

The use of fluid inclusion oils to reconstruct the charge history of petroleum reservoirs – an example from the Taranaki Basin

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Abstract

The hydrocarbon charge history of the McKee oil field (Taranaki Basin) has been investigated by comparing the geochemical signatures of two production oils (POs) from the Toetoe-2D and-1A wells with two fluid inclusion oils (FIOs, 2103 mRT and 2154 mRT) from the Toetoe-2 well. Petrographic analyses, recording the abundance of oil bearing fluid inclusions, suggest these FIOs are part of a palaeo-oil accumulation within the current gas cap. Published geochemical studies in the Taranaki Basin suggest coals of the Palaeogene Kapuni Group are the most likely source rocks for oil reservoired in the Eocene McKee Formation at the McKee Field.

The oils are waxy and paraffinic and show no evidence of biodegradation or water-washing. High Pr/Ph ratios >7, a slight to moderate odd-over-even predominance for high molecular weight *n*-alkanes and a predominance of C₂₉ over C₂₇ and C₂₈ steranes indicate terrestrial source rocks for all of the oils. Biomarker and aromatic maturity parameters suggest that the oils were generated in the peak oil window (VRE ~ 0.8–0.9%), with the POs being slightly more mature.

Although there is a close similarity between the FIOs and the POs, and although the composition of the FIOs is almost identical, subtle differences indicate either that the POs were generated from a slightly different source rock facies compared to the FIOs, or that early expelled oil had a different biomarker composition. Source-related differences can be seen in the higher content of angiosperm-derived biomarkers in the POs compared to the FIOs, including oleanane and various A-ring degraded isomers [de(A)-oleanane, de(A)-lupane and de(A)-ursane], and consequently a lower angiosperm/gymnosperm index (AGI) for the FIOs. Tricyclic terpanes occur in greater abundance in the FIOs compared to the POs. This suggests an early diagenetic influence of marine, saline water, followed by a reworking of organic matter by halophilic bacteria, and is consistent with early generation from a marine-influenced coal.

Overall the fill history of the McKee oil field is relatively simple, but the composition of hydrocarbon charge to the McKee oil field has changed over time. Two charge phases can be differentiated in the McKee oil field. An early petroleum charge still preserved in the FIOs was sourced from coaly source rocks infiltrated by marine water and reworked by halophilic bacteria. The close similarity of the two FIOs indicates that they were trapped from the same palaeo-oil column, located in the current gas zone tested by Toetoe-2. Over time the reservoired oil has been displaced by gas and diluted by a second oil charge from a somewhat different type III source rock facies that lacked the early diagenetic marine influence. However, the close range of AGI and the similarity of many geochemical features points to a local source within the Palaeogene Kapuni Group. The differences between the FIO and the PO could reflect early generation from source rock intervals containing the more labile kerogen, which can be found in marine influenced coals, with the main oil charge being sourced from sections lacking this marine influence and requiring higher maturity levels to achieve

expulsion into the carrier bed. The analyses of these FIOs has enabled a more comprehensive description of the hydrocarbon charge history, and whilst only relatively subtle changes to the interpreted filling history are inferred the similar results underpin the reliability of the MCI technique, allowing more confident application in areas where there are more major geochemical differences between inclusion and production oils.

Introduction

The composition of reservoired petroleum may be the result of a complex charge history, where oils from different source rocks have contributed petroleum charges over a wide maturity spectrum. Over geological time, petroleum charges of different composition tend to form a homogeneous mixture (England *et al.* 1987). In addition, early petroleum charges may have been lost due to seal leakage, tilting, or displacement by subsequent gas charges. All these processes make it difficult to analyse a charge history based on the composition of reservoired or residual oils alone. Therefore, it is desirable to compare the present-day geochemical composition of petroleum with the composition of palaeo-oil charges.

Oils trapped in fluid inclusions commonly occur in present-day and palaeo oil columns, and the analysis of these fluid inclusion oils (FIOs) offers a unique opportunity to gather information on the development of the petroleum composition over time. Numerous geochemical studies have shown source and maturity differences between production oils and FIOs (e.g. Karlsen *et al.* 1993; George *et al.* 1997a, 1997b; Isaksen *et al.* 1998). Most of these studies have indicated a lower maturity for the FIOs compared to the associated production oils. Therefore it is likely that oil inclusions are mainly trapping oil from a first charge of petroleum. The reason for this time-specific trapping of first-charge petroleum is probably due to the dependence of inclusion cementation during diagenesis, because diagenetic processes often slow down once a certain threshold of petroleum saturation is reached (e.g. Worden *et al.* 1998).

Concerns about the comparability of geochemical data obtained from the analysis of petroleum inclusions and crude oils have been raised by the fact that inclusion oils have sometimes been shown to be substantially different to presently reservoired oils (e.g. George *et al.* 1998a; 1998b). Thus, one might argue differences in the composition of inclusion and crude oils reflect differences in the nature of the sample rather than genuine differences between different oil charges. A number of processes are conceivably the reason for such differences, including the fractionation of oil during trapping of inclusions. Some fractionation has been shown to occur during inclusion formation, both by laboratory experiments (e.g. Stasiuk and Snowdon 1997) as well as studies on a suite of naturally occurring oil inclusions (Pang *et al.* 1998).

In this study we will show that comparison of FIOs and crude oils will yield similar results in case histories where there were only minor changes in the composition of early and late petroleum charge during the fill history of a petroleum reservoir. The fluid inclusion geochemical data have been obtained using the Molecular Composition of Inclusions (MCI) technique, following a standardised sample work-up procedure and where rigorously tested against system blanks to rule out the possibility of background contamination. Therefore, this gives confidence in data where more major differences in the composition of FIOs and crude oils have been detected, and where inclusion oils have been analysed using the same analytical procedure.

In this study, analyses have been conducted on samples of production oil and compared with palaeo-oils trapped as fluid inclusions within the sandstone reservoir. A combination of petrographic and geochemical techniques has been applied to produce a more comprehensive evaluation of the filling history of the McKee Field.

