

GEOCHEMISTRY OF OILS AND SOURCE ROCKS OF THE EAST COAST BASIN AND IMPLICATIONS FOR THE TARANAKI BASIN, NEW ZEALAND

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Abstract

Numerous oil seeps in the East Coast Basin, New Zealand have been known since before the time of European settlement and have stimulated much interest in the petroleum prospectivity of the region. However, the identity of the source rocks in this structurally complex area remains unclear. The Paleocene Waipawa Black Shale is a prime candidate because it is of sufficient quality and extent to have generated substantial amounts of petroleum. Furthermore, its mixed marine/terrestrial character is broadly compatible with the chemistry of the seep oils. However, the formation is generally immature in outcrop and, for this reason, studies to date have discounted the Waipawa as a possible source of the East Coast oils and implicated unidentified Cretaceous or Miocene strata.

Here we report the results of a new study comparing seep oils and stains from the north and south of the basin with artificially matured Waipawa shale. Unlike previous studies, we have used Metastable Reaction Monitoring (MRM) GCMS and Compound Specific Isotope Analysis (CSIA) to enable more confident identification of diagnostic molecules such as the 24-n-propyl cholestanes (definitive marine markers) and reveal the influence of particular source components on the n-alkane profile. The results show that a mature analog of the Waipawa Black Shale is a likely source for oil stains in the southern part of the Basin and also that a time equivalent of this unit — or at least a marine shale deposited under similar, specialised conditions — could also have contributed to oil generation in the Taranaki Basin. The well known Waitangi seep oil and others in the north of the East Coast Basin probably represent generation from a more distal and/or older source unit.

Introduction

New Zealand's East Coast Basin extends over 40 000 km² of the North Island (figure 1). It is characterised by a Late Cretaceous to Oligocene passive margin section overlain by a very thick Miocene–Pliocene active margin sequence. Numerous gas seeps, oil seeps, stains and strong impregnations occur throughout the 500 km length of the onshore basin, and these have encouraged exploration, mostly onshore, since 1872. However, there has been relatively little modern exploration and only one well has been drilled offshore. Inability to clearly link the seep and stain oils with a source formation has been a factor in this apparent lack of interest. Most exploration plays have presumed a Cretaceous source rock.

Recently, improved documentation of the distribution of East Coast oil and gas seeps, their host formations, and in particular, their relationship to reservoir and structure has pointed to a source in the lower Tertiary, rather than the Cretaceous (Francis, 1992a,b). Some recent company exploration has developed this play with respect to Tertiary reservoirs and to late Tertiary burial (Francis 1991, 1993). The possibility that an early Tertiary source may have

generated in the East Coast Basin is therefore critical to some play concepts presently being considered or explored.

The best known and most productive seeps occur in the north of the basin near Gisborne, but more than 30 seeps, stains or strong oil impregnations are known elsewhere. This study focuses on two stain oils recovered from sandstones in the south, between Dannevirke and Castlepoint (figure 1). Like many seep and stain oils, these samples are biodegraded and, since the n-alkane profiles have been destroyed, oil–oil and oil–source correlation can only be accomplished via gas chromatographic–mass spectrometric (GCMS) analysis of recalcitrant biomarker compounds. Furthermore, GCMS biomarker analyses give much more information about the nature of the source organic matter, its maturity and the source rock lithology than does gas chromatography alone (the reader is referred to Peters and Moldowan, 1993 for a detailed description of biomarker technology).

Two previous studies have applied biomarker techniques to East Coast oils and sediments. Weston et al. (1988) analysed the Waitangi, Rotokautuku and Totangi seep oils and compared their results to source rock data obtained from unpublished reports. Their main conclusion was that these

three oils from the north of the basin originate from a similar and probably Cretaceous source rock containing both marine and terrestrial organic matter. The assignment of the source age was based on maturity considerations and no match was found between the biomarker profiles of the oils and those of potential sources in the Cretaceous. Johnston et al. (1992) also examined the Rotokautuku and Waitangi oils together with a range of stain oils from the area north and south of

Hawke's Bay. Noting a similarity between stains from the Westcott area and the Waitangi oils, they concluded that the oils from the south and north of the basin had a common source, possibly in the lower Cretaceous. No potential source rocks were analysed but the Waipawa Black Shale and other Tertiary units were considered unlikely candidates because earlier studies had shown them to be immature in outcrop.

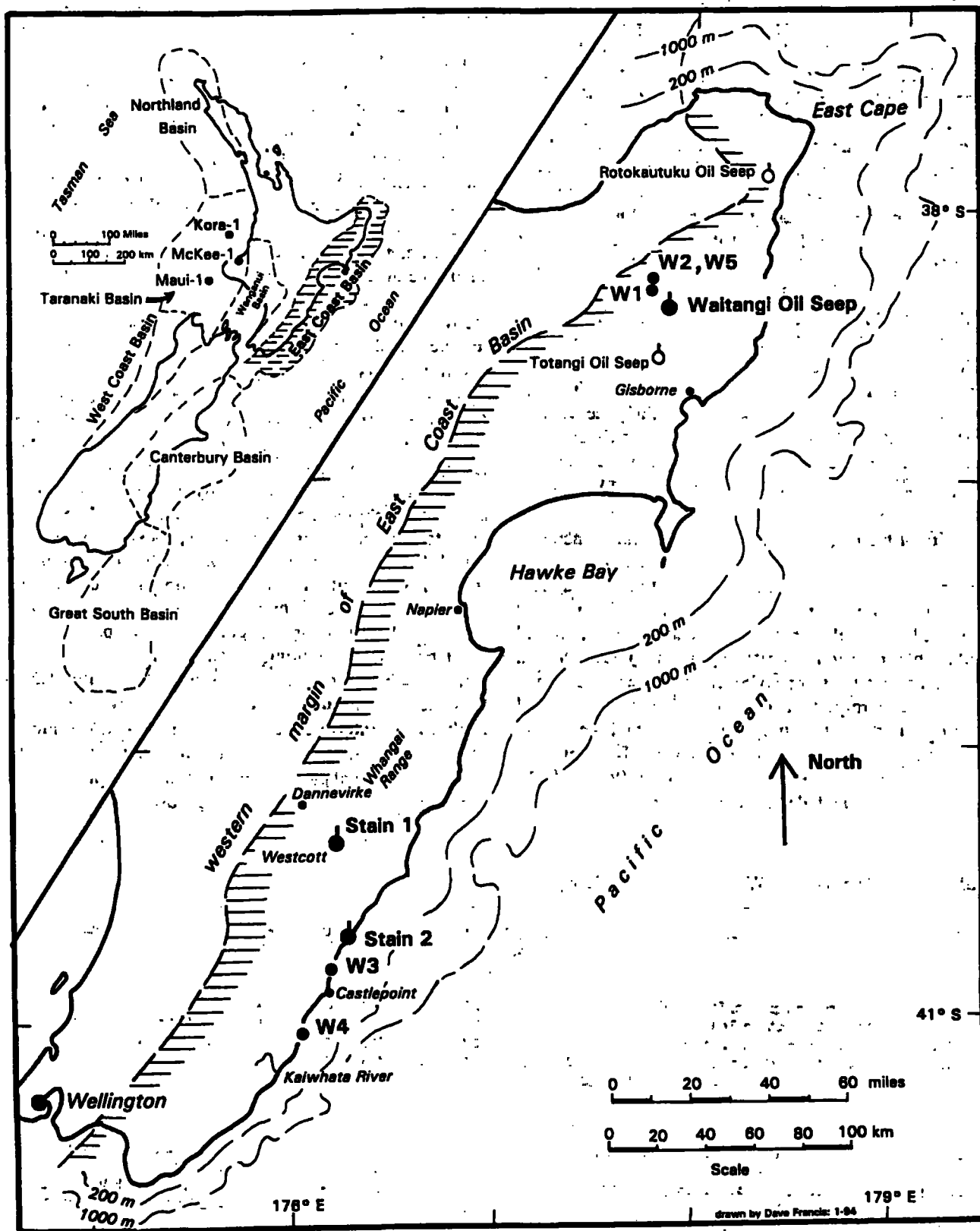


Fig. 1. Sampling locations of oils (Waitangi, stain 1, stain 2) and Waipawa Black Shale (W1 to W5) in the East Coast, and (inset) localities of oil from wells in the Taranaki Basin considered in this study.

