Evaluation of Re-Os geochronology and Os isotope fingerprinting of Late Cretaceous terrestrial oils in Taranaki Basin, New Zealand

Enock K. Rotich[a*], Monica R. Handler[a], Richard Sykes[b], Sebastian Naeher[b], David Selby[c], Karsten Kroeger[b]

[a] *School of Geography, Environment and Earth Sciences, Victoria University of Wellington, PO Box 600, Wellington, 6140, New Zealand*

[b] *GNS Science, 1 Fairway Drive, PO Box 30368, Lower Hutt, 5040, New Zealand*

[c] *Department of Earth Sciences, Durham University, Durham, DH1 3LE, UK*

* Corresponding author. Tel.: +254768268931; e-mail address: rotichenock@gmail.com

Abstract

The rhenium-osmium (Re-Os) isotope system has been applied to several marine and lacustrine petroleum systems worldwide, showing good potential for dating crude oils and correlating them to their source rocks. Here we explore the applicability of the Re-Os geochronometer and Os isotope fingerprinting to terrestrial oils by comparing the Re and Os systematics of Late Cretaceous terrestrial oils from Taranaki Basin, New Zealand, and their correlated coaly source rocks. Comparison is also made with selected Late Cretaceous–Paleocene marine oils and source rocks with varying levels of terrestrial organic matter input.

The asphaltene fractions of nine genetically related terrestrial oils from the Maui, Maari-Manaia and Tui Area fields in offshore Taranaki Basin contain low concentrations of Re (0.18–0.45 ppb) and ^{192}Os (1.3–12.7 ppt) comparable to their correlated Late Cretaceous coaly source rocks (Rakopi and North Cape formations; Re 0.19–0.37 ppb, ^{192}Os 5.3–9.6 ppt). The Re and ^{192}Os concentrations in these terrestrial oils are generally one to two orders of magnitude lower than those in marine-sourced oils from the Kora Field in offshore Taranaki Basin and surface seeps in East Coast Basin.

The ^{187}Re/^{188}Os and ^{187}Os/^{188}Os ratios of the terrestrial oils failed to yield a precise Re-Os isochron age. We attribute this to: (1) insufficient homogenisation of oils with widely variable initial ^{187}Os/^{188}Os (Os_i) values inherited from thick, coaly source rock intervals (up to about 2700 m) within the Maui sub-basin and northern Kahurangi Trough kitchens; (2) insufficient spread of ^{187}Re/^{188}Os values (only 275 units); (3) insufficient time since oil expulsion (modelled to be from approximately 10 Ma to the present day) for the evolution of an isochron; and (4) possible effects of water washing of the oil columns. Although all of the studied oils are water-washed to varying

degrees, there is no definitive evidence that water washing has disturbed the Re-Os systematics.

The Os_i values for the studied terrestrial oils inherited at the modelled time of oil expulsion (approximately 10 Ma) display a wide range (0.47–1.14) and do not provide a unique fingerprint of their Late Cretaceous coaly source rock formations. Osmium isotope compositions therefore appear to have limited potential for broad oil-source rock correlation within the predominantly coal-sourced petroleum systems of Taranaki Basin. The Os_i values may, however, provide useful distinction of the terrestrial oils emanating from the Kahurangi Trough (Tui Area oils) from those of the Maui sub-basin (Maui and Maari-Manaia oils) based on the significantly more radiogenic values of the Tui Area oils (0.84–1.14 compared with 0.47–0.65 from Maui and Maari-Manaia oils). Overall, this study has provided useful insights into the potential application of the Re-Os isotope system to terrestrial, coal-sourced petroleum systems.

Keywords

Re-Os isotopes; terrestrial oils; marine oils; seeps; coaly source rocks; Taranaki Basin; East Coast Basin; New Zealand

1. Introduction

The Re-Os isotope system has been shown to provide accurate and precise depositional ages for both marine and lacustrine organic-rich mudrocks (e.g., Cohen et al., 1999; Xu et al., 2009; Cumming et al., 2012; Liu et al., 2018; Tripathy et al., 2014; Rotich et al., 2020). Prerequisites for valid ages are: 1) the Re-Os isotope systematics must remain a closed system, 2) the initial $^{187}Os/^{188}Os$ (Os_i) compositions

of all samples must be similar, and 3) there must be a sufficient spread in $^{187}Re/^{188}Os$ ratios to define an isochron (Cohen et al., 1999; Cumming et al., 2012). Additionally, studies of natural systems and hydrous pyrolysis experiments have shown that Re and Os are transferred from source rocks to bitumen to oil without significant fractionation, and without significantly affecting Re-Os systematics and Os isotopic composition of the source rock (Selby et al., 2007; Finlay et al., 2012; Rooney et al., 2012; Cumming et al., 2014). Accordingly, the Re-Os geochronometer and Os isotope fingerprinting have shown promising potential both for dating crude oils in marine and lacustrine petroleum systems and for correlating oils to their source rocks (Selby and Creaser, 2005; 2007; Finlay et al., 2011; 2012; Lillis and Selby, 2013; Cumming et al., 2014; Georgiev et al., 2016; 2019; Ge et al., 2018; Liu et al., 2018; Corrick et al., 2019; Scarlett et al., 2019; Meng et al., 2021). However, it remains uncertain exactly which event is being dated. Some studies have linked crude oil Re-Os isochron ages and $^{187}Os/^{188}Os$ compositions to the timing of oil generation (e.g., Finlay et al., 2011; Cumming et al., 2014; Liu et al., 2018), whereas others have linked them to both oil generation and migration (e.g., Lillis and Selby, 2013; Ge et al., 2016; 2018) or oil emplacement (Selby and Creaser, 2005), as identified independently by other age estimation techniques, such as basin modelling and paleomagnetic and radiometric dating (Ar-Ar, U-Pb, Rb-Sr) of hydrocarbon-bearing fluid inclusions and mineral deposits (Christensen et al., 1995; Symons and Arne, 2003; Mark et al., 2010; Lillis and Selby, 2013; Ge et al., 2016; 2018).

The lack of clarity on the event being dated can be attributed to the significant gaps in existing knowledge of the geochemical behaviour and mechanisms that control fractionation of Re and Os in petroleum systems, especially the homogenization of Os isotope composition. For Re-Os hydrocarbon geochronology to work, a complete reset of the isotopic system must happen either during generation, migration or

accumulation, and the system must remain closed throughout subsequent geological time. Most Re-Os hydrocarbon dates obtained so far are not precise enough to clearly distinguish the exact process being dated. Hydrous pyrolysis experiments simulating hydrocarbon generation (Rooney et al., 2012; Cumming et al., 2014) show that, at a local scale, this process is capable of homogenising osmium isotopes as well as fractionating Re/Os ratios, the two conditions necessary for development of an isochron. Experiments have also been conducted to assess the effects of sequential precipitation of asphaltenes on fractionation of Re/Os ratios during migration and charging of oil into reservoirs (Mahdaoui et al., 2013; DiMarzio et al., 2018; Liu et al., 2019). Results show that this process does not appreciably perturb the Re-Os geochronometer, especially when the precipitation of asphaltene is minimal. Interaction of crude oil with formation water and hydrothermal fluids is another potential mechanism that can reset the Re-Os geochronometer as has been shown by oil-water contact experiments (Mahdaoui et al., 2015; Hurtig et al., 2019) and reported in natural systems (Finlay et al., 2010). The oil-water contact experiments reveal that Re and Os can readily transfer from aqueous solutions to oils, especially at high water-oil ratios. Thermal cracking is another process that may reset Re-Os isotope systematics in crude oils, resulting in oil isochrons that record the timing of thermal cracking (production of dry gas and pyrobitumen), rather than generation or migration of oil (Lillis and Selby, 2013; Ge et al., 2016). Similarly, thermochemical sulfate reduction (TSR) has been shown to have caused a reset of the Re-Os geochronometer in oils from the Bighorn Basin, USA, yielding a Re-Os date of 9.24 ± 0.39 Ma, which coincides with the proposed end of TSR as a result of reservoir cooling caused by uplift and erosion at around 10 Ma (Lillis and Selby, 2013).

The comprehensive studies of the Eocene lacustrine Green River Formation source rocks (Cumming et al., 2012) and their derived oils, tar sands and gilsonite deposits

(Cumming et al., 2014) further highlight some of the challenges and uncertainties in Re-Os dating of petroleum systems. While the oils and gilsonite deposits returned Middle Eocene Model 3 isochron ages of 45 ± 31 Ma and 45 ± 42 Ma, respectively, consistent with the range of Re-Os and Ar-Ar depositional dates for the Green River Formation (45.4–50.1 Ma; Cumming et al., 2012), regression of all the samples (oils, gilsonites and tar sands) yielded an isochron age of 19 ± 14 Ma, broadly consistent with a petroleum generation age of ~25 Ma derived from basin models. The large uncertainties in the Re-Os ages of the various petroleum deposits were attributed mainly to very low Os abundances, limited spread in measured $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ ratios, and wide variation in initial $^{187}Os/^{188}Os$ compositions, the latter exacerbated by multiple generation events occurring through a ~3000 m-thick source rock unit (Cumming et al., 2014).

The applicability of the Re-Os isotope system to date and trace crude oils derived from terrestrial (coaly) source rocks has not yet been tested. Terrestrial petroleum systems rarely attain the levels of Os_i homogeneity commonly seen in marine petroleum systems. This is because the source materials for terrestrial source rocks (i.e., detrital silicates and plant debris) have been shown to exhibit heterogeneous Os isotope compositions (Rodushkin et al., 2007; Goswami et al., 2018), and were deposited in bogs or mires far smaller and more restricted than depocenters in the open ocean. Such depositional settings prevent complete mixing and homogenisation of the Os isotope signature before sequestration. Recent studies have indeed provided evidence of heterogeneous initial $^{187}Os/^{188}Os$ ratios in coaly source rocks (Goswami et al., 2018; Rotich et al., 2021). Such variable initial $^{187}Os/^{188}Os$ ratios may be transferred to crude oils during maturation, potentially hindering the application of Re-Os geochronology to terrestrial oils. However, the processes that homogenise Os isotopic composition in marine and lacustrine crude oils, such as primary migration

(Selby and Creaser, 2005), should also apply to coal-sourced oils. In addition, the Os isotopic compositions of these oils may prove useful for oil-source correlation, provided estimates of oil expulsion dates are available through other means, such as basin modelling.

In this study, we explore the possibility of using the Re-Os isotope system to date and trace selected terrestrial oils from offshore Taranaki Basin, New Zealand (Figs 1, 2). These oils have been confidently typed to Late Cretaceous coaly source rocks of the Rakopi and North Cape formations using biomarker compounds (Killops et al., 1994; Sykes et al., 2012; Sykes, 2019). Using results of a previous study of the Re-Os systematics of these source rocks (Rotich et al., 2021) allows us to also assess the potential of Os isotope fingerprinting to correlate terrestrial oils to their source rocks. Further, we investigate the effects of terrestrial organic matter input on the Re-Os isotope system by comparing the Re-Os results for these coal-sourced oils with those for two families of marine oils that differ in their levels of terrestrial organic matter input. The highly distinctive marine oils from the Kora-1 well in northern offshore Taranaki Basin (Fig. 1) are sourced from organic-rich mudstones of the late Paleocene, marine Waipawa Formation (Killops et al., 1994; Sykes et al., 2012), which are very rich in transported terrestrial organic matter (e.g., Schiøler et al., 2010; Field et al., 2018; Naeher et al., 2019). In contrast, the marine seep oils of the northern and southern regions of onshore East Coast Basin (Fig. 1) are more typical marine oils characterised by little terrestrial organic matter input. These seep oils are from an as-yet unknown source, but have biomarker and carbon isotopic characteristics similar to those of the Late Cretaceous–Paleocene Whangai Formation (Murray et al., 1994; Killops, 1996; Rogers et al., 1999; Sykes et al., 2012). The Re-Os isotope systematics of Waipawa and Whangai Formation mudstones have previously been characterised (Rotich et al.,

2020), enabling comparison of the Kora-1 and East Coast Basin seep oils with these source rocks.

2. Geological setting

New Zealand crude oils (including gas condensates) have been grouped into five genetic tribes and 11 families based on chemometric analysis of source-related biomarker and carbon isotope parameters (Sykes et al., 2012). Nine families of terrestrial oils are distinguished mainly by their relative inputs of angiosperm-, gymnosperm- and total higher plant-derived organic matter to the source kerogen, as well as the degree of marine influence within the coal-forming depositional environment. The two marine oil families are distinguished primarily by their carbon isotope signatures and C_{30} sterane contents (Killops et al., 1994; Murray et al., 1994; Killops, 1996; Rogers et al., 1999; Sykes et al., 2012). This study investigates oil accumulations in Taranaki Basin correlated to Late Cretaceous terrestrial source rocks (Family 11) and late Paleocene, marine Waipawa Formation source rocks (Family 41), as well as seep oils in East Coast Basin (Family 42) with source characteristics similar to the Late Cretaceous–Paleocene, marine Whangai Formation (Figs. 1, 2).

2.1. *Taranaki petroleum systems*

Taranaki Basin is the only oil and gas producing basin in New Zealand, with estimated ultimate recoverable reserves of 600 million barrels of oil and condensate and 8.7 trillion cubic feet of gas (MBIE, 2020). The basin covers approximately 330,000 km^2 both onshore and offshore along the west coast of New Zealand's North Island (Figs. 1, 2) and comprises up to 10 km of mid-Cretaceous to recent sedimentary rocks (King and Thrasher, 1996). The main petroleum source rocks are mid-Cretaceous–Eocene coal measures deposited in extensive coastal plain environments. These source rocks were buried to depths sufficient for oil and gas generation and expulsion in the

Neogene (King and Thrasher, 1996; Kroeger et al., 2016). Commercial petroleum accumulations have been encountered at every stratigraphic level from the Paleocene to Pliocene (King and Thrasher, 1996). Most accumulations are trapped in fault-related anticlines that formed in the last 30 to 40 Myr in response to compression associated with subduction of the Pacific Plate to the east of New Zealand (King and Thrasher, 1996; Stagpoole and Nicol, 2008; Reilly et al., 2016; Seebeck et al. 2019; Kroeger et al., 2021).

There are currently 17 producing oil and gas-condensate fields in Taranaki Basin, both on- and offshore (MBIE, 2020). The Family 11 oils studied here are from the offshore Maui, Maari-Manaia and Tui Area fields (Fig. 2), and all have high contents of gymnosperm plant-derived biomarkers that link them to Late Cretaceous coaly rocks of the Rakopi and North Cape formations (Killops et al., 1994; Sykes et al., 2012; Sykes, 2019). These coaly rocks span a wide range of total organic carbon (TOC) from <1% to about 80% and hydrogen index (HI) values are mostly in the range of 200–450 mg HC/g TOC (Sykes and Zink, 2018), indicating high quality, mixed gas- and oil-prone to oil-prone kerogen (classification of Peters and Cassa, 1994). Regional geological models and seismic facies maps indicate these source rocks are present in depocenters of the Maui and Pihama sub-basins to the east, and the Kahurangi Trough to the west (Funnell et al., 2001; 2004; Matthews, 2008; Kroeger et al., 2016; 2021; Fig. 2). Late Cretaceous strata within these depocentres are up to c. 2700 m thick (Seebeck et al., 2019) and are modelled to have been generating and expelling significant quantities of oil and gas from the Late Miocene to the present (Killops et al., 1994; Funnell et al., 2004; Harrison et al., 2013; Kroeger et al., 2016; Pierpont et al., 2017). These hydrocarbons are trapped in Paleocene–Miocene, stacked terrestrial and marine sandstone reservoirs, commonly referred to as the F, D, C and B sands (King and Thrasher, 1996; Funnell et al., 2004). The Paleocene F sands (within the

Farewell Formation) and Early Eocene D sands (Kaimiro Formation) were deposited in nearshore, paralic and fluvio-estuarine environments (Higgs et al. 2012). The Middle–Late Eocene C sands (Mangahewa Formation) consist of coastal plain, shoreface, tidal channel and inner shelf sediments, whereas the Middle Miocene B sands (Moki Formation) comprise basin floor, slope turbidite and channel sandstones (King and Thrasher, 1996; Funnell et al., 2004; Higgs et al. 2012; Kroeger et al. 2019).

