PS Chemometric Classification of Terrestrial Oil Families in Taranaki Basin, New Zealand: Higher Plant Trends and Migration Contamination Effects*

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Abstract

Chemometric analysis of biomarker parameters for more than 200 terrestrial (coal-sourced) oil and gas condensate samples from almost all fields and reservoir zones in Taranaki Basin (New Zealand) has led to an improved classification of genetic oil families but has also identified biomarker contamination effects from entrainment of bitumen during migration. Mid-Cretaceous to Eocene coaly source rocks in Taranaki Basin display broad stratigraphic trends in di- and triterpane distributions that reflect the evolutionary development of higher plants on the Zealandia continent (Killops et al. 1995, 2003). Woody gymnosperm biomass input to coal-forming mires is indicated primarily by the diterpane isopimarane, whereas woody angiosperm input is indicated by the triterpanes oleanane and the ring-A degraded counterparts of oleanane, lupane, and ursane. Stratigraphic changes in the relative abundances of these biomarkers indicate a coal-forming flora relatively poor in total higher plants (i.e., woody gymnosperms and angiosperms) in the mid-Cretaceous to Early Haumurian (Late Cretaceous; c. 100–79 Ma), changing to one dominated by gymnosperms in the Late Haumurian (latest Cretaceous; c. 79–66 Ma), then transitioning to a dominance of angiosperms by the Eocene. In this study, these changing terpane distributions have been utilised in hierarchical cluster and principal component analysis of source-related biomarkers to identify four tribes and seven families of terrestrial oils and gas condensates in Taranaki Basin: one tribe and family derived from the Early Haumurian; one tribe and family from the Late Haumurian; one tribe of two families from the Paleocene–Eocene; and one tribe of three families from the Eocene. Through an iterative process, parameters were selected to minimise non-source-related variations caused by, for example, differences in fluid volatility (i.e., oils vs condensates), maturity, and biodegradation. The resulting oil (and condensate) families model displays strong geographic coherency and provides first-order oil-oil and oil-source rock correlations. However, clear reservoir unit and facies-related trends indicate second-order entrainment of triterpanes and tricyclic terpanes (cheilanthanes) during migration and entrapment, highlighting the need for caution when using such models for correlation at a more detailed level; e.g., for charge analysis.

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CHEMOMETRIC CLASSIFICATION OF TERRESTRIAL OIL FAMILIES IN TARANAKI BASIN, NEW ZEALAND: HIGHER PLANT TRENDS AND MIGRATION CONTAMINATION EFFECTS

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1. INTRODUCTION

Biomarker correlations indicate that mid-Cretaceous to Eocene coaly rocks are the major sources of oil and gas-condensate accumulations in Taranaki Basin (**Figs 1–3**; e.g., Sykes et al. 2012). Broad stratigraphic trends in di- and triterpane distributions through the main coal measure intervals reflect the evolutionary development of higher plants on the Zealandia continent (Killops et al. 1995, 2003). Gymnosperm biomass input to coal-forming mires is indicated primarily by the diterpane isopimarane, whereas angiosperm input is indicated by the triterpanes oleanane and the ring-A degraded counterparts of oleanane, lupane, and ursane. Stratigraphic changes in the relative abundances of these biomarkers indicate a coal-forming flora relatively poor in total higher plants (i.e., gymnosperms and angiosperms) in the mid-Cretaceous to Early Haumurian (Late Cretaceous; c. 100–79 Ma), changing to one dominated by gymnosperms in the Late Haumurian (latest Cretaceous; c. 79–66 Ma), then transitioning to a dominance of angiosperms within the Eocene. These and other stratigraphic changes in biomarker distributions provide time-stamped fingerprints that can be used to infer coaly source rock age and facies and establish oil-oil correlations.

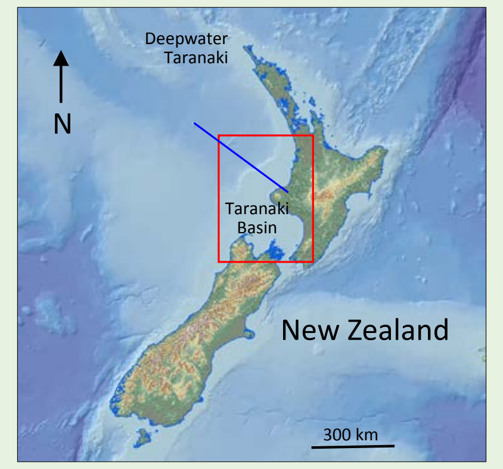

Figure 1 Location of Taranaki Basin. Blue line indicates approximate line of section in **Figure 2**; red box indicates location of paleogeographic maps in **Figure 3**.

