

# Assessing Oil Generation and Expulsion From New Zealand Coals

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## Abstract

Rock-Eval Hydrogen Index (HI) values vary with coal rank and do not give a direct measurement of the oil potential of vitrinite-rich coals. However, oils from coals are characteristically paraffinic and can be considered to derive from a polymethylene (PM) component. The paraffinic oil potential can be determined from an estimation of the relative proportions of carbon present in lignin and PM using a Van Krevelen diagram. Based on this compositional approach, HI values can be calibrated to provide an alternative estimate of paraffinic oil potential. A maximum in HI is generally reached near the onset of oil generation, at Rank(S) 12, from which the polymethylene (PM) contribution can be obtained using the formula  $HI_{PM} = 1.15HI_{max} - 172$ . The onset of oil expulsion can be identified from a variety of geochemical measurements, and occurs in the Rank(S) range ca 12.0-14.5 for coals with paraffinic oil potentials exceeding ca 40% HC/C<sub>org</sub>. Data from Taranaki Basin coals correlate well with the theoretical relationship between BI/HI<sub>PM</sub> and HI<sub>PM</sub>, using bitumen index (BI = S1/TOC) values of 10% HC/C<sub>org</sub> at the start of oil generation and 40% at the onset of oil expulsion, suggesting the HI<sub>PM</sub> model is reasonably accurate for members of the New Zealand coal band. Kinetic modelling of paraffinic oil generation from vitrinite-rich coals may be best approximated by consideration of PM degradation alone.

## Introduction

Although Late Cretaceous and Tertiary coals are recognised as a major source of oils in New Zealand (eg Killops et al 1994), their true hydrocarbon potentials, oil-expulsion thresholds, and kinetics of hydrocarbon-generation are not known with any certainty. We address these problems, using geochemical data from vitrinite-rich coals recovered as cuttings from petroleum exploration wells in the Taranaki Basin, and from a sequence of coal horizons in Tara-1 well in the Great South Basin, which spans a depth range of over 2 km (Killops et al 1997).

In lignified remains, the major constituents of vitrinite, the dominant aliphatic units are C<sub>1</sub>-C<sub>3</sub>, and so it might be expected that vitrinite-rich coals would generate only gaseous hydrocarbons, in the absence of a significant contribution from liptinites. However, maceral composition is not necessarily a good guide to the chemical composition of coals (Powell et al 1991). The presence of amorphous, hydrogen-rich, material, which cannot be recognised by microscopy, probably explains the oil potential of vitrinite-rich coals, particularly those rich in desmocollinite (Clayton et al 1991). Such material includes

polymethylenic biomacromolecules like cutan and suberan, which are expected to yield the paraffinic oils characteristic of coals (Powell 1988; Powell et al 1991).

The New Zealand coal band is a good example of a predominantly vitrinite-rich coal series (generally ≥80% vitrinite; eg Black 1980). The bottom of the New Zealand coal band broadly coincides with the bottom of the type III kerogen trend and also with a band of vitrinite genesis based on European and American Carboniferous coals (Figure 1a). It marks the boundary between high-H coals (often liptinite-rich) and low-H coals (inertinite-containing). The New Zealand coal band is not unique; vitrinite-rich coals from Japan and the Mahakam Delta, Indonesia, plot as bands overlapping it on Van Krevelen diagrams (Suggate and Boudou 1996), as do many vitrains from Australia. On the basis of compositional similarities, the oil generation and expulsion characteristics of all these coals should be similar.

In order to compare variation in the geochemical parameters of coal samples from a number of locations and to correlate these parameters with the onset of oil generation and expulsion, it is necessary to use a thermal

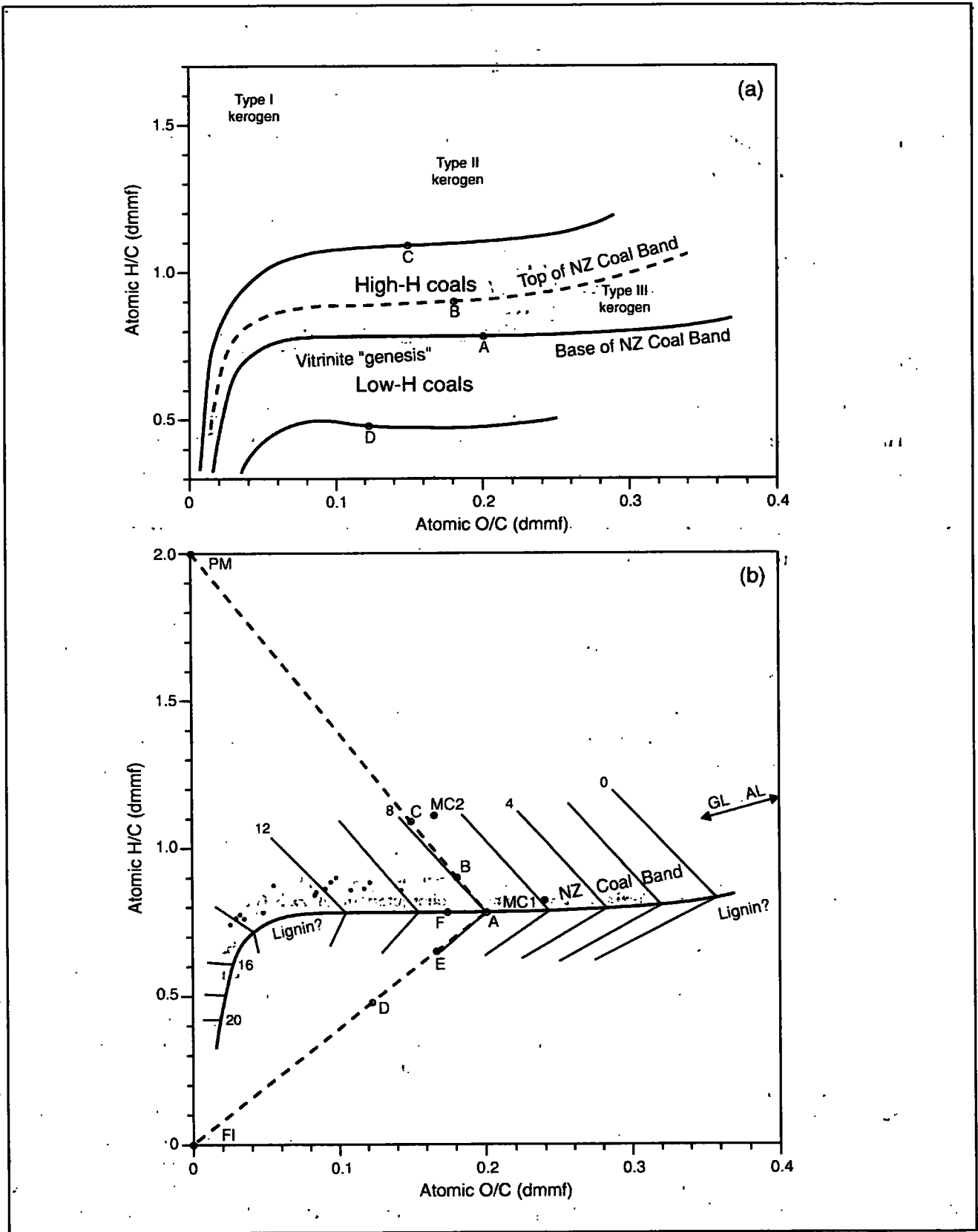


Figure 1. Van Krevelen diagrams showing the New Zealand coal band. (a) Relationship between the New Zealand coal band, the main kerogen types (light-tone; after Béhar and Vandembroucke, 1986) and Van Krevelen's band of vitrinite genesis (dark-tone band; Van Krevelen, 1961). (b) New Zealand coal band and isoRank(S) contours in relation to lignins and fossil woods. [See text for discussion of A-F; PM = polymethylene; FI = fusinitic inertinite; MC1 and MC2 are Maramarua coals; unlabelled points are Tara coals; GL and AL are modelled gymnospermous and angiospermous lignins (Hatcher, 1990).]

maturity scale that is independent of variations in organic matter type. Rank(S) provides such a maturity scale (Figure 1b; Suggate and Boudou 1993); with units representing approximately equal increments of temperature (ca 10°C for a heating rate of 3°/Ma). An empirical, approximate relationship between Rank(S) and vitrinite reflectance (VR) has been established for the VR range 0.5-1.0%: Rank(S) = (17.87 - 3.25/VR - 0.5/VR<sup>2</sup>).

## Petroleum Potential and Rock-Eval Analysis

Rock-Eval is a quick and convenient method for examining the petroleum potential of source rocks, and its application and limitations have been documented (eg Orr 1983; Peters 1986). Coals present particular problems because their abundant pyrolysis products tend to produce a response outside the linear range of the flame ionisation detector (FID) which measures S1 and S2, and so small samples are preferable (ca 10 mg; eg Bostick and Daws 1994). Most coals yield hydrogen indices (HI) of <300% HC/C<sub>org</sub>, but it is believed that the hydrocarbon potential of coals is generally overestimated by open pyrolysis systems like Rock-Eval, in which thermally-cleaved fragments can escape from the kerogen (Peters 1986; Schenck and Horsfield 1993). In this article HI is preferred to S2 when describing petroleum potential, because it normalises the potential to C content, allowing comparison of coals of different maturities and ash content. Similarly, bitumen (ie oil-like components) will be considered as S1/TOC (hereafter referred to as bitumen index, BI).

