# A COMPARISON OF SOME CRUDE OILS AND POTENTIAL SOURCE ROCKS OF THE EAST COAST BASIN, USING GEOCHEMICAL BIOMARKERS

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## Abstract

Organic geochemical biomarkers have been characterised from a selection of outcrop and oil seep samples from three regions of the East Coast, North Island, New Zealand.

Oils from the Rotokautuku and Waitangi seeps in the region north of Gisborne are shown to be mainly mature marine oils with a minor and less mature terrestrial component. The overall maturity is comparable to that of the terrestrial South Taranaki Basin oils.

Analyses of the extracts from possible source formations in inland Hawkes Bay show the organic material from Lower Miocene sediments of the lower Te Hoe River area to have a similar dominant marine character with a maturity comparable to the oil seeps. This mature organic component could represent a marine oil which has migrated into these formations. The nearby Eocene Wanstead Formation and Paleocene Rakauroa Formation are, however, much less mature and cannot be considered as a possible source.

In a wide area of southern Hawkes Bay and Wairarapa, oil impregnates various porous sandstone and fractured argillite formations ranging in age from Lower Cretaceous to Lower Miocene, and situated in structural settings of differing intensities. The maturity and marine character of the organic material extracted from the Lower Miocene formations from Westcott and the Paleocene Whangai Formation near Westcott are similar to that of the oil seeps north of Gisborne and the Lower Miocene formations in the Te Hoe area.

The results suggest a possible common source for this predominantly marine oil which has migrated into these particular formations and which also occurs as surface seeps. Such a source could be a Lower Cretaceous marine formation, with a minor terrestrial component, which has not yet been sampled, or a Lower Miocene formation which has been buried to sufficient depth for oil generation.

## Introduction

The East Coast Basin area (Figure 1) is one of the most stratigraphically and structurally complex sedimentary basins in New Zealand. The occurrence of various oil seeps and potential hydrocarbon-generative source rocks in the East Coast of the North Island has been known for a long time. A number of wells have been drilled but to date no commercial oil or gas accumulations have been found. Other aspects of the geology of the basin are favourable for petroleum exploration (Francis, 1991).

The most significant of the gas and oil seeps are those occurring at Rotokautuku, Waitangi and Totangi, north of Gisborne, which were known to exist before European settlement. Of these, Weston *et al.* (1988) have suggested that the Totangi and Waitangi seeps were sourced from a marginal marine rock.

Also, there are more than 30 recorded localities of oil-impregnated formations from Cretaceous to Miocene in age, in an area from north of Gisborne to southern Wairarapa. Aspects of the geochemistry of these formations have been reported by Jackson (1982) and Fry (1982).

Studies on the source-rock potential of the East Coast Basin suggest that the Eocene to Pliocene sediments have little, if any, source potential with TOC values much less than 1% (Fry, 1982; Jackson, 1982; and Moore, 1988). Generally the dark brown coloured Waipawa Black Shale of Paleocene age which comprises carbonaceous mudstones, has been considered as the most likely source rock. This