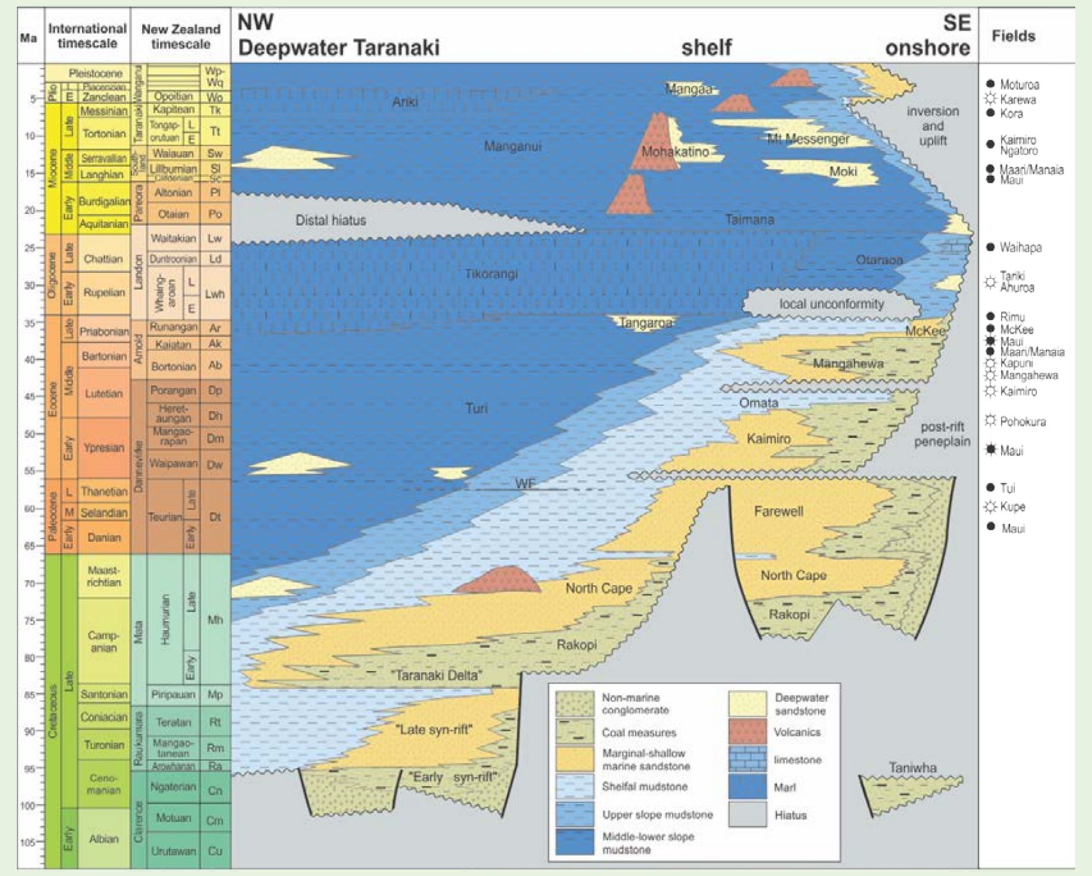

Figure 2 Representative stratigraphic section for Taranaki Basin from NW to SE (**Fig. 1**), highlighting the distribution of mid-Cretaceous (Taniwha Formation) to Late Eocene (Mangahewa Formation) coaly source rock formations in green (Strogen et al. 2017). Mid-Cretaceous to Paleocene coal measures were deposited during the basin rifting phase; Eocene coal measures were deposited during passive subsidence. Key reservoirs are indicated for selected fields in column on right.

Study objective

Employ chemometric analysis of biomarker parameters to develop a robust oil family classification of terrestrial (i.e., coal-sourced) oils and gas condensates in Taranaki Basin for use in oil-oil and oil-source rock correlation.

Scope

This study focuses solely on Taranaki terrestrial oils and condensates. A sub-commercial marine-sourced oil accumulation occurs in the north of the basin (Kora Field), and sub-commercial accumulations, seeps, and shows of terrestrial and marine oils have been extensively analysed from several other New Zealand basins (Sykes et al. 2012). These fluids are not included in this study.

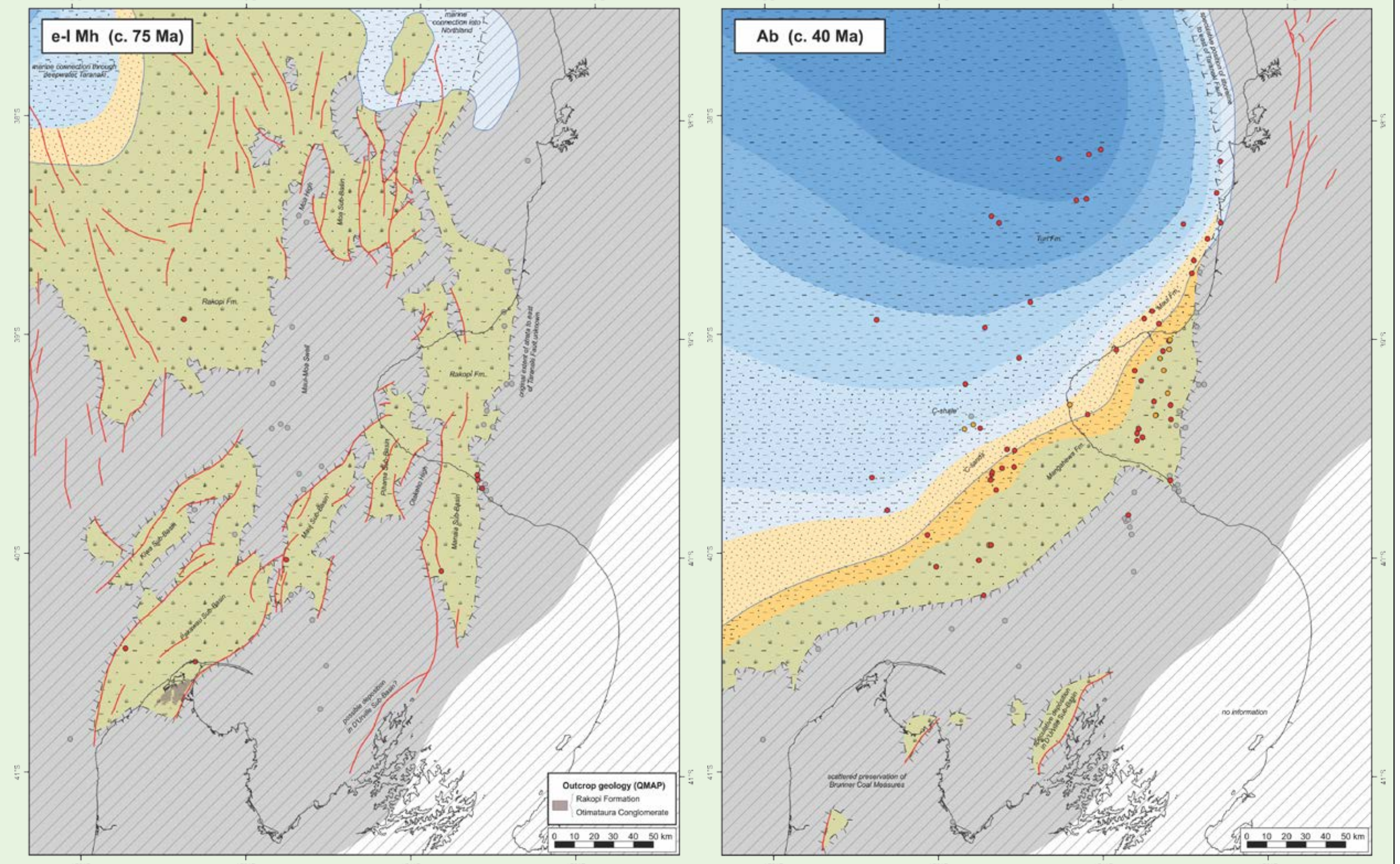

Figure 3 Paleogeographic reconstructions of Taranaki Basin at c. 75 Ma (Early–Late Haumurian) and 40 Ma (Middle Eocene) depicting the broad depositional settings of two of the major coaly source rock units, the Late Cretaceous Rakopi Formation and Middle–Late Eocene Mangahewa Formation (Strogen et al. 2011). Frequent and widespread inundation of variably brackish waters across the low-lying coastal plains influenced the bulk geochemistry, biomarkers, and petroleum potentials of coaly rocks within these and the other coal measure formations (e.g., Sykes et al. 2014).

