval temperature reveal nesting of the curves for the three least mature samples [Rank( $S_r$ ) 5.4–6.6,  $R_o$  0.39–0.45%), followed by progressive offset of curves to higher temperatures for successively more mature samples; i.e. each curve extends beyond the envelope of the preceding sample in the

rank series. This distribution is consistent with the neo-formation of more refractory kerogen with progressive maturation – kerogen that is expected to generate late-stage, high-maturity gas (Dieckmann et al., 2006).

To further test this theory, hydrocarbon generation rate curves were obtained for the non-extracted coals at laboratory heating rates of 0.7, 2, 5 and 15 K/min and discrete activation energy and frequency factor distributions derived following the enhanced kinetics approach of Dieckmann (2005). Initial results are equivocal, probably because of the significant heavy bitumen component of many of the samples. However, irrespective of the kinetics results, the progressive offset of the S2 hydrocarbon generation rate curves beyond the immature envelopes indicates that hydrocarbon generation kinetics obtained from immature samples would likely result in erroneous predictions of petroleum formation histories at geological heating rates (Schenk and Horsfield, 1998).

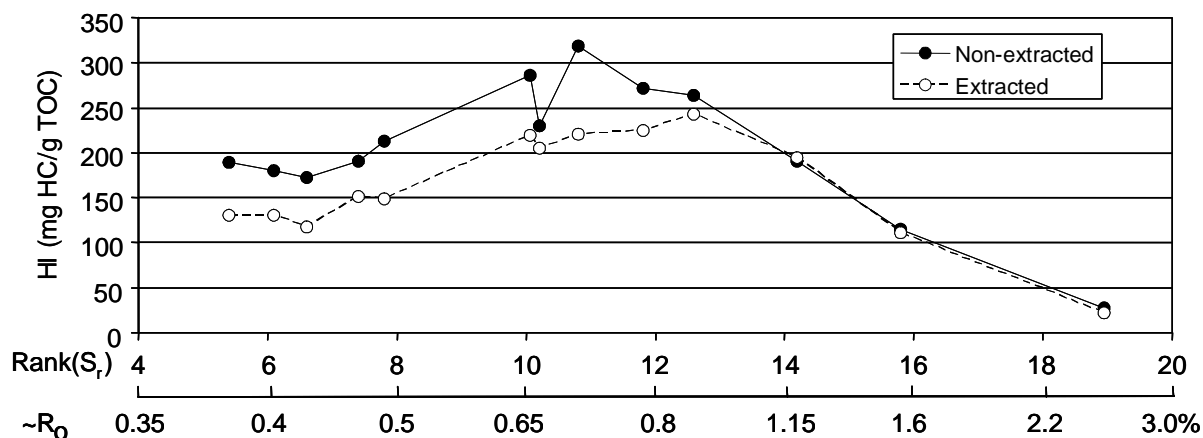


Figure 1. Plot of HI versus Rank( $S_r$ ) and equivalent  $R_o$  for selected coals from the NZ Coal Band, pre- and post-extraction.

## REFERENCES

- Dieckmann V. (2005) Modelling petroleum formation from heterogeneous source rocks: the influence of frequency factors on activation energy distribution and geological prediction. *Marine and Petroleum Geology*, **22**, 375–390
- Dieckmann V., Ondrak R., Cramer B. and Horsfield B (2006) Deep basin gas: New insights from kinetic modelling and isotopic fractionation in deep-formed gas precursors. *Marine and Petroleum Geology*, **23**, 183–199.
- Killops S., Jarvie D., Sykes R. and Funnell R. (2002) Maturity-related variation in the bulk-transformation kinetics of a suite of compositionally related New Zealand coals. *Marine and Petroleum Geology*, **19**, 1151–1168.
- Schenk H.J. and Horsfield B. (1998) Using natural maturation series to evaluate the utility of parallel reaction kinetics models: an investigation of Toarcian shales and Carboniferous coals, Germany. *Organic Geochemistry*, **29**, 137–154.
- Sykes R. and Snowdon L.R. (2002) Guidelines for assessing the petroleum potential of coaly source rocks using Rock-Eval pyrolysis. *Organic Geochemistry*, **33**, 1441–1455.