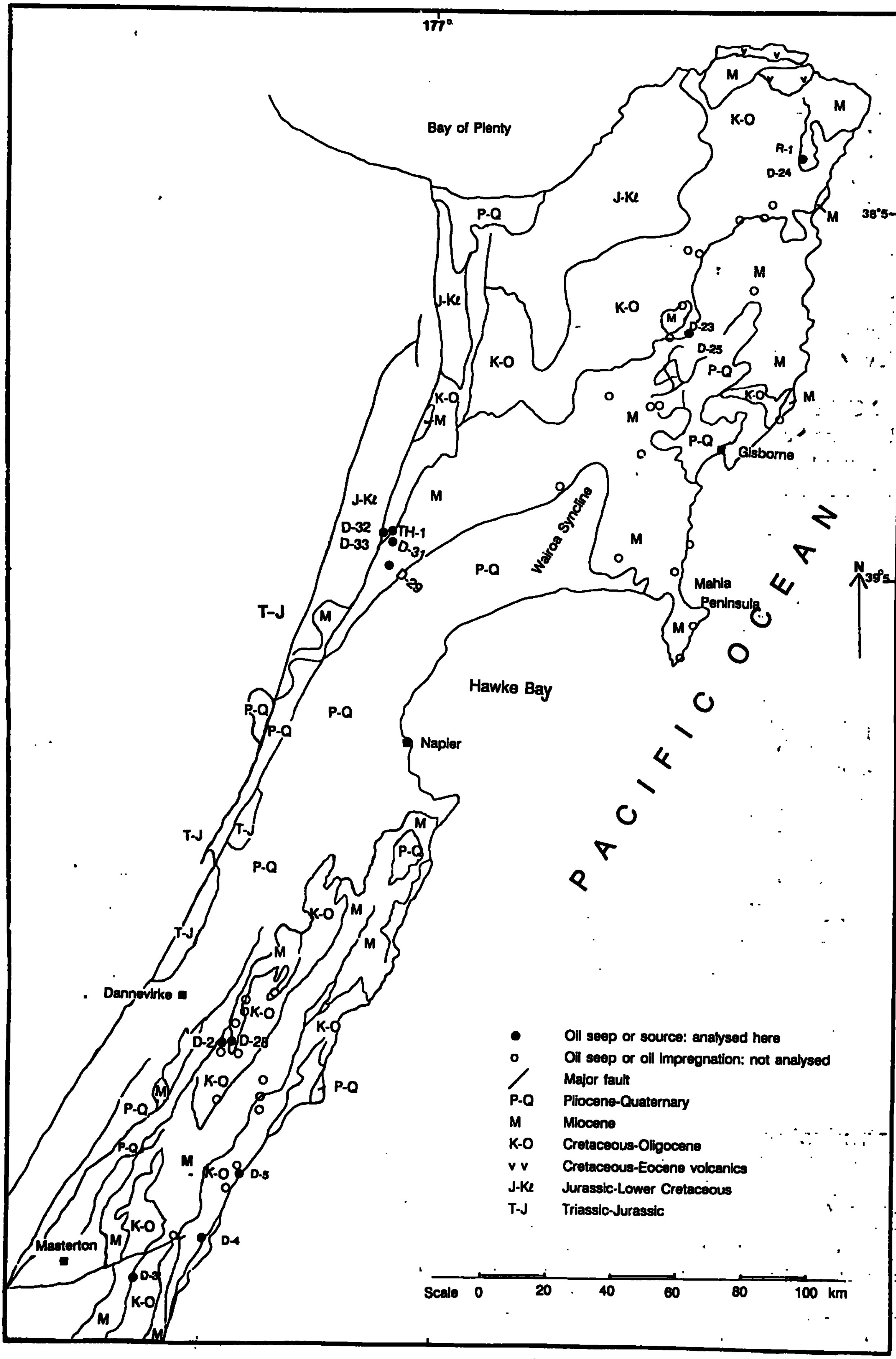


Figure 1: Map of the East Coast study area showing the essential geological formations and sample locations.

formation, with predominately marine type kerogen, has yielded TOC values of up to about 12% and averaging 6%. The oil-generating capacity ranges from about 4-22 kg/tonne (Moore, 1988). However outcrop samples have shown this Waipawa Black Shale to be regionally immature with vitrinite reflectances of about 0.3-0.4%, although the formation may reach suitably higher levels of maturity at greater depths of burial. The Late Cretaceous-Paleocene age Whangai Formation may also be considered as a source rock, and is generally immature to marginally mature. In localised areas, vitrinite reflectances greater than 0.6% have been recorded for this formation (Moore, 1988). It is possible that the Waipawa Black Shale or Whangai Formation sediments have been buried to sufficient depth to generate hydrocarbons, such as those observable as the gas and oil seeps (Figure 1).

This paper presents the results of a preliminary geochemical biomarker study examining the steranes and triterpanes (hopanes) of extracts from oil and sediment samples from three different areas in the East Coast Basin. The samples studied are from the Rotokautuku and Waitangi oil seeps from the area north of Gisborne, plus a number of oil-impregnated formations from the northern Hawkes Bay area and the area between Dannevirke and Masterton. The purpose of the study is to see if such biomarker characterisations and distributions can provide any further definitive information to identify the type and level of maturity of the kerogen or of the oils impregnating these formations, and to establish any correlation between the oil seeps and the formations.

The application of biomarker geochemistry to the study of oils and source rocks is well established (e.g. see Seifert and Moldowan, 1978, 1981; Mackenzie *et al.* 1982; Philp, 1985; Philp and Gilbert, 1987) and has been applied extensively to the Taranaki Basin area (Collier and Johnston, 1991; Johnston *et al.*, 1988, 1990, 1991). For the Taranaki Basin the biomarker data show that the oils and condensates are sourced from terrestrial coals and shales deep within the basin and have migrated to their present shallower reservoirs. The overall similarity in the biomarker distributions in the various Taranaki oils and condensates suggest that they have been generated under similar conditions and from equally similar source rocks. Since the East Coast Basin area is much more structurally and stratigraphically complex it appears unlikely that the overall model for oil generation in this basin would be as consistent as that which is apparent for the Taranaki Basin.

## Samples

Samples for this study were collected from the following seeps and oil-impregnated formations (Figure 1).

**Area 1 - North of Gisborne**

- R1, D24—Oil samples escaping from the shaft of the Rotokautuku-1 well located at, or near, the contact between Miocene and Cretaceous rocks in a structurally complex area. (This well was hand-dug near an oil seep to a depth of 145m in 1881-84).
- D25—Waitangi oil seep, exuding oil, gas and brine. Located on fault contact between gently dipping Lower Miocene and complex Paleocene-Oligocene rocks.

**Area 2 - Te Hoe area, Northern Hawkes Bay**

- TH-1—Rakauroa Formation (above Tahora Formation). Paleocene age.
- D32,D33—Middle Te Hoe river area. Samples collected from the Wanstead Formation (Eocene); D32—hard dark mudstone, D33—muddy glauconitic sandstone.
- D29,D31—Outcrop samples from the Lower Te Hoe river area. D29—Lower Miocene mudstone with a noticeable organic smell. D31—Lower Miocene siltstone with carbonaceous flakes.

**Area 3 - Southern Hawkes Bay-Wairarapa between Dannevirke and Masterton**

- D3—Kerosene Ridge, Blairlogie. Collected from fractured Lower Cretaceous rocks (Springhill and Gentle Anne Formations) immediately below the unconformity with overlying mid-Miocene sandstone.
- D2—Westcott, east of Dannevirke. Sample collected from porous oil-smelling glauconitic sandstone at the top of the Paleocene Whangai Formation.
- D4—Okau Stream, north of Castlepoint. Sample collected from porous oil-smelling greensand enclosed in the Paleocene Waipawa Black Shale, and in a steeply dipping sequence within a complex tectonic zone.
- D5—Kerosene Rock, on the coast south of the Owahanga River. Sample collected from porous oil-smelling glauconitic sandstone at the base of the Oligocene and unconformably overlying the Upper Cretaceous to Eocene formations, in an overturned sequence within a complex tectonic zone.
- D28 - Westcott, east of Dannevirke. Sample collected from porous Lower Miocene kerosene-smelling quartzo-feldspathic sandstone enclosed in siltstone, which unconformably overlies Upper Cretaceous to Oligocene formations. Nearby limestone, sandstone and greensand also smell of kerosene.

## Methods

The organic fractions of the samples were extracted using the procedures described by Johnston *et al.* (1988). The triterpane (hopane) and sterane biomarker distributions were determined by gas chromatography-mass spectrometry (gcms) using the m/z=191 and m/z=217 mass fragmentograms respectively. For some of the extracts, where the organic matter had not been biodegraded, it was possible to determine the relative abundances of the saturated alkane fractions using gas chromatography to give an estimate of the marine and/or terrestrial character of the organic material. Unfortunately for most samples the alkane distribution had been affected by biodegradation. Samples of Waipawa Black Shale collected for this study showed considerable biodegradation and it was not possible to determine their biomarker distributions. The comparisons made in this paper are therefore with the results obtained by Fry (1982) and Jackson (1982).