2. SAMPLES AND METHODS

Samples

- >150 coaly rocks (coals, shaly coals, and coaly mudstones) and carbonaceous, coastal facies mudstones of Jurassic to Eocene age covering all main coal measure formations and from immature to near the end of the gas window [Rank(S_r) 6.1–18.9, R_o 0.45–2.6%, T_{max} 410–537°C].
- >200 terrestrial oil and condensate samples from essentially all fields and key reservoir intervals within the basin (**Figure 2**). The samples comprise a wide range of fluid type from solid, waxy oils to gas condensates (**Figure 4**). Very light condensates with <10 ppm steranes were not included in the chemometric model in order to reduce solubility effects on biomarker parameters. Multiple samples from individual fields and reservoirs were used to increase the reliability of the final chemometric model.

Geochemical methods

- Solvent extraction of rocks to recover extractable organic matter (EOM) fractions. EOM, oil, and condensate samples then de-asphalted.
- Medium pressure liquid chromatography to recover saturated and aromatic hydrocarbon fractions.
- Whole-oil and EOM fractions analysed by gas chromatography with flame ionisation detection (GC-FID) for hydrocarbon distributions.
- Combined saturated and aromatic hydrocarbon fractions analysed by gas chromatography-mass spectrometry (GC-MS) for biomarkers.
- All geochemical analyses of source rock and fluid samples were undertaken by a single laboratory (Applied Petroleum Technology, Norway) to maximise comparability of biomarker data for chemometric analysis.

Chemometric methods

- Approximately 80 source-related biomarker parameters were derived for the source rocks and fluids.
- Parameters were evaluated and chemometric analysis undertaken using *Pirouette* v. 4.5 (Infometrix Inc). The multi-plot function was used to screen out parameters significantly influenced by maturity, differences in fluid volatility (i.e., oils versus condensates), or biodegradation.
- Hierarchical cluster analysis (HCA) was conducted using autoscale pre-processing, Euclidean metric distance, and incremental linkage.
- Principal component analysis (PCA) was undertaken using autoscale pre-processing.
- Parameters with low modelling power (i.e., small loadings on Factors 1–3) were eliminated through numerous iterations of HCA and PCA to arrive at a set of 15 parameters that provides robust, source-based discrimination of oil tribes and families.

Figure 4 Selection of oil and condensate samples used in the study.

3. SOURCE-RELATED BIOMARKER COMPOUNDS AND PARAMETERS

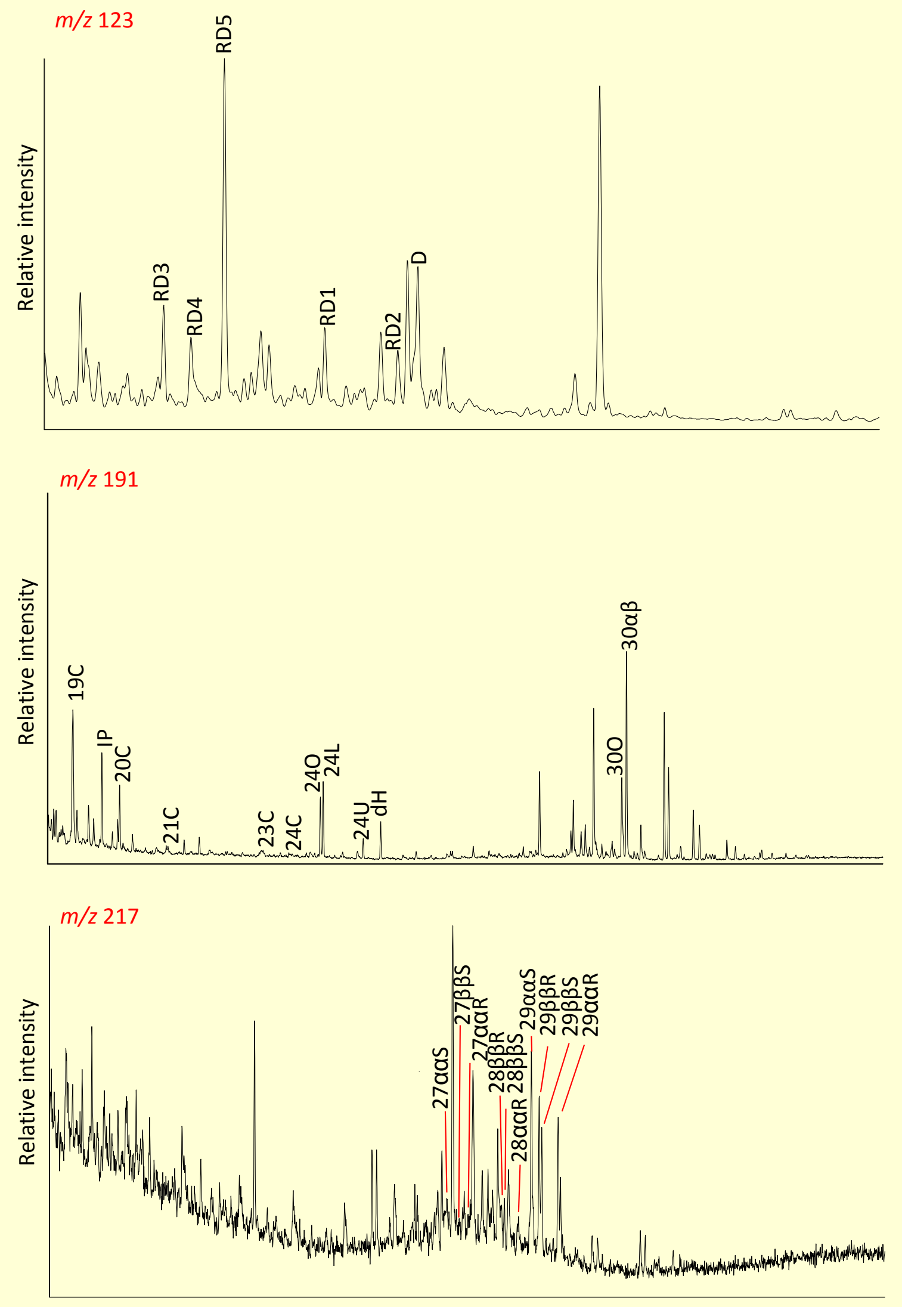

Figure 5 Mass fragmentograms (*m/z* 123, 191, 217) for sample Kahili-1B-ST1 (condensate) with peak identifications of biomarkers used in the HCA/PCA multivariate model.