Geological setting and samples

The Taranaki Basin (Fig. 1) extends over and offshore of the Taranaki Peninsula of New Zealand's North Island and contains a predominantly terrigenous Late Cretaceous to Holocene succession, with an estimated maximum thickness

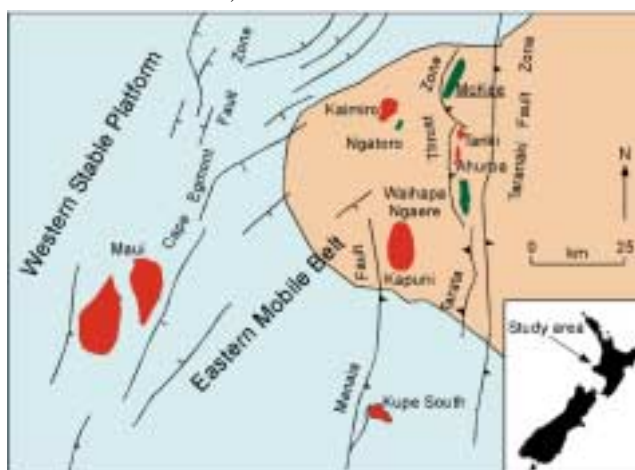


Figure 1: Location map of the Taranaki Basins with major tectonic elements and oil and gas fields.

of ca. 8 km. Most of New Zealand's oil discoveries occur in this basin, and are commonly accompanied by large volumes of gas and condensate. So far all petroleum discoveries have been associated with structural traps developed in the Neogene (Killops *et al.* 1994). In the "Eastern Mobile Belt", extensional structures of the Late Cretaceous-Early Tertiary

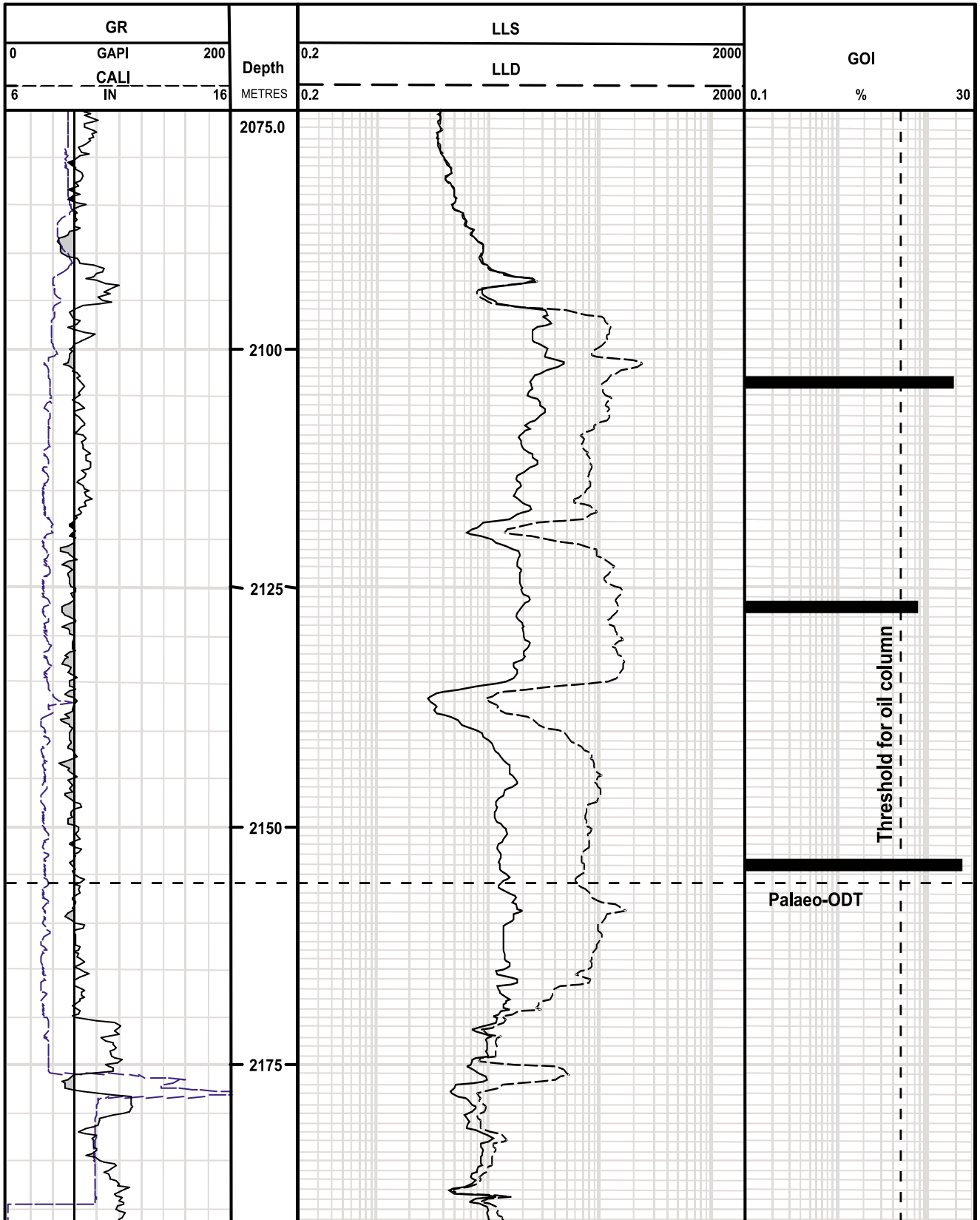


Figure 2: GOI results for Toetoe-2 relative to gamma, caliper and resistivity logs. The threshold for oil accumulation is empirically derived from a database of GOI values from known oil fields (Eadington *et al.* 1996).

period are overprinted by an inversion dated as Early Miocene (King and Thrasher 1992).

The McKee oilfield (PPL 38705) was discovered during drilling of the McKee-2A well in 1980 and is situated in an onshore compartment of the “Eastern Mobile Belt” (Fig. 1).

Petroleum in the McKee oil field is reservoired in the siliciclastic Eocene sediments of the McKee Formation. Previous geochemical studies suggest that the Eocene Mangahewa Formation is the source of petroleum reservoired in the stratigraphically overlying siliciclastic sediments of the McKee Formation (Cook 1988; Killops *et al.* 1994).

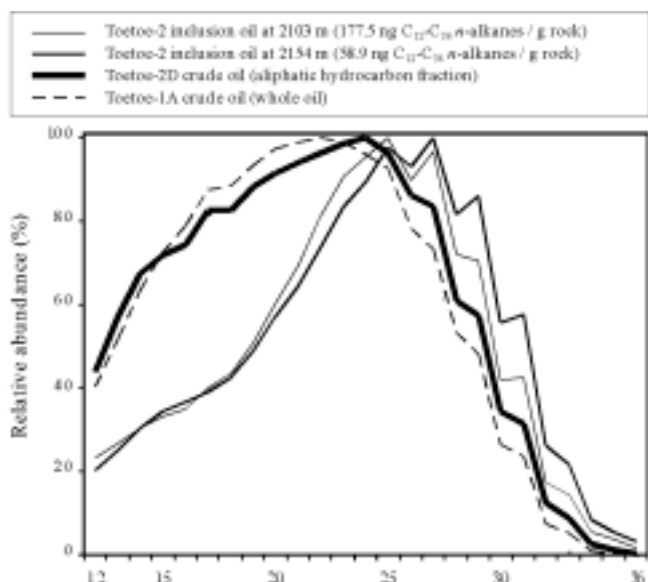


Figure 3: Normalised n -alkane profiles of FIOs and production oils from the Taranaki Basin.

However, the production history of the undercharged McKee oilfield shows a complex reservoir geometry, and indicates substantial compartmentalisation (Rickard 2000). Analyses conducted in this study have focused on the most crestal part of the accumulation, tested by the Toetoe section of the field. The Toetoe hydrocarbon accumulation was initially considered separate from the McKee Field, but the results of more recent drilling has confirmed the connection between the Toetoe area and the rest of the McKee Field (pers. com. David Waghorn, Fletcher Challenge Energy Ltd, 2000).