In the northern part of Taranaki Basin, sub-commercial oil accumulations were discovered in the Kora-1 well that was drilled to target a Miocene-aged submarine volcano (King and Thrasher, 1996; Brett, 2005; Bischoff et al. 2021, Kroeger et al., 2022). These oils are assigned to Family 41 and are geochemically correlated with the late Paleocene Waipawa Formation whose organic matter is derived from both terrestrial higher plants and marine algae (Reed, 1992; Killops et al., 1994; Murray et al., 1994; Killops, 1996; Clayton, 2011; Sykes et al., 2012; Naeher et al., 2019). The Waipawa Formation is primarily gas-condensate-prone on account of its large proportion of terrestrial organic matter, dominated (66–98%) by woody phytoclasts (Naeher et al., 2019). Nonetheless, its strong geochemical correlation with the Kora oils and a number of oil seeps and stains in the southern Hawke's Bay to Wairarapa region of East Coast Basin (Fig. 1) indicates some oil potential, presumably from subordinate contributions of marine, algal-derived kerogen. The two principal reservoir units in the Kora Field are the Eocene Tangaroa Formation, which comprises deep-water submarine fan sandstones, and volcaniclastic rocks intercalated in the Miocene Mohakatino Formation (Reed, 1992; Brett, 2005; Bischoff et al. 2021).

2.2. *East Coast Basin petroleum systems*

East Coast Basin is located both on- and offshore along the eastern margin of North Island and northeastern South Island, covering about 120,000 km^2 (Fig. 1). The basin

has numerous onshore oil and gas seeps and stains indicating the presence of active petroleum systems (Field et al., 1997). Late Cretaceous–Paleocene carbonaceous mudstones of the marine Whangai and Waipawa formations have been identified as the most promising source rocks, although no commercial accumulations of oil or gas linked to either formation have yet been discovered in the basin (Field et al., 1997; Hollis and Manzano-Kareah, 2005). The Waipawa Formation has a maximum known thickness within the basin of c. 80 m and has relatively high TOC contents, averaging 3.6 wt.% (n=99), and moderate HI values, averaging 245 mg HC/g TOC (n=87; Hollis and Manzano-Kareah, 2005; Field et al., 2018). These values indicate very good potential for mixed oil and gas. The formation appears thermally immature to marginally mature throughout at least the onshore part of the basin (Moore, 1989; Field et al., 1997; Hollis and Manzano-Kareah, 2005), where it has been geochemically linked to minor oil seeps and stains assigned to Family 41 in the southern Hawke's Bay and Wairarapa regions (Fig. 1, Murray et al., 1994; Killops, 1996; Rogers et al., 1999). Both the Waipawa and Whangai formations are, however, modelled to have higher thermal maturities offshore, in the Hikurangi subduction margin (Kroeger et al., 2015).

The Whangai Formation is up to c. 1500 m thick and appears to have generally poor to fair potential for gas only (Hollis and Manzano-Kareah, 2005). Overall, Whangai Formation carbonaceous mudstones have mean TOC and HI values of 0.56 wt.% (n=284) and 159 mg HC/g TOC (n=188), respectively, although individual values are as high as 1.7 wt.% and 377 mg HC/g TOC (Hollis and Manzano-Kareah, 2005). Multiple seep oils in the Raukumara Peninsula and Marlborough regions of the northern and southern onshore East Coast Basin (Fig. 1), respectively, including the Waitangi and Kaikoura seep oils studied here, are assigned to Family 42, with source organofacies characteristics similar to those of the Whangai Formation (Rogers et al.,

1999; Sykes et al., 2012). However, given the generally low oil potential of this formation, it remains uncertain whether these oils were sourced from an as-yet-undiscovered oil-prone organofacies within the Whangai Formation or from a separate, as-yet-unknown Cretaceous formation with similar source organofacies characteristics.

3. Samples and methods

3.1. *Oil samples*

3.1.1. Origin of samples

Thirteen oil samples representative of the coal-sourced Family 11 and marine-sourced families 41 and 42 were selected from a collection of oils held at GNS Science, Lower Hutt, and the National Core Store, Featherston, New Zealand (Table 1). The nine Family 11 oils are from the Maui, Maari-Manaia and Tui Area fields, which are spread over c. 75 km across the offshore Taranaki Basin (Fig. 2). The Maui and Tui Area oils are from the Paleocene and Eocene F and D sands reservoirs, whereas the Maari-Manaia oils are from the much shallower, Miocene B sands reservoir. The Tui Area fields consist of three separate, c. 10–12 m thick oil accumulations, forming the Pateke, Amokura and Tui pools (Fig. 2), all within the same F10 sand. These pools represent a fill-spill chain shallowing to the south (i.e. from Pateke to Tui) over a lateral distance of c. 10 km (Matthews et al., 2008). The Maui B well oil sample is also from the F sands, whereas the Maui-1 well oil is from the D sands. The marine Family 41 oils are from the two different reservoirs penetrated in the Kora-1 discovery well in northern offshore Taranaki Basin (Fig. 1; Reed, 1992). The Kora-1(A) oil is from the Eocene Tangaroa Formation sandstone reservoir whereas the Kora-1(B) oil is from the Miocene Mohakatino Formation reservoir comprising volcaniclastic sediments. The marine Family 42 oil samples are from the Waitangi and Kaikoura surface seeps

in the Raukumara Peninsula and Marlborough regions of northern and southern East Coast Basin, respectively (Fig. 1).

3.1.2. Oil sample properties and quality

All of the oil samples studied here have previously been analysed for their bulk compound groups (i.e., saturated and aromatic hydrocarbons, resins and asphaltenes), whole-oil hydrocarbon distributions, saturated and aromatic biomarkers, and stable carbon isotope compositions of the saturated and aromatic hydrocarbon fractions (Sykes and Zink, 2018; GNS Science unpublished results). This enabled initial selection of samples based on the assigned oil family, oil quality and asphaltene content. Asphaltene content is considered important for sample selection because the asphaltene fraction typically contains the majority (up to 98%) of the Re and Os in crude oils (Selby et al., 2007; Georgiev et al., 2016; Liu et al., 2019), but New Zealand coal-sourced oils are typically low in asphaltenes (<3%; Sykes and Zink, 2018). Sample selection therefore favoured those oils with higher asphaltene contents.

Studies of the Re-Os isotope system and geochronology of crude oils should ideally use pristine oils that are unaltered from the original oil that charged the host reservoirs. However, crude oils are commonly altered by processes such as biodegradation and water washing, either within the reservoir or surface seeps (Peters et al., 2005, and references therein). In addition, oil samples are typically missing some volatile low molecular weight hydrocarbons (i.e., “front-ends”) as a result of less-than-ideal sample collection and storage procedures. While the loss of volatiles is unlikely to have a significant impact on the Re and Os budget, this may not be the case with biodegradation and water washing. Biodegradation is the alteration of crude oil by microbial organisms primarily through the process of oxidation which produces carbon dioxide and other partially oxidized by-products, such as organic acids (Peters et al.,

2005). For biodegradation to occur, specific conditions that support microbial life must exist. These include reservoir temperatures of less than ~80°C, availability of water and inorganic nutrients, water salinity of less than ~100–150 parts per thousand and presence of microorganisms (Wenger et al., 2002; Peters et al., 2005; Wang et al., 2016). A scale of 1 (least altered) to 10 (most altered) has been developed to rank the extent of biodegradation of crude oil based on differing resistance of its components to microbial attack (Peters and Moldowan, 1993; Peters et al., 2005). On this scale, level 1 is assigned to slightly biodegraded oils, level 2 to moderately biodegraded oils, level 3 to heavily biodegraded oils and levels 4–10 to severely biodegraded oils (Peters et al., 2005). Water washing is the removal of the more water-soluble constituents of crude oil, especially light alkanes and low molecular weight aromatic hydrocarbons such as benzene and toluene (Palmer, 1984). It occurs when crude oils come in contact with water in reservoirs, during migration and/or during production. Water washing is an important consideration in Re-Os studies of crude oils because contact experiments have demonstrated that Re and Os can readily transfer between aqueous solutions and oils (Mahdaoui et al., 2015; Hurtig et al., 2019), raising the possibility that mixing of oil with formation or surface waters may disturb the Re-Os systematics (Finlay et al., 2010).

The Tui Area and Maui B oils have *n*-alkane distributions typical of largely unaltered New Zealand coal-sourced oils apart from the usual loss of some gas- (C_1–C_4) and gasoline-range (C_5–C_8) homologues due to evaporation (Fig. 3a). In contrast, the Maui-1 oil displays a smooth and more substantial loss of short-chain *n*-alkanes up to nC_{15}, probably as a result of poor sample handling at some point since the oil was first discovered and sampled in 1969. This artificial loss of short to medium chain length *n*-

alkanes is not expected to have affected Re and Os because they largely reside within the asphaltene fraction.

In contrast, the loss of *n*-alkanes in the Maari-MR8A and Manaia-2 oils is more irregular and extends up to at least nC_{25} (Fig. 3a). This pattern of loss of *n*-alkanes, commencing in the short- to medium-chain *n*-alkanes and then extending to long-chain *n*-alkanes, is typical of biodegradation (Peters et al., 2005). Cross-plots comparing the concentrations of nC_8 and nC_{14} to less easily biodegraded cyclic and branched (isoprenoid) hydrocarbons of similar boiling points (Fig. 4) confirm these samples are biodegraded to levels 2–3 of Peters et al. (2005). These Maari-Manaia oils are from the shallower Moki Formation B sands, with reservoir temperatures of 50–52°C (Sykes et al., 2011), conducive for biodegradation, whereas the remaining Family 11 oils are from the F and D sands with reservoir temperatures of c. 112–125°C (Sykes et al., 2011), well beyond the upper temperature limit of 60–80°C for significant biodegradation (Peters et al., 2005). The apparent slight biodegradation of the Maui-1 oil indicated in Figure 3a is more likely an artefact of the significant loss of short-chain *n*-alkanes experienced by this sample (Fig. 3a).

Although the Tui and Maui oils are not biodegraded, they are variably water-washed, as are the biodegraded Maari-Manaia oils. This is indicated by their preferential loss of the more water-soluble aromatic hydrocarbons compared to branched and cyclic hydrocarbons of similar boiling point. Cross-plots comparing relative concentrations of C_6–C_8 cyclic and branched hydrocarbons to aromatic hydrocarbons (Fig. 5a) and benzene and toluene to nC_6 and nC_7, respectively (Fig. 5b), show largely consistent relative levels of water washing using the two sets of parameters. The Maui-1 sample appears to have spurious results due to its large loss of short-chain *n*-alkanes (Fig. 3a). Amongst the other terrestrial oils, the Maui B and all of the Tui Area oils appear

more water-washed than the Maari-MR8A oil, despite not being biodegraded. The thin (10–12 m) oil columns in the Pateke, Amokura and Tui pools overlie a strong aquifer (NZOP, 2005), and the relative levels of water washing indicated by the loss of aromatic hydrocarbons (Pateke>Amokura>Tui) match the present-day direction of hydrodynamic flow between the fields, from Pateke to Tui.

Amongst the marine oil samples, the Kora-1(A) and Waitangi Seep samples have both experienced significant loss of short-chain *n*-alkanes up to about C_{15}–C_{16} (Fig. 3b). This will likely have affected the parameters on which the assessments of biodegradation (Fig. 4) and water washing (Fig. 5) are based. The Kora-1(A) oil is unlikely to be biodegraded given that it is from a depth of 3128–3182 m within the Tangaroa Formation with temperatures of approximately 110 °C (Kroeger et al., 2022). In contrast, there is negligible loss of short-chain *n*-alkanes in the Kora-1(B) oil from the Mohakatino Formation reservoir (Fig. 3b). This oil lies just within the indicated fields of biodegradation in Figure 4, but as the reservoir temperature is 68°C (Sykes et al., 2011), any biodegradation is likely to be minimal. This sample also appears to be amongst the least water-washed of the oil samples (Fig. 5). Lastly, the Kaikoura Seep oil is the most biodegraded of the oil samples, with almost all of the *n*-alkanes having been lost (Fig. 3b), indicating biodegradation to level 3 (Fig. 4b).

3.2. *Source rock samples*

Samples representative of potential or similar source rocks that generated the oils studied here (Rakopi, North Cape, Waipawa and Whangai formations) have previously been analysed for Re and Os concentrations and isotopic compositions (summarised in Table S1; Rotich et al., 2020; 2021). The samples from Rakopi and North Cape formations comprise coals and a coaly mudstone, ranging in TOC from 12.9 to 68.4 wt.% and HI from 183 to 350 mg HC/g TOC (Table S1). These samples were originally

collected from various outcrops in the Collingwood district of northwest Nelson (Fig. 1). The marine source rock samples from the Waipawa and Whangai formations are all mudstones. The Waipawa mudstones are significantly richer in TOC (1.7–9.7 wt.%) and contain higher quality organic matter (HI 164–375 mg HC/g TOC) than those from the Whangai Formation (TOC 0.84–1.08 wt.%, HI 112–232 mg HC/g TOC; Table S1). These samples were obtained from a drill core from well Orui-1A in the Wairarapa region (Fig. 1) and several outcrop locations (Taylor White section, Angora Road and Blacks Quarry) in the southern Hawke's Bay and Northland regions of North Island (Fig. 1).

3.3. *Methods*

3.3.1. Asphaltene precipitation

The asphaltene fraction contains the majority of Re and Os in crude oil, and in most cases possesses Re-Os isotopic compositions that are representative of the whole oil (Selby et al., 2007; Georgiev et al., 2016; DiMarzio et al., 2018; Liu et al., 2019). Separation of this fraction therefore pre-concentrates these elements and allows for more precise Re and Os analyses to be undertaken. This is especially important for New Zealand coal-sourced oils, given their typically very low asphaltene contents (Sykes and Zink, 2018).

Asphaltenes precipitation from the bulk oil samples was carried out at GNS Science's Organic Geochemistry Laboratory using methods reported in Speight (2004) and Selby et al. (2007). Stock oils were thoroughly mixed to remove heterogeneities caused by density segregation during storage. Many of the coal-sourced crude oils from New Zealand are solid at room temperature due to their medium to very high wax contents. Therefore, the first step in the separation process involved heating the solid stock oils to about 50°C to obtain a viscous liquid that was thoroughly mixed prior to

sub-sampling. The subsamples (~1 g) were placed in pre-heated glass vials where an excess of *n*-heptane (40 ml) was added and thoroughly mixed before continuous, gentle agitation overnight (at least 12 h) at room temperature using an orbital shaker. The contents of the vials were then centrifuged at 3500 rpm for 10–15 min to allow complete separation of precipitated asphaltene and soluble maltene fractions. Maltene fractions were decanted to waste while the remaining residues (asphaltene fractions) were transferred into pre-weighed glass vials and dried overnight on a hot plate at 60°C. Depending on asphaltene content, the above steps were repeated 2 to 30 times per sample to obtain the required amount of asphaltene (~250 mg) for Re-Os analysis.

3.3.2. Re-Os analysis

Rhenium and Os analyses of the asphaltene fraction of the oil samples were undertaken at Durham University's laboratory for Source Rock and Sulfide Geochronology and Geochemistry in 2018 following previously published protocols (e.g., Selby et al., 2007; Liu et al., 2019). In brief, asphaltene fractions (150–200 mg) were transferred into Carius tubes using small amounts of chloroform ($CHCl_3$; ≤1 ml) and dried on a hot plate at 60°C overnight to evaporate the $CHCl_3$. After complete solvent removal, a known amount of ^{190}Os and ^{185}Re mixed tracer solution and inverse *aqua-regia* digestion mixture (3 ml 12 N HCl + 6 ml 15.5 N HNO_3) were sequentially added, the tube sealed and then placed in an oven at 220°C for 24 h. The Os fraction was extracted and purified from the inverse *aqua-regia* solution using solvent extraction ($CHCl_3$ and back extraction in HBr) and micro-distillation methods, respectively, whereas the Re fraction was extracted using anion exchange chromatography (HCl-HNO_3). The obtained Re and Os fractions were then loaded onto nickel and platinum wire filaments, respectively, and their isotopic compositions measured on the Thermo Scientific TRITON negative thermal ionisation mass

spectrometer (N-TIMS; Creaser et al., 1991) housed at the Arthur Holmes Laboratory, Durham University. The total procedural blanks over the course of this study were 2.41 ± 0.07 pg Re and 0.12 ± 0.05 pg Os, with an average $^{187}Os/^{188}Os$ of 0.26 ± 0.01 (2 SD, n = 4). The average $^{185}Re/^{187}Re$ value for the Re standard solution was 0.5989 ± 0.0016 (2 SD, n = 10), which is in excellent agreement with previously published data (e.g., Cumming et al., 2014; Liu et al., 2019). The average $^{187}Os/^{188}Os$ value for the in-house Durham Romil Osmium Standard (DROsS) was 0.16084 ± 0.00043 (2 SD, n = 8), consistent with previously published data from other laboratories (0.16078 ± 0.00024, Liu and Pearson, 2014; 0.16091 ± 0.00015, van Acken et al., 2019). The uncertainties reported here include those from asphaltene weighing, blank elemental and isotopic compositions, spike calibration, and the precision of the repeated standard measurements.