HI data are presented for coals from Tara-1 in Figure 2, and an average trend is shown by the solid line, its extension to maturity extremes being based on data for New Zealand coals in general. HI reaches a maximum of ca 250% HC/C<sub>org</sub> at Rank(S) ca 12-13. Such maxima are not exhibited by other kerogen types, but appear to be characteristic of all coals and type-III kerogens (in the range R<sub>m</sub> ca 0.65-0.8%; Durand and Paratte 1983; Teichmüller and Durand 1983; Suggate and Boudou 1993; Bostick and Daws 1994). They are not expected, if a particular coal has an intrinsic petroleum potential which remains constant until oil generation commences. This variation in HI has thwarted attempts to derive a simple empirical relationship between HI and atomic composition (Powell et al 1991). Mass balance calculations based on atomic composition suggest that CO<sub>2</sub> loss from the average member of the New Zealand coal band accounts for an HI increase of no more than 10% HC/C<sub>org</sub> (Killops et al 1996), and water evolution (or uptake) has no effect on HI. Yet HI increases by at least 100% HC/C<sub>org</sub> up to Rank(S) ca 12. The expected trend in HI is shown by the bold broken line in Figure 2. Hydrocarbon generation should result in a significant decrease in HI, and so may commence near the maximum in HI. In Figure 2 it is assumed to occur at Rank(S) 12 (discussed later). Can a meaningful hydrocarbon potential be obtained from HI<sub>max</sub>, or does it vary dramatically with rank?

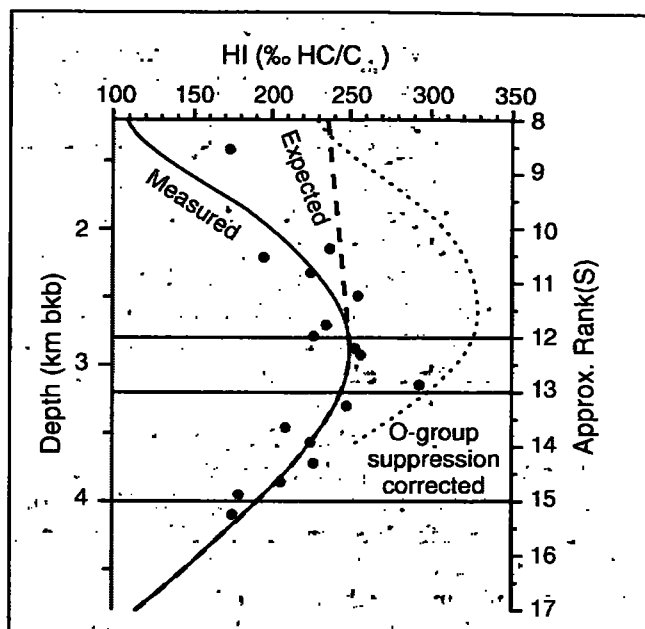


Figure 2. Variation in hydrogen index with depth in Tara-1 well: (Average trend of samples represented by solid line; modelled trends shown by bold broken line; faint broken line gives potential correction of observed HI trend for O-group suppression.)

The cause for the apparent suppression of HI below Rank(S) 12 has not been established unequivocally. One possible explanation is variation in suppression of the FID signal during Rock-Eval analysis (Boudou et al 1994). The FID responds to C atoms, and the direct C measurement is usually subjected to a correction factor based on the average H/C ratio in the expected products, so that S2 provides an estimate of hydrocarbon yield (C is assumed to comprise 83% by weight of products in the Tara data in Figure 2). However, ionisation is suppressed to varying degrees by C-bonded electronegative atoms. Consequently, the amount by which C yields are underestimated by a FID depends on the type and number of functional groups present (Sternberg et al 1962). In immature New Zealand coals O is the main cause of signal suppression. The effects of O-group suppression should be large in lignin products and negligible in PM products. Based on the maturity-related variation in O-group content of the average New Zealand coal (Killops et al 1996 and references therein) and reported suppression factors (Jorgensen et al 1990), and allowing for CO<sub>2</sub> evolved during the S3 measurement, the faint broken line in Figure 2 shows the possible effects of O-group suppression on the measured HI. Correction for O-group suppression is of the right magnitude to account for the observed HI variation, but does not produce the expected trend.

Direct O-group suppression may not be the only or even the main factor controlling HI. Structural rearrangements within coal during diagenesis, as proposed for Mahakam coals (Boudou et al 1994), may lead to an increase in potentially hydrocarbon-generating units. A possible mechanism is the recombination of thermally-cleaved fragments with kerogen before expulsion occurs, in what

would effectively be a closed pyrolysis system. For example, the methyls liberated from methoxy groups during early diagenesis (discussed later), rather than contributing to early methane generation, may migrate elsewhere on the kerogen structure, whereupon they are not subject to O-group suppression. Such rearrangements may reflect progression towards thermodynamic equilibrium in a closed system. Types I and II kerogen should also exhibit O-group suppression, but the greater hydrocarbon potentials and lower O contents presumably obscure its effect, and a maximum in HI near the onset of catagenesis is not observed.

Other factors affect HI values. The pyrolysis conditions used to measure the S1 peak do not remove all solvent-extractable components from coals (eg Orr 1983). This effect can be seen for three samples from Tara-1 in Figure 3. The least mature sample appears to be on the verge of entering the oil window, whereas the other two samples are within the oil window (and post expulsion onset, discussed below). A significant proportion of the S2 peak of the least mature sample is solvent extractable (ca 13%), but the effect of this material on HI diminishes with increasing maturity (Figure 3b). This material appears to be partially represented by the shoulder on the low-temperature side of the S2 peak (Figure 3a). The shoulder may be present at all maturities, but can only be distinguished as the main S2 peak moves to higher  $T_{max}$  with increasing maturity. If it represents a symmetrical peak (half toning, Figure 3a), it accounts for ca 7% of S2 (ca 10% of  $C_{org}$ ). If the extractable material is considered an oil component, HI may overestimate the residual petroleum potential by ca 10% (on top of any other effects) as the oil window is approached. However, the material is not typical of the hydrocarbons in coal-sourced oils, and so it should probably be considered a true part of the residual kerogen (ie part of S2).

Rock-Eval TOC is little affected by solvent extraction, even though some 36% of the TOC value is derived from the S2 peak in the least mature sample in Figure 3 and subject to O-group suppression. It has been suggested that it is more appropriate to use ultimate analysis C content in computing HI rather than the Rock-Eval TOC (Newman et al 1997). However, from the above discussion of HI behaviour, it is not clear that such HI values would provide a more accurate estimate of petroleum potential. Rock-Eval appears to give accurate results for the residual (non-hydrocarbon generating) C measurement, upon comparison with proximate analysis fixed-C (daf) for Tara coals (Figure 4a). In contrast, Rock-Eval TOC ( $C_{org}$ ) values are lower by some 6-8% than ultimate analysis values throughout the maturity range (Figure 4b). This could be due to suppression of the S1 and S2 measurements, because the ultimate  $C_{org}$  values were determined as  $CO_2$  by IR and so were not subject to FID signal-suppression. The suppression does not decrease with rising maturity, as expected for simple O-group suppression, so another factor must operate.

Because Rock-Eval residual C values seem accurate and because  $S1 \ll S2$  for coals in the Rank(S) range 10-15 in Tara-1, the main cause of the  $C_{org}$  discrepancy is under-representation of C loss by the S2 measurement. S2 values can be corrected for this under-representation, based on the difference between  $C_{org}$  values from ultimate analysis and Rock-Eval. The corresponding corrected HI values are shown in Figure 4c. They exhibit a greater spread than the original data, but there is an apparent trend of approximately constant HI up to Rank(S) ca 12-13 followed by a decline, as originally expected (Figure 3). The measured  $HI_{max}$  is ca 82% of the corrected value [comparable to the  $HI_{max}$  correction of Boudou et al (1994) for O-group suppression based on HI and OI values].

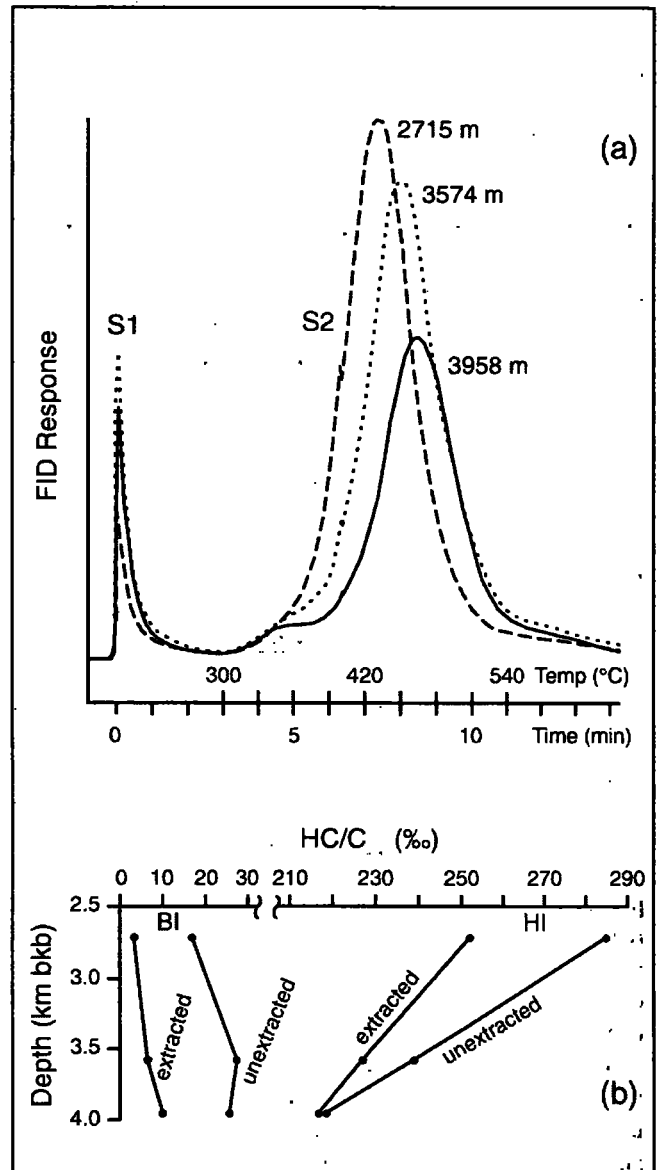


Figure 3. Rock-Eval data for three coal samples from Tara-1 well. (a) Pyrograms for unextracted samples (half-tone area represents potential kerogen-degradation products not liberated during S1 measurement). (b) Variations in BI and HI between solvent extracted and non-extracted aliquots.