Peak identifications

m/z ion 123

RD3	Rearranged drimane #3
RD4	Rearranged drimane #4
RD5	Rearranged drimane #5
RD1	Rearranged drimane #1
RD2	Rearranged drimane #2
D	8β-drimane

Note the marine-derived C_{21}, C_{23}, and C_{24} cheilanthanes (tricyclic terpanes) are no longer used in the chemometric model but are referred to in Figure 14 in relation to migration contamination.

m/z ion 191

19C	$C_{19}H_{34}$ tricyclic terpane
IP	Isopimarane
20C	$C_{20}H_{36}$ tricyclic terpane
21C	$C_{21}H_{38}$ tricyclic terpane
23C	$C_{23}H_{42}$ tricyclic terpane
24C	$C_{24}H_{44}$ tricyclic terpane
dO	10β-de-A-oleanane
dL	10β-de-A-lupane
dU	10β-de-A-ursane
dH	$C_{24}H_{42}$ tetracyclic terpane
30O	18α-oleanane
30αβ	17α, 21β-hopane

m/z ion 217

27ααS	5α, 14α, 17α, 20(S)-cholestane
27ββS	5α, 14β, 17β, 20(S)-cholestane
27ααR	5α, 14α, 17α, 20(R)-cholestane
28ααS	24-methyl-5α, 14α, 17α, 20(S)-cholestane
28ββR	24-methyl-5α, 14β, 17β, 20(R)-cholestane
28ββS	24-methyl-5α, 14β, 17β, 20(S)-cholestane
28ααR	24-methyl-5α, 14α, 17α, 20(R)-cholestane
29ααS	24-ethyl-5α, 14α, 17α, 20(S)-cholestane
29ββR	24-ethyl-5α, 14β, 17β, 20(R)-cholestane
29ββS	24-ethyl-5α, 14β, 17β, 20(S)-cholestane
29ααR	24-ethyl-5α, 14α, 17α, 20(R)-cholestane

Biomarker parameters in HCA/PCA model

Gymnosperm input parameters

IP2	IP/(IP+20C)
IP2a	IP/(IP+19C+20C)
IP4	IP/(IP+19C)

Angiosperm input parameters

A1	30O/(30O+30αβ)
A17	(dO+dL+dU)/(dO+dL+dU+dH)
A18	(30O+dO+dL)/(30O+dO+dL+30αβ)

Total higher plant input parameters

IPA1	(IP+dO+dL+dU)/(IP+dO+dL+dU+19C+20C)
IPA4	(IP+dO+dL+dU)/(IP+dO+dL+dU+19C)
IPA5	(IP+dO+dL+dU)/(IP+dO+dL+dU+20C)

Marine influence parameters

S13	$C_{27}/(C_{27}+C_{28}+C_{29})$ ααR+ααS+ββS steranes
S15	$C_{29}/(C_{27}+C_{28}+C_{29})$ ααR+ααS+ββS steranes

Drimane parameters

D1	RD3/(RD5+RD3)
D2	RD5/(RD3+RD4+RD5)
D3	RD2/(RD2+D)
D4	(RD1+RD2)/(RD1+RD2+D)

4. CHEMOMETRIC MODEL AND HIGHER PLANT BIOMARKER TRENDS

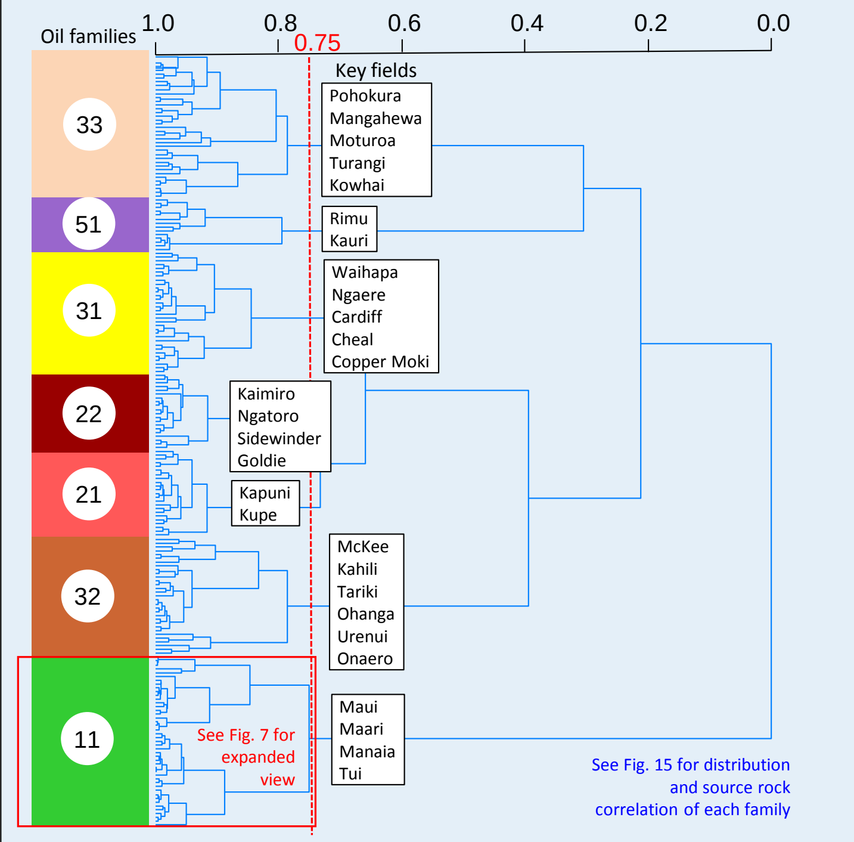

Figure 6 HCA dendogram for 203 Taranaki oil and condensate samples, defining four tribes and seven families of terrestrial oils at a similarity index of 0.75.

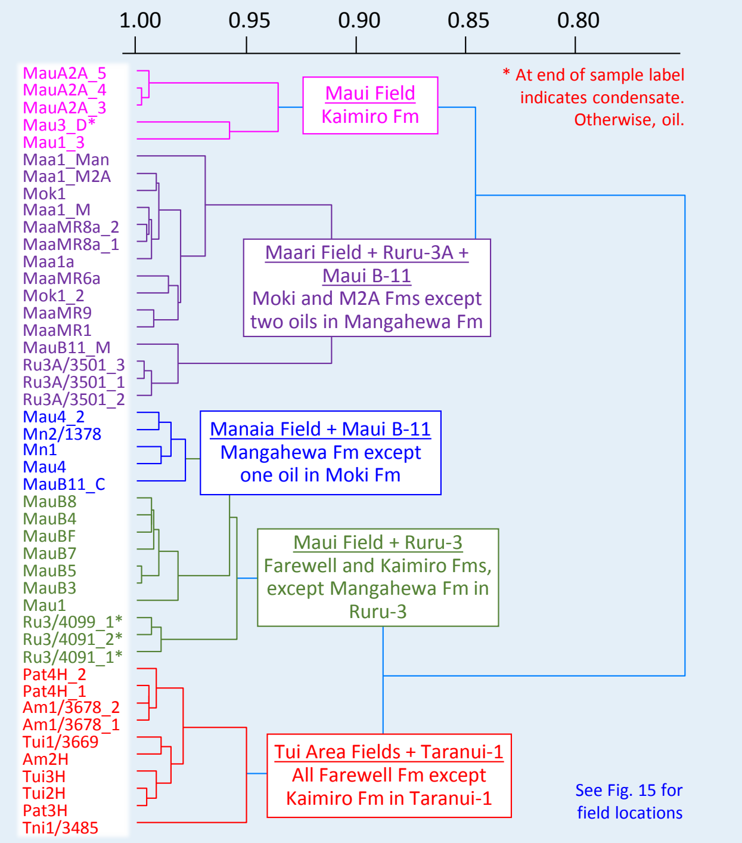

Figure 7 HCA dendogram for 45 Family 11 oils and condensates showing clustering of samples by field and reservoir formation (see **Fig. 2**).