Rhenium and Os analysis of the source rock samples were undertaken on powdered aliquots of the whole rock material at the same time and at the same laboratory as the oils (Rotich et al. 2020; 2021). Rhenium and Os concentrations are quoted with respect to the whole rock, whereas the Re and Os concentrations of the oils are with respect to the asphaltene fraction.

4. Results

Twelve of the 13 oil samples have low asphaltene contents, ranging from 0.9 to 2.4 wt.% (Table 1). In contrast, the asphaltene content of the Kaikoura Seep oil is higher (15.5%), which is attributed to its more advanced degree of biodegradation, enriching the asphaltene fraction through the loss of *n*-alkanes and other hydrocarbons. For all oil samples, there is no significant direct relationship between asphaltene content and Re and Os concentrations present in the asphaltene fractions (Fig. 6a, b), which range from 0.18 to 5.90 ppb Re, 3.4 to 400.2 ppt Os and 1.3 to 149.9 ppt ^{192}Os (Table 1),

the latter being a measure of Os concentration unaffected by the radiogenic ingrowth of ^{187}Os. Rhenium and ^{192}Os concentrations in the terrestrial Family 11 oils range from 0.18 to 0.45 ppb and 1.3 to 12.7 ppt (Fig. 7a), respectively, mirroring the low concentrations of these elements in their potential Rakopi and North Cape Formation coaly source rocks (0.19–0.37 ppb Re and 5.3–9.6 ppt ^{192}Os; Fig. 7b, Table S1). The low Re and Os concentrations in these terrestrial oils, coupled with their low asphaltene contents, made precise Re and Os measurements difficult, with blank corrections ranging from 3.8 to 10.5% for Re and 1.2 to 21.1% for Os. In contrast, the asphaltene fractions of the marine oils (families 41 and 42) contain significantly higher concentrations of both Re (0.91–5.90 ppb) and ^{192}Os (14.1–149.9 ppt; Fig. 7a), mirroring, again, the higher concentrations of these elements in the marine mudstones of the Waipawa and Whangai formations (3.6–62.3 ppb Re and 55.4–228.2 ppt ^{192}Os; Fig. 7b).

The Re and ^{192}Os concentrations in the asphaltene fraction of the oils are strongly correlated (R^2=0.93) across the full set of 13 oils (Fig. 7a), with generally much higher concentrations of both elements in the marine-sourced oils. The Re and ^{192}Os concentrations in the terrestrial (coaly) and marine source rocks also show a strong correlation (R^2=0.91) across the full sample set, with the marine source rocks having greater concentrations than the terrestrial rocks (Fig. 7b). This is especially true for the Waipawa Formation mudstones, which have consistently higher concentrations of Re and ^{192}Os than the Whangai Formation mudstones. This suggests that the enrichments of both elements are closely related in both the oils and the source rocks.

The asphaltene fractions of the Family 11 oils have ^{187}Re/^{188}Os ratios ranging from 31.1 to 306.0 and ^{187}Os/^{188}Os ratios from 0.514 to 1.164 (Table 1). These ratios show no recognisable linear trend on an isochron diagram (Fig. 8). Within this oil family, the

Tui Area oils exhibit higher (i.e., more radiogenic) $^{187}Os/^{188}Os$ ratios (0.854–1.164) and a smaller range in $^{187}Re/^{188}Os$ ratios (108.6–135.7) compared to those collected from the Maui and Maari-Manaia fields ($^{187}Os/^{188}Os$ 0.514–0.681 and $^{187}Re/^{188}Os$ 31.1–306.0; Table 1, Fig. 8). The $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$ values for the asphaltene fraction of the marine oils from families 41 and 42 range from 0.693 to 0.907 and 78.3 to 208.9, respectively (Table 1).

5. Discussion

5.1. *Evaluation of Re and Os geochronology of terrestrial oils*

The Family 11 oils were analysed to assess whether Re-Os geochronology can be applied to terrestrial oils from Taranaki Basin. However, $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ ratios for these nine oils do not display any linear relationship on an isochron diagram (Fig. 8), thus precluding a reliable Re-Os isochron date for this collection of terrestrial oils.

Studies have suggested that the processes of oil generation and migration lead to homogenisation of $^{187}Os/^{188}Os$ ratios and development of a Re-Os isochron in crude oils (e.g., Selby and Creaser, 2005; Lillis and Selby, 2013; Liu et al., 2018). For example, Re-Os data obtained from oil sand deposits of Alberta, Canada, yield an age of 111.6 ± 5.3 Ma, which is in agreement with burial history models predicting petroleum generation and migration at 110 Ma (Selby and Creaser, 2005). Similarly, Re-Os dates for bitumen from the Polaris Mississippi Valley-type Zn–Pb deposit (Selby et al., 2005) coincide with Rb–Sr sphalerite and paleomagnetic ages for the mineralization of the Polaris deposit suggesting that the Re-Os isotope systematics record the timing of bitumen migration. Lillis and Selby (2013) also presented Re-Os data for crude oils from the Phosphoria petroleum system that yield an age of 211 ± 21 Ma consistent with the timing of oil generation and migration. Rhenium-osmium

isotope data for crude oils from the Duvernay petroleum system in Canada yield an age of 66 ± 31 Ma, which is consistent with basin modelling derived timing of hydrocarbon generation from the Duvernay Formation (Liu et al., 2018). If generation and migration are the only processes needed for development of an oil isochron, then the lack of a linear relationship for the Family 11 oils suggests that: (1) there was insufficient homogenisation of the oils generated from coaly source rock intervals with widely variable initial $^{187}Os/^{188}Os$ (Os_i) values and Re abundance, the latter resulting in heterogeneous $^{187}Os/^{188}Os$ values over time as the ^{187}Re decays, (2) there is an insufficient spread in $^{187}Re/^{188}Os$ values, (3) the Re-Os isotope systematics of the oils were subsequently disturbed, and/or (4) there has been insufficient time since homogenisation for the evolution of an isochron. It should be noted that wide scatter on Re-Os isochron diagrams is not restricted to terrestrial oils, having previously been documented in oils from marine and lacustrine systems (e.g., Cumming et al., 2014; Liu et al., 2018).

Various scenarios have been proposed for charging of the Tui Area, Maui and Maari-Manaia fields, with potential Late Cretaceous terrestrial kitchens including the Maui and Pihama sub-basins, the Kahurangi Trough and a local Maari sub-basin beneath the Maari structure (Fig. 2; Funnell et al., 2001; 2004; Matthews, 2002; 2008; Kroeger et al., 2016; 2021; Reilly et al., 2016; Smith et al., 2016; Seebeck et al., 2019). The more recent basin modelling studies favour charging of the Tui Area Field from the northern Kahurangi Trough; the Maui Field, primarily from the Maui sub-basin, with migration across the Cape Egmont Fault Zone; and the Maari-Manaia Field primarily from the Maui sub-basin, potentially with a subordinate local fluid contribution from the small Maari sub-basin (Fig. 2; Smith et al., 2016; Kroeger et al., 2016, 2021; Seebeck et al., 2019). In all cases, the abundance of gymnosperm-derived diterpene biomarkers within the oils indicates derivation from Late Cretaceous coaly rocks of the

Rakopi and North Cape formations (Killops et al., 1994; Sykes et al., 2012; Sykes and Zink, 2018; Sykes, 2019). These formations have a maximum combined thickness of up to ~2700 m (Seebeck et al., 2019) and their coaly rocks display considerable variation in initial $^{187}Os/^{188}Os$ (Os_i) values and Re abundance. While the full range of Os_i values for these formations is unknown, calculated values for eight coaly rock samples analysed are 0.82–1.24 for Rakopi Formation (at 78 Ma) and 0.31–0.46 for the younger North Cape Formation (at 67 Ma) (Rotich et al., 2021). The difference between the two formations is attributed primarily to changing contributions of Os from weathering of upper continental crust (Rakopi Formation) and freshly erupted mafic rocks (North Cape Formation) (Table S1; Rotich et al., 2021). Rhenium abundances for the above eight coaly rock samples are low, varying from 0.19 to 0.37 (Table S1). However, as the source kitchens for the Tui Area, Maui and Maari-Manaia oils are on the order of 50 km apart and several hundred meter-intervals of coaly source rocks can lie within the oil window at any given time, it is highly likely that the expelled oils would have varied widely in Re abundance and initial Os isotope compositions. It is, therefore, not entirely unexpected to see such scatter in $^{187}Os/^{188}Os$ values on the isochron diagram (Fig. 8), especially given that the nine oils were likely generated from different coal measure intervals in two separate depocentres (i.e., northern Kahurangi Trough and Maui sub-basin).

Notably, even the five Tui Area oils display significant variation in $^{187}Os/^{188}Os$ values (0.85–1.16, Table 1), despite being from a single spill-fill chain that links the Tui, Amokura and Pateke accumulations. Either these accumulations were filled from separate, sequential charges of oil from different source rock intervals of the Rakopi Formation, with incomplete homogenisation of $^{187}Os/^{188}Os$ compositions through migration and accumulation, or the Os isotope compositions were subsequently disturbed within the reservoir.

One reason for selecting the nine Family 11 oil samples from different fields was to maximise the likelihood of achieving a sufficient spread in $^{187}Re/^{188}Os$ ratios (Fig. 2; Selby and Creaser, 2005). The obtained $^{187}Re/^{188}Os$ values for the asphaltene fractions of these oils, however, vary by only 275 units, which is low when compared to most oils successfully dated using the Re-Os geochronometer (up to 1500 units; e.g., Selby and Creaser, 2005; Selby et al., 2005; Finlay et al., 2011; Lillis and Selby, 2013; Cumming et al., 2014; Liu et al., 2018). Asphaltenes obtained from southern Australian asphaltites have produced reliable Re-Os oil isochrons with a much lower spread in $^{187}Re/^{188}Os$ ratios (~147 units) than the Family 11 oils (Corrick et al., 2019; Scarlett et al., 2019). However, as the asphaltites from that study were generated in the mid-Cretaceous (104 ± 12 Ma; Corrick et al., 2019; Scarlett et al., 2019), they would have radiogenically evolved more to better define an isochron compared to the Family 11 oils, which, as discussed below, only commenced expelling significant oil since the Late Miocene (Kroeger et al., 2016; 2021). Indeed, when the Re-Os isotope data for the Maui and Maari-Manaia oils are forward modelled to, for example, 100 Ma in the future, a good correlation is obtained (Table 1). Not so for the Tui Area oils as high variation in Os_i values and a small range in $^{187}Re/^{188}Os$ values hinder any correlation. We therefore consider that the lack of an isochron fit for the Family 11 oils is largely due to a combination of high variation in Os_i values inherited from different Late Cretaceous coaly source rock intervals, an insufficient spread in $^{187}Re/^{188}Os$ values, and insufficient time since oil expulsion for the evolution of an isochron, although other factors discussed below may have also contributed.

Another potential cause of data point scatter on crude oil Re-Os isochron diagrams is disturbance of the Re-Os systematics within the reservoir through processes such as thermochemical sulfate reduction (TSR; Lillis and Selby, 2013), biodegradation and water washing. TSR is a redox reaction that occurs in reservoirs containing anhydrite

or another source of sulfate, whereby petroleum is oxidized to carbon dioxide and sulfate is reduced to hydrogen sulfide (Goldstein and Aizenshtat, 1994; Walters et al., 2015). There is, however, no evidence of TSR having affected the Family 11 oils, which show no detectable H_2S and only low CO_2 in bottom hole and separator PVT samples (Sykes et al., 2011). Similarly, of the nine Family 11 oils, only the two Maari-Manaia oil samples (Maari-MR8A and Manaia-2) are biodegraded, but only to levels 2–3 (Section 3.1.2). The $^{187}Os/^{188}Os$ values of these two oils do not stand out from those of the other Family 11 oils, and their $^{187}Re/^{188}Os$ values are only slightly higher. Biodegradation to levels 2–3 is likely restricted to hydrocarbons in the maltene fraction, sparing the more resistant asphaltene fraction within which much of the Re and Os resides. Biodegradation can therefore also be discounted as a significant process affecting the Re-Os systematics of these oils, consistent with the findings of other studies of biodegraded oils and tar sands (Selby and Creaser, 2005; Finlay et al., 2011; Lillis and Selby, 2013).

Contact experiments have demonstrated that Re and Os can readily transfer between aqueous solutions and oils (Mahdaoui et al., 2015; Hurtig et al., 2019), and all of the Tui Area, Maui and Maari-Manaia oils in this study appear to have been water-washed to varying degrees (Fig. 5). The Re-Os systematics of these low Re- and Os-bearing oils may be more vulnerable to the adverse effects of water washing because water-oil ratios of less than 100 (based on estimated concentration levels of 4 ppt Re and 0.07 ppt Os in groundwaters) would be required to completely overprint their Re-Os systematics (e.g., Colodner et al., 1993; Paul et al., 2010; Mahdaoui et al., 2015). Such water-oil ratios are likely in conventional petroleum systems, such as in offshore Taranaki Basin, because reservoir rocks are commonly fully saturated with formation water prior to the ingress of oil (Magoon and Dow, 1994; Levorsen, 2001). Moreover, in the case of the Tui Area oils, the three pools of oil overlie an aquifer with a strong

bottom water drive (NZOP, 2005; Matthews et al., 2008), which would help sustain Re and Os concentration and isotope ratio gradients across the oil-water interface. The relative degree of water washing indicated between the three oil pools (Pateke>Amokura>Tui) matches the present-day direction of hydrodynamic flow from Pateke to Tui, and would account for the consistent difference in $^{187}Os/^{188}Os$ ratios between the four Pateke and Tui oils if the $^{187}Os/^{188}Os$ composition of the formation water is approximately 0.8 or lower (Fig. 8). However, there are currently no Os isotope data for formation water in Taranaki Basin to support this assumption, and $^{187}Os/^{188}Os$ values for formation waters elsewhere are generally more radiogenic (>1; Paul et al., 2010; Hnatyshin, 2018). Furthermore, it has been shown that formation waters in deep subsurface aquifers are generally severely depleted in Re and Os (Hnatyshin, 2018), and thus crude oils may not gain appreciable Re and Os from any interaction with these waters. This is evident in crude oils from the Duvernay petroleum system in the Western Canada Sedimentary Basin whose $^{187}Os/^{188}Os$ compositions are much lower than estimated $^{187}Os/^{188}Os$ values for formation fluids in the basin, and thus, less likely to have been impacted by interaction with these fluids (Liu et al., 2018). Therefore, there is no definitive evidence to indicate whether any of the variation in $^{187}Os/^{188}Os$ ratios amongst the Tui Area oils or the other Family 11 oils can be attributed to water washing, rather than incomplete homogenisation of highly variable initial $^{187}Os/^{188}Os$ values.