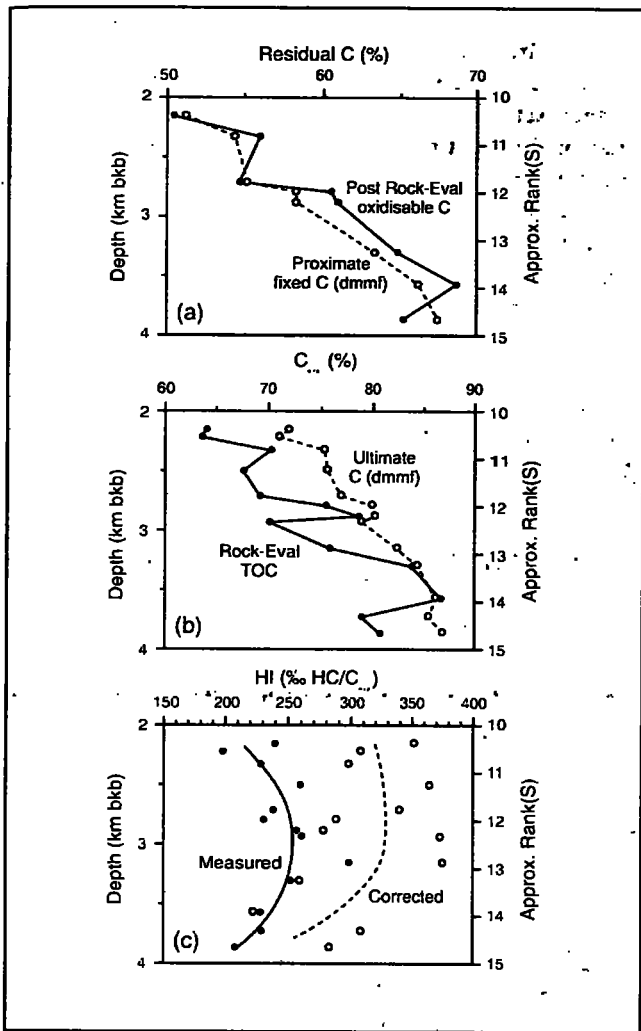


Figure 4. Comparison of data from Rock-Eval with those from proximate and ultimate analyses of Tara coals (dmmf = dry mineral-matter-free). (a) Post Rock-Eval oxidisable C and proximate fixed C. (b) Rock-Eval TOC and ultimate C content. (c) Measured and corrected HI [based on adding  $\Delta C_{org}$  values from (b) to S2].

To summarise, Rock-Eval appears to provide reasonable TOC values, but there are several factors that can affect S2 (and hence HI), so it is not clear how accurately the measured or corrected HI values near the onset of oil generation represent the true hydrocarbon potential. Not all the C-containing compounds released during the S2 measurement will contribute to natural hydrocarbon accumulations. Mass balance calculations based on observed atomic CHO variations for the average member of the New Zealand coal band suggest the total amount of hydrocarbons generated during catagenesis is 220-290% HC/C<sub>org</sub> (Killops et al 1996), similar to the range spanned by measured and corrected HI<sub>max</sub> values.

## Hydrocarbon Potential and Elemental Analysis

It has been suggested that, because oils from coals are highly paraffinic, estimates of the petroleum potential of coals would be more accurate if based on the paraffinic

component (Powell et al 1991; Smith et al 1994). It is possible to estimate paraffinic oil potential from Van Krevelen diagrams, provided: the oil-generating component can be approximated by (CH<sub>2</sub>)<sub>n</sub> (polymethylene); the polymethylene contribution can be estimated; direct generation of methane from polymethylene is negligible. To determine the polymethylene contribution requires a baseline of zero polymethylene to be identified, corresponding to predominantly lignin and its diagenetic products. An interesting property of the isoRank(S) lines is the sharp change in gradient at the base of the New Zealand coal band (Figure 1b). It can be explained if the base of the New Zealand coal band represents the trend for pure lignin, and coals lying above it comprise mainly mixtures of lignin and polymethylenic material (PM; Figure 1b), whereas those below contain mixtures of lignin with fusinite-like inertinite (FI; Figure 1b). PM in immature samples has an atomic H/C ratio of 2, and FI is a large polyaromatic structure with an effective H/C ratio of 0, so isoRank(S) lines for immature samples extrapolate to H/C = 2 and H/C = 0 from the lignin trend. With increasing maturity, as the main down-turn in the New Zealand coal band is approached, isoRank(S) lines above the proposed lignin trend extrapolate to successively lower atomic H/C values, which can be interpreted as the result of PM cracking and the consequential disproportionation of H into *n*-alkanes.

On this basis, C<sub>PM</sub>:C<sub>lignin</sub> in an immature coal [up to Rank(S) ca 12] is given by its position on the line joining pure PM (H/C = 2) to the lignin evolution line at the required Rank(S) value. For example, at Rank(S) 8, the upper boundary of the New Zealand coal band (B, Figure 1) corresponds to a C<sub>PM</sub>:C<sub>lignin</sub> ratio of 10:90, whereas the upper limit of high-H coals (C, Figure 1) represents ca 26:84 C<sub>PM</sub>:C<sub>lignin</sub> and the lower limit of low-H coals (D, Figure 1) represents ca 39:61 C<sub>PM</sub>:C<sub>lignin</sub>. The hydrocarbon potential of the PM component of a lignin-PM mixture is obtained by multiplying the theoretical HI value for pure PM (1167% HC/C<sub>org</sub>) by the proportion of C<sub>PM</sub> present, which amounts to 117% HC/C<sub>org</sub> for B. The PM-derived oil potential does not take into account possible contributions of resins and lignin/tannins. Resin contributions appear to be minor, but would cause paraffinic oil potential to be underestimated slightly because H/C ratios are <2 for resin components. Such underestimations are offset by some gaseous hydrocarbon production (H/C >2) during the primary cracking of PM, which has not been taken into account in our model.

That the Rank(S) scheme works for New Zealand coals suggests that this simplified compositional picture is a reasonable approximation. Mixtures of all three components would tend to blur the Rank(S) distinctions. For example, a mixture of Rank(S) 8 samples of B and E with a C<sub>PM</sub>:C<sub>lignin</sub>:C<sub>FI</sub> of 13:79:8 would plot at point F rather than A, at Rank(S) ca 9. Such ternary mixtures would cause a problem for the Rank(S) scheme, but they appear to be uncommon. The question remains whether there is a

discrete lignin trend. It is recognised that cellulosic material degrades rapidly and makes only minor contributions to woody material after the initial phase of peatification (eg Stout et al 1988; Hatcher et al 1989). Lignin is the major surviving woody component; that from gymnosperms is predominantly derived from coniferyl alcohol, bearing one methoxy group per aromatic ring, whereas that from angiosperms also contains a proportion of sinapyl units, bearing two methoxy groups. The compositional trend from gymnospermous to angiospermous lignin (GL-AL, Figure 1b) is almost perpendicular to isoRank(S) lines and might be predicted to interfere severely with the Rank(S) scheme, because Eocene New Zealand coals are predominantly derived from angiosperms whereas their Late Cretaceous counterparts are mainly of gymnosperm origin (eg Killips et al 1995). However, demethylation of methoxy groups occurs during early diagenesis (Hedges et al 1985; Hatcher 1990), so lignin compositions probably rapidly converge, permitting the application of the Rank(S) scheme to angiosperm- and gymnosperm-derived coals on Van Krevelen diagrams.