Methods

To elucidate the filling history of the McKee oilfield, two fluid inclusion techniques have been applied. The evaluation of fluid inclusion populations contained in these samples was initially achieved by petrographic evaluation of thick sections (70-80 μm) prepared from selected core and cuttings samples. The abundance of oil inclusions was determined for each sample using the Grains containing Oil Inclusions (GOI) technique of Eadington *et al.* (1996). These analyses allowed samples with abundant oil inclusions to be identified for subsequent geochemical analysis of the included oil.

Following petrographic analysis, two cuttings samples were selected and their FIOs were extracted for detailed geochemical analysis. These were then compared with the geochemical composition of production oils taken from the Toetoe-2D (sampled in August 2000), and Toetoe-1A wells, both located in the south-western part of the McKee oilfield.

The oil trapped within inclusions in quartz grains of the reservoir sandstone was extracted and analysed according to the MCI technique. A detailed description of this technique is provided in George *et al.* (1998c). Briefly, the core or cutting samples were mechanically (using mortar and pestle) and chemically (using hydrogen peroxide and hydrochloric

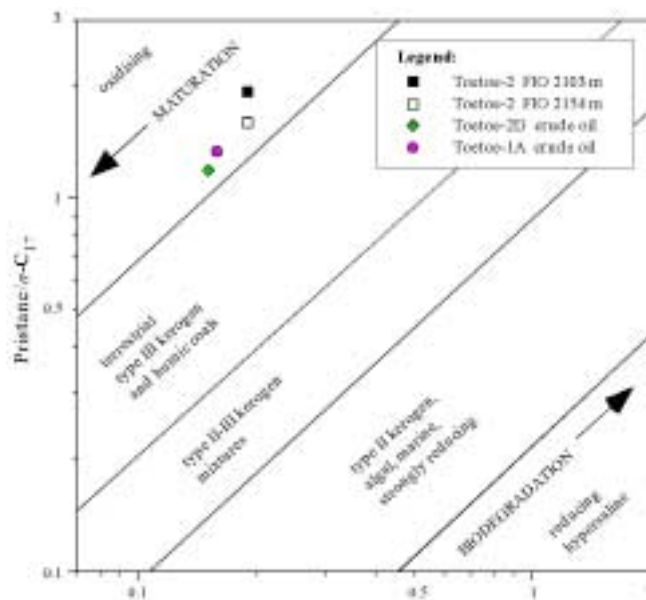


Figure 4: Distribution of pristane/ n -C₁₇ versus phytane/ n -C₁₈ for the FIOs and production oils from the Taranaki Basin. Interpretation fields adopted from Hunt (1996, p. 542).

acid) disintegrated, and quartz grains were separated from other lithologies using magnetic separation. Potential surface contaminations on the quartz grains were removed using successive treatments of solvents, hot hydrogen peroxide and chromic acid, and quartz grains were not crushed until a final outside solvent rinse was analysed and deemed to be clean. The quartz concentrates were crushed under solvent (dichloromethane) to release oil from the inclusions into the solvent (off-line analytical technique). For each FIO extract the level of background contamination was determined by preparing and analysing a system blank under exactly the same conditions.

The FIOs and production oils were analysed by gas chromatography-mass spectrometry (GC-MS) using an AutoSpecQ system (George *et al.* 1998c). The GC was fitted either with a DB5MS or a DB5 60 m fused silica column (i.d. 0.25 mm, film thickness 0.25 μm). Quantification was carried out using single ion monitoring (SIM) and metastable reaction monitoring (MRM). Peak identifications of diterpanes and A-ring degraded angiosperm markers were verified using mass spectra from magnet-scan runs (50-550 amu).

Petrographic results

Three sandstone samples from the currently gas-bearing reservoir tested by the Toetoe-2 well were selected for GOI analyses. All three samples have high GOI values, ranging from 7.2% to 21.8% (Fig. 2). These values are above an empirical threshold for oil accumulation (Eadington, *et al.* 1996) and are interpreted to reflect the presence of a palaeo-oil column within these currently gas filled sandstones. Early oil accumulation, subsequently displaced by a later gas charge, represents the likely charge history. The lack of the samples with GOI values consistent with high water saturation (GOI <1%) precludes determination of a palaeo-

oil water contact, so the results only define a palaeo-oil down to at 2154 mRT (Fig. 2).

Geochemical results

The two samples selected from the Toetoe-2 well for MCI analysis have elevated GOI values (16.7% at 2103mRT and 21.8% at 2154mRT). The results presented below summarise results that have been outlined in more detail in a comparison of two fill histories from the Gippsland Basin (Blackback oil field) and the Taranaki Basin (McKee oil field) (Volk *et al.* 2001).

n-Alkanes and isoprenoids

Yields of *n*-alkanes in the FIOs were determined using an internal squalane standard. Yields for the Toetoe-2 FIOs are more than 60 times higher than that in the system blanks when

comparing the signals of *n*-C₁₂₋₃₆ alkanes (177.5 and 58.9 ng *n*-C₁₂₋₃₆ / g quartz for samples 2103 mRT and 2154 mRT, respectively). Together with the very low level of background noise in all other examined mass chromatograms this gives confidence in the quality of the data discussed in this paper.

Both FIOs are dominated by waxy *n*-alkanes, with maxima at *n*-C₂₅ and *n*-C₂₇ and a slight (production oils) to moderate (FIOs) odd-over-even predominance (Fig. 3). Carbon preference indices (CPI₂₆₋₃₂) range between 1.18 (Toetoe-1A production oil) and 1.25 (Toetoe-2 FIO 2103 mRT; Table 1). The production oils from the Toetoe wells have similar distributions of *n*-alkanes compared to the FIOs in the same well, except that the FIOs have greater odd-over-even predominance. Pristane/phytane values are > 7 for all samples (Table 1), consistent with a terrestrial, oxic source facies for all of the oils (Fig. 4). The Pr/*n*-C₁₇ and Ph/*n*-C₁₈ ratios are

Table 1: Geochemical parameters based on saturated hydrocarbons.