The Waipawa Black Shale (more correctly a carbonaceous siltstone) is easily the most widespread, oil-prone unit in the East Coast Basin. It was deposited during the Paleocene when a regional marine transgression produced conditions of reduced oxygen flow, abnormal salinity and elevated water temperature (Walley, 1992). Organic rich time-equivalents occur in many other parts of New Zealand including offshore north Taranaki (e.g. Ariki-1 well), offshore south Canterbury (Galleon-1 well), the Northland Basin (Hay, 1960) and the Great South Basin (Fleming, 1978) and possibly also in New Caledonia (Walley, 1992 and references therein). In the East Coast Basin, outcrop exposure occurs from near East Cape in the north to the area of the Kaiwhata River in the south and from the western margin to the coast. The thickness of the formation is generally 20–30 m but it is relatively thin (2–4 m) in the west and very thick (70 m) near the coast at Castlepoint. It is absent or substantially thinned below an Eocene unconformity around the Whangai range, south of Hawke's Bay. Leckie et al. (1992) estimate that "at least 500 km³" of the Waipawa Black Shale exists in the offshore East Coast Basin.

Although the Waipawa is immature in outcrop, its maturity as determined by Rock Eval analysis varies regionally (Moore, 1988, Leckie et al., 1992), as might be expected from the complex tectonic regime. Some samples from the north of the basin have a maturity approaching the window for oil generation and more mature placement can be expected to occur along the basin axis. The petroleum yield of mature Waipawa Black Shale would far exceed that of any Cretaceous unit recognised to date.

The aim of the present study was to determine whether a mature analog of the Waipawa Black Shale could have generated some of the seep oils and stains found throughout the basin. Closed-system pyrolysis of immature material was used to simulate natural petroleum generation and metastable reaction monitoring (MRM) GCMS and compound specific isotope (CSIA) techniques were used to examine the pyrolysates and compare them to the stain and seep oils. Early in the study we realised that there were strong similarities between some East Coast Basin oils and the Kora-1 oil of the North Taranaki Basin (Reed, 1992). This oil has been included for comparison.

Methods

Samples

Table 1 and figure 1 give details of the samples used in this study. The two stain oils from the Westcott and Okau Stream locations are equivalent to the samples labelled D28 and D4 respectively by Johnston et al., (1992). They were recovered by hand crushing the sandstone matrix and sonicating in dichloromethane.

Immature samples of Waipawa Black Shale were collected from two outcrop locations in the north and two in the south of the basin. A further composite sample (W5) was created by combining equal weights of subsamples from the top, upper middle, lower middle and bottom of the Waipawa as it appears at the Te Weraroa stream bank site (i.e. site W2).

Artificial maturation (pyrolysis)

The sediment samples were broken into small pieces (but not crushed) and sealed into a stainless steel Parr reactor. They were then heated at 330°C for 72 hours, generating a liquid petroleum, gas and some char. Water was not added and it should be noted that the method is closed system but not "hydrous" pyrolysis. The extractable organic matter was recovered by rinsing the inside of the reactor and the shale residue with dichloromethane.

Analytical techniques

The methods used have been described in detail elsewhere (Summons and Capon, 1991; Hayes et al., 1990). Briefly, the oils and pyrolysates were separated into saturate, aromatic and polar fractions by column chromatography on silica. The saturate fractions were analysed by capillary gas chromatography on a non-polar column and by GCMS in the metastable reaction monitoring mode (MRM-GCMS). The MRM-GCMS method is superior to the more common selected ion monitoring (SIM) GCMS mode because it allows deconvolution of biomarker families into molecular mass families and largely eliminates the problem of overlapping and co-eluting peaks. This makes it possible (for example) to accurately and separately quantify C27, C28 etc. ring desmethyl steranes. The lower level of background interference renders MRM-GCMS more sensitive than SIM-GCMS — an important factor when analysing sediment pyrolysates, where the concentration of cyclic biomarker compounds is often low.

Table 1. Details of Oil and Waipawa Black Shale samples.

Name	Location	TOC %	S1	S2	HI	OI	Tmax °C	Comments
Waipawa Shale samples								
W1	Road cutting exposure, Tamdale Rd.	3.9	0.7	14.4	369	< 5	414	Rock Eval/TOC data for the immature samples before closed system pyrolysis
W2	Stream bank outcrop, Te Weraroa stream	4.4	2.5	20.2	463	< 5	421	
W3	Exposed shore platform, near Castlepoint	3.5	0.4	8.3	236	24	412	
W4	Exposed shore platform, approx. 30 km sth. of W3	2.5	0.2	3.5	143	40	420	
W5	Top - middle - bottom depth composite from W2 site							
Oils and Stains								
Stain 1	Westcott area, oil stained Miocene sandstone							Same locn. as D28 of Johnston et al. (1992)
Stain 2	Oil stained glauconitic sandstone, Okau Stream bed, near Castlepoint.							Totally enclosed in Waipawa Shale. = D4 of Johnston et al. (1992)
Waitangi seep	Waitangi oil seep, near Waitangi-1 well							
Kora Oil	Kora-1 well, offshore North Taranaki Basin							

Compound specific isotope analysis (CSIA) is an improvement over isotope measurements made on the bulk oil or the saturate, aromatic and polar fractions. The method uses a combination of high resolution gas chromatography and an on-line isotope ratio mass spectrometer to measure the $^{13}\text{C}/^{12}\text{C}$ ratio of individual compounds (Hayes et al., 1990). The most common application in petroleum geochemistry has been the generation of n-alkane isotope profiles (e.g. Bjoroy et al., 1992) but there is increasing application to other classes of compounds (e.g. Freeman et al., 1989, Collister et al., 1992). For the present study, only the n-alkane isotope ratios were determined and the analyses were carried out on an n-alkane fraction separated from the bulk saturates using silicalite molecular sieve (Hoering and Freeman, 1984). All carbon isotope ratios are expressed relative to the $^{13}\text{C}/^{12}\text{C}$ ratio of the Pee Dee Belemnite in the standard delta (δ) notation.

Except where otherwise noted, the interpretation of biomarker and isotope data in this paper follows *The Biomarker Guide* (Peters and Moldowan, 1993).

Results and Discussion

Stain and seep oils

Gas chromatograms for stain 1, the Waitangi oil and the Kora oil are shown in figure 2. Table 2 lists some quantitative parameters derived from the liquid and gas chromatographic analyses. The gas chromatograms for the stain oils show that both are lightly to moderately biodegraded with stain 1 having lost the n-alkanes and stain 2, having lost both the n-alkanes and the more resistant isoprenoid alkanes, being the more extensively altered of the two. The chromatogram for stain 2 is not included in figure 2 as it is devoid of peaks and provides no useful information. The only source information available from the gas chromatogram for stain 1 is the pristane/phytane ratio and this too must be treated with caution since it may have been altered by the biodegradation. However, the value (3.0) is consistent with deposition of the source rock under oxic or mildly dysoxic conditions (Peters and Moldowan, 1993 and references therein).

The gas chromatographic data for the Waitangi and Kora oils are in accord with previous reports (Johnston et al., 1992, Weston et al., 1988, Reed, 1992) in that the n-alkane profiles and pristane/phytane ratios are typical of mature oils generated from a mixture of marine and terrestrial matter.

The pristane/phytane ratios are again consistent with deposition under oxic to dysoxic conditions, although we concur with Peters and Moldowan (1993) and ten Haven et al., (1987) that values in the range 1 to 3 are ambiguous and must be interpreted with caution. The isoprenoid/n-alkane ratios for both the Kora and Waitangi oils are higher than those normally observed for marine oils, even where there is a subsidiary contribution from terrestrial organic matter. This feature may be the result of light biodegradation.

Biomarker profiles for stain 1, the Waitangi oil and the Kora oil are shown in figure 3 and selected source, maturity and lithology parameters for these samples and stain 2 are listed in table 3. There is no evidence that biodegradation has significantly affected the biomarker profiles for either of the stain oils.