Contours of the percentage of  $C_{PM}$  in a PM-lignin mixture obtained from the proposed model are shown by solid lines in Figure 5; they are almost thermal evolution lines. A further set of contours, representing the trends in the fractional weight of coal (dmmf) that can be converted to paraffinic oil, are shown by the broken lines in Figure 5, together with the corresponding contours (shown as faint broken lines) derived from Saxby's empirical model for coals (Saxby 1980; Saxby and Shibaoka 1986). Although the contours of fractional coal conversion to oil for the two models have similar gradients over most of the maturity range in Figure 5, those of Saxby give slightly higher potentials, mainly because they represent total oil potential. Total petroleum potential is very difficult to predict because of the varying H/C ratios of potential precursors and products. Mass balance calculations suggest the average member of the New Zealand coal band may yield 80-110%  $CH_4/C_{org}$  (Killips et al 1996). A  $^{13}C$  NMR-based structural model for subbituminous coal suggests most of the propyl groups of lignin have been retained during diagenesis, so if they are subsequently eliminated as methane during catagenesis, there could be

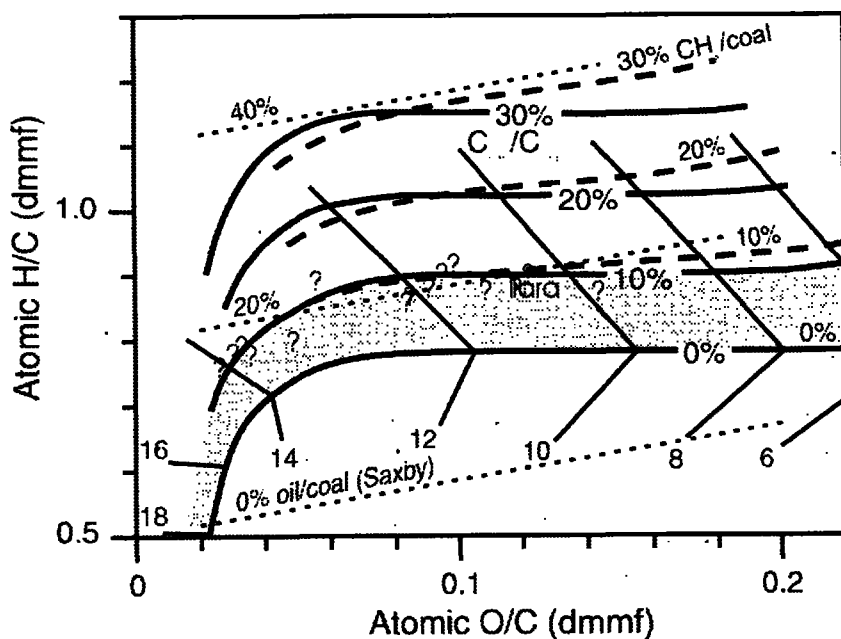


Figure 5. Potential oil yields of coals based on atomic CHO composition. [Solid lines = oil/ $C_{org}$  for PM-derived oil (ie  $C_{PM}/C_{org}$ ), 0% = lignin evolution line. Bold broken lines = oil/coal weight % for PM-derived oil. Faint broken lines = Saxby's total oil/coal weight yield (Saxby, 1980; Saxby and Shibaoka, 1986).]

as much as 350 kg/tC<sub>org</sub> methane generated. However, pyrolysis studies of Mahakam and North Sea coals suggests that only ca 30% CH<sub>4</sub>/C<sub>org</sub> is generated under open pyrolysis conditions (Béhar et al 1997).

## Recognising Oil Generation and Expulsion Thresholds

In Figure 6 various geochemical parameters are plotted against depth/Rank(S) for coals from Tara-1 well (biomarker data were obtained from coal-rich cuttings samples). BI exhibits a scatter above ca 3.2 km depth, but is reasonably constant at greater depth. The higher, constant value can be interpreted as representing the saturation capacity of coal for bitumen and that expulsion begins near 3.2 km depth, or Rank(S) 13. BI values vary widely at shallower depth because of coal-type variation and trapping of migrated hydrocarbons. The variability in BI above ca 3.2 km in Tara-1 makes the onset of oil generation difficult to establish with certainty using this parameter alone.

The appearance of petroleum-like material in New Zealand coals occurs at Rank(S) 9-10 (Suggate and Boudou 1993), but the geochemical parameters in the lower part of Figure 6 provide little evidence for significant generation of the component distributions characteristic of New Zealand coal-sourced oils until Rank(S) ca 12. For example, CPI in the C<sub>25</sub>-C<sub>31</sub> range is high (>1) in immature coals, reflecting the contribution of leaf epicuticular waxes to the *n*-alkanes in the initial bitumen. Cracking of PM results in *n*-alkanes with CPI = 1, so the CPI of bitumen is expected to decrease as the contribution of *n*-alkanes from PM cracking rises, reaching a minimum when expulsion and effective flushing of initial bitumen has occurred. Such a maturity-related trend has been reported for a suite of German Carboniferous bituminous coals (Radke et al 1980) and for Mahakam coals (Bjørøy et al 1988). CPI values appear to begin declining above Rank(S) 12 for Tara coals (Figure 6). Similarly, the bitumen in immature Tara coals generally contains high proportions of 17 $\alpha$ (H)-homohopanes, presumably derived from decarboxylation of 31,32-bishomohopanoic acid, whereas the hopanes of coal-derived oils are dominated by 17 $\alpha$ (H)-hopane (Killops et al 1994). The proportion of 17 $\alpha$ (H)-hopane does not increase noticeably until nearly Rank(S) 12.5.

Without absolute quantification of biomarkers in initial bitumen and thermally-generated hydrocarbons, it is not possible to discount that changes in biomarker parameters only become apparent at the onset of oil expulsion rather than at the onset of generation. However, the fact that generated oils are more paraffinic ( $f_1$ , sats/aroms; Figure 6) than the initial bitumen suggests that the onset of distinct changes in 30 $\alpha\beta$ /(30 $\alpha\beta$ +31 $\alpha\beta$ ) and CPI in Figure 6 probably represents the start of significant paraffinic oil generation, at Rank(S) ca 12 (VR ca 0.65%). This assumes that the kinetics of biomarker and *n*-alkane generation from kerogen are virtually identical. It can also be

speculated from the recently proposed structures for cutan and related components (eg McKinney et al 1996) that the ester-bonded polymethylene chains would be released by decarboxylation before cracking of these long chains occurs (Alexander et al 1992). This release of PM chains might help to explain the appearance of petroleum-like substances at Rank(S) 9-10. Functional group and NMR data for New Zealand coals suggest the proportion of C in ester groups is at most 25% at Rank(S) 9 and falls to no more than 8% at Rank(S) 12. Expulsion of paraffinic oil should cause a decrease in the atomic H/C ratio and an increase in the aromatic fraction of the <sup>13</sup>C NMR signal ( $f_1$ ; Newman et al 1988) of bulk coal samples (including residual bitumen), together with an increase in the saturates/aromatics ratio of extracted hydrocarbons. These trends occur at Rank(S) 13-14 in Figure 6. At the onset of expulsion the contribution of initial bitumen should decrease, although some geochemical parameters may not show this effect as markedly as other because of variations in the abundance of individual components in the initial bitumen compared with the thermally-generated bitumen. It might also be expected that the effects of the initial bitumen would linger after the onset of expulsion until flushing is complete, so not all geochemical parameters will necessarily reach their values in thermally-generated oil at the onset of expulsion. From Figure 6, expulsion appears to begin in Tara coals at Rank(S) 13, and flushing is effectively complete by Rank(S) 14, consistent with data from coal-sourced New Zealand oils (half-tone bands, Figure 6).

Expulsion-related effects may account for the observed discontinuities in compositional trends of bitumen extracted from some German bituminous coals at R<sub>m</sub> ca 0.9% (Radke et al 1980), which corresponds to Rank(S) ca. 13.5. Similarly, BI has been found to reach a maximum at ca 0.9% R<sub>m</sub> in a range of other coals (Teichmüller and Durand 1983), consistent with the onset of expulsion.

## Biomarker Maturity Parameters

Various biomarker parameters are represented in Figure 6 which have been considered indicators of maturity (eg Peters and Moldowan 1993). For some time it has been thought that thermally-induced isomerisations account for the observed variations in stereochemistry at C-22 and C-17/C-20 in hopanes, and at C-20 and C-14/C-17 in steranes, resulting in an increase in the relative amounts of the more thermodynamically-stable configurations with rising thermal stress until equilibria are established. So the apparent decrease in the ratios 31 $\alpha\beta$ S/(31 $\alpha\beta$ S+31 $\alpha\beta$ R) and 30 $\alpha\beta$ /(30 $\alpha\beta$ +30 $\beta\alpha$ ) for hopanes and 20S/(20S+20R) for steranes at Rank(S) >13 in Figure 6 is unexpected. However, it can be explained by a combination of differences in isomer distributions between initial bitumen and thermally generated hydrocarbons, and variation in the relative rates of generation from kerogen and subsequent thermal