	Toetoe-2 FIO (2103 mRT)	Toetoe-2 FIO (2154 mRT)	Toetoe-2D crude oil	Toetoe-1A crude oil
Pr/Ph ‡	9.3	7.5	7.9	8.4
Pr/ <i>n</i> -C ₁₇ ‡	1.92	1.58	1.19	1.32
Ph/ <i>n</i> -C ₁₈ ‡	0.19	0.19	0.15	0.16
CPI ₂₆₋₃₂ ‡	1.25	1.24	1.19	1.18
8β(H)-drimane/ <i>n</i> -C ₁₅ Δ	0.010	0.007	0.007	0.005
8β(H)-homodrimane/ <i>n</i> -C ₁₆ Δ	0.017	0.014	0.009	0.022
8β(H)-phyllocladane/ <i>n</i> -C ₂₀ Δ	0.004	0.0013	<0.001	<0.001
Σ(dO+dL+dU+O)/C ₃₀ αβ ¶	0.76	0.64	0.74	1.02
dU : dL : dU (%) ¶	21:34:45	26:33:41	19:36:45	17:37:46
Σ(diterpanes)/C ₃₀ αβ §	0.17	0.12	0.23	0.31
AGI (Killops <i>et al.</i> 1995) §	4.3	5.6	3.2	3.3
IP/C ₃₀ αβ ¶	0.03	0.02	0.03	0.03
C ₂₄ tetracyclic terpane/C ₃₀ αβ hopane ¶	0.07	0.05	0.09	0.01
C ₂₄ tetracyclic terpane/C ₂₃ tricyclic terpane ¶	1.25	1.07	11.6	3.4
Ts/Tm	0.61	0.83	0.31	0.33
C ₃₀ */C ₃₀ αβ hopane	0.13	0.14	0.13	0.11
28,30-BNH/C ₃₀ αβ hopane	n.d.	n.d.	0.04	0.05
C ₂₉ 25-norhopane/C ₂₉ αβ	0.03	0.03	0.06	0.05
Oleanane (+ ? lupane)/C ₃₀ αβ hopane	0.59	0.72	0.84	0.91
C ₂₉ ab hopane/C ₃₀ αβ hopane ¶	0.56	0.58	0.55	0.58
Total homohopanes/C ₃₀ ab hopane ¶	2.0	2.5	2.1	2.1
C ₃₀ hopanes αβ/(αβ+βα)	0.91	0.89	0.91	0.91
C ₃₂ hopanes αβ 22S/(22S+22R)	0.61	0.60	0.59	0.60
C ₂₇ : C ₂₈ : C ₂₉ ααα 20R (%) steranes †	41:14:45	46:16:38	9:24:67	7:13:80
C ₂₉ aaa R sterane/C ₂₇ ααα R sterane	1.07	0.81	7.5	10.7
C ₃₀ /(C ₂₇ +C ₂₈ +C ₂₉) ααα 20R steranes (%)	n.d.	n.d.	0.51	0.43
C ₂₇ ba diasteranes/(ααα+αββ steranes)	0.48	0.36	1.48	1.49
C ₂₉ βα diasteranes/(ααα+αββ steranes)	0.95	0.75	1.12	1.14
C ₂₉ ααα 20S/(20S+20R) steranes	0.50	0.47	0.47	0.43
C ₂₉ αββ/(αββ+ααα) steranes	0.52	0.52	0.50	0.50

Ratios are calculated from MRM data, (*m/z* M⁺ → 191, 217 for terpanes and steranes), except for ‡ (*m/z* 85), Δ (*m/z* 85 and 123), ¶ (*m/z* 191), § (*m/z* 123 and 191), and † (*m/z* 217). For peak identification, see the captions to Figs 4, 5 and Table 2.

higher for the FIOs, which suggests the FIOs are less mature than the production oils.

Aliphatic biomarkers

The distributions of pentacyclic hopanes in oils from the McKee oilfield are very similar, and for the two FIOs are almost identical (Fig. 5). The ratio of total homohopanes/ C_{30} 17 α (H)-hopane ranges from 2.1 to 2.5 for all of the oils, and no enhanced abundance of C_{35} hopane is discernible in any of the oils (Fig. 5). The abundance of 2 α -methylhopanes is also low. Maturity-related hopane ratios (e.g. the hopane/moretane ratios and the 22*S*/(22*S*+22*R*) homohopane ratios) have reached equilibrium values (Table 1). The Ts/Tm ratio is significantly higher for the FIOs (0.61 and 0.83) than for the production oils (0.31 and 0.33).

Oleanane and oleanoids are present in all of the investigated FIOs and production oils (Fig. 5). Under the chromatographic conditions applied in this study (DB5MS and DB5 columns) lupane co-elutes with oleanane. However, the A-ring degraded counterparts are readily resolved (Fig. 6). Pentacyclic triterpanes such as oleanane, lupane, ursane and other oleanoids are derived from a woody angiosperm precursor flora and are characteristic of Tertiary terrestrial oils in New Zealand (Woolhouse *et al.* 1992). Oleanane (+ lupane?) is abundant in both the production oils and the FIOs (Fig. 5), but to a greater extent in the production oils (oleanane/ C_{30} 17 α (H)-hopane = 0.84 and 0.91) than in the FIOs (0.59 and 0.72; Table 1). Consistent with this observation, the relative abundances of the A-ring degraded angiosperm markers 10 β (H)-de-A-oleanane, 10 β (H)-de-lupane and 10 β (H)-de-ursane are higher in the production oils than in the inclusion oils (Fig. 6). The most significant difference between the FIOs and the production oils can be found in the distribution of tricyclic terpanes (cheilanthanes). The C_{23} - C_{25} tricyclic terpanes are present in moderate relative abundance in the FIOs, but only in very low abundance in the Toetoe-2D and Toetoe-1A production oils (Table 1 and Fig. 6).

The distributions of steranes is shown in Figure 7 for two representative oils from the McKee oilfield. The proportion of C_{29} steranes is higher for the Toetoe-1A and Toetoe-2D production oils (C_{29}/C_{27} $\alpha\alpha\alpha$ 20*R* steranes = 10.7 and 7.5) than the FIOs (1.07 and 0.81; Table 1). The C_{29} $\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ sterane ratio appears not to have quite reached its equilibrium value, ranging from 0.50 to 0.52 for all of the oils from the McKee oilfield (Table 1). However, the C_{29} 20*S*/(20*S*+20*R*) sterane ratio is lower for the Toetoe-1A production oil (0.43) than for the other oils from the McKee oilfield (0.47–0.50; Table 1).

In the oils from Toetoe 2 and 2D the bicadinanes W, T and R (e.g. Sosrowidjojo, 1996) were monitored in the MRM transitions m/z 412 \rightarrow 369 and m/z 370 \rightarrow 191 (not shown). The relative abundance of these compounds is low, and they are slightly more abundant in the production oil than the FIOs. T is the most abundant bicadinane, and makes up more than 50% of bicadinanes in all of the oils.