The maturation parameters typically used in triterpane and sterane biomarker studies have been well documented (e.g. see Seifert and Moldowan, 1978, 1981; Philp and Gilbert, 1987; Johnston *et al.*, 1988; Collier and Johnston, 1990). In summary the extent of maturation can be assessed from a consideration of the following (refer to Table 1, Figures 2 and 3a):

| | |
|---|---|
| **Steranes** | |
| 1 | $C_{27}$ (20S) 13β(H) 17α(H) diacholestane |
| 2 | $C_{27}$ (20R) 13β(H) 17α(H) diacholestane |
| 3 | $C_{27}$ (20S) 5α(H) 14α(H) 17α(H) cholestane |
| 4 | $C_{29}$ (20S) 24-ethyl 13β(H) 17α(H) dicholestane |
| 5 | $C_{27}$ (20R) 5α(H) 14β(H) 17β(H) cholestane |
| 6 | $C_{27}$ (20S) 5α(H) 14β(H) 17β(H) cholestane |
| 7 | $C_{27}$ (20R) 5α(H) 14α(H) 17α(H) cholestane |
| 8 | $C_{29}$ (20R) 24-ethyl 13β(H) 17α(H) dicholestane |
| 9 | $C_{29}$ (20S) 24-ethyl 5α(H) 14α(H) 17α(H) cholestane |
| 10 | $C_{29}$ (20S) 24-ethyl 5α(H) 14β(H) 17β(H) cholestane |
| 11 | $C_{29}$ (20S) 24-ethyl 5α(H) 14β(H) 17β(H) cholestane |
| 12 | $C_{29}$ (20R) 24-ethyl 5α(H) 14α(H) 17α(H) cholestane |
| **Triterpanes** | |
| A | 18α(H)-22,29,30 trisnorhopane ($T_s$) |
| B | 17α(H)-22,29,30 trisnorhopane ($T_m$) |
| C | $C_{29}$ 17α(H) 21β(H) norhopane |
| D | $C_{29}$ 17α(H) 21β(H) norhopane |
| D | $C_{29}$ 17α(H) 21α(H) normoretane |
| E | $C_{30}$ 17α(H) 21β(H) hopane |
| F | $C_{30}$ 17β(H) 21α(H) moretane |
| G,H | $C_{31}$ 22A, 22R 17α(H) 21β(H) homohopane |
| I,J | $C_{32}$ 22S, 22R 17α(H) 21β(H) bishomohopane |
| K,L | $C_{33}$ 22S, 22R 17α(H) 21β(H) trishomohopane |
| M | $C_{30}$ triterpane (unidentified - present in low maturity sediments) |
| N | $C_{29}$ 17β(H) 21β(H) norhopane |
| O | $C_{30}$ 17β(H) 21β(H) hopane |

Table 1: Identification of Sterane, Diasterane and Hopane Biomarker Peaks in the GCMS Mass Fragmentograms (as shown in Figures 2 and 3a)

**Low Levels of Maturity**

(i) The presence of 17β(H),21β(H) norhopanes and hopanes (peaks N, O).

(ii) The presence of the unidentified $C_{30}$ triterpane (peak M).

**Increasing Levels of maturity**

(i) The depletion of 17β(H)21β(H) norhopanes, mortanes and the unidentified $C_{30}$ triterpane.

(ii) A decrease in the 17β(H)21α(H) mortane / 17 (H)21β(H) hopane ratio (peaks D/C and F/E).

(iii) An increase in the S/S+R ratio of the $C_{31}$ and higher order hopanes, to a value of 60% at the base on the oil-generation window (peaks G/G+H, I/I+J, K/K+L).

(iv) An increase in the S/S+R ratio for the 5α(H)14 β(H)17β(H)$C_{27}$, ($C_{28}$) and $C_{29}$ steranes, to a value of about 50% in the middle of the oil-generation window (peaks 3/3+7, 9/9+12).

(v) An increase in the content of the 5α(H)14β(H)17β(H) steranes to the total 5α(H)14α(H)17α(H) + 5α(H)14β(H)17β(H) steranes (peaks 5+6/3+5+6+7, 10+11/9+10+11+12). This ratio, which is referred to as the %ββsteranes, increases to a value of about 75% towards the upper levels of the oil-generation window.

**Source Characterisation**

In addition, geochemical biomarkers can be used to provide an assessment of the marine or terrestrial nature of the source material and produced hydrocarbons. The marine nature is reflected by the relative predominance of $C_{27}$ steranes and diasteranes over the respective $C_{29}$ members. Also the presence of specific biomarker components such as oleanane are indicative of terrestrial origin.

## Results and Discussion

In general the alkane, triterpane and sterane distributions for the oil seeps and for the organic extracts from the East Coast formations studied here, are significantly different from those oils and possible source rocks of the Taranaki Basin area (Johnston *et al.*, 1988, 1990; Collier and Johnston 1990). The most notable feature is that the Taranaki Basin samples are terrestrial and have a predominance of $C_{29}$ steranes and diasteranes, whereas the East Coast samples are mainly marine in character with a small terrestrial component, as shown by the bimodal nature of the saturated alkane distributions and the predominance of $C_{27}$ steranes and diasteranes. The odd-even predominance of the alkane distributions, where measurable, show the marine components to be more mature than the minor terrestrial component. In addition, if it is assumed that the $C_{27}$ steranes essentially reflect the marine components and the $C_{29}$ steranes reflect the terrestrial components, a consideration of the S/S+R ratio and the %ββvalues for the $C_{27}$ and $C_{29}$ steranes confirm this greater maturity for the marine components. The detailed geochemical biomarker data for each area are discussed below.