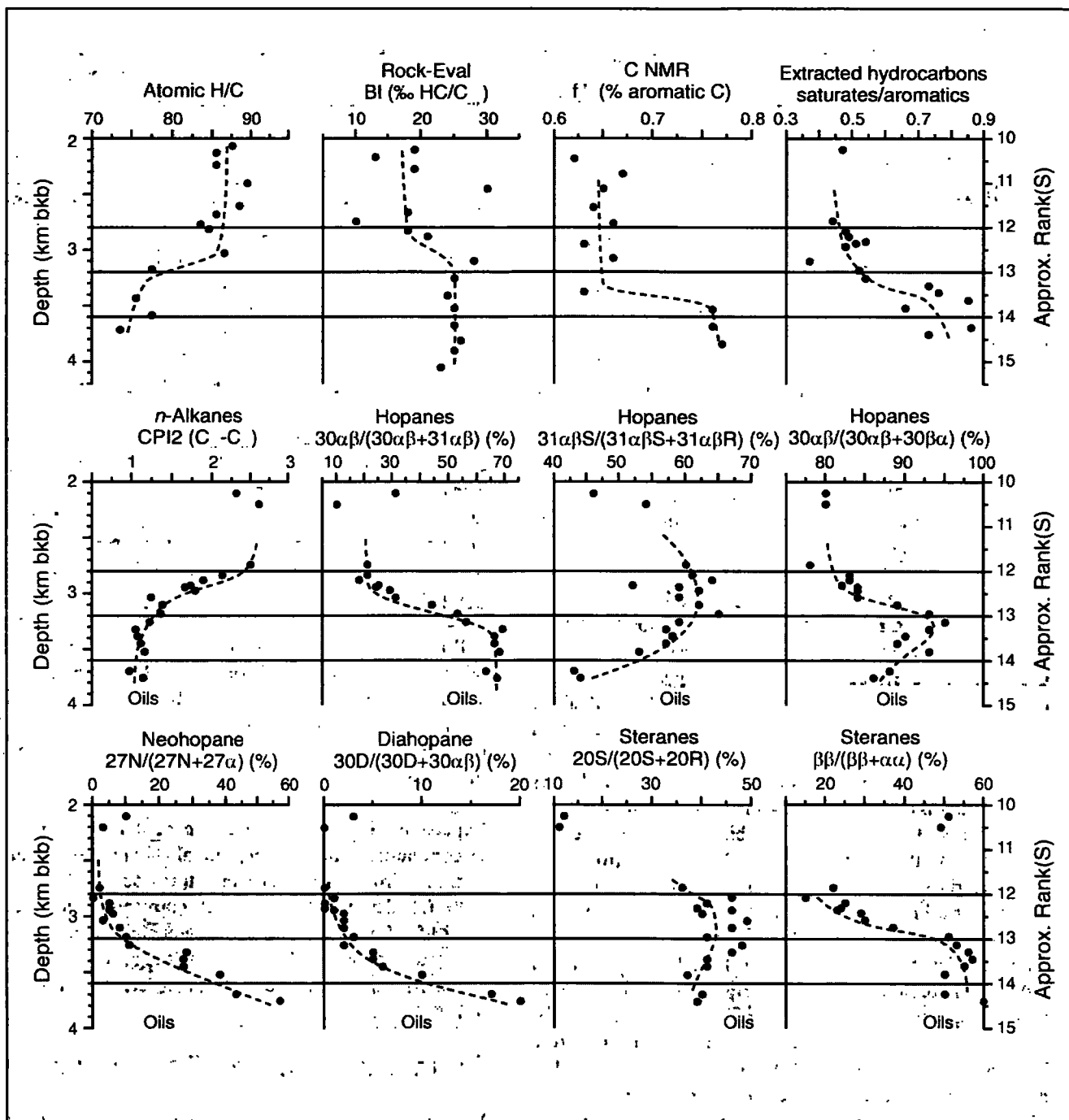


Figure 6. Depth trends in various geochemical parameters for coals in Tara-1 well. [ $^{13}\text{C}$  NMR data and  $f'$  after Dickinson et al, 1991. CPI2 based on  $m/z$  183 responses for  $\text{C}_{25}$ - $\text{C}_{31}$   $n$ -alkanes (after Marzi et al, 1993). Hopane ratios based on  $m/z$  191 response;  $27\alpha$  and  $30\alpha\beta = \text{C}_{27}$  and  $\text{C}_{30}$   $17\alpha(\text{H})$ -hopanes;  $30\beta\alpha = 17\beta(\text{H})$ -moretane;  $31\alpha\beta\text{S}/\text{R} = 22\text{S}/\text{R}-17\alpha(\text{H})$ -homohopane;  $27\text{N} = \text{C}_{27}$   $18\alpha(\text{H})$ -neohopane;  $30\text{D} = 17\alpha(\text{H})$ - $15\alpha$ -methyl- $27$ -norhopane. Sterane ratios based on  $m/z$  217 response:  $20\text{S}/\text{R} = 20\text{S}/\text{R}$  epimers of  $5\alpha(\text{H}), 14\alpha(\text{H}), 17\alpha(\text{H})$ - $24$ -ethylcholestane,  $\beta\beta = 5\alpha(\text{H}), 14\beta(\text{H}), 17\beta(\text{H})$ - $24$ -ethylcholestanes,  $\alpha\alpha = 5\alpha(\text{H}), 14\alpha(\text{H}), 17\alpha(\text{H})$ - $24$ -ethylcholestanes. Half-tone bands represent parameter ranges for New Zealand coal-sourced oils.]

destruction of individual components (eg Peters et al 1990; Farrimond, et al 1996). Thermal destruction of biomarkers is a major factor close to dykes (eg Farrimond et al 1996), and may affect saturates in general more than aromatic hydrocarbons (Clayton and Bostick 1986). Under more normal heating rates, apparent concentrations of hopanes and steranes in the Upper Devonian Duvernay Formation of Western Canada decrease as  $T_{\text{max}}$  exceeds ca  $440^\circ\text{C}$

(Requejo 1994), which corresponds to Rank(S) ca 13 in New Zealand coals (Suggate and Boudou 1993).

Significant thermal destruction of biomarkers is unlikely at Rank(S) <13, so isomerism may play a role in initial bitumen, which is retained within coal for considerable time at elevated temperatures prior to expulsion. At Rank(S) >13 thermal stability appears to become the dominant factor, in view of the rapid increase in relative

abundance of neohopanes and diahopanes (Figure 6). This is because kerogen is not thought to be important in the origin of 27N (Farrimond et al 1996) and predicted thermal stability increases in the order 17 $\alpha$ (H)-hopanes <18 $\alpha$ (H)-neohopanes <17 $\alpha$ (H)-diahopanes (Moldowan et al 1991). Once expulsion commences, it is anticipated that the residence time of biomarkers in bitumen within coal is short, so there is little time for isomerism to occur before migration results in a significant decrease in temperature. Consequently, the apparent decline in maturity parameter values between Rank(S) 13 and 14 could be at least partly attributable to a lower apparent maturity for freshly evolved biomarkers than for those in the initial bitumen, due to steric hindrance of isomerism in kerogen-bound biomarkers (eg Peters et al 1990).

The variation in hopane C number with coal rank in New Zealand petroleum exploration wells has been known for some time (Johnston et al 1988; Collier and Johnston 1991) and has also recently been reported for a series of Eocene coals from the West Coast region of New Zealand (Newman et al 1997). A ternary plot of 17 $\alpha$ (H)-hopane C-number distribution is presented in Figure 7 for Tara samples and for coals from various wells in Taranaki Basin. Approximate positions of isoRank(S) lines are shown, but there is some spread in data, particularly at Rank(S) <12.5, and so the boundaries are indicative only. The majority of New Zealand coal-sourced oils plot in the Rank(S) range 13.0-13.5 (half-toning, Figure 7). The trend for coal samples in Figure 7 is approximately linear with increasing maturity up to the proposed onset of oil expulsion, and indicates that 29 $\alpha\beta$  and 30 $\alpha\beta$  are generated from kerogen in similar amounts, and greater than 31 $\alpha\beta$ , up to Rank(S) ca 13, resulting in a dilution of the pronounced 31 $\alpha\beta$  contribution in initial bitumen. A similar trend of decreasing 31 $\alpha\beta$ , and at higher maturity a relative increase in 30 $\alpha\beta$ , has been noted by Farrimond et al (1996). The apparent relative increase in 30 $\alpha\beta$  above Rank(S) ca 13 could reflect changes in the distribution of generated hopanes and/or differences in thermal degradation rates. The trend does not appear to be affected by whether coals expel oil (eg Tara) or not (eg Toko, as discussed below). However, it may be due at least partly to the effect of unidentified co-eluting components during GC-MS analysis, which are initially in relatively low abundance but are of higher thermal stability than the regular hopanes (cf neo/diahopanes).

## Factors Controlling Oil Expulsion

Chemical adsorption is considered an important control on the expulsion of oil from coals (eg Sandvik et al 1992; Pepper and Corvi 1995b). A general oil expulsion threshold value of 100% HC/C<sub>org</sub> for BI has been suggested (Pepper and Corvi 1995b), but it appears rather high for New Zealand coals (Figures 6 and 8; Sandvik et al 1992), although values up to 80% HC/C<sub>org</sub> have been recorded for the Walloon coal measures of Australia (Khorasani and Michelsen 1991). It is possible that the

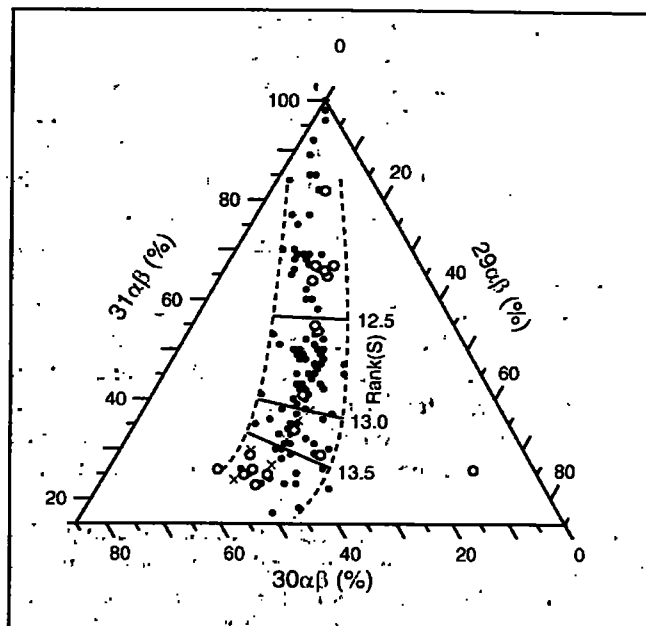


Figure 7. Ternary plot of the relative abundance of C<sub>29</sub>, C<sub>30</sub> and C<sub>31</sub> (22S+22R) 17 $\alpha$ (H)-hopanes in coals from various wells. (Based on m/z 191 response. o = Tara coals; x = Toko coals; • = other Taranaki Basin coals. Half-toning = province of coal-sourced oils in Taranaki Basin. Additional data after Crisp, 1986.)

effects of adsorption are modified by those of porosity, but there are problems of obtaining meaningful porosity data for in-situ coals (eg Killops et al 1996). Coal porosity is probably no more than ca 5% at 4-5 km depth, so if 1 t C<sub>org</sub> is equivalent to ca 1.5 t coal occupying ca 1.15 m<sup>3</sup>, pore volume could total 0.06 m<sup>3</sup> and accommodate up to 75 kg oil (in the absence of water). In practise, it is difficult to distinguish between petroleum that is unbound in pores and that chemically adsorbed. However, the fact that BI does not decrease significantly upon onset of expulsion argues against mass draining of over-pressured pores and for dominance of adsorption.