The sterane distributions for the stain oils show three characteristics typical of marine oils, these being the dominance of the C_{27} over the C_{29} members, the presence of C_{30} ring A-desmethyl steranes (i.e. the 24-n-propyl cholestanes) and the presence of dinosterane isomers (figure 3). The most diagnostic of these characteristics is the presence of the C_{30} , 24-n-propyl cholestanes. These compounds are derived from precursor molecules found in marine chrysophyte algae and they appear to be definitive and specific markers for marine organic matter (Moldowan et al., 1990, 1985). Their abundance in oils and sediments can be expressed as the " C_{30} Index" (Peters and Moldowan, 1993) which is the proportion (or percentage) of C_{30} steranes relative to the total desmethyl steranes (i.e. sum of C_{27} - C_{30} dia- and regular steranes). The C_{30} indices for stain oils 1 and 2 are 28% and 24% respectively (table 3, parameter 4). Moldowan et al. (1985) determined the C_{30} index for a set of 24 oils of known marine affinity from Canada, Australia, Spain, Greece, Italy and various parts of the USA. Although the sample set was relatively small, the oils were chosen so as to be representative of a much larger set. Since the highest value for the C_{30} index obtained in this study was 11% (average 5%) the higher values obtained for the East Coast stain oils must be considered exceptional and very characteristic. It is significant, therefore, that the only other oil so far found to have such a high abundance of C_{30} steranes is the Kora-1 oil from the North Taranaki Basin (Reed, 1992 and table 3). By contrast, the Waitangi oil has a more "normal" C_{30} index of 5%.

Table 2. Extract, bulk composition and gas chromatographic data for oils and sediment pyrolysates.

Sample	% EOM	ppm HC	Sat/Aro	Pr/C ₁₇	Ph/C ₁₈	Pr/Ph	CPI	Comments
Pyrolysates								
W1	0.14	1023	0.25	0.22	0.12	2.4	1.05	
W2	0.38	2520	0.46	0.37	0.17	2.4	0.99	
W3	0.26	1255	0.19	0.14	0.07	2.6	1.00	
W4	0.12	312	0.17	0.19	0.08	2.2	.85	
W5	0.15	938	0.19	0.18	0.07	3.0	.89	
Oils and Stains								
Stain 1	-	-	0.99	ndp	ndp	3.0	ndp	Light-moderately biodegraded
Stain 2	-	-	1.2	ndp	ndp	ndp	ndp	Moderately biodegraded
Waitangi Seep	-	-	3.5	1.8	0.58	2.6	1.06	Lightly biodegraded ?
Kora Oil	-	-	1.8	1.3	0.56	2.7	1.05	Lightly biodegraded ?
ndp: No determination possible								

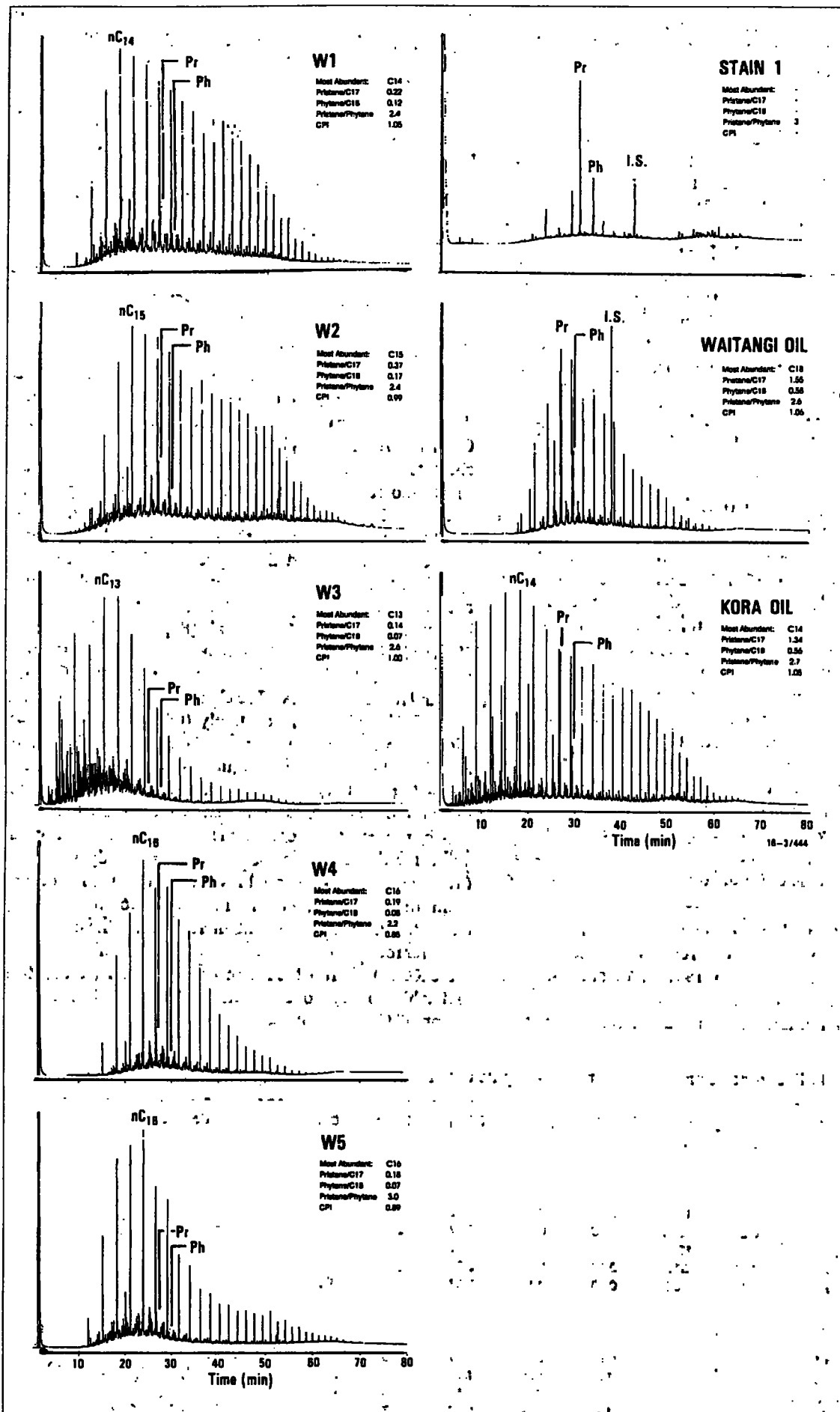


Fig. 2. Gas chromatograms of the saturate fractions of oils and pyrolysates. Pr = Pristane, Ph = Phytane, I.S. = internal standard, CPI = carbon preference index.

A terrestrial organic matter contribution to the stain oils is shown by the presence of oleanane, a compound derived from precursors found in the flowering plants (angiosperms). The presence of this compound also constrains the age of the source rock to late Cretaceous or younger, when the angiosperms-eclipsed gymnosperms as the main higher plant group. The oleanane/C₃₀ hopane ratio (parameter 11, table 3) is similar for both stain oils and of the same order as the value for the Kora oil. By contrast, only traces of oleanane were detected in the Waitangi oil and, indeed, at this level it was not possible to confirm the presence of this compound using the standard mass spectrometry tests (Peters and Moldowan, 1993).

Another reasonably unusual and therefore characteristic marker in both stain oils is 28,30 bisnorhopane. This compound (for which the strict nomenclature is 28,30 dinorhopane) is best known from its occurrence in the Kimmeridge shales and associated oils from the North Sea and is typical of marine source rocks deposited under anoxic conditions (Grantham et al., 1980, Curiale et al., 1985). Several studies have suggested that it is a component of the free source rock lipids rather than being incorporated in the kerogen, as is the case for other hopanoid compounds. Dilution by catagenetic hydrocarbons would then explain why its relative concentration is often much lower in an oil than in the immature source rock (e.g. Curiale et al., 1985). However, in previous studies of the Waipawa Black Shale (unpublished) we have found 28,30 bisnorhopane to be present in pyrolysates of isolated, solvent-washed kerogens, as well as in bitumens and stain oils. The Kora oil contains traces of 28,30 bisnorhopane but we could not reliably detect this compound in the Waitangi oil (figure 3, table 3).