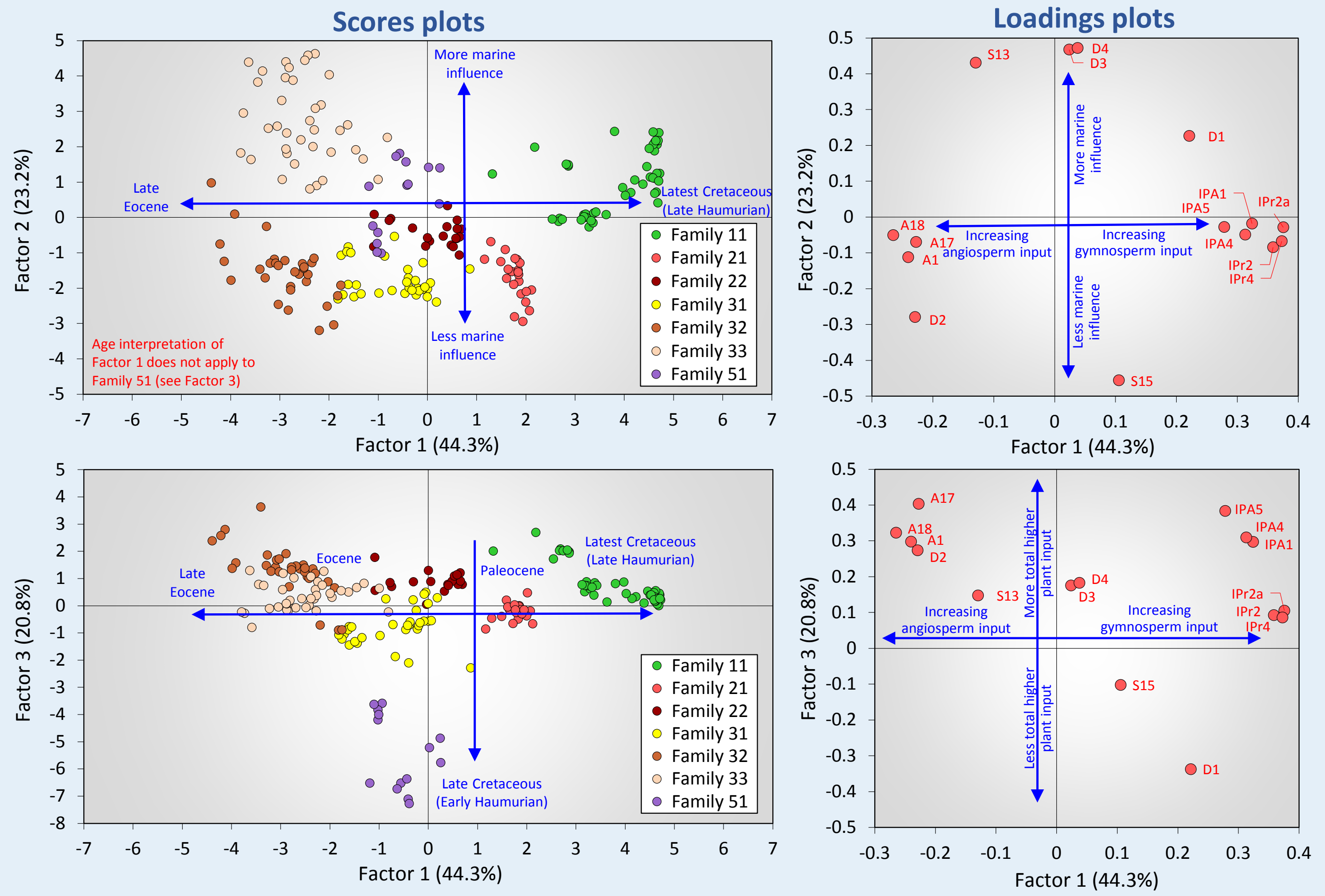

Figure 8 PCA scores and loadings plots on Factors 1–3 for Taranaki terrestrial oils and condensates, with samples coloured according to oil family groupings in **Figure 6**. Interpretation of scores and loadings on each factor is based on corresponding plots for coaly rock extracts (not shown here; Sykes et al. 2012).

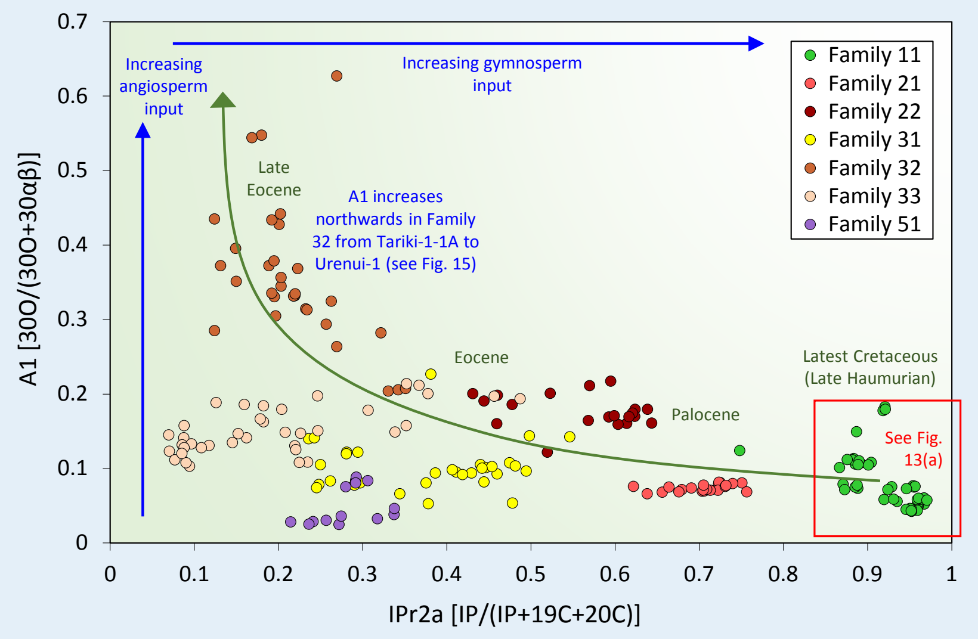

Figure 9 Cross-plot of gymnosperm input parameter IPr2a (based on isopimarane) and angiosperm input parameter A1 (based on oleanane) with age interpretation from coaly rock extracts.