Although paraffinic hydrocarbons have the lowest adsorption affinities among petroleum components, the degree of saturation of adsorption sites, particularly by aromatic hydrocarbons and NSO compounds, prior to the main phase of oil generation may be important in determining the expulsion thresholds of waxy oils (Horsfield et al 1988; Sandvik et al 1992; Pepper and Corvi 1995b). So the amount of initial bitumen, which tends to be aromatic and NSO-rich, is likely to be important. The saturates:aromatics ratio for bitumen extracted from Tara coals is ca 0.5 in immature coals and tends towards a maximum of ca 0.8 at higher maturity (Figure 6). If this is simply the effect of diluting initial bitumen with thermally-generated paraffins, expulsion requires ca 60% increase in bitumen content, which is similar to the observed increase in BI (from ca 15 to 25% HC/C<sub>org</sub>; Figure 6). This is a small amount, and could suggest that only a little PM is necessary in some coals for paraffinic oil to be expelled. However, it ignores the potential generation (and adsorption) of aromatic

hydrocarbons, which would raise the required amount of petroleum to be generated. It is not certain that expelled oil has a saturates:aromatics ratio approaching unity, because oil accumulations in Taranaki Basin have higher values, even when secondary migration distances are relatively short (Killips et al 1994). It is also not clear if the aromatics in Tara coal bitumens represent adsorbed components from either the initial bitumen or early-generated hydrocarbons (mainly from lignin and tannins), or whether they are a consequence of continuing generation (and expulsion) of aromatics throughout the oil window. Results from Mahakam coals suggest that aromatics are generated early, before paraffins (Bjørøy et al 1988), and that preferential adsorption of aromatics from initial bitumen may account for the observed saturates:aromatics ratios.

To examine whether Rock-Eval data can be used to predict oil expulsion, analysis was undertaken of coal data from a number of exploration wells in Taranaki Basin. Data were restricted to one source (Crisp 1986) to avoid inter-laboratory variations, and the trends in the Rank(S) range of interest are shown in Figure 8. In general, the expected trends in Rock-Eval data are observed, but there is considerable data spread, attributable to differences in coal composition within and between wells. The hopane parameter  $30\alpha\beta/(30\alpha\beta+31\alpha\beta)$  also exhibits a spread of data, influenced by variations in both the bacterial activity affecting initial bitumen, and the degree of bacteriohopanoid incorporation into kerogen. Coals from Toko-1 well may be close to the limiting potential for oil expulsion, because HI is generally low but BI/HI is high and still increasing at Rank(S) 13.5 (Figure 8), suggesting expulsion has yet to occur.  $HI_{max}$  in the Toko coals is ca

200‰  $HC/C_{org}$ , which has been proposed as a general threshold value for oil expulsion from coals (Pepper and Corvi 1995b). In comparison, HI is high for Tara coals, whereas BI/HI values are low and constant above Rank(S) 13 (Figure 8) because only a small proportion of PM has to be converted to exceed the oil-expulsion threshold.

Comparison of BI (equivalent to  $C_{bitumen}/C_{PM+lignin}$ ) and BI/HI (equivalent to  $C_{bitumen}/C_{PM}$ ) trends suggest that the adsorption capacities of PM and lignin are similar. It would be convenient if Rock-Eval data, routinely obtained during petroleum exploration, could be used to model the expelled amount of paraffins. The main problem is determining whether generation of aromatics and NSO compounds has to be included, or whether a reasonably accurate picture can be obtained from consideration of paraffinic components only. Previous models have considered coals as one member of a range of kerogen types and corresponding expulsion thresholds have been based on bulk petroleum (eg Pepper and Corvi 1995b). The typical saturation value of BI at the onset of oil expulsion for New Zealand coals is 20-40‰  $HC/C_{org}$  (Figure 8; Sandvik et al 1992). BI measures predominantly PM-derived hydrocarbons (after oil expulsion begins), so for oil expulsion to occur  $HI_{PM}$  must be >20‰  $HC/C_{org}$ . Alternatively, for oil expulsion to occur it appears  $HI_{max}$  has to be >200‰  $HC/C_{org}$  (discussed above), so  $HI_{PM}$  must be >40‰  $HC/C_{org}$  ( $C_{PM}:C_{lignin}$  ca 4:96) on the basis of the Tara coal calibration from elemental composition. From these estimates of limiting  $HI_{PM}$  it is likely that only coals within the upper part of the New Zealand coal band and above (ie higher H/C ratio, Figure 1) will expel oil.

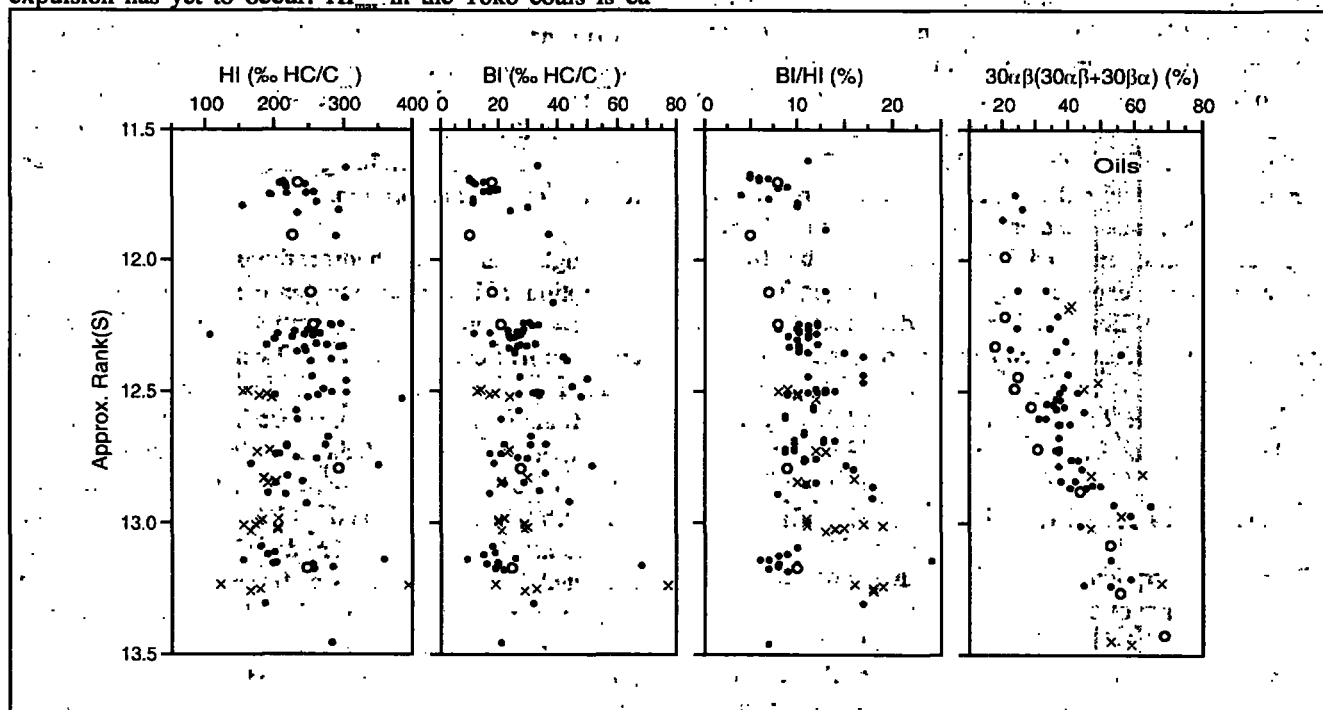


Figure 8. Rank-related trends in Rock-Eval and hopane data for coals from various wells in Taranaki Basin. (o = Tara coals; x = Toko coals; • = other Taranaki Basin coals. Rock-Eval data for wells in Taranaki Basin after Crisp, 1986. Additional hopane data after Crisp, 1986; Johnston et al, 1989; Collier and Johnston, 1991.)

## Obtaining paraffinic hydrocarbon potential from $HI_{max}$

The PM contribution to total HI ( $HI_{PM}$ ) can be calculated for vitrinite-rich coals lying above the lignin evolution line in Figure 1 if the lignin contribution to HI ( $HI_{lignin}$ ) is known. For Tara coals,  $HI_{max}$  is ca 250‰ HC/C<sub>org</sub>,  $C_{PM}$  is predicted to be ca 8.5% from Figure 1b, so  $HI_{PM}$  should be 99‰ HC/C<sub>org</sub>. The  $HI_{lignin}$  contribution to  $HI_{max}$  is, therefore, 151‰ HC/C<sub>org</sub> for 91.5%  $C_{lignin}$ , so pure lignin should have an  $HI_{max}$  of 165‰ HC/C<sub>org</sub>. For any vitrinite-rich coal for which  $HI_{max}$  can be measured or predicted using Figure 5,  $C_{PM}/C_{org} = (HI_{max} - 165)/1002$ , and  $HI_{PM} = 1167(HI_{max} - 165)/1002$ . An expulsion threshold value for  $HI_{PM}$  of 40‰ HC/C<sub>org</sub> is used to predict amounts of expelled paraffinic oil from the relationship between  $HI_{max}$  and  $HI_{PM}$  for vitrinite-rich coals in Figure 9. For coals capable of exceeding the saturation BI value, expulsion occurs over a limited Rank(S) range: between the onset of paraffinic oil generation at ca 12 and the onset of significant cracking to gas at ca 14.5 (equivalent to an in-situ temperature of ca 160°C; Mackenzie and Quigley 1988; Sandvik et al 1992), as similarly proposed by Suggate and Boudou (1993).