5.2. *Some comments on the actual event being dated*

The terrestrial oils in this study did not yield a Re-Os isochron. However, this does not discount the possibility of isochrons being obtained for terrestrial oils elsewhere. Should an isochron emerge, it is important to consider what actual event or process is being dated—oil generation, migration or emplacement—particularly if the assigned

age is critical for establishing temporal relationships between elements of a petroleum system. Most studies of marine and lacustrine oils have assigned isochron ages to the time of oil generation (e.g., Cumming et al., 2014; Liu et al., 2018). However, the process of oil generation is confined to the host kerogen generating the oil (Pepper and Corvi, 1995a), thus the heterogeneity of source rock $^{187}Os/^{188}Os$ composition will still exist within the generated oil residing within the source rock interval (Selby and Creaser, 2005; Selby et al., 2007; Finlay et al., 2011; Rooney et al., 2012; Cumming et al., 2014; Liu et al., 2018). Adequate homogenisation of $^{187}Os/^{188}Os$ ratios, which is a requisite condition for forming a Re-Os isochron, can only occur with the mixing of oil that results from expulsion, migration and accumulation. For the more oil-prone, marine and lacustrine source rock organofacies, oil expulsion and primary migration tend to be efficient and in geological terms, are thought to occur relatively soon after the onset of generation (Pepper and Corvi, 1995a; Liu et al., 2018). Moreover, secondary migration is also generally an efficient process (Pepper and Corvi, 1995b), occurring over relatively short periods of geological time. Thus, for marine and lacustrine oils, it may be satisfactory to equate Re-Os isochron ages with oil generation, but it still remains that homogenisation will not commence until migration proceeds upon expulsion.

The distinction between the timing of generation and migration is more critical for terrestrial oils because coaly organofacies tend to be both more heterogeneous and less efficient expellers of oil (Pepper and Corvi, 1995b). In coaly source rocks with oil potential, there is typically a significant time lag between the onset of oil generation and when the kerogen pore saturation threshold is reached to enable expulsion. The lag duration will depend on, among other things, source rock quality (mainly HI) and the burial and thermal histories, but can be 40 Myr or more (Pepper, 1991; Pepper and Corvi, 1995b; Zhao and Cheng, 1998; Wilkins and George, 2002; Sykes et al.,

2014). This is consistent with generation and expulsion histories extracted from the model of Kroeger et al. (2022) for the Maui sub-basin and the Kahurangi trough (Fig. 9). We therefore propose that Re-Os isochron ages for terrestrial oils date the onset of expulsion (i.e., start of migration) and that for oil-source fingerprinting, oil Os_i values for undisturbed systems should match the $^{187}Os/^{188}Os$ composition of the source rock at the time of oil expulsion (Os_e), rather than generation (Os_g).

5.3. *Os isotope fingerprinting of Family 11 terrestrial oils*

Given that oil expulsion from the central Maui sub-basin and northern Kahurangi Trough is modelled to have commenced only within approximately the last 13 to 3 Myr (Fig. 9; Kroeger et al., 2016; 2021), we consider 10 Ma as the average oil expulsion date for the purpose of calculating the Os_i and Os_e values from the present-day Re-Os data for the oil and source rock samples, respectively. The use of an average oil expulsion date does not affect the outcome of Os isotope fingerprinting because Os_i and Os_e values will generally co-vary with changing oil expulsion dates, especially when the $^{187}Re/^{188}Os$ values exhibited by both the terrestrial oils and source rocks are low (≤ 306 for the samples studied here; Cumming et al., 2014).

The Os_i values for the Family 11 terrestrial oils collectively display a wide range from 0.47 to 1.14, with a mean value of 0.78 (Table 1; Fig. 10). Although these values overlap much of the range of Os_e values (0.38–1.38, mean = 0.81) for their inferred Late Cretaceous Rakopi and North Cape Formation source rocks (Table S1), they also show considerable overlap with the Os_e values of Paleocene (Farewell Formation) and Eocene (Mangahewa Formation) coaly rocks (Fig. 10). Moreover, they also overlap the Os_i values for the Family 41 and 42 marine oils and their potential Waipawa and Whangai source rocks, respectively. The Os_i values of the terrestrial oils in this study are thus not sufficiently specific to provide a unique fingerprint of their Late Cretaceous

coaly source rock formations on their own. Osmium isotope compositions therefore appear to have limited potential for broad oil-source rock correlation within the predominantly coal-sourced petroleum systems of Taranaki Basin.

Within Family 11, the Tui Area oils exhibit notably higher (more radiogenic) Os_i values (0.84–1.14) than oils from the Maui and Maari-Manaia fields, which have only moderately radiogenic Os_i values (0.47–0.65). This difference is inferred to be a direct result of generation from different Late Cretaceous coaly source rock intervals within the northern Kahurangi Trough and Maui sub-basin, possibly with greater relative contributions from the Rakopi and North Cape formations to the Tui Area and Maui/Maari-Manaia oil fields, respectively (Fig. 10). Rakopi Formation coaly sediments appear to have more radiogenic Os compositions, possibly reflecting greater input from weathering of upper continental crust, whereas North Cape Formation coaly sediments have less radiogenic Os compositions, possibly from weathering of freshly erupted mafic rocks (Rotich et al., 2021). The most recent basin models identify Rakopi Formation as the principal source rock unit in both the Maui sub-basin and Kahurangi Trough based on coaly source rock distribution, volume and maturity (Kroeger et al., 2016; 2021). However, the less radiogenic Os compositions of the oils in the Maui and Maari-Manaia fields may reflect a greater, though still subordinate, contribution from the North Cape Formation.

Whilst the difference in Os_i values between the Tui Area and the Maui and Maari-Manaia oils may add further support for the derivation of these oils from different sub-basins, it is evident from the wide variation in Os_i values amongst the Family 11 oils that more oil and source rock Re-Os isotopic data are needed to better constrain the underlying controls on the $^{187}Os/^{188}Os$ compositions of the terrestrial oils.

5.4. *Os isotope fingerprinting of Family 41 and 42 marine oils*

Wide variation in initial $^{187}Os/^{188}Os$ compositions is also reported to have hampered petroleum geochronology and oil-source correlation in some lacustrine (Cumming et al., 2014) and marine (Liu et al., 2018) petroleum systems. The marine oils of this study provide a further example. The average age of 10 Ma used to calculate Os_i and Os_e values for fingerprinting the Family 11 terrestrial oils and their source rocks is also deemed appropriate for comparing the Family 41 and 42 marine oils and their potential source rocks. Family 41 oils from the Kora Field (Fig. 1) are modelled to have been expelled from the Late Paleocene Waipawa Formation from the Miocene (15 Ma) to present day (Brett, 2005; Clayton, 2011; Kroeger et al., 2022). Similarly, thermal maturity models from a number of sites in East Coast Basin indicate potential generation and expulsion of Family 42 oils from the Whangai Formation from the Miocene to Pliocene (Field et al., 1997; Schlumberger, 2017).

The calculated Os_i values at 10 Ma for the two Family 41 oils from Kora-1 are markedly different (Fig. 10). The Kora-1(A) oil from the Eocene Tangaroa Formation sandstone reservoir has a moderately radiogenic Os_i value (0.66), consistent with the calculated Os_e values (0.48–0.68) for the Waipawa Formation source rock samples (Fig. 10). In contrast, the Os_i value (0.90) for the Kora-1(B) oil from the Miocene Mohakatino Formation volcaniclastic reservoir is significantly more radiogenic. Both oils have the distinctive heavy carbon isotopic signature and high C_{30} sterane content that are diagnostic of the Waipawa Formation, and were undoubtedly sourced from this unit (Reed, 1992; Killops et al., 1994; Killops, 1996; Rogers et al., 1999; Sykes et al., 2012; Naeher et al., 2019). As the Waipawa Formation is estimated to be <30 m thick in the vicinity of Kora Field (Clayton, 2011), it is reasonable to assume that the entire thickness of the formation would lie within the oil expulsion window at the same time,

thus leaving two possible scenarios to explain the high Os_i value of the Kora-1(B) oil: 1) the Re-Os systematics of this oil have been disturbed, or 2) this oil was derived from a different fetch or drainage area of the Waipawa Formation to that of the Kora-1(A) oil. The latter is consistent with the modelling results of Kroeger et al. (2022) which suggest that the Miocene Kora-1(B) accumulation was charged late, in the Plio-Pleistocene and quite possibly from a fetch area further away from the volcano unaffected by magmatic heating.

Disturbance of the Re-Os systematics through thermochemical sulfate reduction (Lillis and Selby, 2013) can be discounted because the Kora-1(B) oil shows no detectable H_2S or CO_2 in bottom hole PVT sample (Sykes et al., 2011). Any biodegradation in the Kora-1(B) sample is also considered minimal (Fig. 4). Disturbance through interaction with reservoir formation waters (Mahdaoui et al., 2015; Hurtig et al., 2019) seems unlikely because most volcanic rocks have non-radiogenic $^{187}Os/^{188}Os$ compositions (generally <0.3; e.g., Lassiter and Luhr, 2001; Suzuki and Tatsumi, 2006), whereas the Kora-1(B) oil, reservoired in volcaniclastic rocks, has a distinctly more radiogenic Os_i value (0.90) than the Kora-1(A) oil (0.66).

No Waipawa Formation mudstone samples of sufficient size for Re and Os isotope analysis are available from the immediate vicinity of Kora Field. However, in their study of the Re-Os systematics of Waipawa Formation in East Coast Basin (Fig. 1), Rotich et al. (2020) suggested that scatter in $^{187}Os/^{188}Os$ values within the Taylor White section may have been caused by localised variation in seawater Os_i values related to the episodic and localised influx of large amounts of terrestrial organic matter (Naeher et al., 2019). Such influxes may have supplied high loads of continental-derived Os with more radiogenic $^{187}Os/^{188}Os$ compositions, not only within the Taylor White section but also, potentially, within the respective fetch areas for the Kora-1(A)

and (B) oils. Without further data, however, the cause of the higher Os_i value of the Kora-1(B) oil compared to those of the Kora-1(A) oil and Waipawa mudstone samples, remains uncertain.

Similarly, the underlying cause of the higher Os_i values of the Family 42 Waitangi (0.78) and Kaikoura (0.86) seep oils compared to the Os_e values of the potential Whangai Formation source rock (0.46–0.58; Fig. 10) remains unknown. The Os_e values are from the upper (Paleocene) section of the Whangai Formation, which could possibly explain the less radiogenic values given that seawater $^{187}Os/^{188}Os$ composition in the Paleocene ranged from 0.3 to 0.4 (Peucker-Ehrenbrink and Ravizza, 2012). Deeper sections (Late Cretaceous) of the Whangai Formation would likely exhibit more radiogenic Os_e values because Late Cretaceous seawater $^{187}Os/^{188}Os$ composition ranged from 0.6 to 0.7 (Peucker-Ehrenbrink and Ravizza, 2012). However, these sections generally have very poor oil generation potential (Field et al., 1997; Hollis and Manzano-Kareah, 2005). Therefore, the mismatch of $^{187}Os/^{188}Os$ compositions lends further support to previous suggestions that the Family 42 seep oils are not derived from known organofacies of the Whangai Formation. Rather, they are more likely to have originated from another Late Cretaceous marine source unit with similar biomarker and carbon isotope compositions as the Whangai Formation.

6. Conclusions

This is the first study of the Re-Os systematics of terrestrial (coal-sourced) oils. Although a radiometric age could not be determined, the study nonetheless provides useful insights into the potential application of Re-Os geochronology and Os isotope fingerprinting in coal-sourced petroleum systems. Nine genetically related terrestrial oils (Family 11) from offshore Taranaki Basin contain similar, low concentrations of Re

and ^{192}Os as their correlative Late Cretaceous coaly source rocks (Rakopi and North Cape formations). The Re and ^{192}Os concentrations in these terrestrial oils are generally one to two orders of magnitude lower than those in marine oils from Taranaki (Family 41) and East Coast (Family 42) basins.

The $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ ratios of the Family 11 terrestrial oils do not display a linear relationship and hence did not yield a Re-Os isochron age. We attribute this to: (1) insufficient homogenisation of widely variable initial $^{187}Os/^{188}Os$ (Os_i) values and Re abundance inherited from thick, coaly source rock intervals (up to about 2700 m) within the Maui sub-basin and northern Kahurangi Trough kitchens; (2) insufficient spread of $^{187}Re/^{188}Os$ values (only 275 units); (3) insufficient time since oil expulsion for the evolution of an isochron (expulsion is modelled from approximately 10 Ma to the present day); and (4) potentially, water washing of the oil columns. Although the oil samples are all water-washed to varying degrees, there is no definitive evidence that water washing has disturbed the Re-Os systematics. We recommend that future Re-Os studies of terrestrial oils be done on simple, well-characterised systems with a single source rock, relatively fast petroleum generation, well-defined migration pathways and limited post-generation alterations.

Most previous studies of marine and lacustrine oils have assigned Re-Os isochron ages to the time of oil generation. However, as adequate homogenisation of $^{187}Os/^{188}Os$ ratios can only occur with the mixing of oil that results from expulsion, migration and accumulation, isochron ages correspond best to the timing of oil expulsion. This distinction between the timing of oil generation and migration is more critical for terrestrial oils because of the typically longer time lag between the onset of oil generation and expulsion from coaly source rocks, which, in the case of the Family 11 study oils, is modelled to be up to about 40 Myr. Longer lag times are possible in

other (sub-)basins, depending on, among other things, coaly source rock quality and the burial and thermal histories. We therefore suggest that Re-Os isochron ages for terrestrial oils should date the onset of expulsion (i.e., start of migration) and that for oil-source correlation, calculated oil Os_i values should match the calculated $^{187}Os/^{188}Os$ ratios of the source rock at the time of oil expulsion (Os_e), rather than generation (Os_g).

Calculated Os_i values for the Family 11 study oils display a wide range and do not provide a unique fingerprint of their Late Cretaceous coaly source rock formations. Os isotope compositions therefore appear to have limited potential for broad oil-source rock correlation within the predominantly coal-sourced petroleum systems of Taranaki Basin. Nonetheless, the observed Os_i values are distinct between two sub-basins which, consistent with basin modelling, suggest charge of the Tui Area Field and the Maui and Maari-Manaia fields from different source kitchens. Significantly higher (more radiogenic) Os_i values of the Tui Area oils may indicate a charge predominantly from the Rakopi Formation in the Kahurangi Trough, whilst the less radiogenic Os_i values of the Maui and Maari-Manaia oils may suggest a greater contribution from the North Cape Formation in the Maui sub-basin, although further samples are needed to confirm this.

Acknowledgements

This study and the PhD scholarship awarded to EKR were primarily funded by the Ministry of Business, Innovation and Employment (MBIE), New Zealand, as part of the GNS Science-led research programme “Understanding petroleum source rocks, fluids, and plumbing systems in New Zealand basins: a critical basis for future oil and gas discoveries” (Contract C05X1507). We thank Antonia Hoffman, Geoff Nowell and Chris Ottley of Durham University, Roger Tremain and Andy Phillips of GNS Science,

and Bruce Charlier and Luisa Ashworth of Victoria University of Wellington for their technical assistance. Special thanks to all the staff at the National Core Store in Featherston for providing access and assistance during oil sub-sampling. We thank Katz Suzuki, Candace Martin and Warren Dickinson for feedback on an earlier version of the manuscript. This contribution has benefited from thoughtful and constructive comments of two anonymous reviewers, and the editorial handling of Professor Quanyou Liu.