## **BIOMARKER AND CARBON ISOTOPE SYSTEMATIC IN CENOZOIC COAL AND FOSSIL WOOD OF CENTRAL EUROPE**

Achim BECHTEL<sup>1,2</sup>, Reinhard F. SACHSENHOFER<sup>2</sup>, Reinhard GRATZER<sup>2</sup>, Andreas LÜCKE<sup>3</sup> and Wilhelm PÜTTMANN<sup>4</sup>

*1. Department of Mineralogy & Petrology, University of Bonn, Poppelsdorfer Schloss, D-53115 Bonn, Germany*

*2. Department of Applied Geosciences & Geophysics, University of Leoben, Peter-Tunner-Str. 5, A-8700 Leoben, Austria*

*3. Institute for Chemistry and Dynamic of the Geosphere V: Sedimentary Systems (ICG V), Research Center Jülich, D-52425 Jülich, Germany*

*4. Institute of Atmospheric and Environmental Sciences, Department of Analytical Environmental Chemistry, J. W. Goethe-University, Georg-Voigt-Str. 14, D-60054 Frankfurt a.M., Germany*

In the light of recent findings, biomarker and carbon isotope systematic in coal and fossil wood are expected to provide valuable information for the reconstruction of floral assemblages and paleoenvironmental changes during the Cenozoic. Carbon isotope analyses of terrigenous organic matter have been used to reconstruct changes in the isotopic composition of upper ocean and atmospheric carbon reservoirs (Arens et al., 2000). Carbon isotope values of cellulose from tree-rings and fossil wood have also been related to climatic change (e.g. temperature, humidity) via water-use efficiency of land plants.

In this study, we report on biomarker and carbon isotope analyses of coal, resinates, woody macrofossils, and extracted cellulose obtained from lignite deposits of Central Europe (Austria, Bulgaria, Germany, Hungary, Slovenia) covering the time interval from Early Eocene to Pliocene. The concentration of diterpenoid biomarkers (including abietane-, pimarane-, isopimarane-, beyerane-, kaurane-, and phyllocladane-type hydrocarbons) relative to the sum of diterpenoids plus triterpenoid hydrocarbons, containing the structures typical of the oleanane-, the ursane-, or the lupane-skeleton, are used as proxies for the contribution of gymnosperms versus angiosperms to peat formation. Our results demonstrate that bulk organic matter of coal and coaly sediments is influenced by varying contributions of angiosperms and gymnosperms, by different isotopic composition of land plant tissue (e.g. leaves, wood, bark), as well as by microbial activity. The concentration ratios of terpenoid biomarkers in coal seams indicate the predominance of angiosperms in the peat-forming vegetation during Eocene and Early Oligocene, whereas Late Oligocene to Pliocene coals are derived from gymnosperm-dominated (i.e. coniferous) sources. The results are in general agreement with paleobotanical records and demonstrate the potential of biomarker analyses in paleoecological studies.

The  $\delta^{13}\text{C}$  variations found in resinites, fossil wood and wood cellulose support their capability to trace paleoenvironmental conditions. In contrast to fossil wood,  $\delta^{13}\text{C}$  values of cellulose from woody macrofossils are only negligibly influenced during decomposition. The carbon isotope analyses demonstrate isotopic trends of land plants parallel to the marine record during the Tertiary (Zachos et al., 2001). Furthermore, co-variations of  $\delta^{13}\text{C}$  of coals, fossil wood from gymnosperms, and wood cellulose with climatic changes (i.e. mean annual temperature, mean annual precipitation) reconstructed from paleobotanical data from eastern Germany are noticed (Krutzsich et al., 1992; Eissmann, 1994; Krutzsich, 2000). We propose that the observed patterns were primarily produced by variations of the isotope ratios of oceanic and atmospheric carbon reservoirs, and additionally modified by climatic changes due to their influence on plant physiology. Thus, the terrestrial carbon isotope record indicates changing  $\delta^{13}\text{C}$  values of atmospheric  $\text{CO}_2$  associated with atmospheric  $p\text{CO}_2$  and paleoclimate. Carbon isotope studies on fossil wood of known taxa and on their cellulose provide a powerful tool in reconstructing the isotopic record of land plants and its implication for environmental changes during the Earth's history.