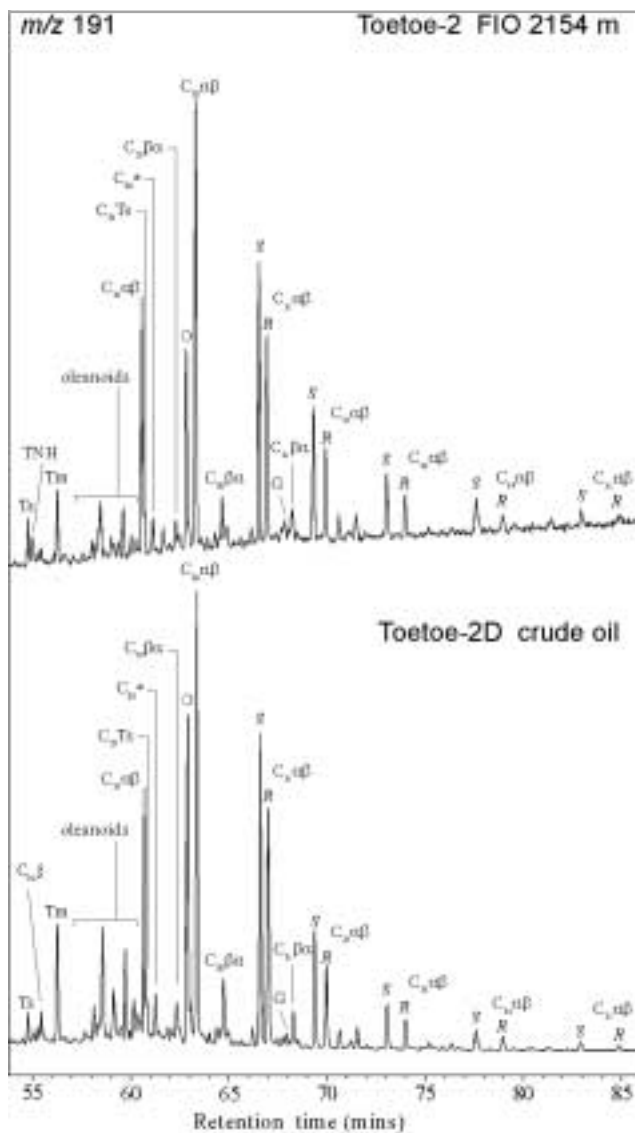


Figure 5: Partial m/z 191 mass chromatograms showing the hopane distribution in Toetoe-2 FIO (2154 mRT) and Toetoe-2D production oil. Peak assignments define stereochemistry at C-22 (*S* and *R*); $\alpha\beta$ and $\beta\alpha$ denote 17 α (H)-hopanes and 17 β (H)-moretanes respectively. Ts = C_{27} 18 α (H),22,29,30-trisnorhopane, TNH = C_{27} 25,28,30-trisnorhopane, C_{30} § = re-arranged C_{30} hopane, Tm = C_{27} 17 α (H),22,29,30-trisnorhopane, BNH = 28,30-bisnorhopane, C_{29} Ts = 18 α (H)-30-norneohopane, G = gammacerane, C_{30}^* = 17 α (H)-diahopane, O = oleanane.

Bicyclic sesquiterpanes and tri- and tetracyclic diterpanes are characteristic biomarkers in some oils from the Taranaki Basin (e.g. Weston *et al.* 1989). Most of the diterpanes are believed to originate from a woody gymnosperm flora (Killops *et al.* 1995). Production oils in the McKee oilfield have a similar distribution of diterpanes to the FIOs from the same field, except that they contain significantly more 19-nor-isopimarane (Volk *et al.* 2001).

From the Late Cretaceous to the Middle Tertiary, a shift from a gymnosperm-dominated flora to an angiosperm-dominated flora occurs in the Taranaki Basin. This age-related shift in the precursor flora of terrestrial organic matter can be quantified using an angiosperm-gymnosperm-index (AGI, Killops *et al.* 1995).

Table 2: Peak assignments for steranes, diasteranes and methylsteranes in the MRM M⁺ → m/z 217 chromatogram

Peak	Sterane, diasterane and methylsterane assignments	Abbreviation
a	13β(H),17α(H)-diacholestane (20S)	C ₂₇ βα 20S diasterane
b	13β(H),17α(H)-diacholestane (20R)	C ₂₇ βα 20R diasterane
c	13α(H),17β(H)-diacholestane (20S)	C ₂₇ αβ 20S diasterane
d	13α(H),17β(H)-diacholestane (20R)	C ₂₇ αβ 20R diasterane
e	5α(H),14α(H),17α(H)-cholestane (20S)	C ₂₇ ααα 20S sterane
f	5α(H),14β(H),17β(H)-cholestane (20R)	C ₂₇ αββ 20R sterane
g	5α(H),14β(H),17β(H)-cholestane (20S)	C ₂₇ αββ 20S sterane
h	5α(H),14α(H),17α(H)-cholestane (20R)	C ₂₇ ααα 20R sterane
i	24-methyl-13β(H),17α(H)-diacholestane (20S)*	C ₂₈ βα 20S diasterane
j	24-methyl-13β(H),17α(H)-diacholestane (20R)*	C ₂₈ βα 20R diasterane
k	24-methyl-13α(H),17β(H)-diacholestane (20S)	C ₂₈ αβ 20S diasterane
l	24-methyl-13α(H),17β(H)-diacholestane (20R)*	C ₂₈ αβ 20R diasterane
m	24-methyl-5α(H),14α(H),17α(H)-cholestane (20S)*	C ₂₈ ααα 20S sterane
n	24-methyl-5α(H),14β(H),17β(H)-cholestane (20R)	C ₂₈ αββ 20R sterane
o	24-methyl-5α(H),14β(H),17β(H)-cholestane (20S)	C ₂₈ αββ 20S sterane
p	24-methyl-5α(H),14α(H),17α(H)-cholestane (20R)	C ₂₈ ααα 20R sterane
q	24-ethyl-13β(H),17α(H)-diacholestane (20S)	C ₂₉ βα 20S diasterane
r	24-ethyl-13β(H),17α(H)-diacholestane (20R)	C ₂₉ βα 20R diasterane
s	24-ethyl-13α(H),17β(H)-diacholestane (20S)	C ₂₉ αβ 20S diasterane
t	24-ethyl-13α(H),17β(H)-diacholestane (20R)	C ₂₉ αβ 20R diasterane
u	24-ethyl-5α(H),14α(H),17α(H)-cholestane (20S)	C ₂₉ ααα 20S sterane
v	24-ethyl-5α(H),14β(H),17β(H)-cholestane (20R)	C ₂₉ αββ 20R sterane
w	24-ethyl-5α(H),14β(H),17β(H)-cholestane (20S)	C ₂₉ αββ 20S sterane
x	24-ethyl-5α(H),14α(H),17α(H)-cholestane (20R)	C ₂₉ ααα 20R sterane

* = isomeric peaks (24S and 24R).

$$AGI = \frac{m/z\ 191\ (dO + dL + dU + c)}{m/z\ 191\ (IP)}$$

A key to the compound abbreviations is given in Figures 5 and 6, and SD is the sum of diterpanes as defined in the caption of Figure 8. AGI values have been calibrated using source rocks of known age (chemostratigraphy) and can be used to estimate the source age of oils. In Figure 8 AGI values are plotted together with data from a sequence of source rock extracts ranging from the Late Eocene to the early Late Cretaceous and sampled from various wells in the Taranaki Basin (Killops *et al.* 1995). The AGI for oils from the McKee oilfield are similar, with values of 4.3 and 5.6 for the FIOs, and 3.2 and 3.3 for the production oils (cf. Table 1). A comparison with data from Killops *et al.* (1995) suggests a Late to Mid Eocene depositional age for the source rocks of the oils. This supports the hypothesis that oils in the McKee Formation have been charged from the subjacent Mangahewa Formation.