Figures

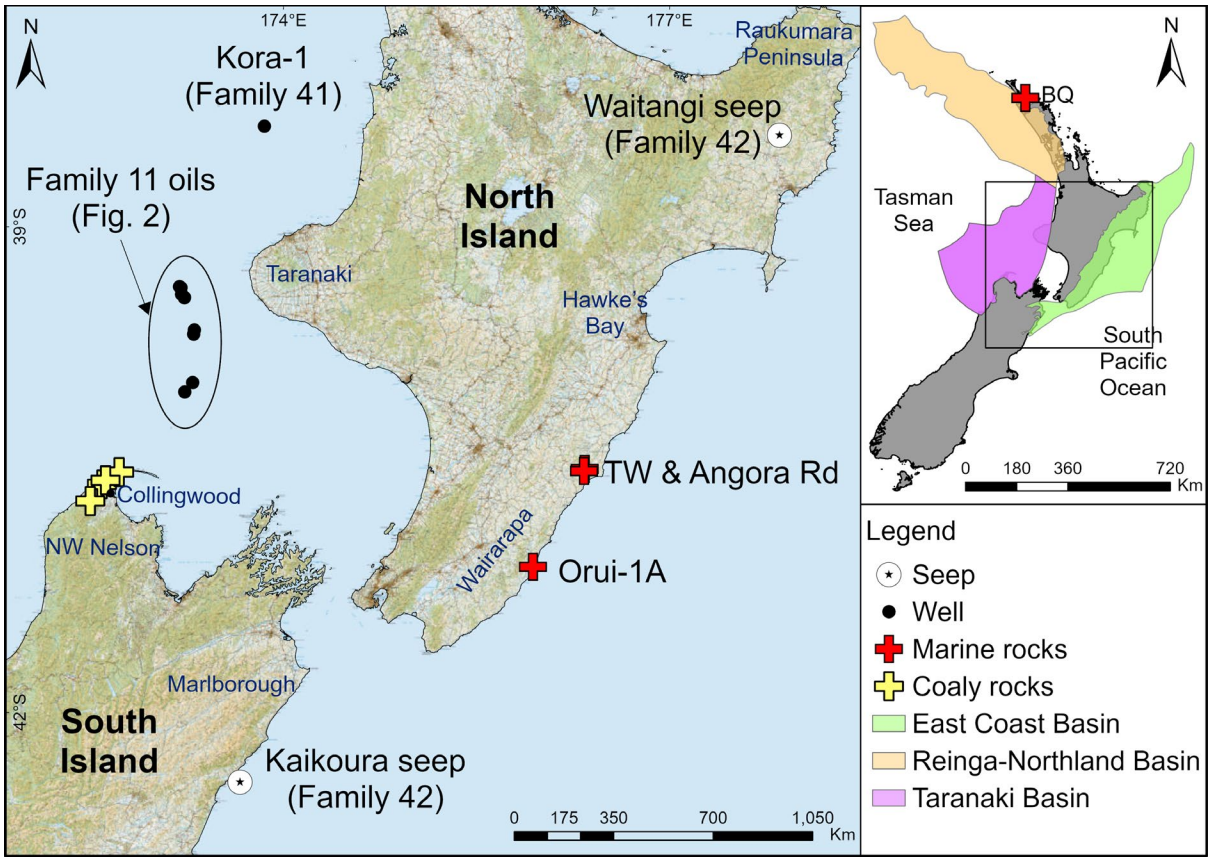

Fig. 1. Locality map of the studied oil and source rock samples in the Taranaki and East Coast basins and onshore Northland. TW = Taylor White outcrop; BQ = Blacks Quarry outcrop.

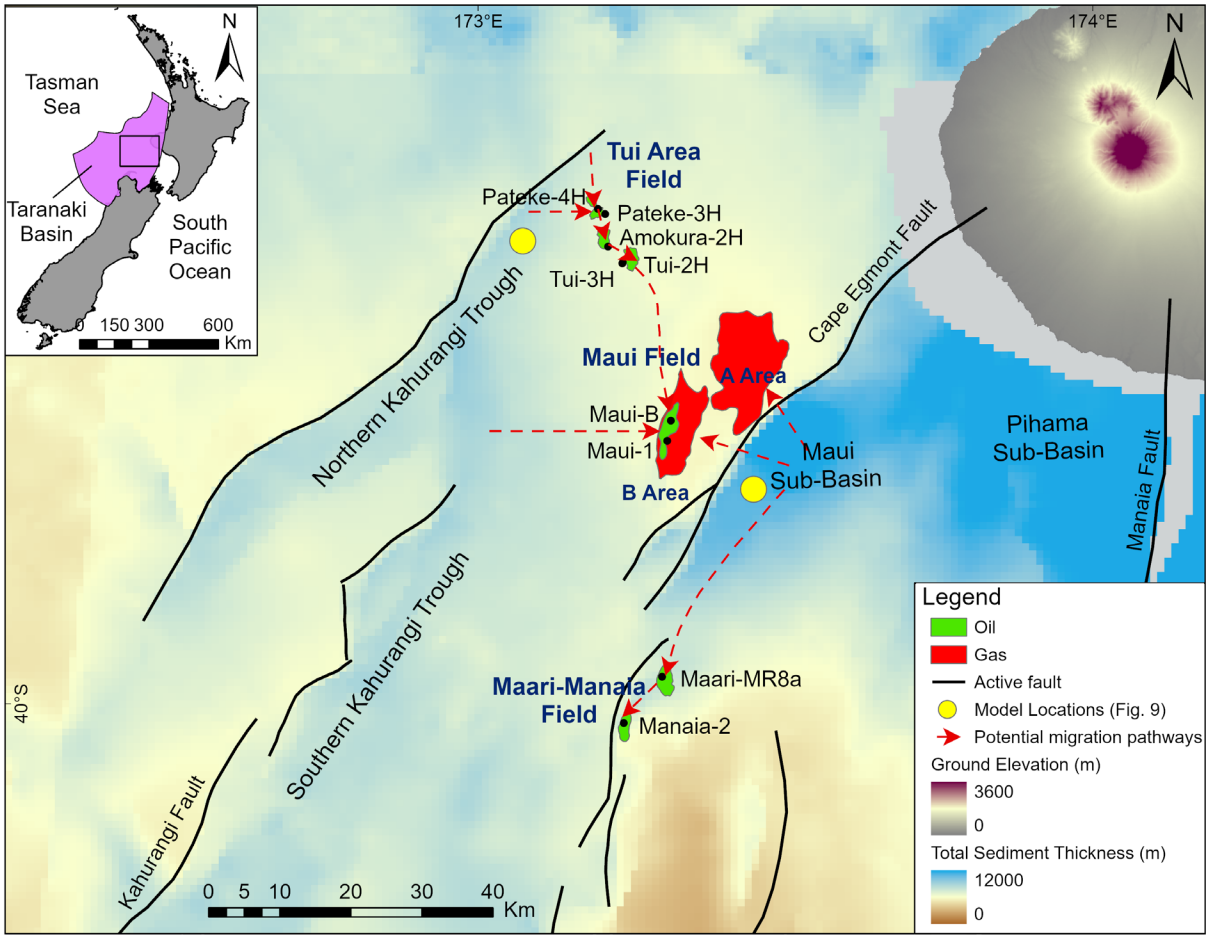

Fig. 2. Detailed map of Taranaki Basin showing distribution of the studied Family 11 oils, oil and gas fields, potential migration pathways and major faults bounding Late Cretaceous sub-basins in which Rakopi and North Cape Formation coal measures are mapped (Matthews, 2008; Bull et al., 2016; Kroeger et al., 2016; 2021). The yellow dots mark the locations where oil and gas generation and expulsion histories in Figure 9 were modelled.

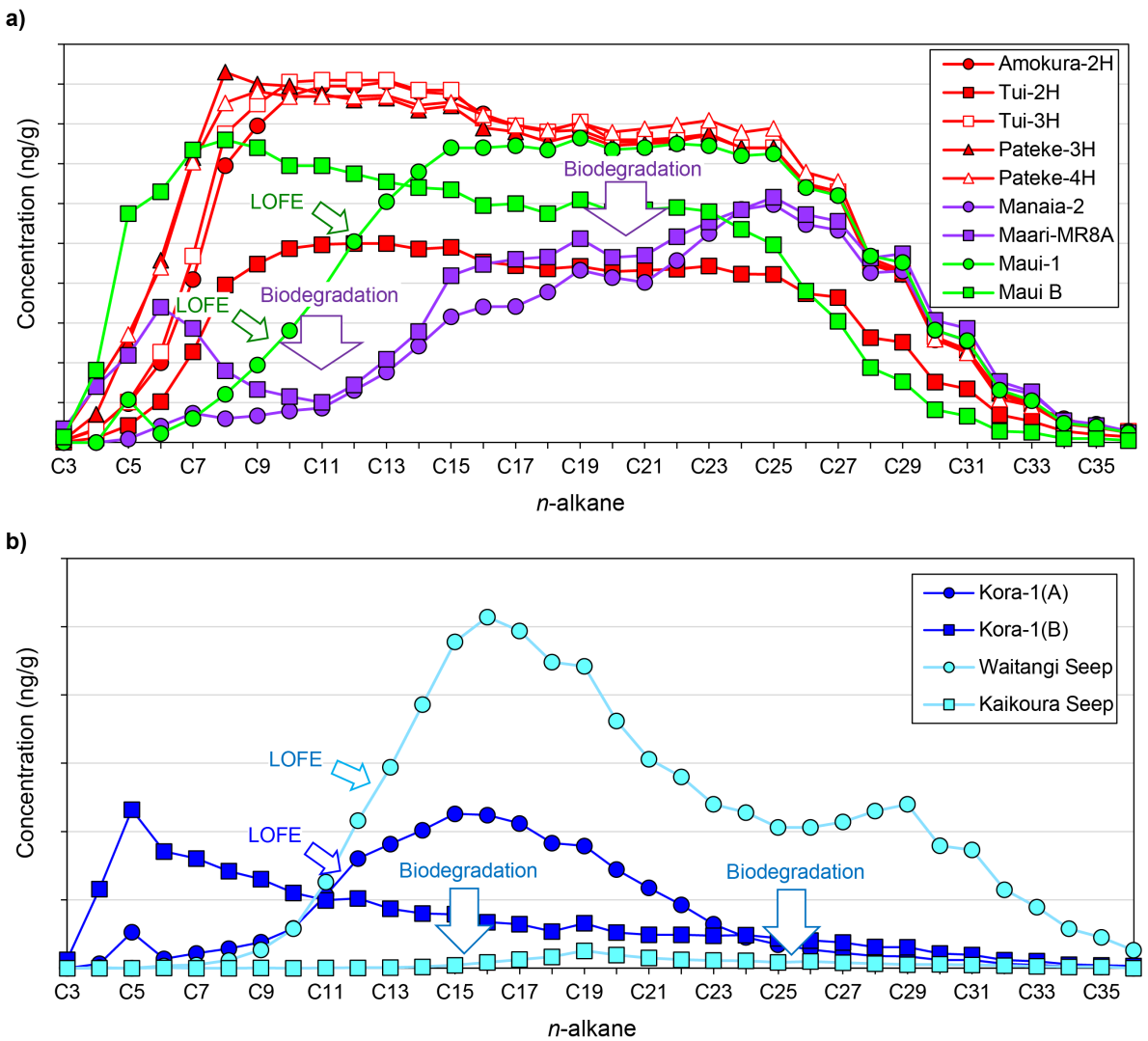

Fig. 3. *n*-alkane distributions of the (a) terrestrial and (b) marine study oils (data from Sykes and Zink, 2018; and GNS Science unpublished results). LOFE = loss of front-ends through evaporation.

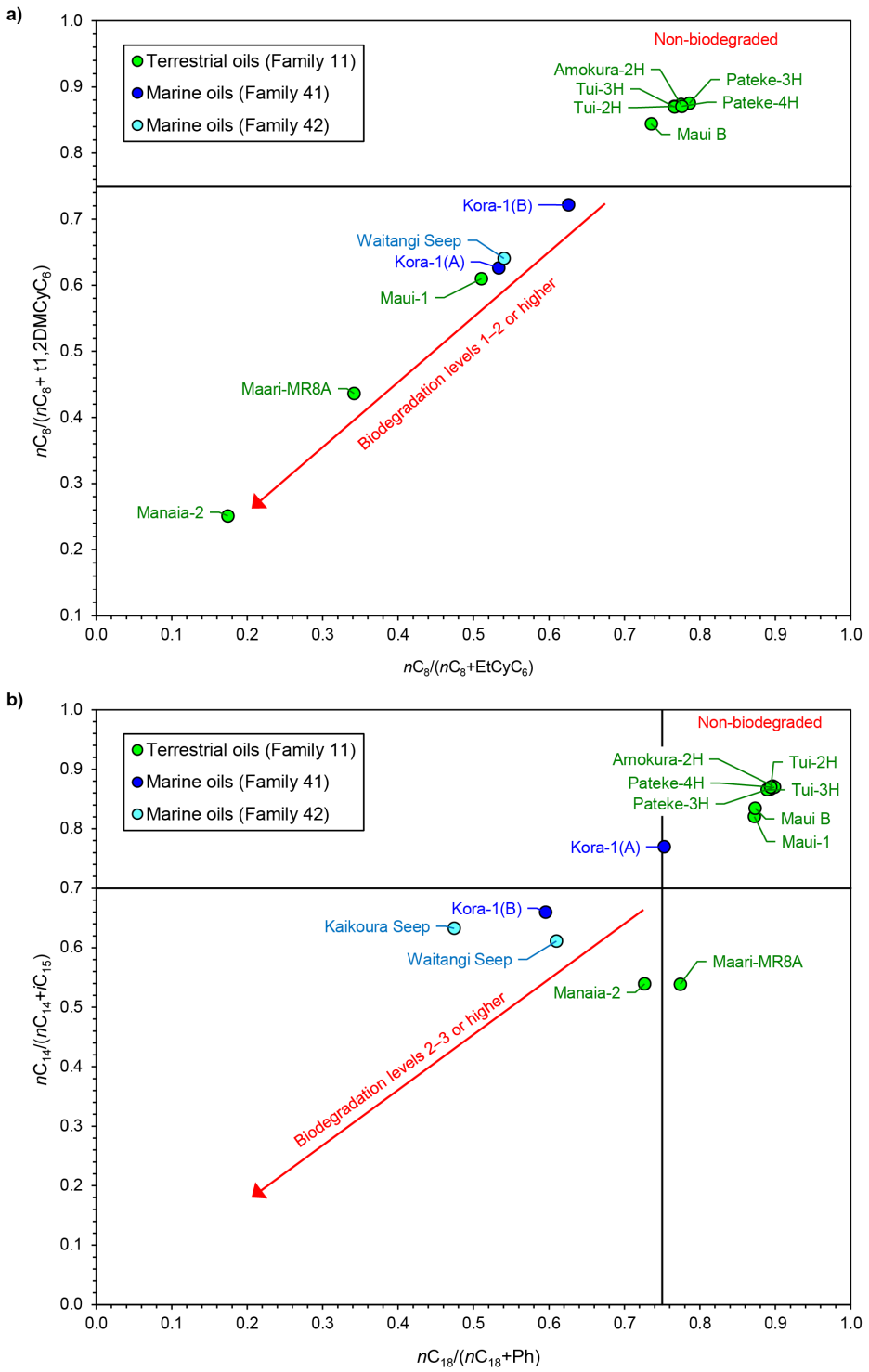

Fig. 4. Biodegradation of the terrestrial and marine study oils to (a) levels 1–2 or greater and (b) levels 2–3 or greater indicated by ratios of *n*-alkanes, cycloalkanes and isoprenoids. nC_8: *n*-octane; *t*-1,2DMCyC_6: *trans*-1,2-dimethylcyclohexane; EtCyC_6: ethylcyclohexane; nC_{14}: *n*-tetradecane; nC_{18}: *n*-octadecane; iC_{15}: *iso*-pentadecane; Ph: phytane. Biodegradation levels are those of Peters et al. (2005).