**Area 1: North of Gisborne**

The biomarker data show that both the Rotokautuku and Waitangi oils are predominately marine in character. The saturated alkane distributions show the dominant marine component to be significantly more mature than the minor terrestrial component. The sterane distributions for both oils show that the $C_{27}$ sterane and diasterane components occur in significantly greater abundance than the $C_{29}$ steranes and diasteranes, which indicates a dominant marine source (Figure 2). It is unlikely that this terrestrial component is related to the source of the oil, but rather is probably a contaminant from sediments through which the oil has migrated.

As discussed above, a consideration of the $C_{27}$ %ββsteranes compared with the $C_{29}$ %ββvalues shows that the dominant marine component in the Rotokautuku oil is more mature than the terrestrial component. For the Waitangi seep the dominant marine component has a similar level of maturity to that of the Rotokautuku oil but the minor terrestrial component is slightly more mature in the Waitangi seep. This result suggests either these oils have a slightly different source or that they have migrated through different sedimentary formations to their present locations.

The triterpane distributions also indicate these oils to be mature, and although mainly marine in nature, they have a maturity level comparable to that of the Taranaki Basin oils. This is particularly evident for the Rotokautuku sample, but is more difficult to assess fully for the Waitangi samples because of the biodegradation present.

It is of considerable interest to note that both the maturity and source biomarker data for these two oil seep samples match closely those data from the Westcott samples D2 (collected from the Paleocene glauconitic sandstones at the top of the Whangai Formation) and D28 (collected from the Lower Miocene sandstone). There is no such similarity with the more organic rich but much less mature D4 sample of glauconitic sandstone enclosed in the Waipawa Black Shale

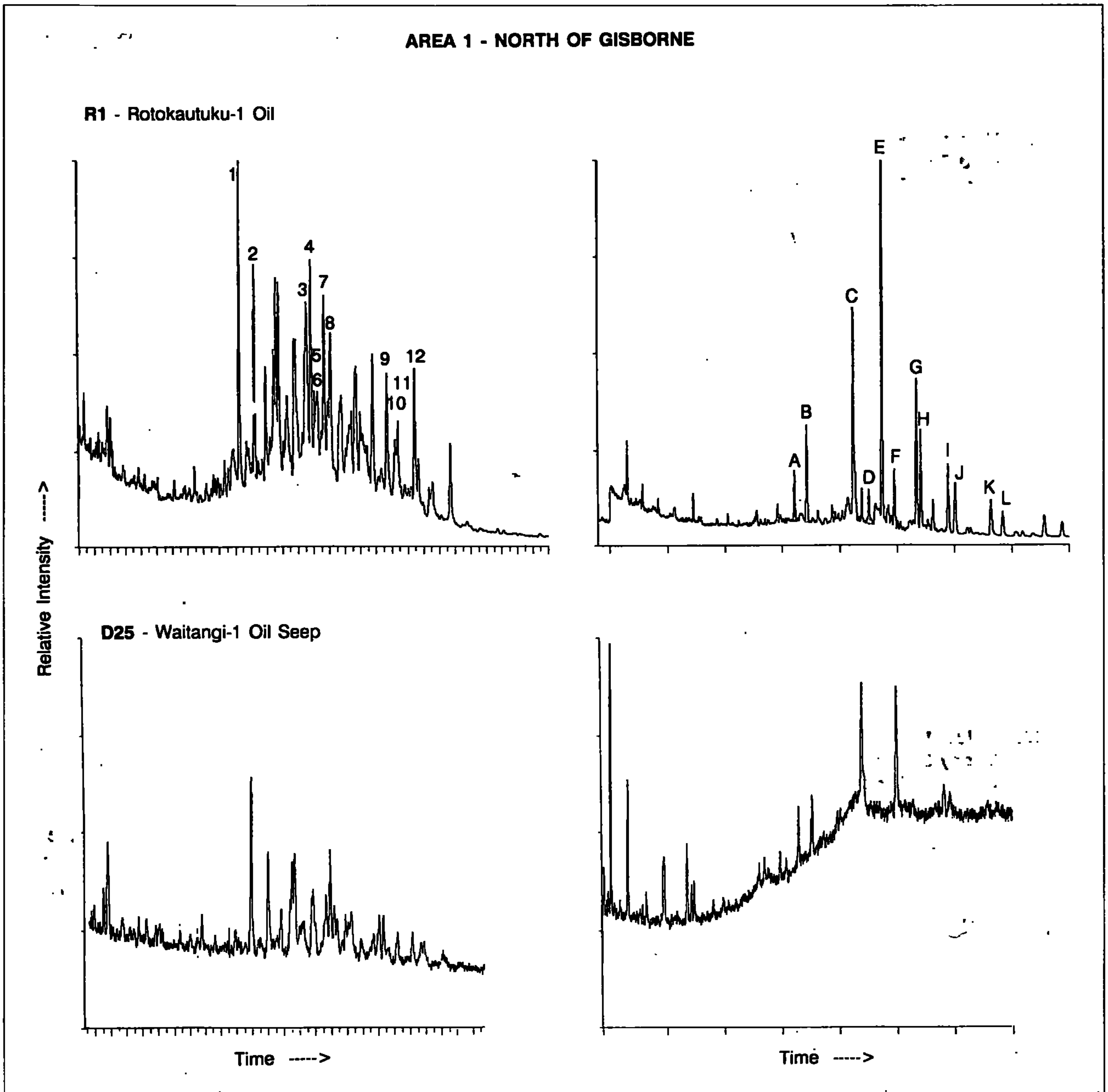


Figure 2: Sterane and triterpane gcms mass fragmentograms for the Rotokautuku and Waitangi oil seeps, Area 1 North of Gisborne. The peak identifications are given in Table 1.

sample studied here, or with the Waipawa Black Shale sample reported by Fry (1982). This suggests the Paleocene-Late Cretaceous Whangai formation or similar could be the source for the Rotokautuku and Waitangi oil seeps rather than the Paleocene Waipawa Black Shale. The presence of minor terrestrial biomarkers suggest a small terrestrial component in dominantly marine formations.