Although there are many points of similarity between the stains from the Castlepoint and Westcott areas (i.e. stains 1 and 2 respectively); table 3 shows that they are not identical. The most significant differences are the higher relative abundance of neohopanes (parameters 13 and 14) and $\alpha\beta\beta$ steranes (parameters 8 and 9) in stain 2. Both of these features are influenced by both source and maturity and it would be difficult to distinguish between the two effects. However, given that the two stain oils are similar on most other source indications, the differences probably indicate a

more advanced maturity for the rock which generated stain 2. This is also borne out by the maturity dependent sterane epimer ratios (parameters 6 and 7). Another possibility is that incipient biodegradation of biomarkers has occurred for stain 2. In its earliest stages, biomarker degradation mimics the effects of increased maturity and normally begins with the C₂₇ $\alpha\alpha\alpha$ steranes.

To summarise, we find that stain oils 1 and 2 have a very similar or common source and that they are strikingly similar to the Kora oil from the north Taranaki Basin. All three oils were derived from a rather unusual marine/terrestrial facies which is no older than late Cretaceous. By comparison, the Waitangi seep oil and (by implication) others from the North of the basin probably arise from a more distal and/or older source facies. These findings partly contradict those of Johnston et al. (1992) who postulated a common source for the Waitangi oil and the Westcott stain (stain 2) and a different source for the Okau Stream stain (stain 1). Furthermore, sterane epimeric ratios in the Waitangi oil are similar for C₂₉ and C₂₇ members, so that there is no evidence for the differential maturity of "marine" vs. "terrestrial" components, as reported by these workers.

Artificial maturation of Waipawa Black Shale and comparison with the oils

Table 2 summarises the quantitative results for closed system pyrolysis of Waipawa Black Shale samples and figure 2 shows the gas chromatograms of the saturate fractions of the pyrolysates. All samples produced good yields of hydrocarbons with the best yield obtained from sample W2 (Te Weraroa Stream). This is as predicted by the Rock Eval/TOC results (table 1) which show it to be the most oil prone sample. The depth composite (W5) from the same site gave less than half the yield, suggesting that there is considerable variation in the quality of the Waipawa shale through its depositional section. This variability is also apparent in TOC/Rock-Eval data for an outcrop section near Angora (Leckie et al., 1992 and pers. comm.) which shows organically richer horizons at the top and bottom of the formation separated by a less rich layer in between. Foraminiferal data for this Angora section indicate changes in the depositional environment through the Waipawa section (Leckie et al., 1992, H. Morgans, pers. comm.) Taken together with visual

Table 3. Selected biomarker parameters for oils and sediment pyrolysates.

Parameter	Pyrolysates			Oils and Stains				Indication (Primary, Secondary)
	W2	W4	W5	Stain 1	Stain 2	Waitangi Seep	Kora oil	
1 % C ₂₇ Steranes	28	41	35	29	29	33	24	Source
2 % C ₂₈ Steranes	17	20	19	18	22	40	17	Source
3 % C ₂₉ Steranes	24	29	25	25	24	22	23	Source
4 % C ₃₀ Steranes	31	10	22	28	24	5	35	Source
5 Dia/Total C ₂₉ Steranes	0.38	0.27	0.22	0.42	0.37	0.43	0.38	Source, Lithology
6 C ₂₉ S/S+R Steranes	0.46	0.42	0.30	0.42	0.48	0.60	0.52	Maturity
7 C ₂₇ S/S+R Steranes	0.38	0.40	0.31	0.45	0.59	0.52	0.48	Maturity
8 $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ C ₂₉ Steranes	0.25	0.46	0.32	0.39	0.57	0.54	0.52	Maturity, Source
9 $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ C ₂₇ Steranes	0.14	0.16	0.18	0.31	0.53	0.52	0.53	Maturity, Source
10 C ₂₉ $\alpha\beta$ Hop/C ₃₀ $\alpha\beta$ Hop	2.16	2.18	5.33	0.74	0.61	0.63	0.48	Source, Maturity
11 Oleanane/C ₃₀ $\alpha\beta$ Hop	0.13	0.04	0.16	0.11	0.12	0.05	0.16	Source
12 28,30 BNH/C ₃₀ $\alpha\beta$ Hop	0.97	0.41	0.10	0.40	0.78	< 0.02	0.03	Source, Maturity
13 C ₂₉ Neohopane/C ₂₈ Hopane	< 0.05	0.15	< 0.05	0.32	0.42	0.39	0.35	Maturity, Source
14 T ₂₇ /T _m	0.17	0.13	0.12	0.67	1.37	1.53	1.60	Maturity, Source
15 Hopanes/Steranes	0.92	0.83	1.42	0.19	0.10	0.44	0.19	Source, Maturity