In summary, although there are many similarities between the biomarkers of the oils from the McKee oilfield, and the

composition of the FIOs is almost identical to each other, slight differences between the FIOs and the production oils indicate that there is some source variation.

Aromatic hydrocarbons

The overall distributions of monitored aromatic hydrocarbons (alkylbenzenes, alkyl-naphthalenes, alkylphenanthrenes, alkylbiphenyls, alkyl-dibenzothiophenes and alkylpyrenes) in oils from the McKee oilfield are similar, and those for the two FIOs are almost identical to each other. A wide range of molecular parameters based on the distribution of naphthalenes, phenanthrenes, biphenyls and dibenzothiophenes have been evaluated, providing information on maturity and source (Table 3).

Alkylbenzenes are the most abundant compound class of the total aromatic hydrocarbon fraction and make up 54% to 62% of the aromatics. The abundance of alkylbenzenes decreases with increasing alkyl-substitution. The abundance of alkyl-naphthalenes is also very high (33% to 40%). The abundance of sulphur-aromatic compounds such as dibenzothiophenes is low, and the phenanthrene/dibenzothiophene ratio is high for all of the oils from the McKee oilfield (6.8 to 10.4; Table 3). Low sulphur contents

Table 3: Geochemical parameters based on aromatic hydrocarbons.

	Toetoe-2 FIO (2103 mRT)	Toetoe-2 FIO (2154 mRT)	Toetoe-2D crude oil	Toetoe-1A crude oil
^a MNR	2.2	2.2	2.1	2.2
^b DNR-1	7.6	7.4	8.4	9.4
^c TNR-1	1.02	1.06	1.18	1.11
^d TMNr	0.41	0.42	0.50	0.44
^e TeMNR	0.55	0.56	0.57	0.56
^f PMNr	0.40	0.41	0.39	0.43
log (1,2,5-TMN/1,3,6-TMN)	0.02	0.01	-0.11	-0.02
log (1,2,7-TMN/1,3,7-TMN)	-0.25	-0.28	-0.36	-0.37
^g MPI-1	0.65	0.70	0.79	0.86
^h %R _c from MPI-1	0.79	0.82	0.87	0.92
ⁱ MPDF	0.52	0.52	0.53	0.52
^j DPR-x	0.37	0.37	0.29	0.35
^k MBpR	31	28	159	1294
3-MBp/4-MBp	2.5	2.5	3.1	3.6
^l DMBpR-x	13	6	n.d.	17
^m DMBpR-y	21	16	n.d.	38
ⁿ MDR	5.2	4.3	2.5	5.8
^o DMDR	0.42	0.43	0.60	0.54
P/DBT	6.9	8.0	10.4	6.8

- ^a MNR=methylnaphthalene ratio (2-MN/1-MN).
^b DNR-1=dimethylnaphthalene ratio 1 ([2,6+2,7-DMN]/1,5-DMN).
^c TNR-1=trimethylnaphthalene ratio 1 (2,3,6-TMN/[1,4,6+1,3,5-TMN]).
^d TMNr=trimethylnaphthalene ratio (1,3,7-TMN/[1,3,7-TMN+1,2,5-TMN]).
^e TeMNR=tetramethylnaphthalene ratio (1,3,6,7-TeMN/[1,3,6,7+1,2,5,6-TeMN]).
^f PMNr=pentamethylnaphthalene ratio (1,2,4,6,7-PMN/[1,2,4,6,7+1,2,3,5,6-PMN]).
^g MPI=methylphenanthrene index {1.5 x [3-MP+2-MP]}/[P+9-MP+1-MP]).
^h R_c=calculated reflectance (0.6 x MPI-1+0.4).
ⁱ MPDF=methylphenanthrene distribution fraction ([3-MP+2-MP]/SMPs).
^j DPR-x (1,7-DMP/1,7+1,3+3,9+2,10+3,10-DMP).
^k MBpR=methylbiphenyl ratio (3-MBp/2-MBp).
^l DMBpR-x=dimethylbiphenyl ratio x (3,5-DMBp/2,5-DMBp).
^m DMBpR-y=dimethylbiphenyl ratio y (3,3'-DMBp/2,3'-DMBp).
ⁿ MDR=methyldibenzothiophene ratio (4-MDBT/1-MDBT).
^o DMDR =methyldibenzothiophene ratio (4,6-DMDBT/[3,6+2,6-DMDBT]).
P/DBT=phenanthrene/dibenzothiophene.

are typical for oils sourced from terrestrial source rocks (Hughes *et al.* 1995).

The distribution of aromatic hydrocarbons in the McKee oilfield suggests a maturity in the mid oil window for all of the oils, with the production oils probably being slightly more mature than the FIOs. For example, MPI ranges between 0.65 (2103 mRT FIO) and 0.86 (Toetoe-1A production oil) for samples from the McKee oilfield, with the values being higher in the production oils than in the FIOs. This corresponds to a calculated reflectance of ~0.8% R_c for the FIOs and ~0.9% R_c for the production oils (Radke and Welte 1983). The distribution of methyl-, dimethyl- and ethylbiphenyls in mature oils and sediments favours the more

stable *meta*-substituted isomer compared to compared to *ortho*-substituted (Alexander *et al.* 1986, Cumbers *et al.* 1987). The distribution of alkylbiphenyls consistently suggests a higher maturity for the McKee oilfield production oils compared to the FIOs.

The methyldibenzothiophene ratio (MDR) gives values between 4 and 6 for the oils from the Taranaki Basin, except for the production oil from Toetoe-2D (2.5; Table 3). These MDR values correspond to ~0.8-0.9% vitrinite reflectance equivalent (VRE) according to a correlation published by Radke (1988), and to a somewhat lower maturity for production oil from the Toetoe-2D well (~0.7%). However, the maturity-related dimethyldibenzothiophene ratio (George *et al.* 2001) suggests that the maturity of the production oils is higher than the maturity of the FIOs (Table 3).

The relative abundance of 1,2,7-trimethylnaphthalene (TMN) is high in oils from the McKee oilfield (Fig. 9). This is consistent with the presence of oleanoids in these oils, as 1,2,7-TMN has been reported to originate from the structural degradation of these angiosperm-derived biomarkers (Strachan *et al.* 1988). Although oleanoids are more abundant in the production oils relative to the FIOs, the 1,2,7-TMN/1,3,7-TMN ratio is higher in the Toetoe FIOs compared to the Toetoe production oils (Fig. 9). However, as the 1,2,7-TMN/1,3,7-TMN ratio decreases with increasing maturity, and the production oils are more mature than the FIOs, this phenomenon can be attributed to maturity.