**Area 2: Te Hoe, Northern Hawkes Bay**

Biomarker data (Figure 3b) for the TH-1 sample from the Rakauroa Formation show a greater predominance of $C_{27}$ steranes and diasteranes compared with $C_{29}$ steranes suggesting stronger marine character than for the Area 1 samples. It is also significant that for TH-1 the S/S+R and %ββ ratios of the $C_{29}$ steranes show this minor terrestrial component to be much more mature than the dominant marine component (compare the $C_{27}$ steranes). The maturity level of the terrestrial component is comparable to that of the deep Pakawau coals and oils of the Taranaki Basin (Johnston and Collier, 1991). The marine component is much less mature as shown by the low S/S+R ratio and %ββvalue for the $C_{27}$ steranes. The low level of maturity is also evident from the presence of ββ hopanes (Figure 3a), which indicate a maturation level consistent with that of late diagenesis or early catagenesis and hence lower than that required for oil generation.

The D32 and D33 samples from the Eocene Wanstead Formation are similar to the Rakauroa Formation (TH-1), also showing both marine and terrestrial characters (Figures 3a and 3b). However there is a greater abundance of the $C_{29}$ steranes relative to the $C_{27}$ steranes in the D32 and D33 samples than there is in the TH-1 sample, thereby indicating a larger terrestrial component in D32 and D33. The low S/S+R ratio and %ββ values show both the marine and terrestrial components to be of low maturity, which is again confirmed by the presence of ββ hopanes (Figure 3a).

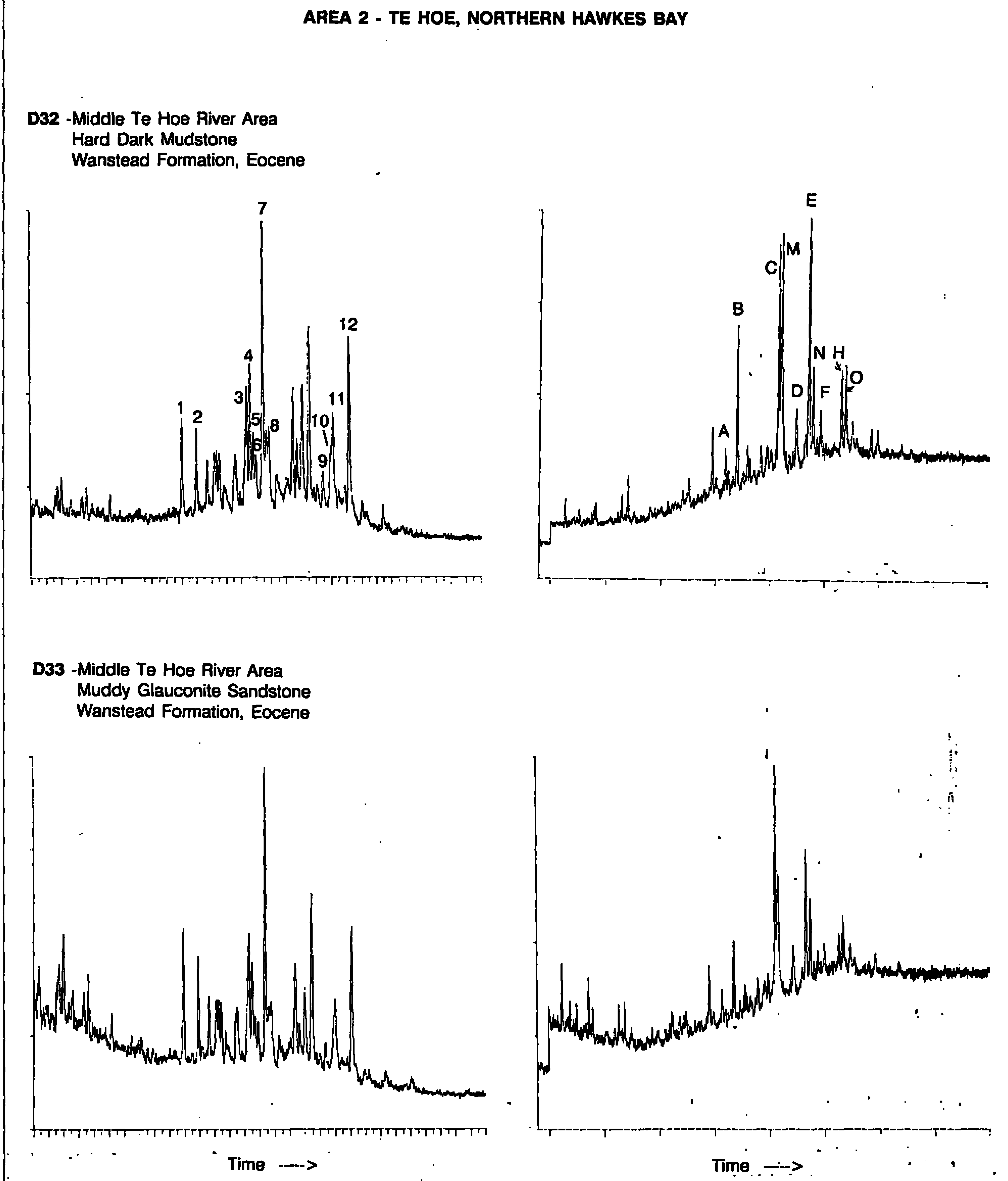


Figure 3a: Sterane and triterpane gcms mass fragmentograms for extracts of outcrop samples from Area 2 - Te Hoe and Northern Hawkes Bay: D32 and D33. The peak identifications are given in Table 1.

It is interesting that ßß hopanes have not been observed in any of the coals or terrestrial shales of the Kapuni or Pakawau formations of the South Taranaki Basin, even at low levels of maturity (shallow depths) and comparable sterane S/S+R ratios and %ßß values. However, such ßß hopanes have been reported previously in samples from various formations in the East Coast area (Fry, 1982; Jackson, 1982). This difference probably reflects the corresponding difference between the source types for these two basins.