Geographic and stratigraphic trends in gymnosperm, angiosperm, and total higher plant (gymnosperm + angiosperm) input parameters largely reflect source rock age and, to lesser degrees, source rock depositional environment and migration contamination (**Figs 9**, **10**, **13**). The relatively low angiosperm input in Family 33 fluids (**Fig. 9**), for example, is inferred to reflect reduced terrestrial input in Eocene coastal facies source rocks, whilst the northwards increase in angiosperm input in Family 32 fluids may reflect increased preservation of oleanane and related triterpanes in Eocene marine-influenced coaly rocks (Sykes et al. 2014) and/or progressive younging of the source rock unit to the north.

5. HIGHER PLANT BIOMARKER TRENDS AND MIGRATION CONTAMINATION EFFECTS

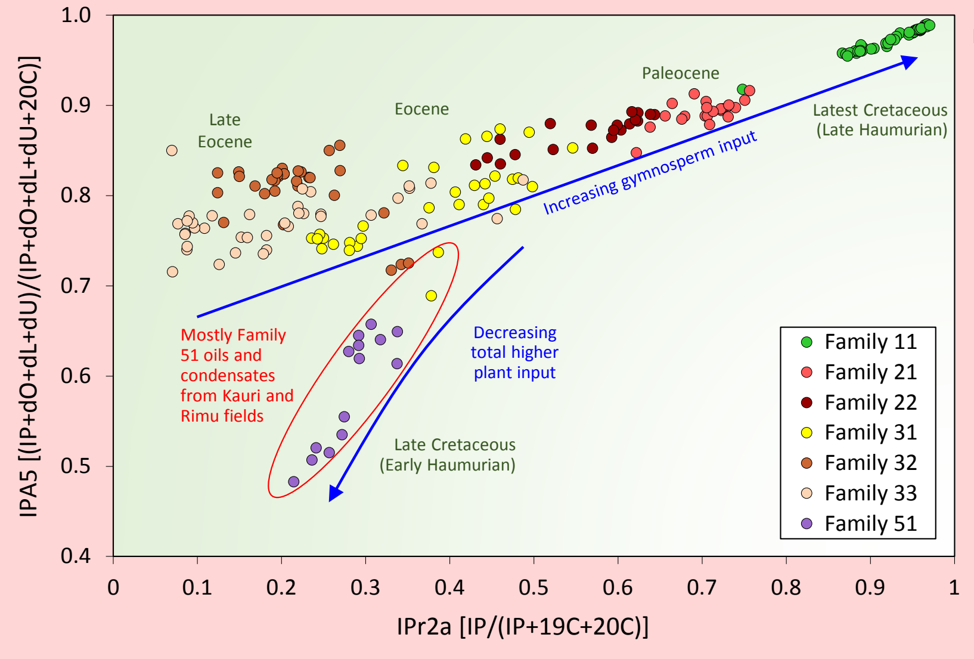

Figure 10 Family 51 oils and condensates in Kauri and Rimu fields display lower contents of both gymnosperm and angiosperm biomarkers. This signature of lower total higher plant input is a feature of New Zealand coaly rocks of Jurassic to Early Haumurian (Late Cretaceous) age. Early Haumurian rocks are recorded in some Rimu Field wells.

Angiosperm and gymnosperm biomarkers of the oils and condensates provide indications of source age (**Fig. 9**, **Fig. 10**). Rearranged drimanes provide information both on source age and depositional environment (**Fig. 11**, **Fig. 12**). Tight clustering of oils and condensates in some fields and wells **(Fig. 11)** in which other biomarkers show more variation highlights the potential value of drimanes for oil-oil correlation.

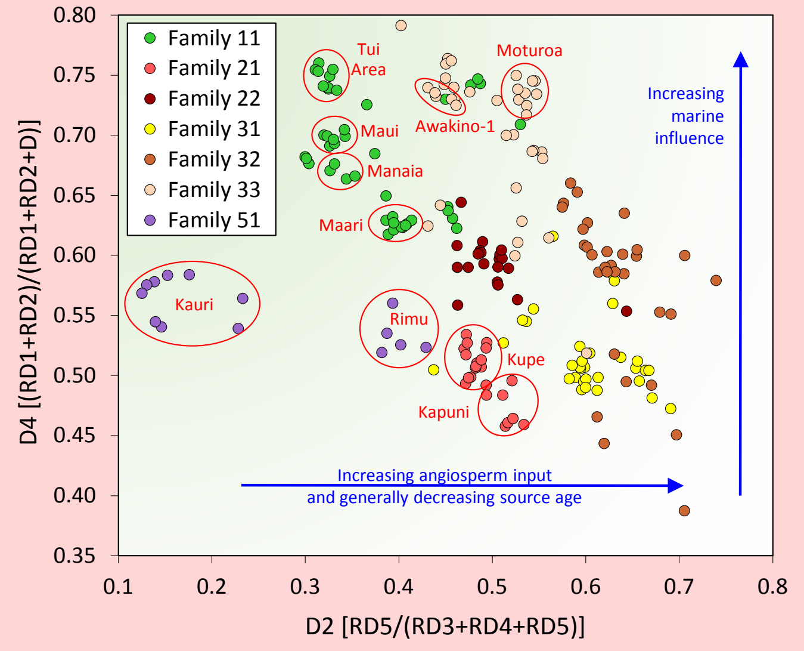

Figure 11 Cross-plot of drimane parameters D2 and D4 reveals tight clustering of oils and condensates in many fields. Examples are highlighted.

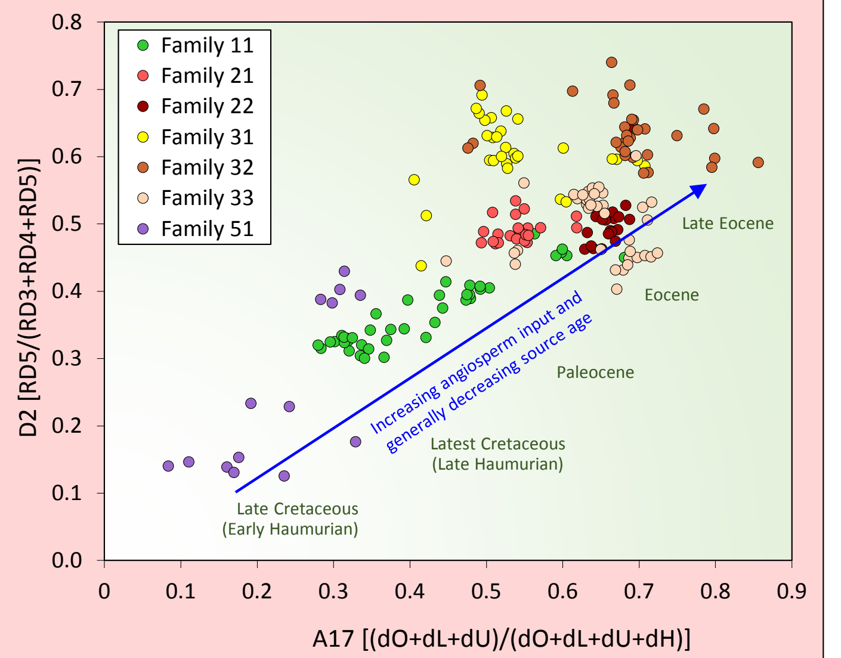

Figure 12 General correlation of the angiosperm parameter A17 and drimane parameter D2 supports an origin for the rearranged drimane RD5 from degradation of oleanoids (Nytoft et al. 2009).