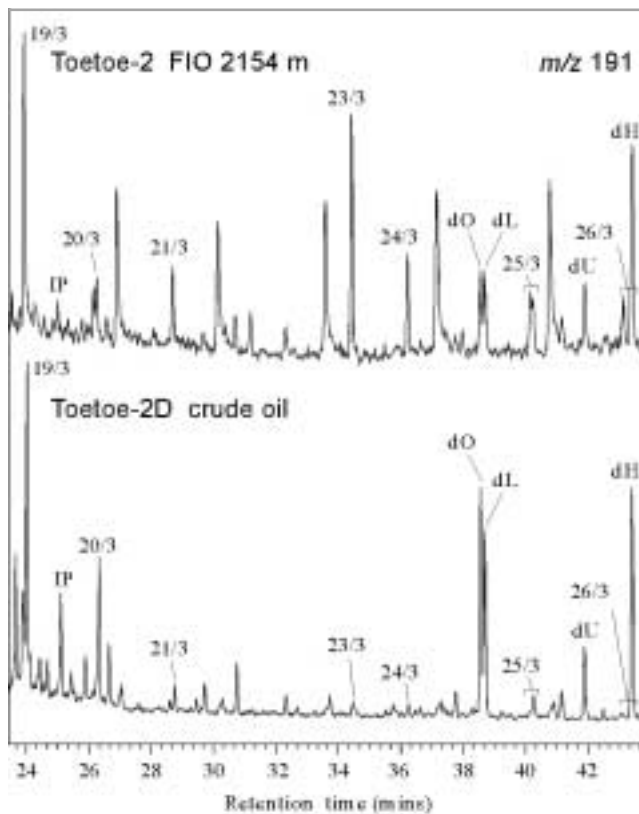


Figure 6: Partial m/z 191 mass chromatograms of the Toetoe-2D production oil and Toetoe-2 (2154 mRT) FIO, showing the distribution of tri- and tetra-cyclic terpanes, ring-A-degraded angiosperm markers and the gymnosperm marker isopimarane. 19/3 = C_{19} tricyclic terpane, etc., IP = isopimarane, dO = 10 β (H)-de-A-oleanane, dL = 10 β (H)-de-A-lupane, dU = 10 β (H)-de-A-ursane, dH = 18(H)-de-E-hopane (C_{24} tetracyclic terpane).

Discussion

Source and maturity characterisation

The geochemical composition of the production oils and two FIOs from the McKee oilfield is relatively similar, and the composition of the two FIOs is almost identical. A terrestrial source rock is indicated by many geochemical characteristics, such as the waxy and paraffinic character of the oils, high Pr/Ph values, high CPI values, and high relative abundances of C_{29} steranes and oleanoids. No evidence of biodegradation or water washing such as a depletion of n -alkanes together with a hump of UCM, or the presence of 25-norhopanes, has been found for either the FIOs or the production oils from the McKee oilfield. AGI values fall in a narrow range and are somewhat higher for the FIOs than for the production oils (Table 1). However, the differences between these AGI values are too small to allow a confident conclusion as to whether the production oils have been generated from a higher or a lower stratigraphic level than the FIOs.

Although the FIOs and the production oils from the McKee oilfield are very similar, and the FIOs are almost identical in their geochemical composition, there are some indications of source variability. These include the higher abundance of

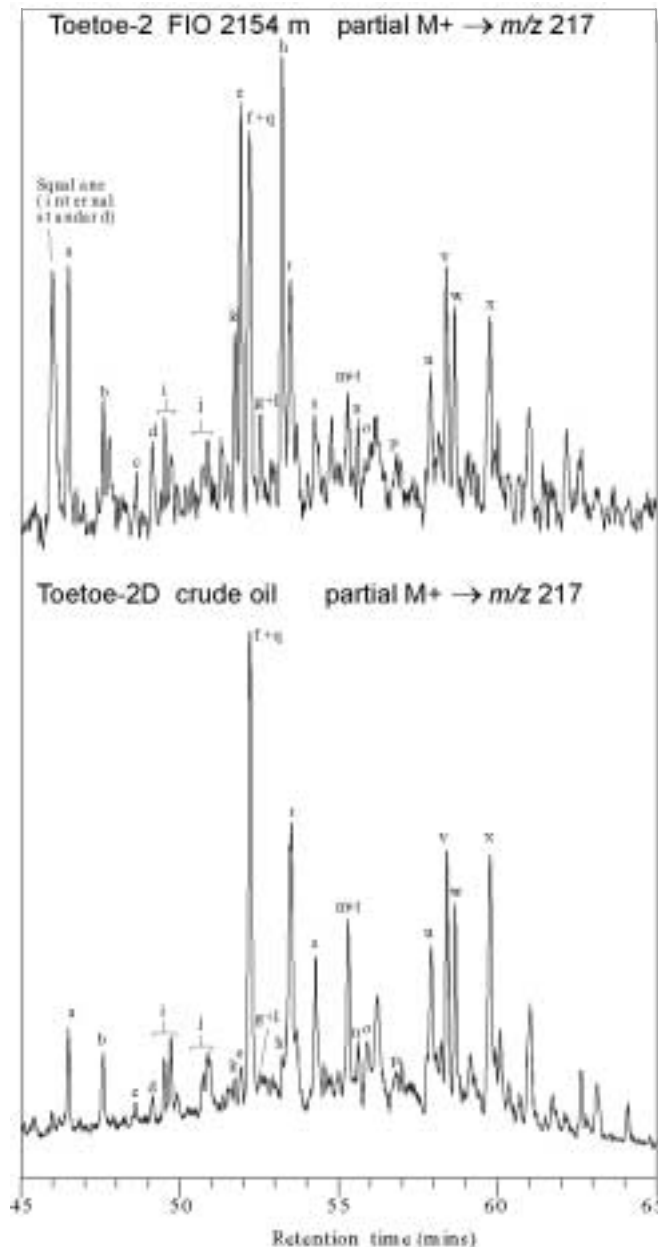


Figure 7: Partial $M^+ \rightarrow m/z$ 217 MRM chromatograms of Toetoe-2 FIO (2154 mRT) and Toetoe-2D production oil. Peak assignments are defined in Table 2.