It is therefore unlikely that the Eocene Wanstead or Rakauroa formations can be considered as potential source rocks.

In contrast, the samples D29 and D31 from the Lower Miocene of the Te Hoe River area are much more mature than the above Area 2 samples, as shown by the higher sterane S/S+R ratios and %ßß values, absence of hopanes and the higher S/S+R hopane ratios. (Figure 3a). Both D29 and D31 have a greater abundance of $C_{27}$ steranes and

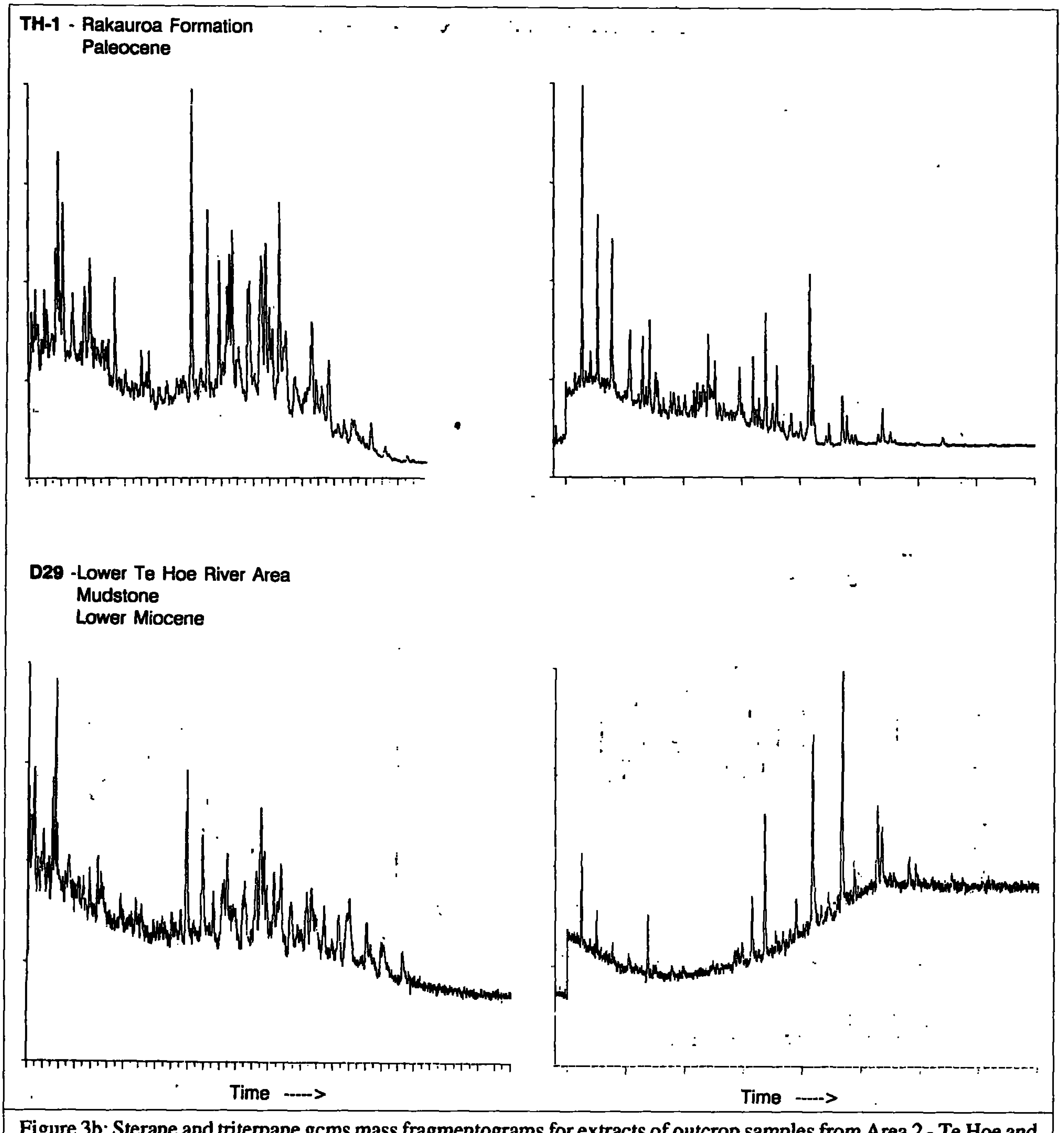


Figure 3b: Sterane and triterpane gcms mass fragmentograms for extracts of outcrop samples from Area 2 - Te Hoe and Northern Hawkes Bay: TH-1 and D29. The peak identifications are given in Table 1.

diasteranes than $C_{29}$, which again reflects a dominant marine character. The biomarker distributions of the D29 and D31 samples are in fact similar to those of the Rotokautuku and Waitangi oil seeps, which suggests a marine oil similar to that of the seeps has migrated through the Lower Miocene formations. Alternatively, but much less likely, these Lower Miocene formations could be considered as a possible source for the East Coast oil seeps, in particular those from Rotokautuku and Waitangi (Figures 2 and 3a).

The high maturity of the extracts from the Miocene formations compared to the low maturity for the Eocene formations in the same general area is problematical, and suggests there is preferential migration of a predominantly marine oil into these Miocene sediments, from a greater depth in the basin to the east.