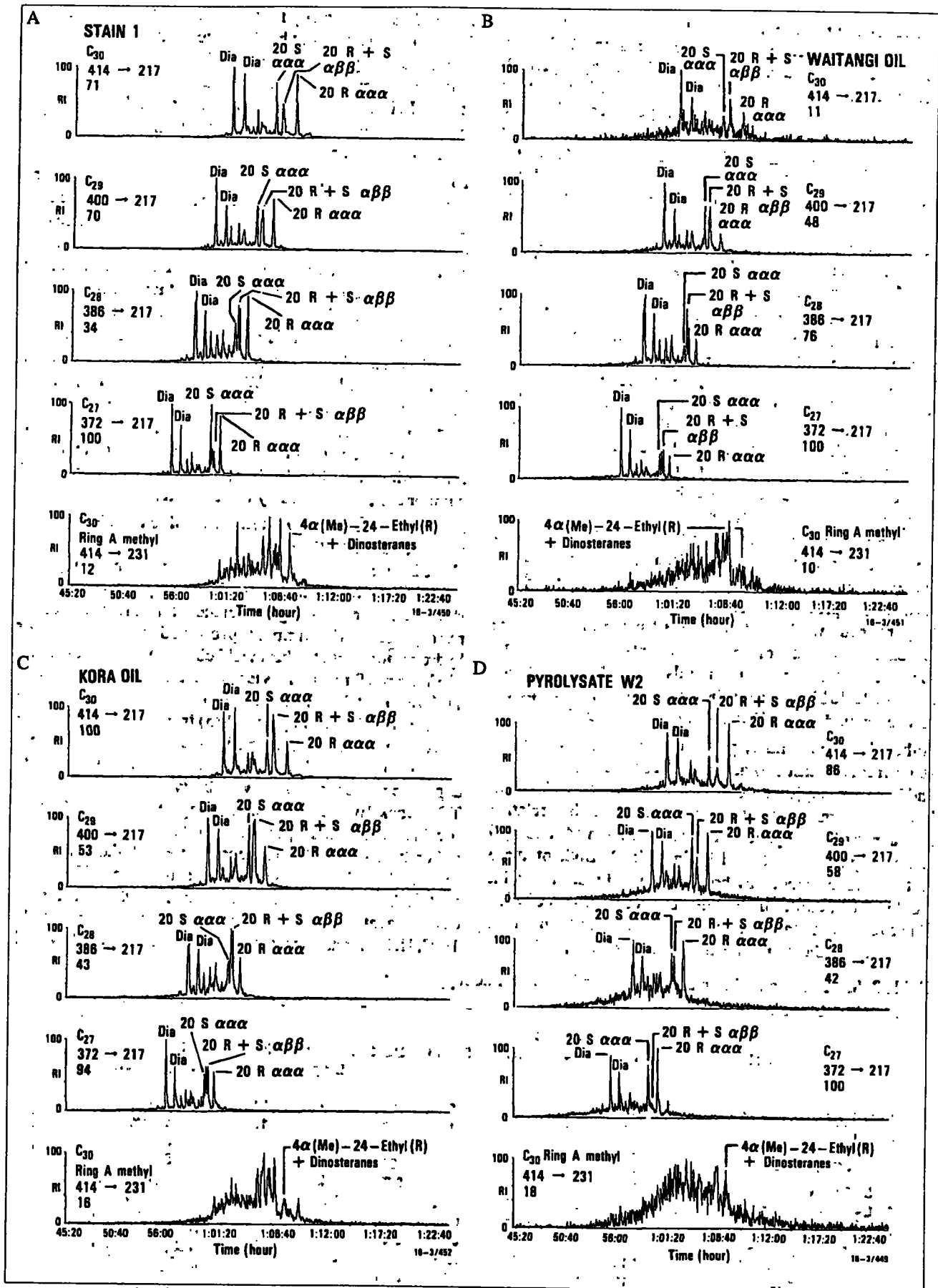
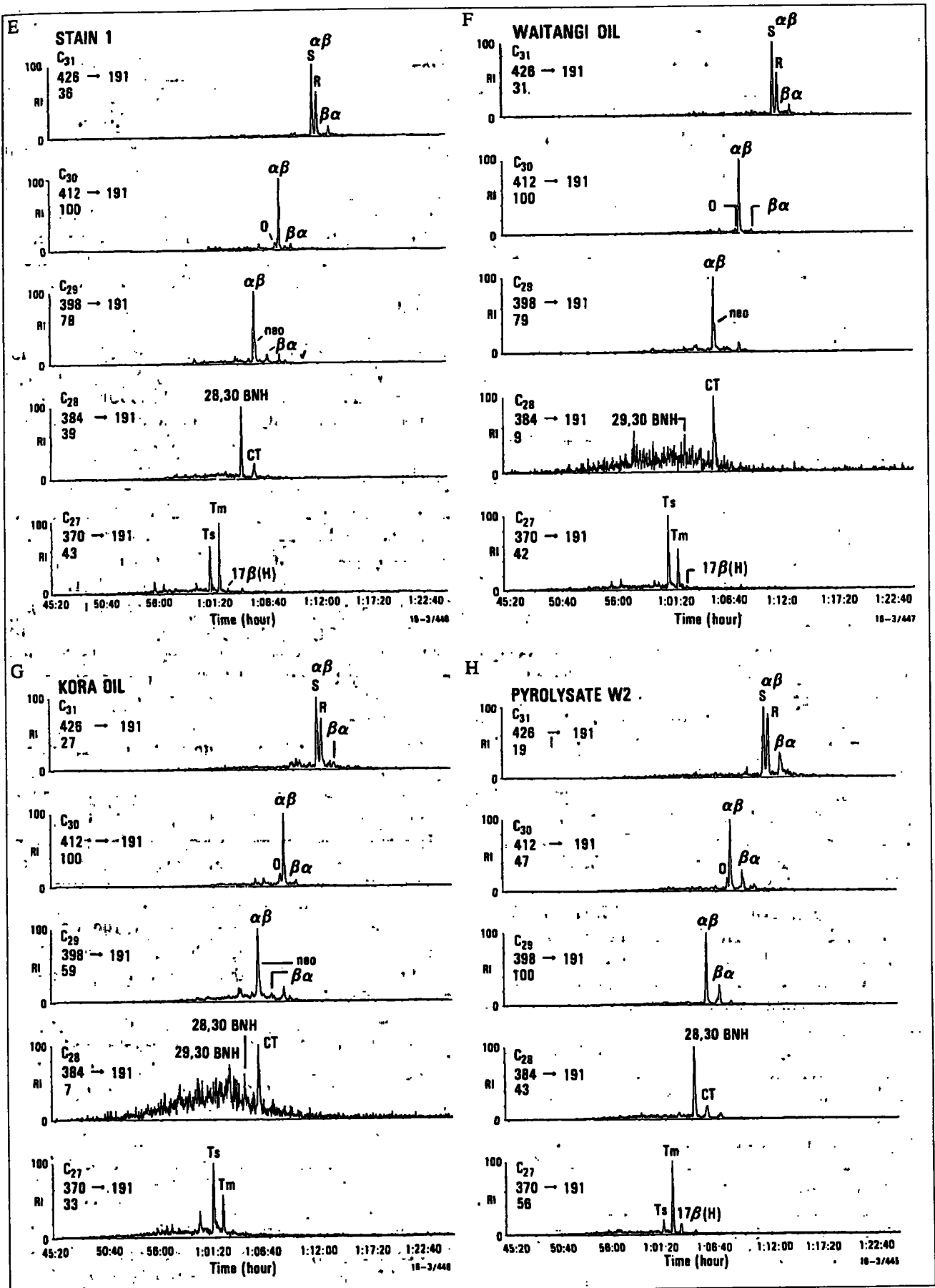
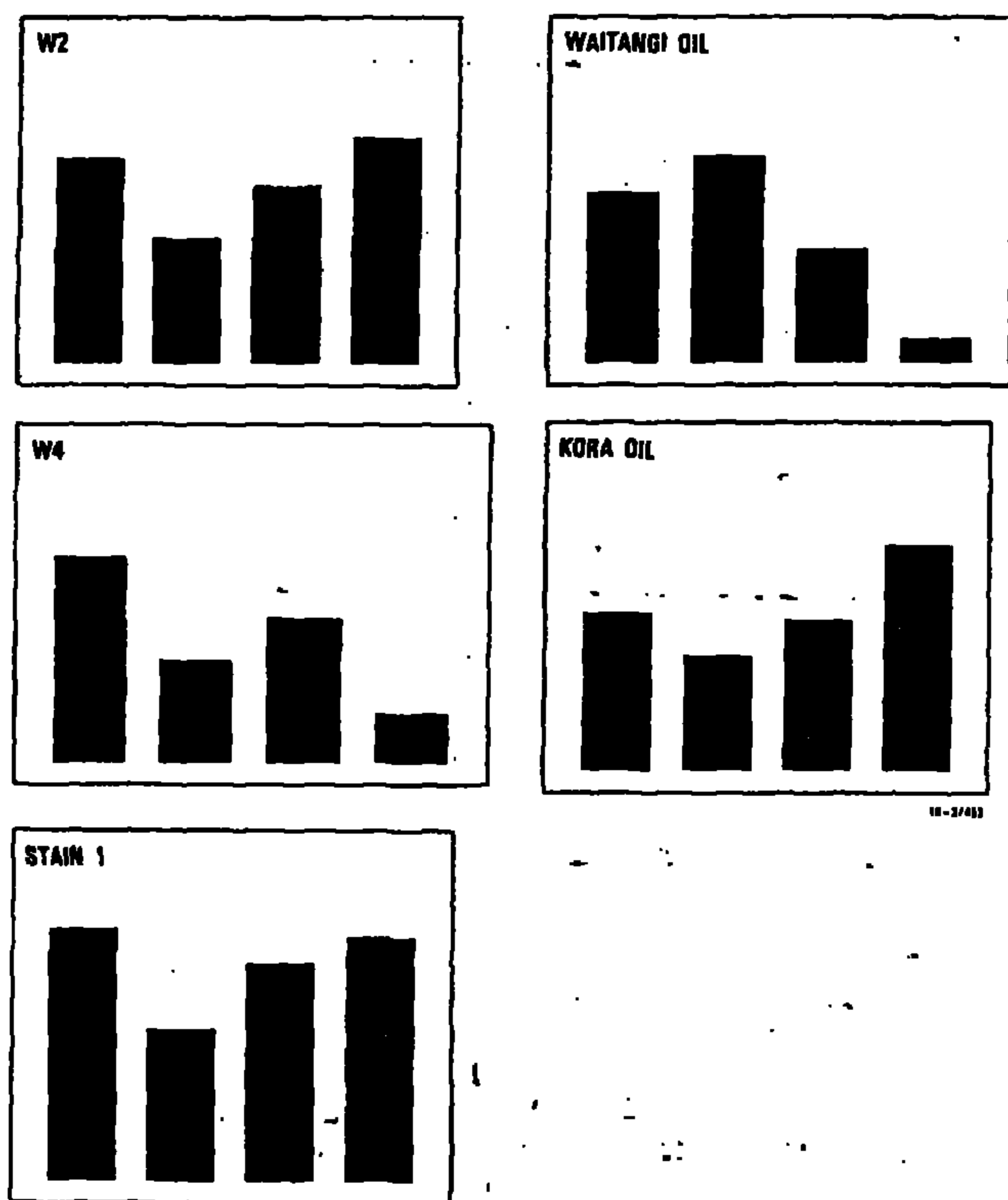