## REFERENCES

- Arens, N.C., Jahren, A.H., Amundson, R., 2000. Can C3 plants faithfully record the carbon isotopic composition of atmospheric carbon dioxide? *Paleobiology*, 261, 137-164.
- Eissmann, L., 1994. Leitfaden der Geologie des Präquartärs im Saale-Elbe-Gebiet. DEUQUA-Tagung 1994, Leipzig. *Altenberger naturwissenschaftliche Forschung*, 7, 11-53.
- Krutzsich, W., 2000. Stratigraphische Tabelle Oberoligozän und Neogen (marin – kontinental). *Berliner geowissenschaftliche Abhandlungen*, E 34, 153-165.
- Krutzsich, W., Blumenstengel, H., Kiesel, Y., Rüffle, L., 1992. Paläobotanische Klimagliederung des Alttertiärs (Mittelozeän bis Oberoligozän) in Mitteldeutschland und das Problem der Verknüpfung mariner und kontinentaler Gliederungen (klassische Biostratigraphien – paläobotanisch-ökologische Klimastratigraphie – Evolutions-Stratigraphie der Vertebraten). *Neues Jahrbuch für Geologie und Paläontologie, Abhandlungen*, 186, 137-253.
- Zachos, J., Pagani, M., Sloan, L., Thomas, E., Billups, K., 2001. Trends, rhythms, and aberrations in global climate 65 Ma to Present. *Science*, 292, 686-693.

## OILS SOURCED FROM PERMIAN COALS - GEOCHEMICAL EVIDENCE FROM SYDNEY BASIN OIL SEEPS AND SHOWS

Manzur AHMED<sup>1</sup>, Herbert VOLK<sup>1</sup>, Simon C. GEORGE<sup>2</sup>, Mohinudeen FAIZ<sup>1</sup> and Linda STALKER<sup>3</sup>

*1. CSIRO Petroleum, PO Box 136, North Ryde, NSW 1670, Australia*

*2. Australian Centre for Astrobiology, Macquarie University, Sydney, NSW 2109, Australia*

*3. CSIRO Petroleum, PO Box 1130, Bentley, WA 6102, Australia*

Oil from coal is still the subject of considerable debate, with unambiguous examples of commercial petroleum accumulations due to coal source rocks largely limited to Late Mesozoic and Cenozoic southern hemisphere examples (Wilkins and George, 2002). Petersen and Nytoft (2006) suggested that this may be due to floral control on oil generation potential, linked to the evolution of land plants. These authors also reported on some Permian coals from the Australian Cooper and Sydney Basins that may have marginal oil generation potential. In the coal-rich Sydney Basin (Australia), the presence of a petroleum system has been known for decades from the occurrences of numerous oil seeps and oil shows encountered during coal mining and the drilling of coal exploration wells (e.g. Philp and Gilbert, 1986). Nevertheless, whether these oils were sourced from coals or from other shaly source-rocks interbedded within the Coal Measures is not yet clearly established. This study assesses the organic geochemical and petrological characteristics of selected coal samples from the Late Permian Illawarra Coal Measures, fine-grained sediment samples from above and within the Coal Measures, and oil samples from the Early Triassic sandstones overlying the Coal Measures, in order to investigate if these oils are related to the coals.

Organic geochemical and petrological data demonstrate that the Sydney Basin coals (vitrinite reflectance values from 1.0 to 1.4 %) have higher hydrogen indices, higher liptinite contents and much higher organic matter extractabilities than the fine-grained sediments in the section. Biomarker evidence such as the high relative abundances of pristane, C<sub>19</sub> and C<sub>20</sub> tricyclic terpanes, C<sub>24</sub> tetracyclic terpane and C<sub>29</sub> steranes and diasteranes indicates that the oil shows and seeps were sourced from higher plant dominated organic matter deposited in an oxic environment. This is corroborated by the low abundances of dibenzothiophenes, and the absence of extended tricyclic terpanes and gammacerane in these samples. The source and maturity-specific biomarkers and aromatic hydrocarbon distributions of the oils exhibit notable affinities to those of the coals (Fig. 1). The affinity of the oils to the coals is also demonstrated by the similarities in bulk carbon isotopic compositions of the total oils and the coal extracts ( $\delta^{13}\text{C}_{\text{Oil}} = -24.7$  to  $-23.1$  ‰ and  $\delta^{13}\text{C}_{\text{Extract}} = -26.3$  to  $-25.3$  ‰) and carbon