A test of the accuracy of  $HI_{PM}$  determination is shown in Figure 10. The behaviour of  $BI/HI_{PM}$  vs  $HI_{PM}$  can be predicted, as in Figure 10a. For this prediction, conditions are determined by the best fit to the coal data: initial BI is set at 10‰ HC/C<sub>org</sub> and expulsion takes place when BI reaches 40‰ HC/C<sub>org</sub> (ie 30‰ HC/C<sub>org</sub> of  $HI_{PM}$  has been converted to oil). All coals initially start on the lower margin of the shaded area and follow evolutionary paths shown by the arrowed lines. A break in gradient of the coal trends occurs at the onset of expulsion, whereupon the trends follow the upper margin of the shaded area until oil cracking becomes significant. All coals fall within the shaded area in the absence of significant oil cracking (which causes  $BI/HI_{PM}$  to decrease rapidly).

(Based on an expulsion threshold  $HI_{PM}$  value of 40‰ HC/C<sub>org</sub> for two pure lignin HI values of 150 and 165‰ HC/C<sub>org</sub>.)

$BI/HI_{PM}$  tends to infinity as  $HI_{PM}$  approaches zero, and to a common saturation threshold value as  $HI_{PM}$  becomes large. The same HI data for Taranaki Basin and Tara coals used in Figure 8 are converted to  $HI_{PM}$  values in Figure 10b. In order to calculate  $HI_{PM}$  values, it is assumed that over the Rank(S) range 11.5-13.5 pure lignin has an almost constant HI value of 150‰ HC/C<sub>org</sub> (which provides the best fit for all coal data), and that the HI value for a given coal is also effectively constant (ie equivalent to  $HI_{max}$ ). All but two of the 109 coals follow the expected trend, suggesting the approximations involved and the underlying model of  $HI_{PM}$  prediction are reasonable. In comparison, the corresponding plot  $BI/HI$  vs  $HI$  shows no obvious trend (Figure 10c).

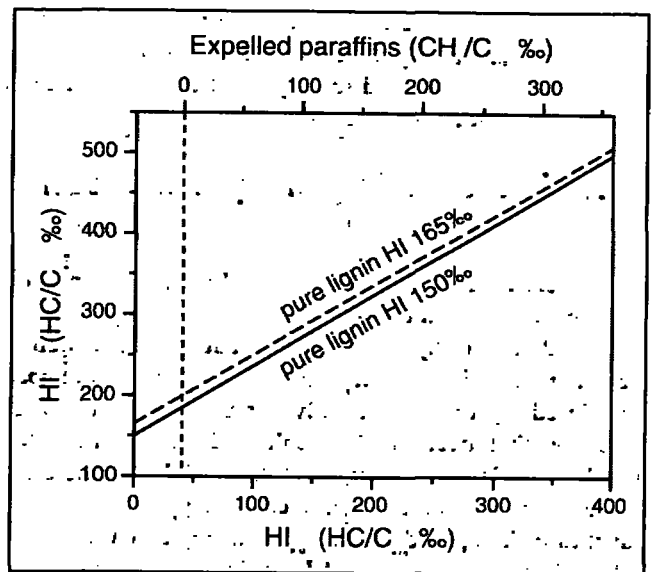


Figure 9. Predicted polymethylene contribution to  $HI_{max}$  and corresponding paraffinic oil expulsion potential.

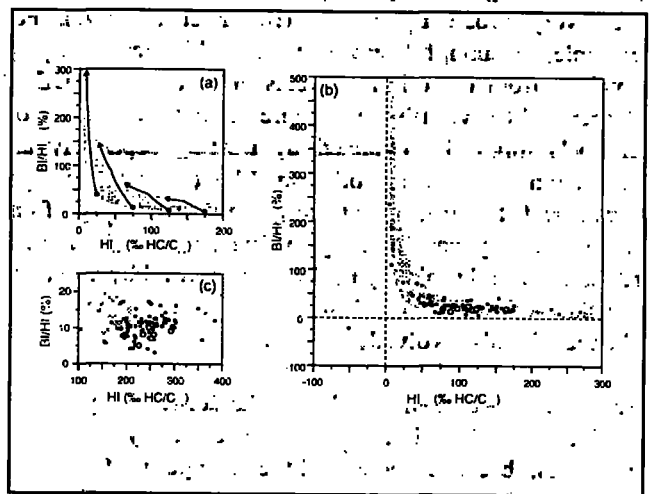


Figure 10. Relationships between BI and polymethylene contribution to HI. (a) Predicted  $BI/HI_{PM}$  vs  $HI_{PM}$ . (For initial  $BI = 10‰ HC/C_{org}$  and expulsion at  $BI = 40‰ HC/C_{org}$ . Examples of coal evolution trends shown by arrowed lines). (b)  $BI/HI_{PM}$  vs  $HI_{PM}$  for coals in relation to predicted trends. (c)  $BI/HI$  vs  $HI$  data for coals in (b). (o = Tara coals; x = Toko coals; • = other Taranaki Basin coals. Taranaki Basin HI data after Crisp, 1986.)

The expulsion threshold used appears reasonable for the Taranaki Basin data, and suggests that most Toko coals have marginal expellable oil potential (Figure 10b). Tara coals lie towards the lower margin of the predicted envelope, although they expel oil by Rank(S) 13, which suggests that the expulsion limit is lower for these coals. This may be caused by the influence of differences in analytical procedures between the two sample sets. Although the model in Figure 10a requires conversion of only 30‰ HC/C<sub>org</sub> for oil expulsion to occur, for coals of marginal oil potential the  $HI_{PM}$  limit may be nearer 40‰ HC/C<sub>org</sub>, as suggested above, because the oil expulsion

threshold moves towards higher maturity with decreasing PM content and expulsion may not occur before the remaining PM is cracked to very short-chain components (ie gases at surface conditions).

## Kinetic Modelling of Hydrocarbon Generation

The uncertainties in the factors controlling expulsion of oil from coal are no more significant than those associated with prediction of hydrocarbon generation rates. As well as general reservations about whether rapid pyrolysis in open or closed systems accurately simulates the types of reactions that occur under geological heating rates (eg Landais and Monthieux 1988; Ritter et al 1995), there are some specific problems with coals. Approximating the kinetics of kerogen degradation by a single  $A$  value for a relatively restricted range of  $E_{act}$  values appears to permit reasonable extrapolation of laboratory heating rates to geological thermal regimes for kerogens dominated by one hydrocarbon-generating component, but not for coals with their very broad  $E_{act}$  ranges (Béhar et al 1997). For example, meaningful gas generation kinetics were not obtained from the oil-prone coals of organofacies DE of Pepper and Corvi (1995a). A more accurate representation of coals might be obtained by treating separately the generation of paraffinic oil from PM, aromatic oil from lignin and tannins, naphthenic and aromatic oil from resins, and dry gas from lignin. Even so, some of these reactions would probably not be characterised by a discrete  $A$  value and narrow  $E_{act}$  distribution, due to the variety of chemical bonds involved.

The cracking of PM should be characterised by a very small range of  $E_{act}$ , similar to that for secondary cracking of  $n$ -alkanes, because there is little change in C-C bond energy with position in a polymethylene chain. The balance between long-chain, liquid products and short-chain, gaseous products is, therefore, primarily determined by probability: as the cracking reactions progress, relatively more short-chain components will be randomly produced because the proportion of shortened polymethylene chains increases. Above ca 160°C it seems that the major products are methane and other short-chain alkanes (Mackenzie and Quigley 1988; Sandvik et al 1992). PM cracking is apparently reflected in the sharp maximum in the  $E_{act}$  frequency distribution for the group E kerogen of Tegelaar and Noble (1994) at 55-57 kcal/mol ( $A = 6.5 \times 10^{14} \text{ s}^{-1}$ ). This kerogen group generates abundant  $n$ -alkane/alkene pairs upon pyrolysis, and is considered to contribute to New Zealand and similar coals, together with group G kerogen (Tegelaar and Noble 1994). The latter is thought to represent pure vitrinite, yielding mainly lignin components upon pyrolysis, but it exhibits considerable variation in generation characteristics. It has a broad  $E_{act}$  distribution (53-63 kcal/mol,  $A = 9.5 \times 10^{14} \text{ s}^{-1}$ ), but still with a maximum at 56-57 kcal/mol consistent with a slight PM contribution.

The effects of varying PM and lignin contributions on the kinetic parameters obtained from Pyromat analysis of total pyrolysate, using KINETICS optimisation software, can be seen in Figure 11a for Eocene coals MC1 and MC2 from the Maramarua coalfield. Sample MC1 appears to be virtually pure lignin, whereas MC2 contains hydrogen-rich material, based on their positions in Figure 1b. Although MC2 contains abundant liptinite, PM appears the major component on the basis of predominant, characteristic  $n$ -alkane/alkene pairs upon pyrolysis-GC analysis. Therefore, the  $E_{act}$  spike at 53 kcal/mol ( $A = 8.8 \times 10^{13} \text{ s}^{-1}$ ) in MC2 probably reflects PM contribution. A similar spike is absent from M/1L, although there are some minor contributions from  $n$ -alkanes/alkenes, testifying to the difficulty of obtaining vitrinite completely free of PM. Representative coals from exploration wells in Taranaki Basin exhibit  $E_{act}$  distributions that fall between the extremes of the two Maramarua coals.