Fig. 3. Metastable Reaction Monitoring (MRM)-GCMS chromatograms of selected oils and pyrolysates. A-D: Steranes. E-H: Triterpanes. Annotations at the top of each trace show the carbon number of compounds appearing in that trace, the MRM reaction monitored (e.g. 412 Δ 191 records C₃₀ triterpanes) and the vertical scale factor (RI = relative intensity). Other annotations as follows: "S" and "R" denote the stereochemistry of hopane and sterane chiral centres, "Dia" = diahopane or diasterane, "O" = oleanane ($\alpha + \beta$), " $\alpha\beta$ " = 17 α (H), 21 β (H) hopanes, " $\beta\alpha$ " = 17 β (H), 21 α (H) hopanes (moretanes), neo



= 18 α (H)-30-norneohopane, "29,30 BNH" = 29,30-bisnorhopane (29,30 dinorhopane), "28,30 BNH" = 28,30-bisnorhopane (28,30 dinorhopane), "T" = 18 α (H)-22,29,30-trisnorneohopane, "T_m" = 17 α (H)-22,29,30-trisnorhopane, "17 β (H)" = 17 β (H) 22-29,30-trisnorhopane, " $\alpha\alpha\alpha$ " = 5 α (H), 14 α (H), 17 α (H) steranes, " $\alpha\beta\beta$ " = 5 α (H), 14 β (H), 17 β (H) steranes, "4 α (Me)-24-ethyl(R)" = the R epimer of the 4 α -ring A-methyl-24-ethyl cholestane, "CT" = crosstalk, a spurious peak caused by interference from another channel.

Fig. 4. Stylised representation of the relative abundance of C_{27} , C_{28} , C_{29} and C_{30} ring A desmethyl steranes in oils and pyrolysates. C_{27} - C_{30} left to right.



examination of the Waipawa Black Shale in outcrop these data indicate that the sectional variation may be at least as great as any geographical variation in quality from north to south. As discussed below, the variation in quality seems to be accompanied by changes in n-alkane and biomarker profiles.

The ratio of saturates to aromatics for the pyrolysates (table 2) was lower than for the oils but this is probably an artefact of the pyrolysis method (Peters et al., 1990). Higher heating rates may favour aromatisation reactions (McKenzie et al., 1984, Lewan, 1993).

The n-alkane profiles for samples W1 and W2 from the north of the East Coast Basin are very similar to that of the Kora oil. By contrast, the two samples from the south (W3, W4) and to a lesser extent the composite (W5) gave pyrolysates richer in low boiling point compounds and in fact they resemble gas-condensates. This lighter distribution of n-alkanes is probably due to a reduced contribution of higher plant waxes, relative to samples W1 and W2. Samples W4 and W5 show a pronounced even/odd preference in the n-alkanes — a feature which is often associated with carbonate source rocks. The isoprenoid content of the pyrolysates is typical of unbiodegraded marine oils and the pristane/phytane ratios (2.2–3.0) are similar to those of the oils. The reduced contribution of terrestrial organic matter to samples W3, W4 and W5 is also shown by the lower pristane/ C_{17} and phytane/ C_{18} ratios in their pyrolysates.

Artificial maturation at high temperature typically produces smaller amounts of biomarkers than does natural maturation, and the biomarker content of the pyrolysates was very low. Nevertheless, the extra sensitivity of the MRM-GCMS method provided good data for samples W2, W4 and W5 and these data appear in table 3 (for brevity, only the

chromatograms for sample W2 are included in figure 3). Though quantitative results could not be obtained for the remaining samples, weak mass chromatograms for sample W1 suggest that its composition is similar to that of sample W2. Before discussing the biomarker profiles of the pyrolysates in relation to those of the oils, it must be recognised that artificial maturation does not mimic natural generation perfectly. Some distortion of the biomarker profile is expected to occur and aspects of this have been described in the literature (Seifert, 1978, Rullkötter et al., 1984, Cassani and Eglinton, 1986, Jones et al., 1987, Tannebaum et al., 1986, Peters et al., 1990, Simoneit et al., 1992). Although these studies differed greatly in the pyrolysis conditions used (temperature, pressure, type of sample, hydrous vs. anhydrous etc.) some common features do emerge.

1. Sterane maturity parameters, such as the epimeric ratios are highly variable and depend critically on sample lithology (Tannebaum et al., 1986, Peters et al., 1990). As a result, estimates of the maturity reached before pyrolysis are not meaningful and the isomer ratios in the pyrolysates are not comparable to the pseudo-equilibrium ratios seen in mature oils (Peters et al., 1990)

2. Pyrolysates inevitably contain a higher proportion of moretanes ($\beta\alpha$ hopanes) than do naturally generated oils.

3. The proportion of neohopanes (relative to regular hopanes) is much lower in pyrolysates than in oils. Therefore, T_s/T_m ratios are much lower (parameter no. 14, table 3).

4. The ratio of C_{29} to C_{30} $\alpha\beta$ hopanes (parameter no. 10, table 3) is higher in pyrolysates than in oils. In the study performed by Rullkötter et al. (1984) the ratio in anhydrously pyrolysed bitumens was approximately double that in the original bitumen.

5. The ratio of total hopanes/total steranes is higher in pyrolysates than in oils.

6. Most reports indicate that the compound 28,30 bisnorhopane (28,30 BNH) is a free lipid and so is not found in kerogen pyrolysates, even when present in bitumens and naturally generated oils. However, in earlier studies of the Waipawa Black Shale and of other oil shales we have found this compound in pyrolysates of solvent washed kerogen (Murray et al., unpublished, Boreham et al., 1994). Thus for the present studies involving whole rock samples 28,30 BNH may arise from both the free lipid fraction and from pyrolysis of the kerogen.

7. No major effects on the sterane distribution (i.e. proportions of C_{27} : C_{28} : C_{29} : C_{30} steranes) are observed beyond a slight enhancement of C_{27} abundance at pyrolysis temperatures above 330°C. This means that the sterane distribution is a useful parameter for correlating oils and pyrolysates.

Several of the above effects are apparent in the data for the Waipawa pyrolysates, e.g. the C_{29}/C_{30} hopane ratios are high and outside the range observed for natural oils. Allowing for these artefacts there remains a strong three-way correlation between the pyrolysates, the southern basin stain oils and the Kora oil. This correlation is strongest for the most productive sample (W2) and its main elements are:

1. A close match in the sterane distributions and, in particular, the unusually high abundance of the C_{30} steranes (24-n-propyl cholestanes). A stylised comparison of the sterane distributions appears in figure 4.

2. The presence of 28,30 BNH. This compound is abundant in the stain oils and pyrolysates and is a trace component of the Kora oil biomarkers (figure 3). Experience elsewhere shows that mature oils often contain low concentrations of 28,30 BNH even when generated from rocks rich in this compound (Grantham et al., 1980, Curiale et al., 1985, Curiale and Odermatt, 1989). Both maturity and selective migration effects may be responsible for this phenomenon (Curiale et al., 1985).

3. An oleanane/ C_{30} hopane ratio in the range 0.1–0.2.

4. A narrow range for the ratio of diasteranes/regular steranes (parameter 5, table 3).

The only difference between the pyrolysates and oils which cannot be readily accounted for as a pyrolysis artefact is the lower $\alpha\beta\beta/(\alpha\alpha\alpha+\beta\beta\beta)$ sterane ratio of the pyrolysates (parameters 8 and 9, table 3). However, this parameter is sensitive to maturity and may or may not indicate a true difference in source character.

The biomarker profile of sample W4 does not correlate as well with those of the stain oils or the Kora oil and, in terms of the abundance of C_{30} steranes and oleanane, it is closer to the Waitangi oil. The biomarker profile of the composite sample (W5) is similar to and yet distinct from the profiles for W2, the stain oils and the Kora oil. This sample has a slightly lower proportion of C_{30} steranes, a lower proportion of diasteranes and a higher C_{29}/C_{30} hopane ratio than sample W2. Interestingly, the last two of these parameters are often associated with the influence of carbonate lithology (Peters and Moldowan, 1993) and, as mentioned earlier, this is also suggested by the even/odd preference in the n-alkanes. Calcareous concretions occur in several outcrop exposures of the Waipawa, generally in the middle of the formation.