**Area 3: Southern Hawkes Bay–Wairarapa between Dannevirke and Masterton**

The biomarker distributions of the two Westcott samples, D2 and D28 (Figures 4a and 4b), collected east of Dannevirke, are essentially identical, even though D2 is a glauconitic sandstone from the Paleocene Whangai Formation and D28 is a Lower Miocene sandstone. Both samples show dominant mature marine components, together with minor terrestrial components (Figures 4a and 4b). The $C_{27}$ steranes and diasteranes are also much more abundant than the $C_{29}$ counterparts. Both samples possess kerosene/oil smells. The results therefore collectively suggest the same, or very similar, oils from predominately a marine source have migrated into these Paleocene and Lower Miocene formations. The extracts studied here represent migrated oil

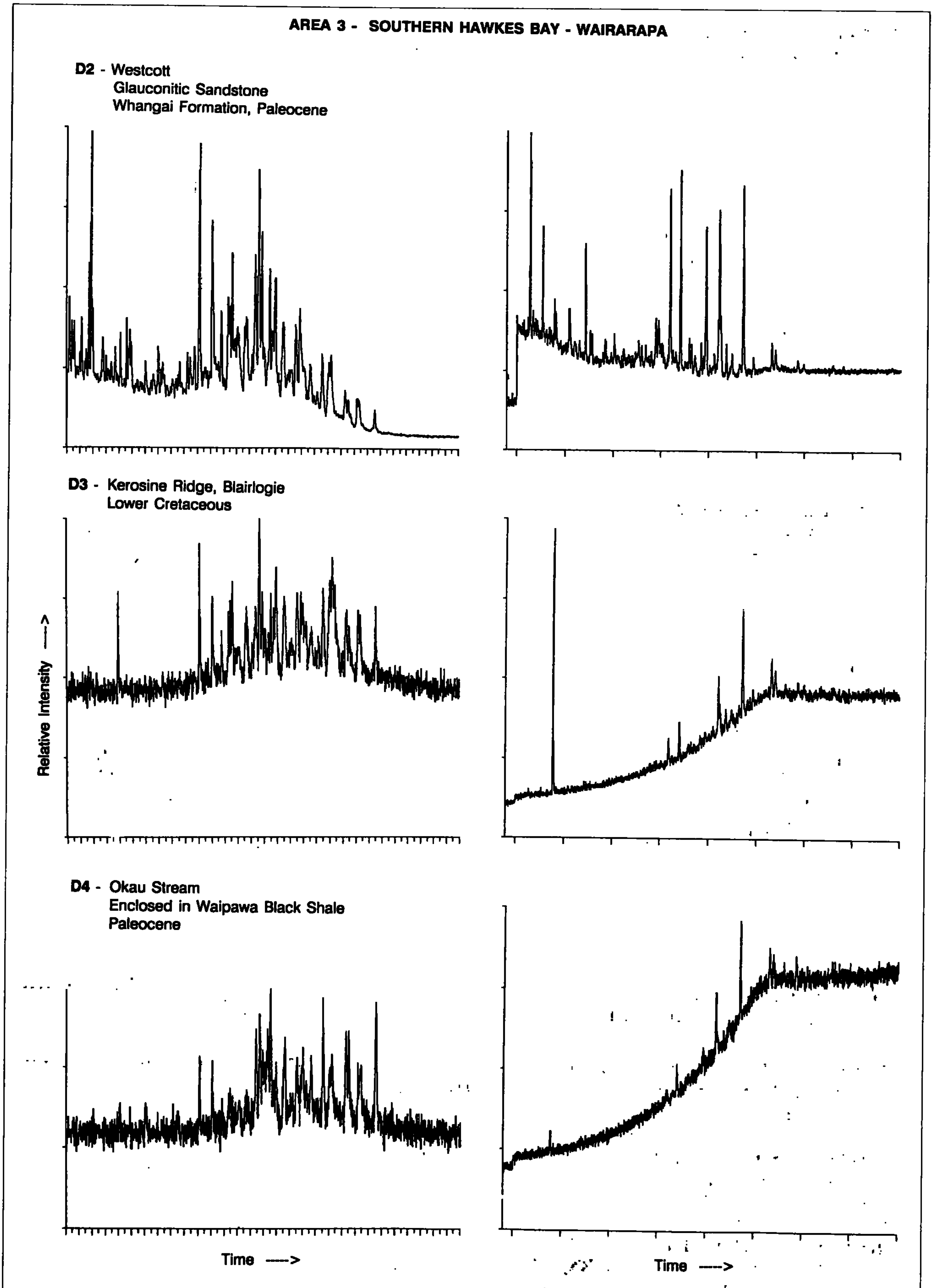


Figure 4a: Sterane and triterpane gcms mass fragmentograms for extracts of outcrop samples from Area 3 - Southern Hawkes Bay - Wairarapa: D2, D3, D4; Waipawa Black Shale (after Fry, 1982).