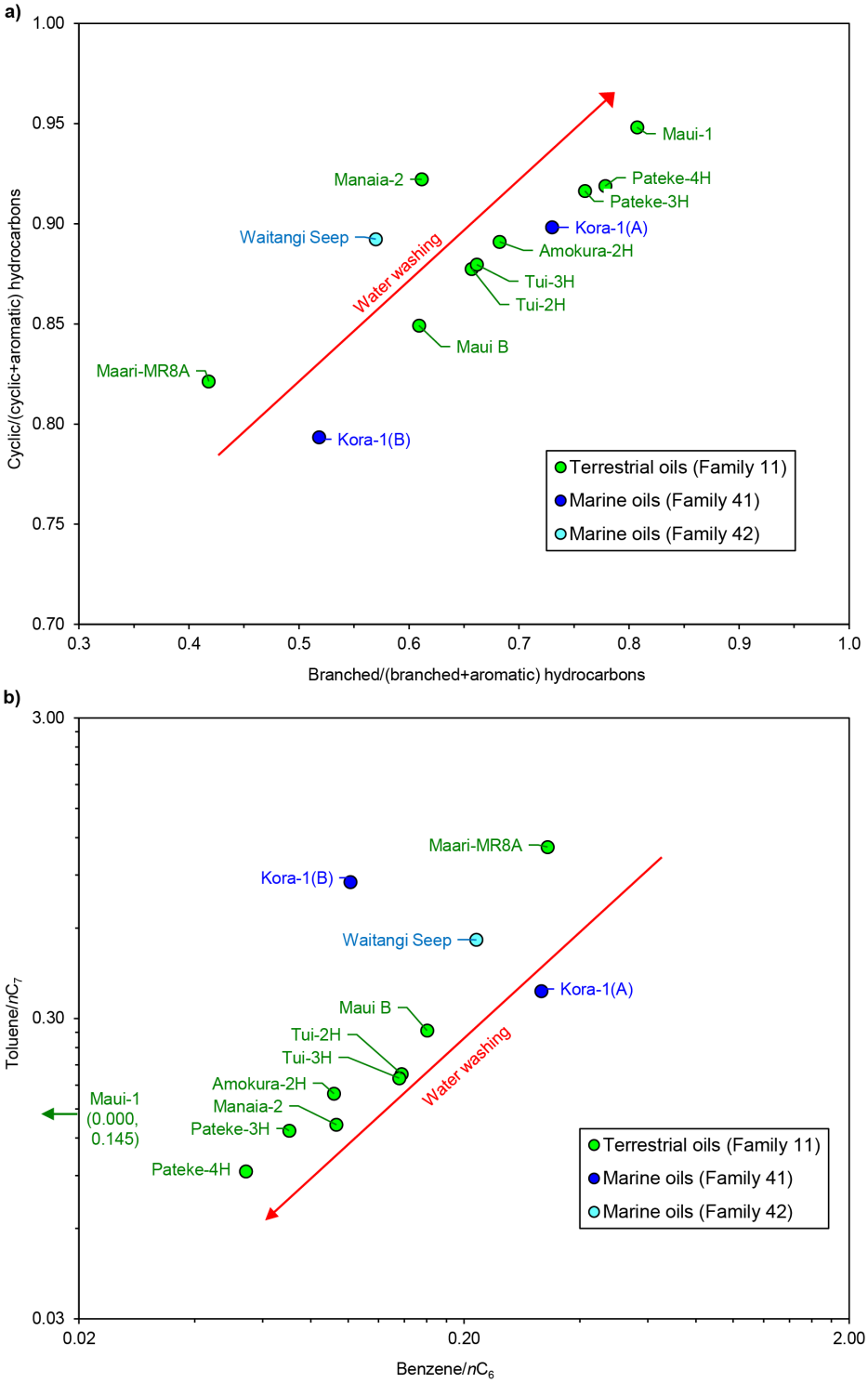

Fig. 5. Relative degree of water washing of the terrestrial and marine study oils indicated by cross-plots based on (a) C_6 to C_8 branched, cyclic and aromatic hydrocarbons, and (b) benzene and toluene aromatic hydrocarbons, *n*-hexane (nC_6) and *n*-heptane (nC_7). The Kaikoura Seep sample cannot be shown on either plot because of the major loss of C_6–C_8 hydrocarbons from biodegradation.

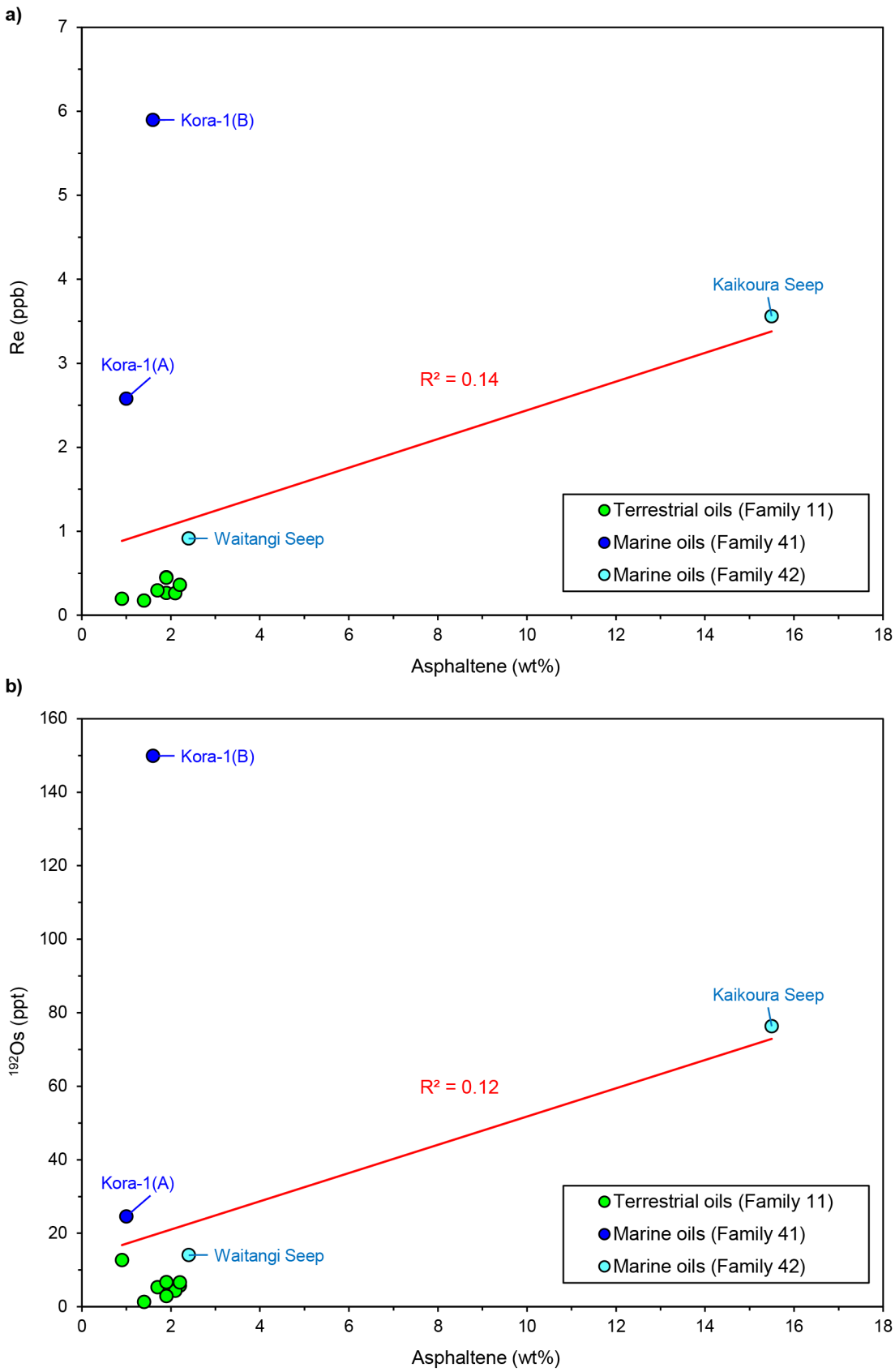

Fig. 6. Cross-plots of (a) Re and (b) ^{192}Os concentrations versus the asphaltene content of oils from families 11, 41 and 42.

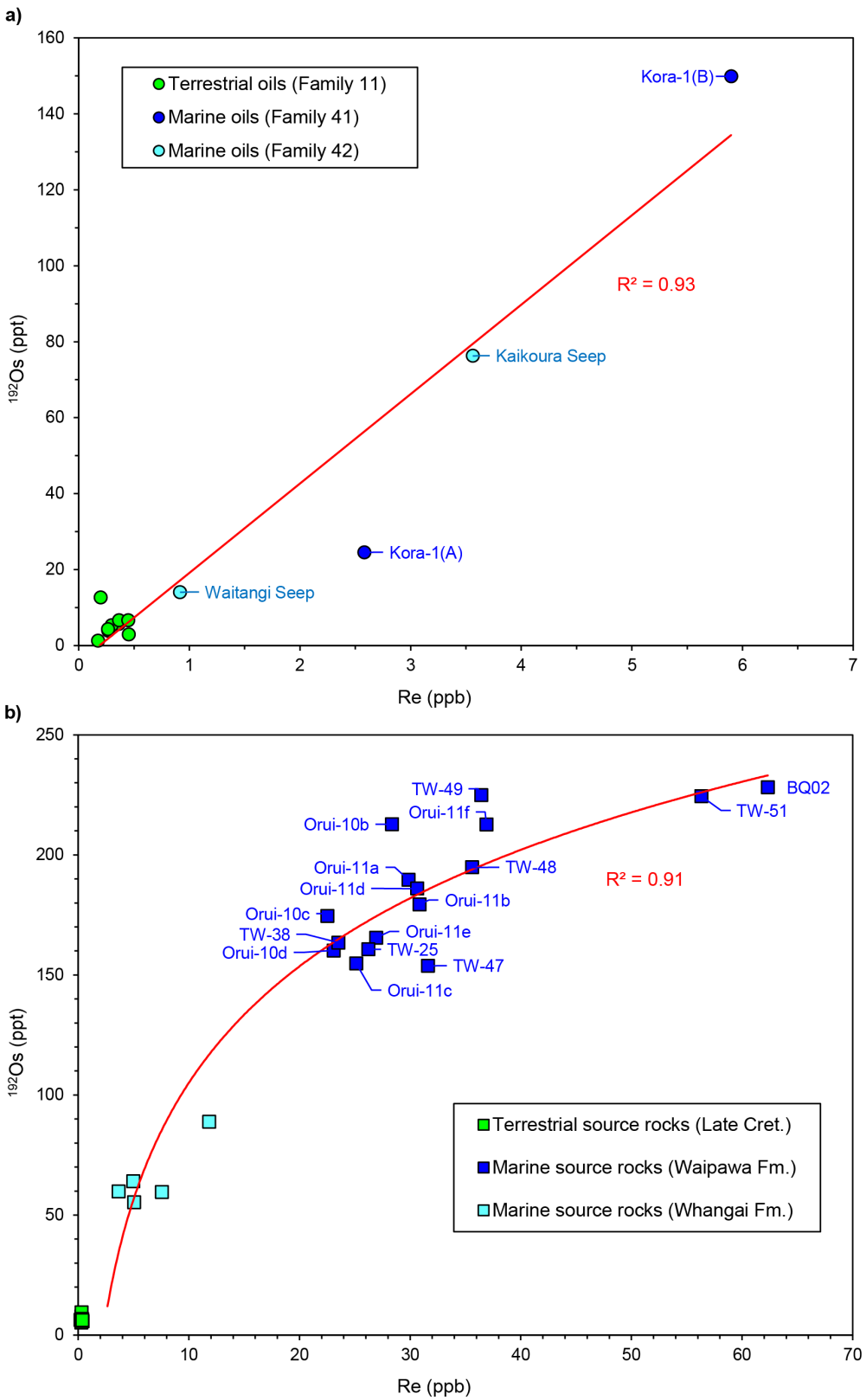

Fig. 7. Cross-plots of Re and ^{192}Os concentrations in (a) the asphaltene fractions of terrestrial (Family 11) and marine oils (families 41 and 42) and b) their correlative or similar source rocks.

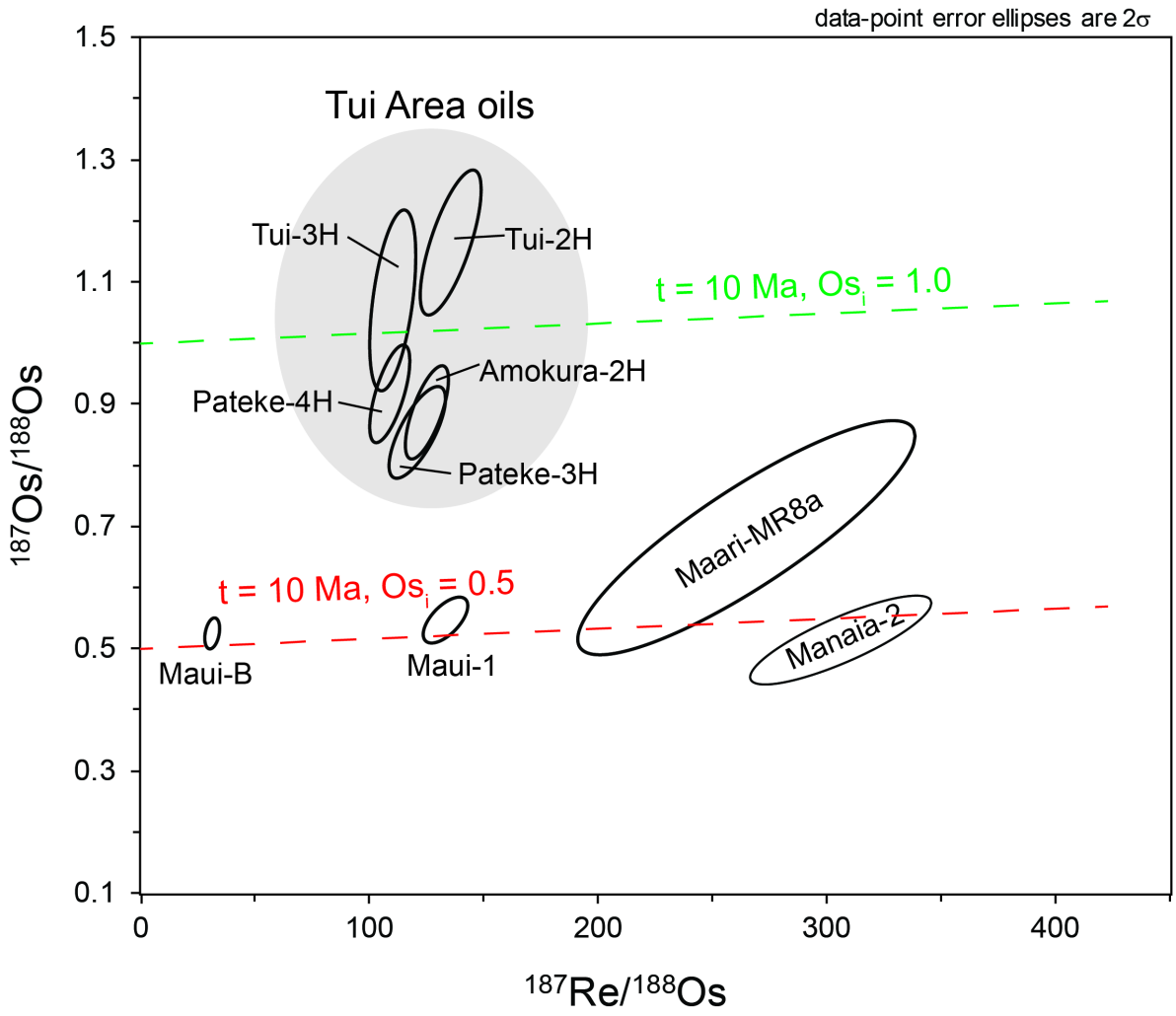

Fig. 8. ^{187}Re/^{188}Os versus ^{187}Os/^{188}Os for the asphaltene fractions of Family 11 terrestrial oils from the Tui Area, Maui and Maari-Manaia fields. Uncertainty ellipses show the 2σ uncertainty. Reference lines with slopes equivalent to the timing of oil expulsion from the central Maui sub-basin and northern Kahurangi Trough (~10 Ma; Kroeger et al., 2021) and Os_i values of 0.5 and 1.0 are shown by the red and green dashed lines, respectively.