The differences between the biomarker profiles of the depth composite and sample W2, though relatively minor, also emphasise the change in character of the Waipawa shale across its section. Kinetic data for kerogen conversion (which will be reported elsewhere) also shows this variation in samples taken from sites very close together geographically. These data suggest that different organofacies within the Waipawa shale may differ by as much as 20°C in the temperature required to induce 50% kerogen conversion. The significance of this for the present work is that the character of a seep or stain oil, which will appear as a site begins to move into the oil window, will probably be that of the more labile facies, even though the less labile one may be more abundant. Furthermore, changes in the character of seep oils could relate to the non-deposition or erosion of the upper part of the Waipawa Black Shale in some parts of the basin. A more detailed study is needed to determine the nature of the geochemical variation through the depositional section of the Waipawa and its relation to bulk chemical, kinetic, paleontological and sedimentological features. The results of such a study could have a major impact on the basin modelling and it would be a worthwhile extension of the present work.

Based on maturity considerations, the source of the Kora oil (Taranaki Basin) was originally assumed to be Cretaceous (Reed, 1992). However, later modelling studies indicate a younger source and a recent review of petroleum systems in the Taranaki Basin attributes the Kora oil to a "Late Paleocene" source (Cook, 1994). Thus, our recognition of

the close similarity between the Kora oil, pyrolysates of the Waipawa Black Shale and some East Coast stain oils may be understood in terms of the regional and widespread deposition of a high quality, marine source rock during the Paleocene. The regional paleogeographic maps compiled by Walley (1992) give an indication of the possible extent of this facies deposited along what was then the western margin of the Pacific Ocean.

As is evident from table 3 and figure 3, the pyrolysates do not match well, in terms of biomarker composition, with the Waitangi oil, (although they are of the same general class). There are some similarities between the Waitangi oil profile and that of pyrolysate W4 and the facies that this sample represents could conceivably have generated the oil. However, the isotopic data (discussed below) suggest that the Waipawa Black Shale is not the source of the Waitangi oil. There are possible source horizons in the Cretaceous strata exposed 60–80 km north of the Waitangi seeps but their presence in the area of the seeps themselves is uncertain. The upper part of the Cretaceous to Paleocene Whangai formation, though less rich than the Waipawa Black Shale, does have fair to good oil potential (Leckie et al., 1992)

Isotopic data

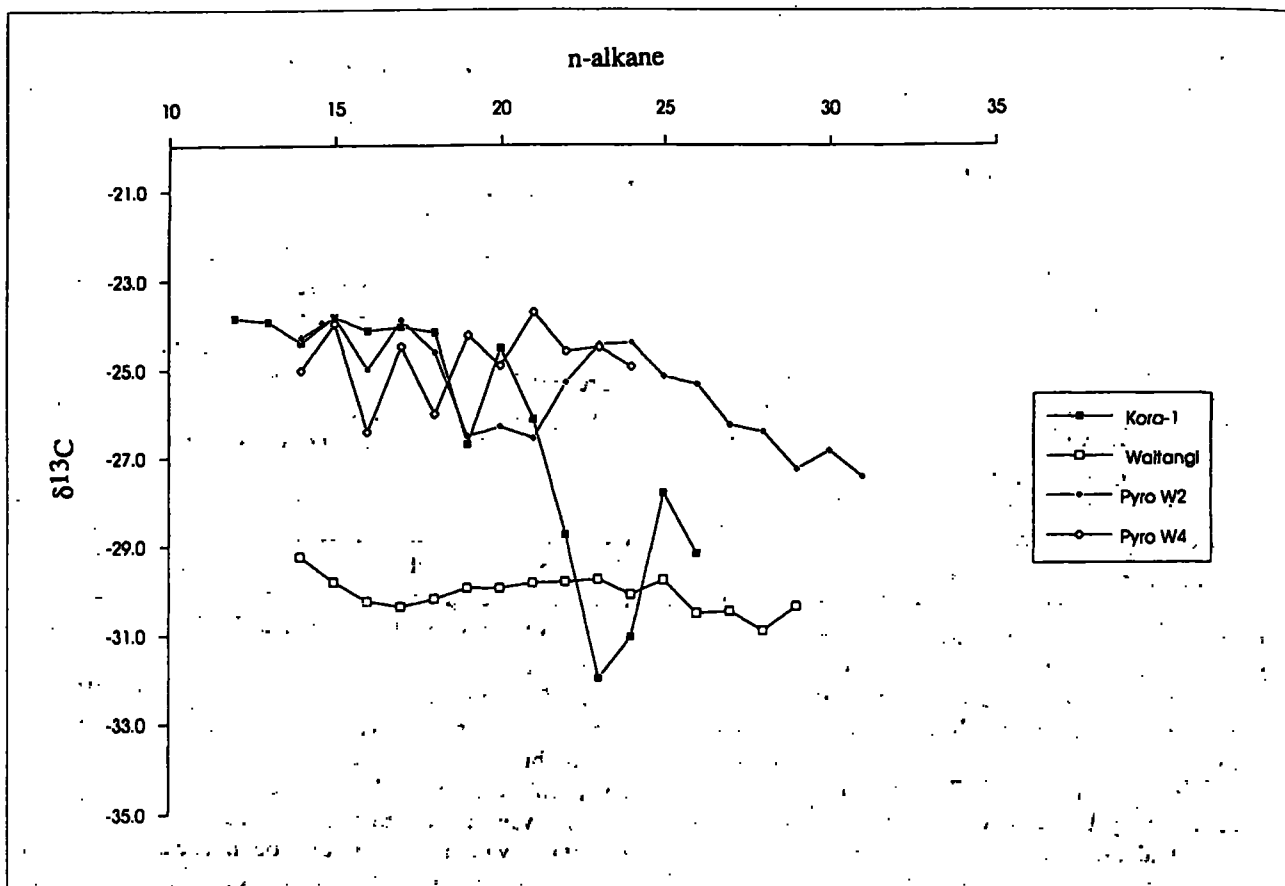
Figure 5 shows n-alkane isotope profiles for the Waitangi and Kora oils and for pyrolysates W2 and W4. As was the case for biomarker data, a comparison of isotope data for oils and pyrolysates must take into account possible artefacts of the pyrolysis method. Because CSIA analysis is a relatively recent innovation, the literature does not deal with this issue to any significant extent. However, the results of Bjorøy et al. (1992) reveal no major differences between the n-alkane isotope profiles of artificially and naturally generated oils, provided the pyrolysis temperature does not exceed 350°C.

As noted by Reed (1992), the Kora oil is characterised by a heavy carbon isotopic signature and figure 5 shows that this is especially so for the shorter-chain alkanes. Isotopic separation between the short and long n-alkanes is exceptional and may result from a significant terrestrial input to the waxy component. By contrast, the n-alkanes of the Waitangi oil are uniformly light. The pyrolysate of sample W2 has a heavy isotopic signature like that of the Kora oil, confirming the similarity noted in the biomarker and alkane/isoprenoid profiles. Because pyrolysate W4 also has a heavy isotopic signature, the facies it represents is unlikely to be the source of the Waitangi oil.

Since biodegradation had removed the n-alkanes from stain oils 1 and 2, n-alkane isotope profiles for these oils do not appear in figure 5. However, in earlier (unpublished) work we measured the bulk isotope composition of stain 2, obtaining values of -23.1‰ and -22.4‰ for the saturate and aromatic fractions respectively. Although it would be unwise to place too much stress on isotope data for biodegraded oils, these values are certainly compatible with the heavy isotopic signature observed for the Waipawa pyrolysates and Kora oil.