Tm, oleanane and the A-ring degraded oleanoids relative to other hopanes in the production oils, and the higher abundance of tricyclic terpanes in the FIOs. There are minor differences in the diterpane distributions between the production oils and FIOs, and the amount of C_{29} relative to C_{27} steranes and diasteranes is greater in the production oils. These differences support the idea that the production oils and the FIOs have been generated from a somewhat different source rock facies. The higher contents of Tm, C_{29} sterane and diasteranes, oleanane and A-ring degraded oleanoids in the production oils are consistent with a more coaly, terrestrially-dominated source facies. Higher levels of tricyclic terpanes in terrestrially-sourced oils have been reported to be typical of a contribution from halophilic bacteria (e.g. Kruger *et al.* 1990; De Grande *et al.* 1993). Therefore, the FIOs containing abundant tricyclic terpanes

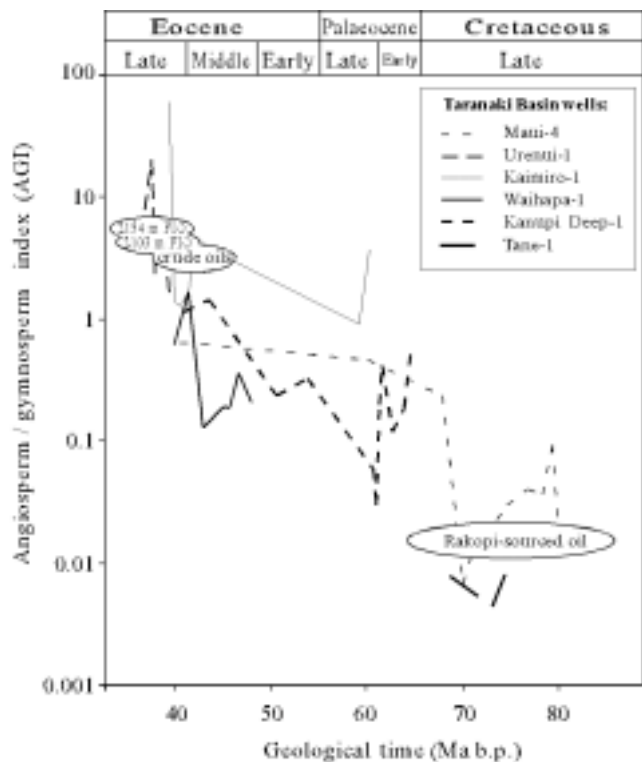


Figure 8: Angiosperm-gymnosperm index (AGI) of FIOs and production oils, compared to an age-related trend of this parameter established on rock extracts from six wells in the Taranaki Basin (Killops *et al.* 1995). Diterpanes used to calculate AGI are 8b(H)-labdane, 4 β (H)-19-norisopimarane, 4 β (H)-18-norisopimarane, rimuane, C₁₉-17-nortetracyclane, *ent*-beyerane, IP=isopimarane, 16 β (H)-phylocladane, abietane and *ent*-16 β (H)-kaurane.

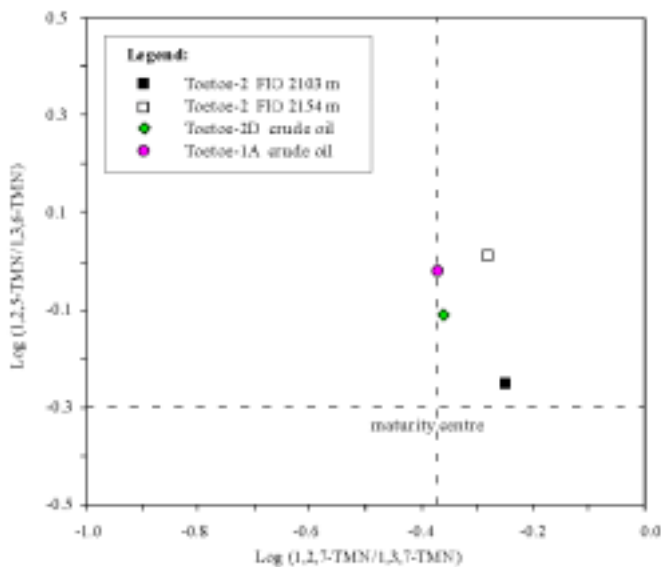


Figure 9: Distribution of log (1,2,5-TMN/1,3,6-TMN) versus log (1,2,7-TMN/1,3,7-TMN). Dashed lines refer to threshold values as defined by Strachan *et al.* (1988) on mature samples from Cape Range-2 (Carnarvon Basin).

at a moderate maturity level may have been generated from the top of a coaly unit, where a marine incursion had halted peat deposition and saline water had infiltrated the underlying terrestrial organic matter. The slightly lower maturity for the McKee oilfield FIOs (~0.8% VRE) compared to the production oils (~0.9% VRE) is consistent with earlier generation from a more thermally labile marine-influenced coal (predominantly trapped in fluid inclusions), followed by main stage generation from a less marine-influenced facies. Source and maturity variations of early charged FIOs and later charged production oils are consistent with recent data on source rock quality variations within type III source rocks of the Mangahewa formation (Sykes 2001). Sykes (2001) showed that coals deposited in an environment with early marine incursions are thermally more labile and more oil-prone than coals that lack such an influence.

Interpreted charge history

The fluid inclusion results indicate a multi-phase charge history where the composition of hydrocarbons changed with time and increasing source rock maturity. An early liquids charge resulted in the accumulation of a palaeo-oil column at the crest of the McKee structure, which was subsequently displaced by gas. Geochemical analyses show that both the reservoired oil (this study and Killops *et al.* 1994) and the FIOs were probably sourced from Eocene coals within the subjacent Mangahewa Formation. There are some significant differences in the distribution of different biomarker classes between the FIOs and the production oils, suggesting variations in source-rock facies; but these are in keeping with the variability expected in a coastal plain depositional setting. In particular, the greater abundance of tricyclic terpanes in the FIOs suggests an early diagenetic influence of marine (*i.e.* saline) water followed by a reworking of organic matter by halophilic bacteria. This is consistent with early generation and expulsion from a marine-influenced coal (predominantly trapped in fluid inclusions), followed by main-stage generation from less marine-influenced coaly sediments. Once again, lower maturity levels would be needed to generate oil from the more labile, reworked terrestrial organic matter compared to the terrestrial coals. The lack of correlation between Taranaki Basin oils and individual coal seams has been related to generation and expulsion from, and averaging of the products from, several different seams (e.g. Johnston *et al.* 1991; Collier and Johnston 1991; Killops *et al.* 1994). In this respect, the McKee oilfield FIOs may be recording a more specific pulse of early migrating oil, rather than the cumulative reservoired production oil, which presumably represents the products of generation and expulsion from several seams over a wider range of maturities.

Conclusions

The McKee oilfield in the Taranaki Basin has experienced a relatively simple, but multi-phased charge history involving both liquid and gas rich charges. The two oil charges, represented by the FIOs and the production oils, have both been generated from the Mangahewa Formation, directly underlying the reservoir in the McKee Formation. However, variations in the distribution of steranes and diasteranes, and in the relative abundance of cheilanthanes, oleanoids

and Tm, indicate that fluid inclusions preferentially trapped earlier-generated oil from terrestrial organic matter that has undergone reworking by halophilic bacteria, probably a marine-influenced coal. The production oils are similar to this first oil charge, but have been effectively expelled from more terrestrial/freshwater-dominated units of the Mangahewa Formation at a later burial stage.

A combination of oil-bearing fluid inclusion and production oil analyses has been shown to be an efficient tool for unravelling the filling history of petroleum reservoirs. In the case history at hand, this approach has shown a simple charge history where only minor changes in the petroleum composition occur with time. This gives confidence in the reliability of results where MCI date indicate more major changes in the petroleum composition of different charge phases, as simple fill histories will result in a similar composition of production and inclusion oils.

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