Transformation curves, representing the rate of conversion of initial petroleum potential (HI) vs temperature at a heating rate of 3°C/Ma, are shown in Figure 11b for the Maramarua coals, together with Eocene (MK1) and Late Cretaceous (Mu4) coals of Rank(S) 12.0-12.5 from exploration wells in Taranaki Basin. The transformation curves for MK1 and Mu4 are of similar shape to MC2, but shifted to slightly higher temperature, because of their higher maturity. The steepness of the main part of the curve reflects the  $E_{act}$  spike due to paraffinic oil generation, hence the shallower gradient for MC1. It is possible to define broad limits for oil expulsion on the plots of HI conversion. BI values are lower than converted HI values, even in the absence of expulsion, because of the restricted range of pyrolysis products measured by S1. If BI is ca 40% HC/C<sub>org</sub> at the onset of oil expulsion, converted HI<sub>max</sub> must be ≥40% HC/C<sub>org</sub> and probably nearer 100%. But converted HI cannot be >200% HC/C<sub>org</sub> if coals with HI<sub>max</sub> values >200% expel oil (because some gas potential remains after temperatures exceed 160°C and oil generation effectively ceases). So the onset of oil expulsion probably begins somewhere between conversion of 100 and 200% HC/C<sub>org</sub> of HI. The temperature limitations on generation of paraffinic oil correspond to Rank(S) values of 12 (onset of generation) and 14.5 (upper stability limit). So overall, expulsion is likely to occur only within the half-tone box in Figure 11b. The transformation curves for the Maramarua and Taranaki Basin coals (Figure 11b) are broadly consistent with this picture. However, it is not clear how accurately the kinetics model the generation of paraffinic oil. As a first approximation, it may be sufficient to model PM degradation alone, once the kinetic parameters have been obtained.

## Summary and Conclusions

It is possible to estimate the paraffinic oil potential of immature vitrinite-rich coals based on a simple compositional model of lignin and polymethylene. The

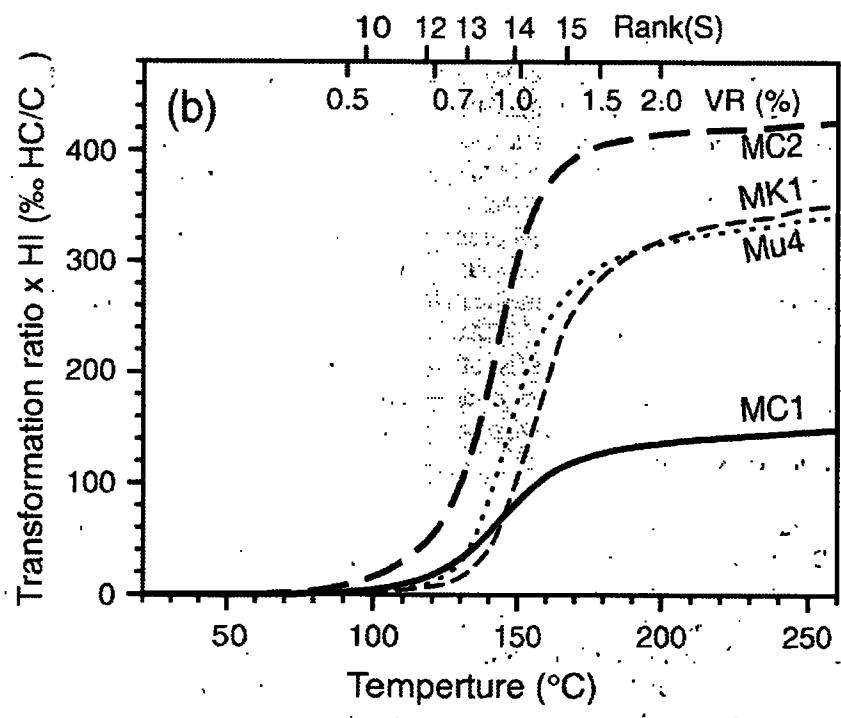
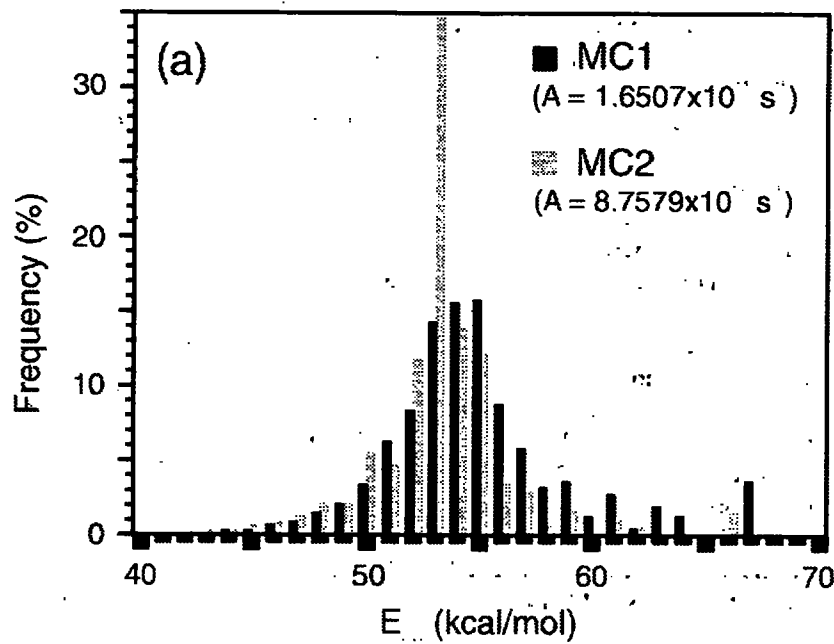


Figure 11. Rock-Eval derived kinetic data for some New Zealand coals. (a) Optimised  $E_{act}$  and  $A$  values for undifferentiated kerogen degradation for two Maramarua coals (MC1 and MC2). (b) Petroleum generation profiles derived from data in (a), based on a uniform heating rate of  $3^\circ\text{C}/\text{Ma}$ . [VR = vitrinite reflectance modelled by Easy% $R_o$  (Sweeney and Burnham, 1990), and corresponding Rank(S) scale derived from the empirical relationship  $\text{Rank}(S) = (17.87 - 3.25/\text{VR} - 0.5/\text{VR}^2)$ . Coal samples as in (a) together with an Eocene coal from McKee-1 well and a Late Cretaceous coal from Maui-4 well, both in Taranaki Basin. Oil expulsion is likely to occur only in the half-tone box.]

proportion of C present as PM in such a mixture can be determined from a Van Krevelen diagram if a discrete lignin evolution trend can be identified. It is proposed that the base of the New Zealand coal band defines this lignin trend.  $HI_{PM}$  is then obtained by multiplying  $C_{PM}/C_{org}$  by the HI of pure PM (1167‰ HC/C<sub>org</sub>). The New Zealand coal band spans a  $C_{PM}/C_{org}$  range of 0-10%, and Tara coals appear to comprise a fairly uniform suite with a  $C_{PM}/C_{org}$  of ca 8.5%.

Rock-Eval HI measurements are affected by an apparent suppression at low maturity, which is partly attributable to O-group suppression of the FID signal, and so mainly varies with O-content of lignin until the onset of oil generation.  $HI_{PM}$  should not be affected by O-group suppression and so should remain almost constant until PM cracking begins. HI reaches a maximum near the onset of oil generation, at Rank(S) 12-13. Various geochemical parameters suggest that, for Tara coals, paraffinic oil generation begins at Rank(S) 12, and expulsion starts at Rank(S) 13. Because oil cracking becomes dominant above Rank(S) 14.5, the potential expulsion window corresponds to Rank(S) 12.0-14.5.

For the Taranaki Basin coals studied, pure lignin appears to have an HI of ca 150‰ HC/C<sub>org</sub> at Rank(S) ca 12. A similar value was obtained from a Van Krevelen diagram for the Tara coals (160‰ HC/C<sub>org</sub>). The  $HI_{PM}$  value for any coal near Rank(S) 12 can then be determined from its  $HI_{max}$  value from the relationship  $HI_{PM} = 1167(HI_{max} - 150)/1017$  (or  $HI_{PM} = 1.15HI_{max} - 172$ ). Oil saturation thresholds at the onset of expulsion, as measured by BI, fall in the range 20-40‰ HC/C<sub>org</sub> for the New Zealand coals analysed. Toko coals ( $HI_{max}$  ca 200‰ HC/C<sub>org</sub>) appear close to the minimum potential required for expulsion of paraffinic oil. A model of oil generation and expulsion was constructed on the basis of  $HI_{PM}$  values, a saturation threshold of 40‰ HC/C<sub>org</sub> and an initial BI of 10‰ HC/C<sub>org</sub>. The variation of BI/ $HI_{PM}$  vs  $HI_{PM}$  was predicted for this model and it correlated well with data from Taranaki Basin coals, suggesting the basis of the model is reasonable.

The variation in HI with rank suggests that any kinetic analysis that relies on FID detection of coal pyrolysate has to be treated with caution. Optimised kinetic data derived from undifferentiated pyrolysate suggests that PM is represented by a narrow  $E_{act}$  distribution towards the lower end of the wide range characteristic of bulk coals. The range of bond-types in such coals suggests that a single A value is unlikely to permit accurate kinetic modelling. As a first approximation, generation of paraffinic oil may be represented by PM degradation alone.

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