isotopic compositions of their individual *n*-alkanes ( $\delta^{13}\text{C}_{n\text{-Alkanes of oil}} = -25.7$  to  $-23.4$  ‰ and  $\delta^{13}\text{C}_{n\text{-Alkanes of Extract}} = -25.6$  to  $-24.6$  ‰), with the exception of the heavier bulk isotopic composition of Metropolitan oil seep and the compound specific isotopic composition of Metropolitan coal extract. Permo-Triassic fine-grained sediments have relatively higher abundances of  $\text{C}_{14}$  and  $\text{C}_{15}$  bicyclic sesquiterpanes,  $\text{C}_{23}$  tricyclics terpane,  $\text{C}_{29}$   $\alpha\beta$  hopane,  $2\alpha$ -methylhopanes,  $\text{C}_{30}$  30-norhopane, 29,30-bisnorhopane,  $\text{C}_{27}$  steranes,  $\text{C}_{27}$  diasteranes and dibenzothiophenes. These distributions suggest a mixed terrestrial and calcareous organic matter input to the fine-grained sediments, which is significantly different from both the oils and the coals (Fig 1).

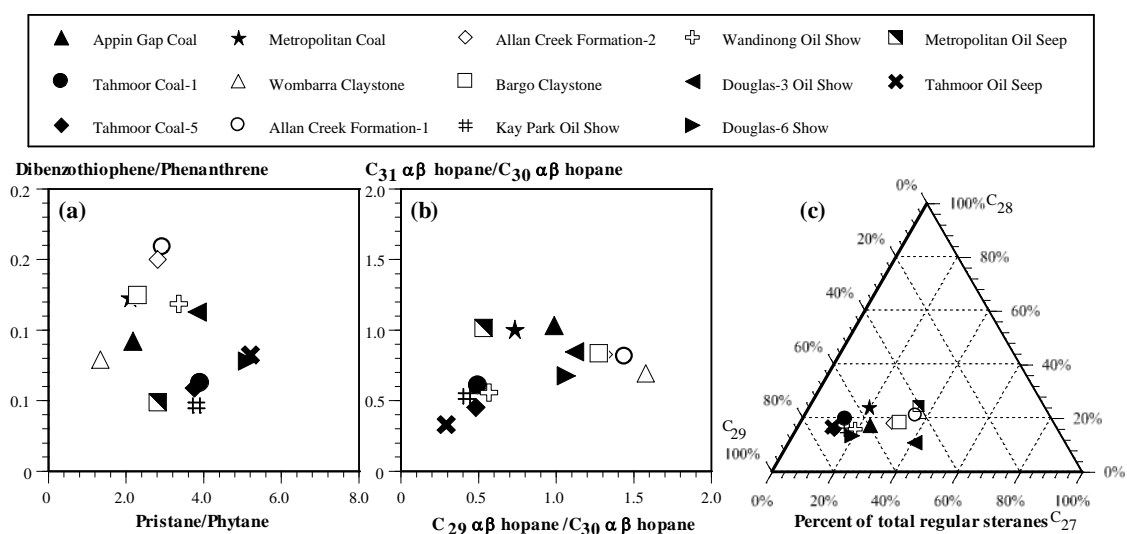


Figure 1. Cross plots of (a) Pristane/Phytane versus Dibenzo[thiophene]/Phenanthrene, (b)  $\text{C}_{29} \alpha\beta$  hopane/ $\text{C}_{30} \alpha\beta$  hopane versus  $\text{C}_{31} \alpha\beta$  hopane/ $\text{C}_{30} \alpha\beta$  hopane and ternary diagram of (c)  $\text{C}_{27}$ ,  $\text{C}_{28}$  and  $\text{C}_{29}$  regular steranes showing the genetic relationship of the oils and coals.

The similar biomarker features, bulk/compound specific carbon isotopic compositions and molecular maturities of the oils and the coals indicate that they are genetically related. This new evidence for generation and expulsion of oil from Permian Coals in the Sydney Basin indicates that this basin may have the potential for commercial oil accumulations in Permian or Early Triassic sandstones.

## REFERENCES

- Petersen, H.I. and Nytoft, H.P. (2006) Oil generation capacity of coals as a function of coal age and aliphatic structure. *Organic Geochemistry*, **37**, 558-583.
- Philp, R.P., and Gilbert, T.D. (1986) Biomarker distributions in Australian oils predominantly derived from terrigenous source material. *Organic Geochemistry*, **10**, 73-84.
- Wilkins, R.W.T. and George, S.C. (2002) Coal as a source rock for oil: A review. *International Journal of Coal Geology*, **50**, 317-361.