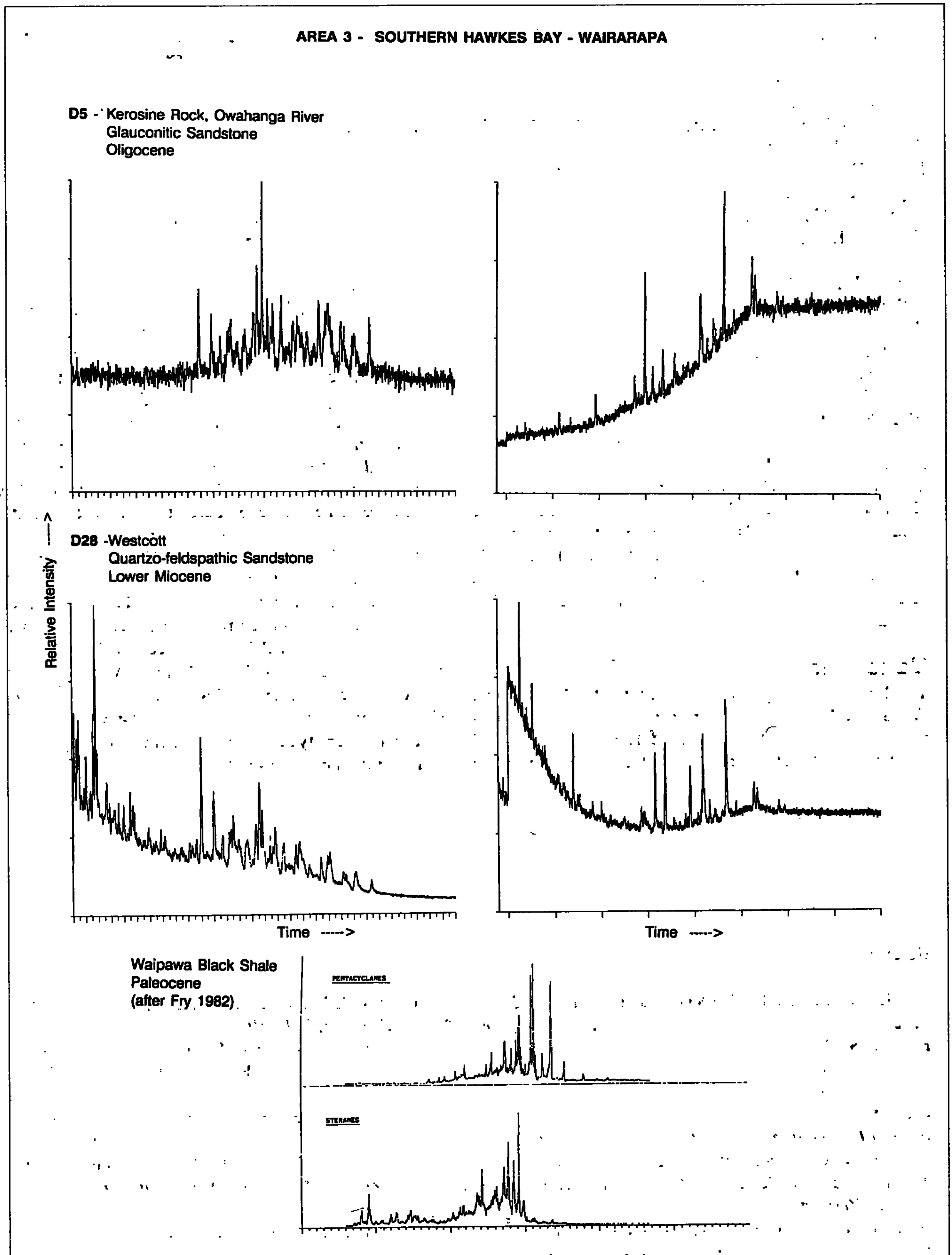


Figure 4b: Sterane and triterpane gcms mass fragmentograms for extracts of outcrop samples from Area 3 - Southern Hawkes Bay - Wairarapa: (b) D5, D28, Waipawa Black Shale (after Fry, 1982).

rather than the *in situ* organic matter of the sediments themselves. It is also significant to note that the biomarker data for the extracts from the Lower Miocene (D29 and D31) sediments of the Lower Te Hoe River Area 2, are very similar to those data for the Lower Miocene sandstone D28 from the Westcott Area 3.

The maturity level of the extracts from D2 and D28 is again comparable to that of the Rotokautuku and Waitangi oil seeps. Interestingly, the $C_{29}$ steranes show slightly different levels of maturity for the more terrestrial component in these Westcott samples to those of the Rotokautuku and Waitangi oil seeps. This difference probably reflects the different migration pathways for the mature marine oil. The D2 and D28 samples show the highest level of maturity for any of the suite of samples studied in this paper.

Sample D3 collected from the Lower Cretaceous rocks at Kerosene Ridge, Blairlogie, also shows the same marine character, but with a slightly larger terrestrial component than the D2 and D28 Westcott samples (Figures 4a and 4b). In the D5 sample from the Oligocene Formation at Kerosene Rock, the marine component is again dominant, but this time both the marine and terrestrial components appear mature.

The D4 sample from the Okau Stream which is a porous oil-smelling greensand enclosed in the Paleocene Waipawa Black Shale is also of similar marine/terrestrial character. The terrestrial component is more pronounced and much less mature than the D2 Westcott formation (Figures 4a and 4b). However, the $C_{27}$ sterane distribution is similar to the above samples for Area 3. Also, the sterane and triterpane biomarker data for this D4 sample are significantly different to those of the very much less mature Waipawa Black Shale reported by Fry (1892) (Figure 4b). The results again suggest that a predominately marine oil, sourced elsewhere, has migrated into this sandstone.

## Conclusion

This biomarker study has shown that the Rotokautuku and Waitangi oil seeps are predominantly mature marine oils with a minor terrestrial components. The maturity level and biomarker distributions match most closely those of the organic extracts obtained from the oil/kerosene-smelling samples of Lower Miocene formations from Westcott and the Te Hoe area, and are also similar to the Paleocene Whangai formation near Westcott. These results collectively suggest a mature marine oil with a probable common source and generated elsewhere, has migrated through the Miocene and Paleocene sediments.

Conversely, biomarker data from extracts of the Waipawa Black Shale, Eocene Wanstead Formation and Paleocene Rakauroa Formation show these formations, as sampled at surface outcrops, to have maturities less than that required for the onset of oil generation, and are therefore unlikely to be the source of this oil.

If the Rotokautuku and Waitangi oil seeps, together with the oil migrated into the Te Hoe Miocene and the formations of Area 3, have a common source, then this source could be a Lower Cretaceous marine (and minor terrestrial) formation which has not yet been sampled, with the oil migrating into all the younger formations. Alternatively, the Rotokautuku and Waitangi seeps could be derived from mature Miocene rocks, and the Te Hoe Miocene samples may, in places, be mature sources. Major overthrusting in Area 3 could have buried the same Miocene source to sufficient generation depth. This is possible given the complex regional tectonic pattern of the East Coast Basin area. However, there is still an unanswered question in the Te Hoe area where the Miocene extracts are more mature than the Paleocene-Eocene, unless migration has occurred more easily in the Miocene formations than in the Paleocene-Eocene and oil has moved 50km or so up-dip from the depths of the Wairoa Syncline.

A more comprehensive biomarker study of this East Coast Basin has commenced to extend the work presented here and to identify the likely source rocks for oil generation and migration pathways in this basin.

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