Migration contamination

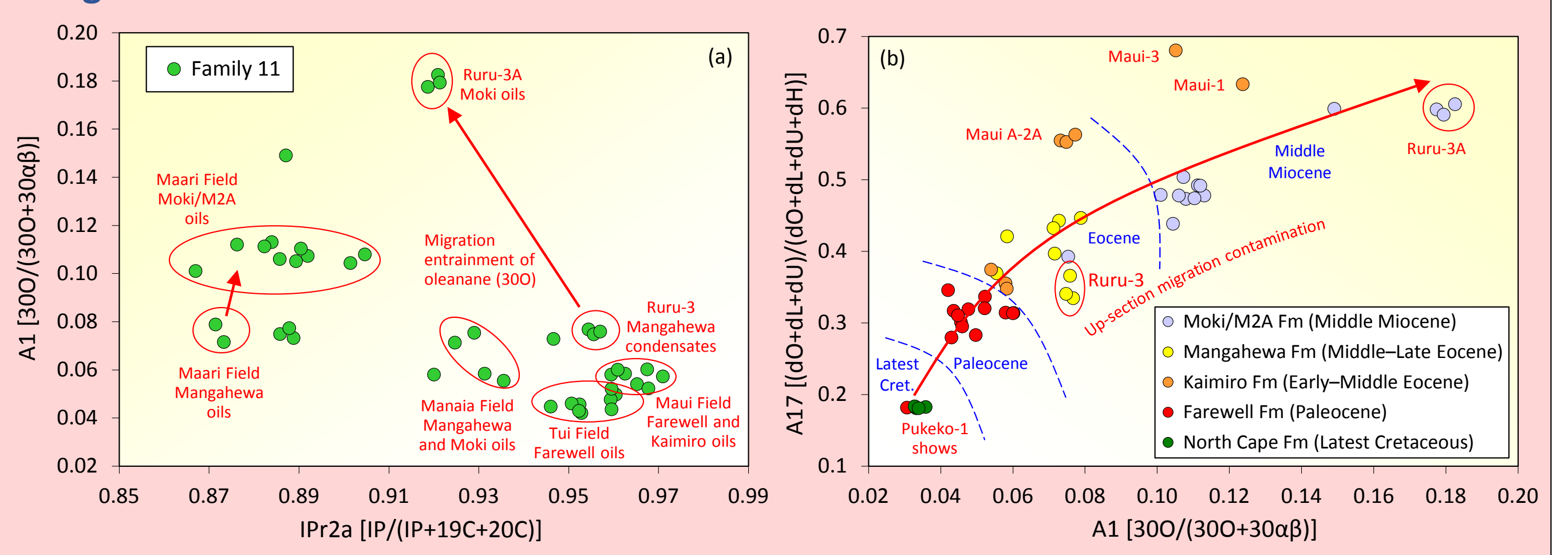

Figure 13 Migration contamination of latest Cretaceous oils and condensates of Family 11 in Maui, Maari, Manaia, and Tui fields and selected wells highlighted by up-section entrainment of angiosperm-derived biomarkers in these generally angiosperm-poor oils. In (b) samples are coloured by reservoir unit.

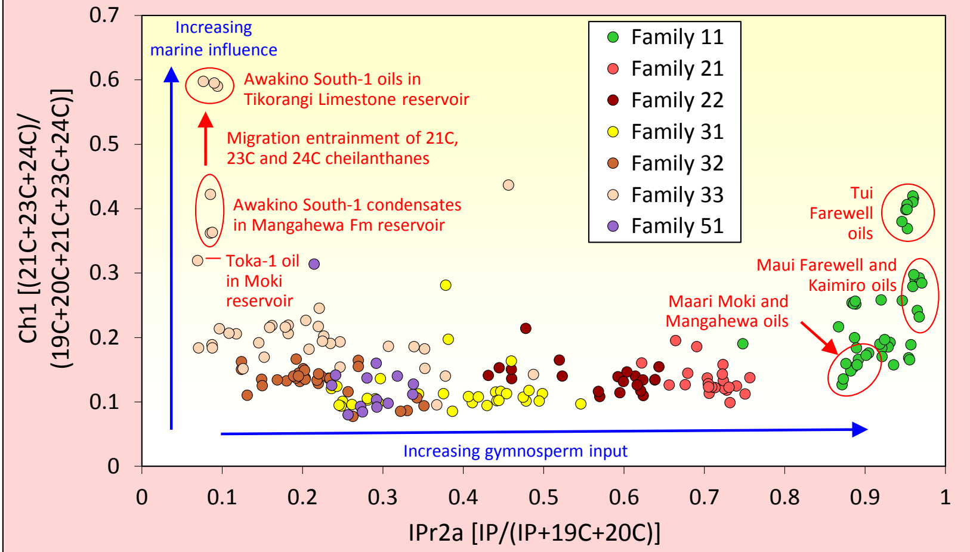

Figure 14 Migration entrainment of cheilanthanes (parameter Ch1) is evident in Awakino South-1, where oils in the Tikorangi Limestone are enriched in marine C_{21}, C_{23}, and C_{24} cheilanthanes, and in Toka-1, where the only Moturoa Field oil reservoired in Moki Formation is also enriched in marine cheilanthanes relative to all other Moturoa oils in Matemateaonga Formation. Migration contamination of cheilanthanes in Maui, Maari, and Tui fields is less certain.

Migration contamination of oils and condensates, including within the reservoir formation, occurs through entrainment of biomarkers. It generally goes unrecognised and even if recognised, it remains problematic for oil-oil correlation and interpretation of source organofacies. The migration entrainment of angiosperm biomarkers (**Fig. 13**) and cheilanthanes (**Fig. 14**) hinders geochemical determination of whether Late Cretaceous oils in Maui, Maari, and Tui fields (**Fig. 15**) are from the same or different kitchen(s).