The very light isotopic composition of the Waitangi oil alkanes supports the view that it originates from a Cretaceous source rock. As figure 5 shows, the $\delta^{13}C$ values for the shorter chain alkanes (which have an algal/bacterial origin and so are least influenced by terrestrial organic matter) are 5–6‰ lighter for the Waitangi oil than for the Kora oil. Dean et al., (1986) found that Cretaceous marine organic matter in

Fig. 5. n-Alkane isotope profiles for Waipawa Black Shale pyrolysates W2 and W4 and for the Waitangi and Kora oils.



sediments at several locations worldwide had $\delta^{13}\text{C}$ values about 5 ‰ lighter than marine matter from later periods.

As part of a wider study of Cainozoic oils we analysed the Maui-1 and McKee oils from the Taranaki Basin (Summons et al., 1993 and in preparation). During this work, we noticed that the Maui-1 oil contains small amounts of C_{30} steranes (C_{30} index approx. 0.02) whereas the McKee oil does not (figure 6). This indicates a subsidiary marine contribution to

the predominantly terrestrial organic matter which generated the Maui oil (Czochanska et al., 1988) and a general trend towards increasing marine influence in the north and west of the Taranaki Basin has been noted previously (Cook, 1988). We wondered whether this marine influence could represent co-sourcing from the same marine facies which gave rise to the Kora oil. The n-alkane isotope profiles (figure 7) show that the Maui oil differs from the McKee oil in displacement of the isotope values for the smaller alkanes toward less negative (i.e. heavier) values. While there could be many reasons for this difference, one possibility is that there is indeed a minor contribution from the Kora source to the Maui-1 oil. Co-sourcing from the Cretaceous Pakawau coals (Rakopi Formation) and a Palaeocene nearshore marine facies would also explain why this oil contains higher plant markers indicative of both gymnosperms (retene, isopimarane etc.) and angiosperms (oleanane). An alternative explanation for the mixed character of the Maui oil is that the source rock was deposited under conditions which were transitional, both in terms of marine/terrestrial influence and floristic composition. Further speculation is not warranted here but a recent reappraisal of oil generation in the Taranaki Basin (Killops et al., this volume) should help to clarify the issue.

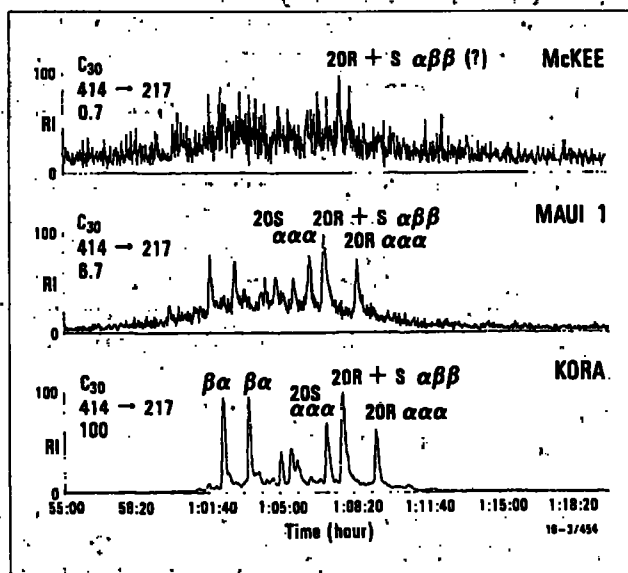


Fig. 6. MRM-GCMS chromatograms showing the presence of C_{30} ring A-desmethyl steranes (24-n-propyl cholestanes) in three oils from the Taranaki Basin. Annotation as for figure 3 except that diasteranes are marked as "β α " steranes.

Conclusions

The results of this study show that the Waipawa Black Shale is a possible and indeed likely source of two stain oils in the south of the East Coast Basin and, hence, that some part of the formation is oil mature. However, because no samples other than those from the Waipawa were analysed in this

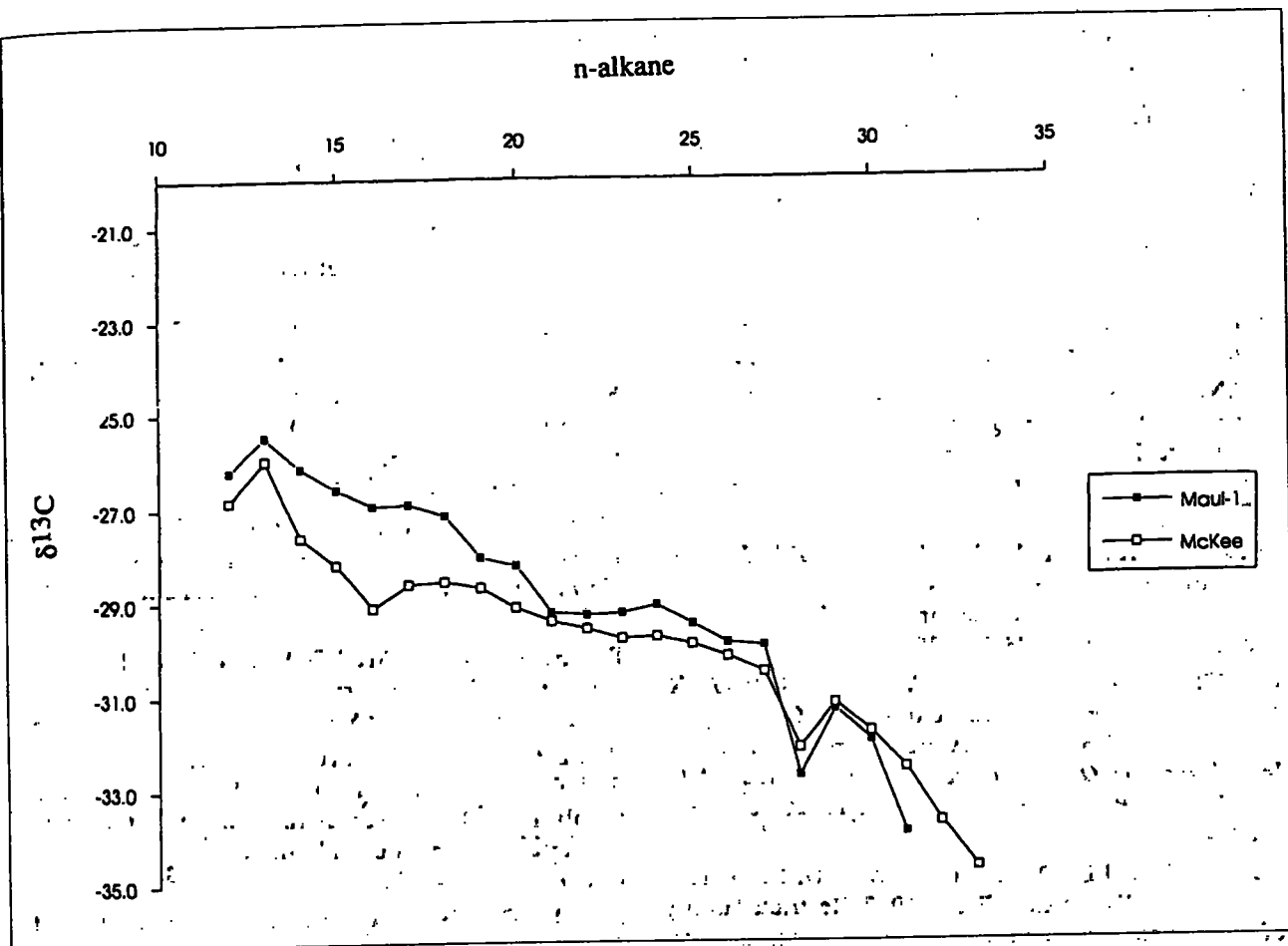


Fig. 7. n-Alkane isotope profiles for the Maui-1 and McKee oils of the Taranaki Basin.

study, we cannot entirely rule out the possibility that another, perhaps older formation was the source of the stains. Nevertheless, any alternative source would need to have the same, rather unusual, molecular and isotopic characteristics as the Waipawa. A time equivalent of the Waipawa Black Shale may also have contributed to oil generation in parts of the Taranaki Basin.

The Waitangi seep oil and those of similar type from the north of the East Coast Basin are chemically and isotopically distinct from the south basin stain oils and probably originate from a marine source rock of Cretaceous age.

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