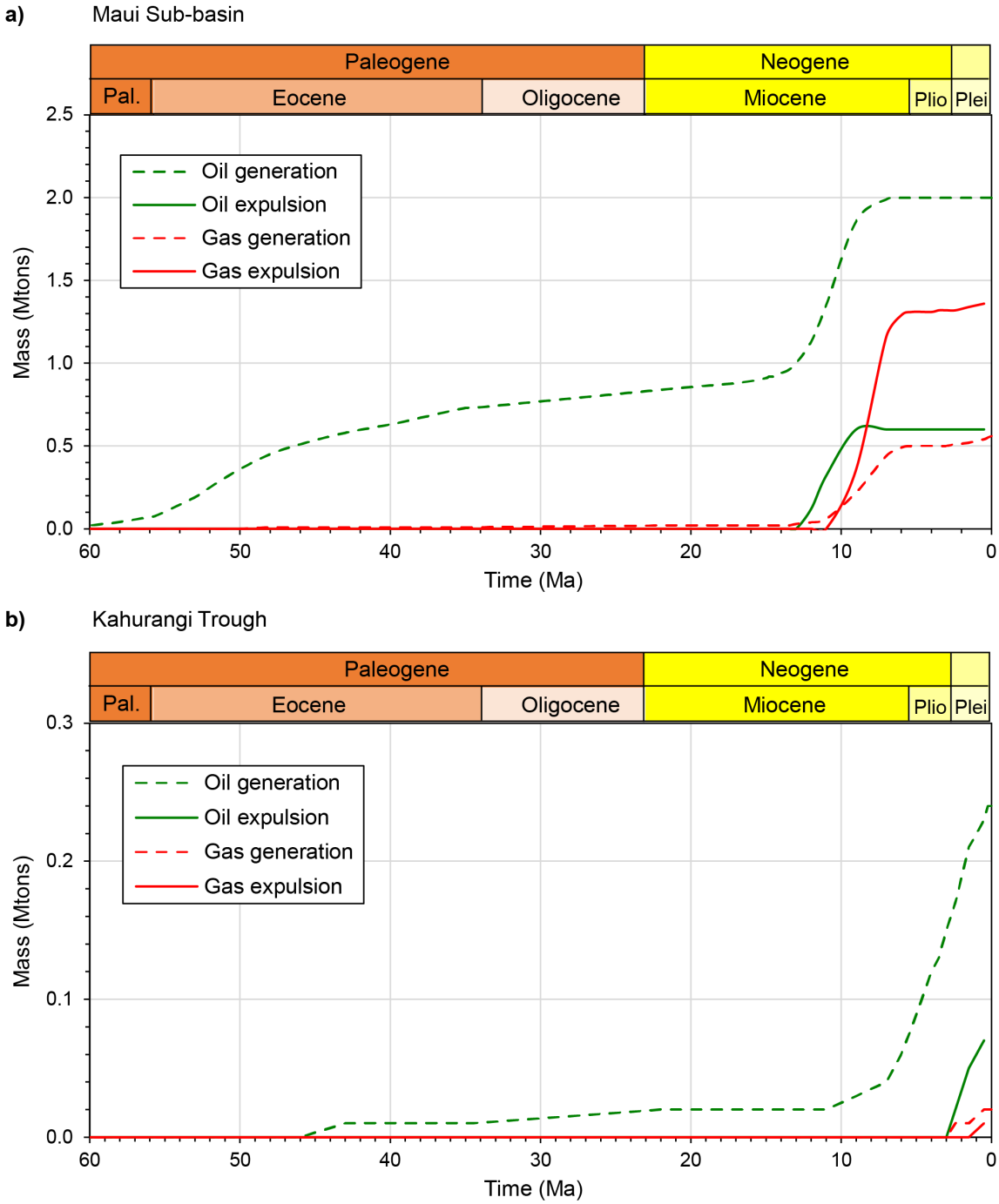

Fig. 9. Modelled oil and gas generation and expulsion histories of Late Cretaceous Rakopi Formation coaly source rocks at selected sites within the (a) central Maui sub-basin and (b) northern Kahurangi Trough. The models show cumulative mass (in megatons) per 200 x 200 m cell using organofacies D/E kerogen kinetics of Pepper and Corvi (1995a).

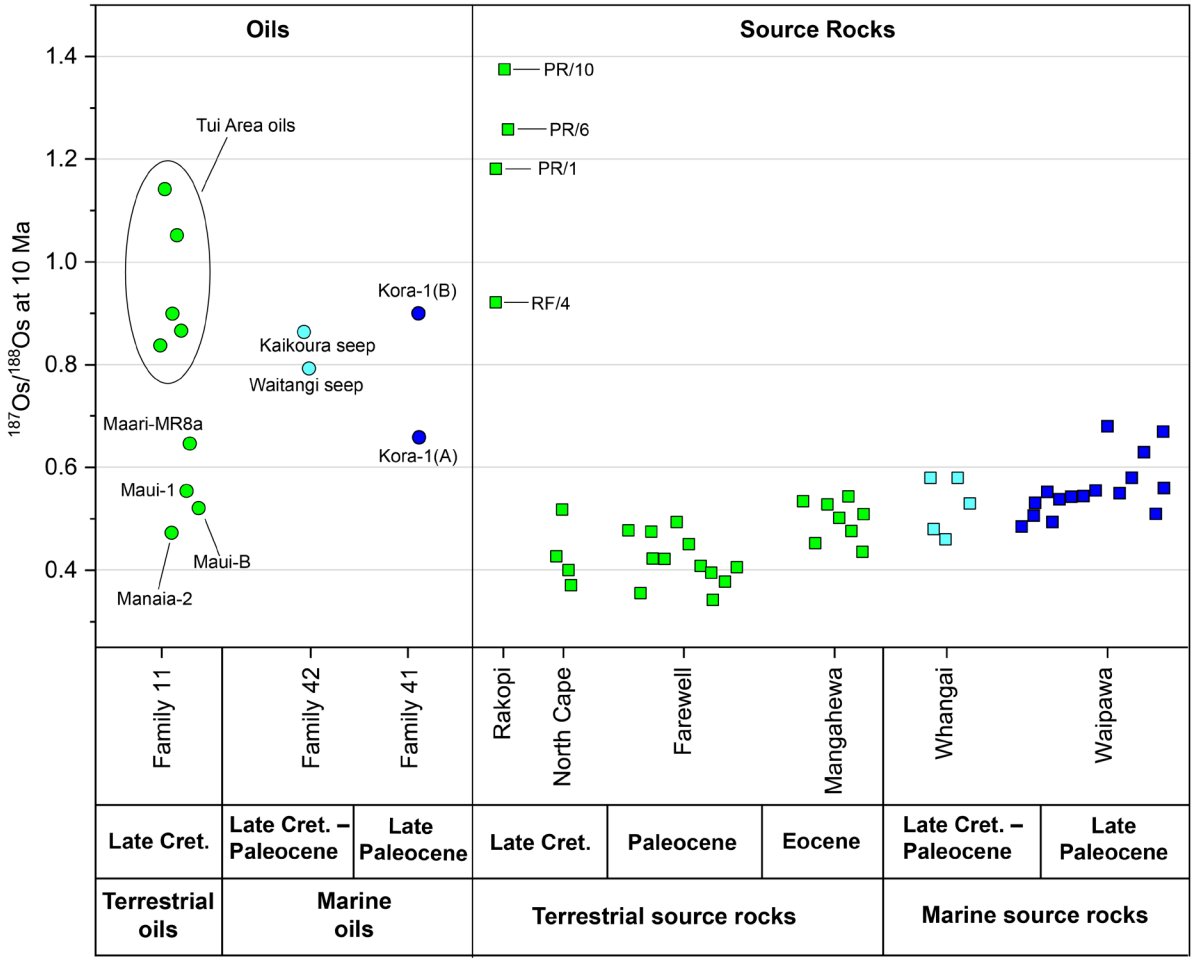

Fig. 10. Comparison of $^{187}Os/^{188}Os$ compositions at the time of oil expulsion (estimated to be ~10 Ma) for the terrestrial and marine oil families and their respective potential source rocks. The $^{187}Os/^{188}Os$ values for Farewell (Paleocene) and Mangahewa (Eocene) Formation coaly rocks are shown for comparison (data from Rotich et al., 2021).

References

Bischoff, A., Fensom, J., Tang, H., Rosetti, M., Nicol, A., 2021. Processes controlling volcanic and epiclastic reservoir formation in a buried polygenetic stratocone. In: Volcanic Processes in the Sedimentary Record: When Volcanoes Meet the Environment. Di Capua A. (Ed.). The Geological Society Special Publications SP520. DOI: 10.1144/SP520-2021-137.

Brett, W., 2005. Hydrocarbon potential of the Kora structure, PEP 38485. Ministry of Economic Development, New Zealand, unpublished Petroleum Report 3346, 32 pp.

Bull, S., Hill, M.G., Strogen, D.P., Arnot, M.J., Seebeck, H., Kroeger, K.F., Zhu, H., 2016. Seismic reflection interpretation, static modelling and velocity modelling of the southern Taranaki Basin (4D Taranaki Project), GNS Science Report 2016/02, GNS Science, Lower Hutt. 91 p.

Christensen, J.N., Halliday, A.N., Leigh, K.E., Randell, R.N., Kesler, S.E., 1995. Direct dating of sulfides by Rb-Sr: A critical test using the Polaris Mississippi Valley-type Zn-Pb deposit. Geochimica et Cosmochimica Acta, 59: 519–5197.

Clayton, C., 2011. 3D Basin modelling of PEP 38485, offshore Taranaki Basin. Ministry of Economic Development, New Zealand, unpublished Petroleum Report 4313, 110 pp.

Cohen, A.S., Coe, A.L., Bartlett, J.M., Hawkesworth, C.J., 1999. Precise Re-Os ages of organic-rich mudrocks and the Os isotope composition of Jurassic seawater. Earth and Planetary Science Letters, 167: 159–173.

Colodner, D., Sachs, J., Ravizza, G., Turekian, K.K., Edmond, J., Boyle, E., 1993. The geochemical cycle of rhenium: a reconnaissance. Earth and Planetary Science Letters, 117: 205–221.

Corrick, A.J., Selby, D., McKirdy, D.M., Hall, P.A., Gong, S., Trefry, C., Ross, A.S., 2019. Remotely constraining the temporal evolution of offshore oil systems. Scientific Reports, 9: 1327.

Creaser, R.A., Papanastassiou, D.A., Wasserburg, G.J., 1991. Negative thermal ion mass spectrometry of osmium, rhenium, and iridium. Geochimica et Cosmochimica Acta, 55: 391–401.

Cumming, V.M., Selby, D., Lillis, P.G., 2012. Re-Os geochronology of the lacustrine Green River Formation: Insights into direct depositional dating of lacustrine successions, Re-Os systematics and paleocontinental weathering. Earth and Planetary Science Letters, 359–360: 194–205.

Cumming, V.M., Selby, D., Lillis, P.G., Lewan, M.D., 2014. Re-Os geochronology and Os isotope fingerprinting of petroleum sourced from a Type I lacustrine kerogen: Insights from the natural Green River petroleum system in the Uinta Basin and hydrous pyrolysis experiments. Geochimica et Cosmochimica Acta, 138: 32–56.

DiMarzio, J.M., Georgiev, S.V., Stein, H.J., Hannah, J.L., 2018. Residency of rhenium and osmium in a heavy crude oil. Geochimica et Cosmochimica Acta, 220: 180–200.

Field, B.D., Uruski, C.I., Beu, A.G., Browne, G.H., Crampton, J.S., Funnell, R.H., Killops, S.D., Laird, M., Mazengarb, C., Morgans, H.E.G., Rait, G.J., Smale, D., Strong, C.P., 1997. Cretaceous–Cenozoic geology and petroleum systems of the East Coast region, New Zealand, Monograph 19, 7 enclosures. Institute of Geological & Nuclear Sciences Limited, Lower Hutt, New Zealand, 301 pp.

Field, B.D., Naeher, S., Clowes, C.D., Shepherd, C.L., Hollis, C.J., Sykes, R., Ventura, G.T., Pascher, K.M., Griffin, A.G., 2018. Depositional influences on the petroleum potential of the Waipawa Formation in the Orui-1A drillhole, Wairarapa. GNS Science report 2017/49, 75 pp.

Finlay, A. J., Selby, D., Osborne, M., Finucane, D., 2010. Fault charged mantle-fluid contamination of North Sea oils: Insights from Re-Os isotopes. Geology, 38: 979-982.

Finlay, A.J., Selby, D., Osborne, M.J., 2011. Re-Os geochronology and fingerprinting of United Kingdom Atlantic margin oil: Temporal implications for regional petroleum systems. Geology, 39: 475–478.

Finlay, A.J., Selby, D., Osborne, M.J., 2012. Petroleum source rock identification of United Kingdom Atlantic Margin oil fields and the Western Canadian Oil Sands using Platinum, Palladium, Osmium and Rhenium: Implications for global petroleum systems. Earth and Planetary Science Letters, 313–314: 95–104.

Funnell, R., Stagpoole, V.M., Nicol, A., Killops, S., Reyes, A.G., Darby, D., 2001. Migration of oil and gas into the Maui Field, Taranaki Basin, New Zealand. In: Hill, K.C., T., B. (Eds.), Eastern Australasian Basins Symposium, A Refocused Energy Perspective for the Future. Petroleum Exploration Society of Australia, pp. 121–128.

Funnell, R., Stagpoole, V.M., Nicol, A., McCormack, N., Reyes, A.G., 2004. Petroleum generation and implications for migration: a Maui Field charge study, Taranaki Basin, 2004 New Zealand Petroleum Conference Proceedings. Ministry of Business, Innovation & Employment (MBIE), New Zealand unpublished petroleum report PR5005, 9 pp.

Ge, X., Shen, C., Selby, D., Deng, D., Mei, L., 2016. Apatite fission-track and Re-Os geochronology of the Xuefeng uplift, China: Temporal implications for dry gas associated hydrocarbon systems. Geology, 44: 491–494.

Ge, X., Shen, C., Selby, D., Wang, J., Ma, L., Ruan, X., Hu, S., Mei, L., 2018. Petroleum-generation timing and source in the northern Longmen Shan thrust belt, Southwest China: Implications for multiple oil-generation episodes and sources. American Association of Petroleum Geologists Bulletin, 102: 913–938.

Georgiev, S.V., Stein, H.J., Hannah, J.L., Galimberti, R., Nali, M., Yang, G., Zimmerman, A., 2016. Re-Os dating of maltenes and asphaltenes within single samples of crude oil. Geochimica et Cosmochimica Acta, 179: 53–75.

Georgiev, S.V., Stein, H.J., Hannah, J.L., Yang, G., Markey, R.J., Dons, C.E., Pedersen, J.H., di Primio, R., 2019. Comprehensive evolution of a petroleum system in absolute time: The example of Brynhild, Norwegian North Sea. Chemical Geology, 522: 260–282.

Goldstein, T.P., Aizenshtat, Z., 1994. Thermochemical sulfate reduction a review. Journal of Thermal Analysis, 42: 241–290.

Goswami, V., Hannah, J.L., Stein, H.J., 2018. Why terrestrial coals cannot be dated using the Re-Os geochronometer: Evidence from the Finnmark Platform, southern Barents Sea and the Fire Clay coal horizon, Central Appalachian Basin. International Journal of Coal Geology, 188: 121–135.

Harrison, A., Reid, E., Smith, N., 2013. PEP 51906 Seismic Interpretation Report. Ministry of Business, Innovation and Employment, New Zealand, unpublished Petroleum Report 4664, 79 pp.

Higgs, K.E., King, P.R., Raine, J.I., Sykes, R., Browne, G.H., Crouch, E.M., Baur, J.R., 2012. Sequence stratigraphy and controls on reservoir sandstone distribution in an Eocene marginal marine-coastal plain fairway, Taranaki Basin, New Zealand. Marine and Petroleum Geology 32, 110-137.

Hnatyshin, D., 2018. Development and application of the Re-Os isotope system to sediment-hosted Zn-Pb ores and sedimentary pore waters (Doctoral thesis, University of Alberta, Edmonton, Canada). https://doi.org/10.7939/R31G0J990

Hollis, C.J., Manzano-Kareah, K., 2005. Source rock potential of the East Coast Basin. Ministry of Economic Development New Zealand, unpublished Petroleum Report 3179, 158 pp.

Hurtig, N.C., Georgiev, S.V., Stein, H.J., Hannah, J.L., 2019. Re-Os systematics in petroleum during water-oil interaction: The effects of oil chemistry. Geochimica et Cosmochimica Acta, 247: 142–161.

Killops, S., 1996. A geochemical perspective of oil generation in New Zealand basins, 1996 New Zealand Petroleum Conference, proceedings, Volume, 1, 179–187. Ministry of Business, Innovation & Employment (MBIE), New Zealand unpublished petroleum report PR5001.

Killops, S.D., Woolhouse, A.D., Weston, R.J., Cook, R.A., 1994. A geochemical appraisal of oil generation in the Taranaki Basin, New Zealand. American Association of Petroleum Geologists Bulletin, 78: 1560–1584.

King, P.R., Thrasher, G.P., 1996. Cretaceous–Cenozoic geology and petroleum systems of the Taranaki Basin, New Zealand, Monograph 13. Institute of Geological & Nuclear Sciences Limited, 243 pp.

Kroeger, K.F., Plaza-Faverola, A., Barnes, P.M., Pecher, I.A., 2015. Thermal evolution of the New Zealand Hikurangi subduction margin: Impact on natural gas generation and methane hydrate formation – A model study. Marine and Petroleum Geology 63, 97-114.

Kroeger, K., Funnell, R., Arnot, M., Bull, S., Hill, M., Sahoo, T., Zhu, H., 2016. Re-assessment of maturity and charge in southern Taranaki Basin (New Zealand) using integrated 3D basin modelling, AAPG/SEG International Conference & Exhibition 2015. Eastern Australian Basins Symposium, Melbourne, Australia, pp. 217–230.