6. OIL FAMILY CLASSIFICATION AND SOURCE ROCK CORRELATION

Chemometric analysis of the selected set of 15 source-related biomarker parameters identifies four tribes and seven families of terrestrial oils and gas condensates in Taranaki Basin (**Fig. 15**): one tribe and family derived from the Lower Haumurian (L. Mh, Late Cretaceous); one tribe and family from the Upper Haumurian (U. Mh, latest Cretaceous); one tribe of two families from the Paleocene–Eocene; and one tribe of three families from the Eocene. Source ages are assigned from comparison with gymnosperm and angiosperm biomarker distributions of coaly source rock extracts (not shown here). Source rock characteristics are inferred from sterane and drimane distributions.

The distribution of oil families and their source rock characteristics show various relationships to the distribution and facies of the inferred source rock units, as seen in the respective paleogeographic maps. The increase in marine influence from Family 31 to Family 33, for example, conforms with that within the underlying Mangahewa Formation, which becomes progressively more marine to the north (see 40 Ma map in **Fig. 3**).

The oil family distributions are also in general accordance with results of petroleum systems modelling. For example, the tight clustering of Family 21 oils and condensates in Kupe and Kapuni fields (**Fig. 8**, **Fig. 9**) is consistent with the model of a common kitchen, although slight differences in drimane distributions (**Fig. 11**) perhaps suggest derivation from different fetch areas within the kitchen.

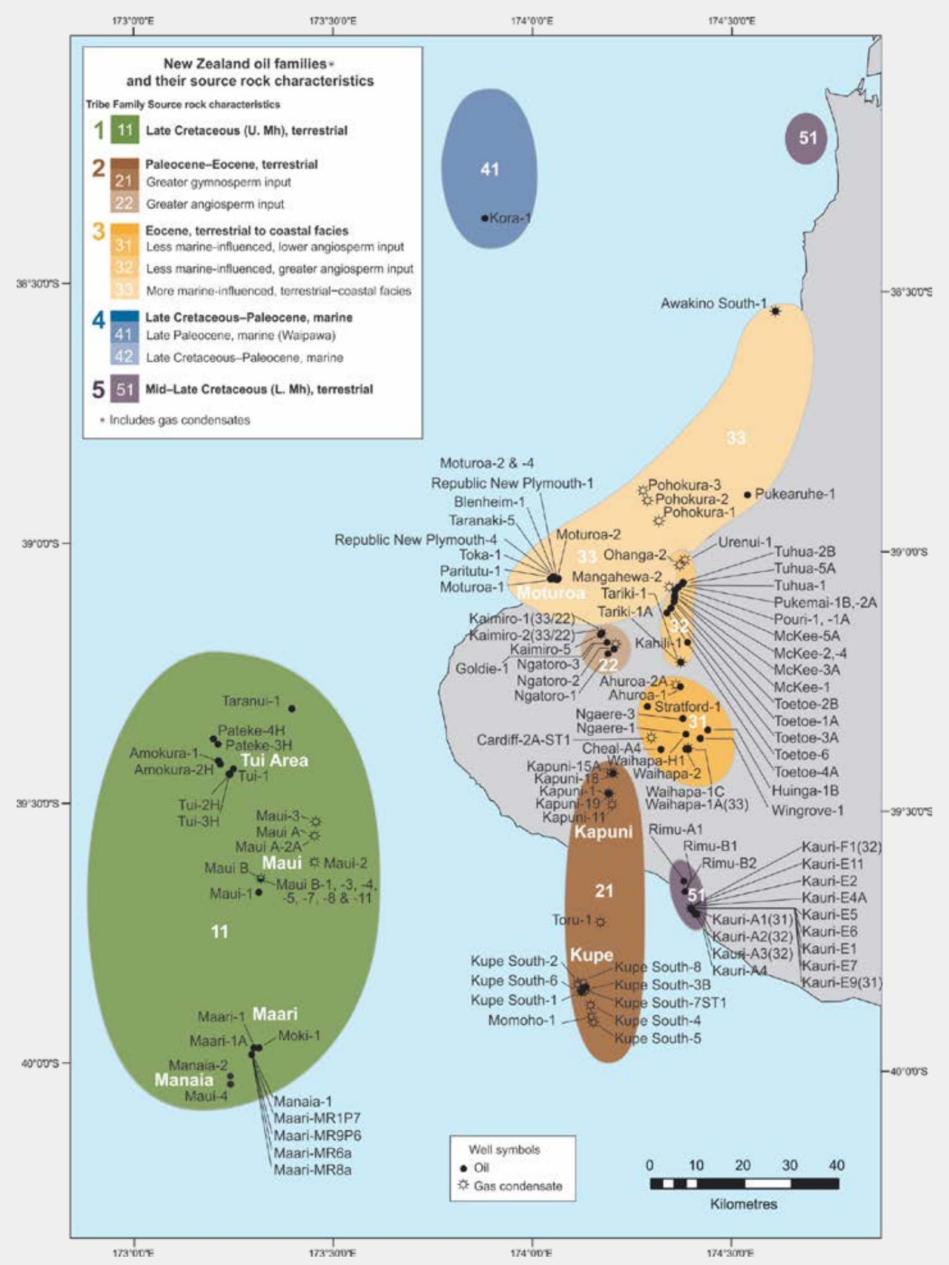

Figure 15 Map of oil family distribution in Taranaki Basin and key to source rock characteristics (updated from Sykes et al. 2012). The map shows only a representative selection of the analysed oils and condensates. The indicated boundaries of the oil families simply encapsulate the member oils and condensates and are not intended to define the geographic extent of each family. The marine Family 41 and 42 oils are not discussed in this poster.

7. CONCLUSIONS

- Evolutionary changes in the composition of gymnosperm and angiosperm higher plants on the Zealandia continent from the mid-Cretaceous to Late Eocene resulted in stratigraphic trends in di- and triterpane distributions through the main coaly source rock formations. These have enabled the development of a robust chemometric classification of terrestrial oil (and gas condensate) families in Taranaki Basin.
- Four tribes and seven families of terrestrial oils and gas condensates are identified: one tribe and family derived from the Lower Haumurian (Late Cretaceous); one tribe and family from the Upper Haumurian (latest Cretaceous); one tribe of two families from the Paleocene–Eocene; and one tribe of three families from the Eocene. Sterane, drimane, and cheilanthane distributions provide additional information on source rock depositional environment and organofacies.
- The oil families are useful for oil-oil and oil-source rock correlation, but clear evidence of migration entrainment of angiosperm and cheilanthane biomarkers highlights a need for caution when correlating and interpreting source rock depositional environment.
- Rearranged drimanes reveal tight clustering of oils and condensates in some fields and wells in which other biomarkers show more variation. This highlights the potential value of drimanes for oil-oil correlation.

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