Kroeger, K.F., Thrasher, G.P., Sarma, M., 2019. The evolution of a Middle Miocene deep-water sedimentary system in northwestern New Zealand (Taranaki Basin): Depositional controls and mechanisms. Marine and Petroleum Geology 101, 355-372.

Kroeger, K.F., Seebeck, H., Thrasher, G.P., Arnot, M., Bull, S., Viskovic, G.P.D., 2021. Reconstruction of rapid charge of a giant gas field across a major fault zone using 3D petroleum systems modelling (Taranaki Basin, New Zealand). Marine and Petroleum Geology, 130: 105121.

Kroeger, K.F., Bischoff, A., Nicol, A., 2022. Petroleum systems in a buried stratovolcano: Maturation, migration and leakage. Marine and Petroleum Geology 141, 105682.

Lassiter, J.C., Luhr, J.F., 2001. Osmium abundance and isotope variations in mafic Mexican volcanic rocks: Evidence for crustal contamination and constraints on the geochemical behavior of osmium during partial melting and fractional crystallization. Geochemistry, Geophysics, Geosystems, 2: 1027.

Levorsen, A.I., 2001. Geology of Petroleum. American Association of Petroleum Geologists Bulletin, Special Publication, Oklahoma, 724 pp.

Lillis, P.G., Selby, D., 2013. Evaluation of the rhenium-osmium geochronometer in the Phosphoria petroleum system, Bighorn Basin of Wyoming and Montana, USA. Geochimica et Cosmochimica Acta, 118: 312–330.

Liu, J., Pearson, D.G., 2014. Rapid, precise and accurate Os isotope ratio measurements of nanogram to sub-nanogram amounts using multiple Faraday

collectors and amplifiers equipped with 1012 Ω resistors by N-TIMS. Chemical Geology, 363: 301–311.

Liu, J., Selby, D., Obermajer, M., Mort, A., 2018. Rhenium–osmium geochronology and oil–source correlation of the Duvernay petroleum system, Western Canada sedimentary basin: Implications for the application of the rhenium–osmium geochronometer to petroleum systems. American Association of Petroleum Geologists Bulletin, 102: 1627–1657.

Liu, J., Selby, D., Zhou, H., Pujol, M., 2019. Further evaluation of the Re-Os systematics of crude oil: Implications for Re-Os geochronology of petroleum systems. Chemical Geology, 513: 1–22.

Magoon, L.B., Dow, W.G., 1994. The Petroleum System—From Source to Trap, 60. American Association of Petroleum Geologists Bulletin, Oklahoma, 644 pp.

Mahdaoui, F., Reisberg, L., Michels, R., Hautevelle, Y., Poirier, Y., Girard, J.P., 2013. Effect of the progressive precipitation of petroleum asphaltenes on the Re-Os radioisotope system. Chemical Geology, 358: 90–100.

Mahdaoui, F., Michels, R., Reisberg, L., Pujol, M., Poirier, Y., 2015. Behavior of Re and Os during contact between an aqueous solution and oil: Consequences for the application of the Re-Os geochronometer to petroleum. Geochimica et Cosmochimica Acta, 158: 1–21.

Mark, D.F., Parnell, J., Kelley, S.P., Lee, M.R., Sherlock, S.C., 2010. $^{40}Ar/^{39}Ar$ dating of oil generation and migration at complex continental margins: Geology, 38: 75–78.

Matthews, E.R., 2002. Implications of Neogene structural development on hydrocarbon prospectivity of the Tui-Maui area, offshore Taranaki Basin, New Zealand., 2002 NZ Petroleum Conference Proceedings. Ministry of Business, Innovation & Employment (MBIE), New Zealand unpublished petroleum report PR5004.

Matthews, E.R., 2008. AWE Taranaki Exploration. 2008 NZ Petroleum Conference Proceedings. Ministry of Business, Innovation & Employment (MBIE), New Zealand unpublished petroleum report PR5007.

Matthews, E.R., Kunjan, B., Osman, N., Shadlow, J., John, Z., Spotkaeff, M., Saicic, M., 2008. Tui Fields Geoscience Review, 2008 New Zealand Petroleum Conference Proceedings. Ministry of Business, Innovation & Employment (MBIE), New Zealand unpublished petroleum report PR5007.

Meng, Q., Wang X., Huo, Q., Dong, Z., Li, Z., Tessalina, S.G., Ware, B.D., McInnes, B.A., Wang, X., Liu, T., Zhang, L., 2021. Rhenium–osmium (Re-Os) geochronology of crude oil from lacustrine source rocks of the Hailar Basin, NE China. Petroleum Science, 18: 1-9

[MBIE] Ministry of Business, Innovation & Employment, 2020. Energy in New Zealand 2020. https://www.mbie.govt.nz/building-and-energy/energy-and-natural-resources/energy-statistics-and-modelling/energy-publications-and-technical-papers/energy-in-new-zealand/ (accessed January 2022).

Moore, P.R., 1989. Stratigraphy of the Waipawa Black Shale (Paleocene), eastern North Island, New Zealand. New Zealand Geological Survey record, 38, 19 pp.

Murray, A.P., Summons, R.E., Boreham, C.J., Reed, J.D., Francis, D.A., 1994. Geochemistry of oils and source rocks of the East Coast Basin and implications for the Taranaki Basin, New Zealand., 1994 New Zealand petroleum conference proceedings. Ministry of Business, Innovation & Employment (MBIE), New Zealand unpublished petroleum report PR5000, Wellington, pp. 338–351.

Naeher, S., Hollis, C.J., Clowes, C.D., Ventura, G.T., Shepherd, C.L., Crouch, E.M., Morgans, H.E.G., Bland, K.J., Strogen, D.P., Sykes, R., 2019. Depositional and organofacies influences on the petroleum potential of an unusual marine source rock: Waipawa Formation (Paleocene) in southern East Coast Basin, New Zealand. Marine and Petroleum Geology, 104: 468–488.

[NZOP] New Zealand Overseas Petroleum Limited, 2005. Tui Area Mining Permit Application - Technical Data. Ministry of Economic Development, New Zealand unpublished petroleum report PR3223, pp. 824.

Palmer, S.E., 1984. Effect of water washing on C_{15+} hydrocarbon fractions of crude oils from Northwest Palawan, Philippines. American Association of Petroleum Geologists Bulletin, 68: 137–149.

Paul, M., Reisberg, L., Vigier, N., Zheng, Y., Ahmed, K.M., Charlet, L., Huq, M.R., 2010. Dissolved osmium in Bengal plain groundwater: Implications for the marine Os budget. Geochimica et Cosmochimica Acta, 74: 3432–3448.

Pepper, A.S., 1991. Estimating the petroleum expulsion behaviour of source rocks: a novel quantitative approach. Geological Society, London, Special Publications, 59: 9–31.

Pepper, A.S., Corvi, P.J., 1995a. Simple kinetic models of petroleum formation. Part I: oil and gas generation from kerogen. Marine and Petroleum Geology, 12: 291–319.

Pepper, A.S., Corvi, P.J., 1995b. Simple kinetic models of petroleum formation. Part III: Modelling an open system. Marine and Petroleum Geology, 12: 417–452.

Peters, K.E., Cassa, M.R., 1994. Applied source rock geochemistry. In: Magoon, L.B., Dow, W.G. (Eds.), The Petroleum System: From Source to Trap. American Association of Petroleum Geologists Memoir, pp. 93–120.

Peters, K E, and Moldowan, J M. 1993. The biomarker guide: Interpreting molecular fossils in petroleum and ancient sediments. Englewood Cliffs, Prentice Hall, 363 pp.

Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide: Volume 2: Biomarkers and Isotopes in Petroleum Systems and Earth History, 2. Cambridge University Press, Cambridge, 700 pp.

Peucker-Ehrenbrink, B., Ravizza, G., 2012. Chapter 8 - Osmium Isotope Stratigraphy. In: Gradstein, F.M., Ogg, J.G., Schmitz, M.D., Ogg, G.M. (Eds.), The Geologic Time Scale. Elsevier, Boston, pp. 145–166.

Pierpont, R., Wunderlich, A., Mayer, J., 2017. PEP 60089 Petroleum system and migration interpretation report. Ministry of Business, Innovation and Employment, New Zealand, unpublished Petroleum Report 5514, 22 pp.

Reed, J.D., 1992. Exploration geochemistry of the Taranaki Basin with emphasis on Kora, 1991 New Zealand Oil Exploration Conference Proceedings. Ministry of Commerce, pp. 364–372

Reilly, C., Nicol, A., Walsh, J.J., Kroeger, K.F., 2016. Temporal changes of fault seal and early charge of the Maui Gas-condensate field, Taranaki Basin, New Zealand. Marine and Petroleum Geology, 70: 237–250.

Rodushkin, I., Engström, E., Sörlin, D., Pontèr, C., Baxter, D.C., 2007. Osmium in environmental samples from Northeast Sweden: Part I. Evaluation of background status. Science of the Total Environment, 386: 145–158.

Rogers, K.M., Collen, J.D., Johnston, J.H., Elgar, N.E., 1999. A geochemical appraisal of oil seeps from the East Coast Basin, New Zealand. Organic Geochemistry, 30: 593–605.

Rooney, A.D., Selby, D., Lewan, M.D., Lillis, P.G., Houzay, J.P., 2012. Evaluating Re-Os systematics in organic-rich sedimentary rocks in response to petroleum

generation using hydrous pyrolysis experiments. Geochimica et Cosmochimica Acta, 77: 275–291.

Rotich, E.K., Handler, M.R., Naeher, S., Selby, D., Hollis, C.J., Sykes, R., 2020. Re-Os geochronology and isotope systematics, and organic and sulfur geochemistry of the middle–late Paleocene Waipawa Formation, New Zealand: Insights into early Paleogene seawater Os isotope composition. Chemical Geology, 536: 119473.

Rotich, E.K., Handler, M.R., Sykes, R., Selby, D., Naeher, S., 2021. Depositional influences on Re-Os systematics of Late Cretaceous–Eocene fluvio-deltaic coals and coaly mudstones, Taranaki Basin, New Zealand. International Journal of Coal Geology, 236: 103670.

Scarlett, A.G., Holman, A.I., Georgiev, S.V., Stein, H.J., Summons, R.E., Grice, K., 2019. Multi-spectroscopic and elemental characterization of southern Australian asphaltites. Organic Geochemistry, 133: 77–91.

Schiøler, P., Rogers, K.M., Sykes, R., Hollis, C.J., Ilg, B., Meadows, D., Roncaglia, L., Uruski, C.I., 2010. Palynofacies, organic geochemistry and depositional environment of the Tartan Formation (Late Paleocene), a potential source rock in the Great South Basin, New Zealand. Marine and Petroleum Geology, 27: 351–369.

Schlumberger, 2017. 1D Petroleum system modelling onshore East Coast Basin, New Zealand. Ministry of Business, Innovation and Employment, New Zealand, unpublished Petroleum Report 5404, 43 pp.

Seebeck, H., Thrasher, G.P., Viskovic, G.P., 2019. Inversion history of the northern Tasman Ridge, Taranaki Basin, New Zealand: implications for petroleum migration and accumulation. New Zealand Journal of Geology and Geophysics, 63: 299–323.

Selby, D., Creaser, R.A., 2005. Direct radiometric dating of hydrocarbon deposits using rhenium-osmium isotopes. Science, 308: 1293–1295.

Selby, D., Creaser, R.A., Dewing, K., Fowler, M., 2005. Evaluation of bitumen as a ^{187}Re-^{187}Os geochronometer for hydrocarbon maturation and migration: A test case from the Polaris MVT deposit, Canada. Earth and Planetary Science Letters, 235: 1–15.

Selby, D., Creaser, R.A., Fowler, M.G., 2007. Re-Os elemental and isotopic systematics in crude oils. Geochimica et Cosmochimica Acta, 71: 378–386.

Smith, N., Wunderlich, A., Mallinson, I., 2016. PEP 51313 - Stage 2 Prospectivity Interpretation Report. Ministry of Business, Innovation & Employment (MBIE), New Zealand unpublished petroleum report PR5332.

Speight, J.G., 2004. Petroleum asphaltenes – part 1: Asphaltenes, resins and the structure of petroleum. Oil & Gas Science and Technology, 59: 467–477.

Stagpoole, V., Nicol, A., 2008. Regional structure and kinematic history of a large subduction back thrust: Taranaki Fault, New Zealand. Journal of Geophysical Research: Solid Earth, 113: B01403.

Suzuki, K., Tatsumi, Y., 2006. Re-Os systematics of high-Mg andesites and basalts from the Setouchi volcanic belt, SW Japan: Implications for interaction between wedge mantle and slab-derived melt. Geochemical Journal, 40: 297–307.

Sykes, R., Andrew, S.M., Joanne, C., 2011. The New Zealand Petroleum PVT Database. GNS Science Data Series 8a. Ministry of Economic Development, New Zealand unpublished petroleum report PR4519.

Sykes, R., Zink, K.-G., Rogers, K.M., Phillips, A., Ventura, G.T., 2012. New and updated geochemical databases for New Zealand petroleum samples, with assessments of genetic oil families, source age, facies and maturity. GNS

Science consultancy report 2012/37, Ministry of Economic Development, New Zealand unpublished petroleum report PR4513, 29 pp.

Sykes, R., Volk, H., George, S.C., Ahmed, M., Higgs, K.E., Johansen, P.E., Snowdon, L.R., 2014. Marine influence helps preserve the oil potential of coaly source rocks: Eocene Mangahewa Formation, Taranaki Basin, New Zealand. Organic Geochemistry, 66: 140–163.

Sykes, R., Zink, K.-G., 2018. The New Zealand Oils Geochemistry Database (Version 2.0). GNS Science Data Series 24a. https://data.gns.cri.nz/pbe/.

Sykes, R., 2019. Chemometric classification of terrestrial oil families in Taranaki Basin, New Zealand: higher plant trends and migration contamination effects. AAPG Datapages, #30628. http://www.searchanddiscovery.com/documents/2019/30628sykes/ndx_sykes.pdf.

Symons, D.T.A., Arne, D.C., 2003. Paleomagnetic dating of mineralization in the Kapok MVT deposit, Lennard Shelf, Western Australia. Journal of Geochemical Exploration, 78-79, 267–272.

Tripathy, G.R., Hannah, J.L., Stein, H.J., and Yang, G., 2014. Re-Os age and depositional environment for black shales from the Cambrian-Ordovician boundary, Green Point, western Newfoundland: Geochemistry, Geophysics, Geosystems, 15: 1021–1037.

van Acken, D., Tütken, T., Daly, J.S., Schmid-Röhl, A., Orr, P.J., 2019. Rhenium-osmium geochronology of the Toarcian Posidonia Shale, SW Germany. Palaeogeography, Palaeoclimatology, Palaeoecology, 534: 109294.

Walters, C.C., Wang, F.C., Qian, K., Wu, C., Mennito, A.S., Wei, Z., 2015. Petroleum alteration by thermochemical sulfate reduction – A comprehensive molecular study of aromatic hydrocarbons and polar compounds. Geochimica et Cosmochimica Acta, 153: 37–71.

Wang, G., Xue, Y., Wang, D., Shi, S., Grice, K., Greenwood, P.F., 2016. Biodegradation and water washing within a series of petroleum reservoirs of the Panyu Oil Field. Organic Geochemistry, 96: 65–76.

Wenger, L.M., Davis, C.L., Isaksen, G.H., 2002. Multiple Controls on Petroleum Biodegradation and Impact on Oil Quality. SPE Reservoir Evaluation & Engineering, 5: 375–383.

Wilkins, R.W.T., George, S.C., 2002. Coal as a source rock for oil: a review. International Journal of Coal Geology, 50: 317–361.

Xu, G., Hannah, J.L., Stein, H.J., Bingen, B., Yang, G., Zimmerman, A., Weitschat, W., Mørk, A., Weiss, H.M., 2009. Re-Os geochronology of Arctic black shales to evaluate the Anisian–Ladinian boundary and global faunal correlations: Earth and Planetary Science Letters, 288: 581–587.

Zhao, C., Cheng, K., 1998. Expulsion and primary migration of the oil derived from coal. Science in China Series D: Earth Sciences, 41: 345–353.