Depositional influences on Re-Os systematics of Late Cretaceous–Eocene fluvio-deltaic coals and coaly mudstones, Taranaki Basin, New Zealand

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Abstract

The factors controlling Re-Os systematics and potential for geochronology in organic-rich sedimentary rocks deposited in fully terrestrial to paralic environments are not well understood. Here we present Re-Os, bulk pyrolysis and sulfur data for coals and coaly mudstones from the Late Cretaceous Rakopi and North Cape, Paleocene Farewell and Eocene Mangahewa formations, Taranaki Basin, New Zealand, to investigate a range of depositional controls on the behaviour of Re and Os in coaly rocks. These rocks were deposited in various fluvial, estuarine and coastal plain environments, and exhibit varying degrees of marine influence, as indicated by total sulfur content, presence of dinoflagellate cysts, and other parameters. The Taranaki coaly rocks have low Re (0.1–1.3 ppb) and Os (14.2–66.2 ppt) concentrations, even for strongly marine-influenced, high-sulfur samples. These low concentrations are similar to those reported for entirely terrestrial coals, but are up to two orders of magnitude lower than in marine-influenced coals from the Matewan coal seam, USA. Unlike the Taranaki coaly rocks and other coals analysed for Re and Os, the Matewan coal seam is directly overlain by a fully marine shale. This suggests that such juxtaposition of depositional environments may be required for enhanced Re and Os enrichment in coals, for example, through drowning of the precursor peat mires by Re- and Os-rich seawater during the deposition of the overlying marine shale.

The initial $^{187}Os/^{188}Os$ (Os_i) compositions of the Taranaki coaly rocks show significant variation. Samples from the Rakopi Formation exhibit radiogenic Os_i values (0.8–1.2), which is expected for coals deposited in fully terrestrial settings and which source Os from weathering of surrounding upper continental crust. In contrast, samples from the progressively younger North Cape, Farewell and Mangahewa formations exhibit significantly less radiogenic Os$_i$ values (0.3–0.5). We attribute this to variable levels of marine influence from moderately radiogenic contemporaneous seawater and a change in sediment source composition following eruption and weathering of nearby subaerial volcanoes between 78 and 72 Ma, after deposition of the Rakopi Formation. The ^{187}Re/^{188}Os vs ^{187}Os/^{188}Os relationship for coaly rocks from the Farewell Formation exhibits significant scatter without any linear trend, precluding Re-Os geochronology. This scatter appears to have resulted from a combination of heterogeneous Os$_i$ (0.1 units) and limited variations in ^{187}Re/^{188}Os (145 units). Improved Re-Os isochroneity is noted in strongly marine-influenced coaly rocks from the Mangahewa Formation, with the ^{187}Re/^{188}Os vs ^{187}Os/^{188}Os relationship yielding an isochron age of 28 ± 16 Ma. Although this age is imprecise, it is within uncertainty of the estimated biostratigraphic age (37 ± 1 Ma) of the rocks.

Keywords:

Marine-influenced coals; terrestrial; Re-Os isotopes; geochronology; Taranaki Basin

1. Introduction

Fluvio-deltaic successions are important components of many sedimentary basins. Their presence, thickness, stacking patterns and geochemical properties record a multi-faceted interplay between changing tectonic regimes, sediment supply and sea-level variations which are integral to the understanding of a basin’s evolutionary development (Sherwood et al., 1992; Flores and Sykes, 1996; Higgs et al., 2012). In addition, fluvio-deltaic coals and coaly mudstones are important economically as sources of energy (coal, oil and gas). For example, the Late Cretaceous–Eocene coal measure sequences of the Taranaki Basin, New Zealand, have sourced essentially all of the 600 million barrels of oil and condensate and 8.4 trillion cubic feet of gas reserves discovered in the basin (Killops et al., 1994; King and Thrasher, 1996; New Zealand Petroleum and Minerals, 2014; MBIE, 2019). However, the full potential of coal measure sequences in basin evolution studies and energy supply cannot be achieved without sound chronological information. Coal-bearing sequences are currently dated using biostratigraphy (Raine, 1984; 2004; Raine and Mildenhall, 2011; Pavlyutkin et al., 2020), chemostratigraphy (Killops et al., 2003; Pearce et al., 2010) and radiogenic isotopes, such as U-Pb zircon and ^{40}Ar/^{39}Ar sanidine crystals from interbedded volcanic-ash layers (Bohor and Triplehorn, 1993; Lyons et al., 2006; Dai et al., 2017a) and ^{87}Sr/^{86}Sr in syngenetic gypsum (Spiro et al., 2019). Generally lacking interbedded volcanic-ash layers, biostratigraphy has been the main tool for assigning relative ages to New Zealand coals and coaly mudstones. However, scarcity of marine microfossils and relatively poor temporal resolution of the existing microspore zonation scheme (Raine, 1984; Raine and Schiøler, 2012) limit the precision of assigned biostratigraphic ages, thus hampering basin-wide, regional and global correlations of time-equivalent facies (Cooper et al., 2004; Raine, 2004; Browne et al., 2008; Crouch and Raine, 2012; Higgs et al., 2012).

Over the last three decades, the Re-Os isotope system has become established as a powerful tool for obtaining depositional ages for organic-rich sedimentary rocks (e.g., Ravizza et al., 1991; Selby and Creaser, 2005; Tripathy et al., 2018). Due to the organophilic nature of Re and Os, organic-rich rocks are significant crustal reservoirs of these elements, much of which is sequestered from the water column during deposition (Cohen et al., 1999; Peucker-Ehrenbrink and Ravizza, 2000; Creaser et al., 2002; Selby and Creaser, 2003; Cohen, 2004). The high concentrations of Re and Os in organic-rich marine rocks, coupled with β-decay of ^{187}Re to ^{187}Os, have enabled precise and accurate radiometric dating of organic-rich sediments. Accordingly, most previous Re-Os studies have focused on marine black shales where Re and Os are sourced primarily from seawater (e.g., Cohen et al., 1999; Selby et al., 2009; Rooney et al., 2010; Bertoni et al., 2014; Geboy et al., 2015; Tripathy et al., 2018; Washburn et al., 2019). In contrast, very few studies have investigated factors controlling Re-Os systematics and geochronology in coal measure sediments deposited in fully terrestrial to paralic depositional environments (Baioumy et al., 2011; Tripathy et al., 2015; Goswami et al., 2018). Whilst peat mire facies, redox conditions, quality of precursor organic matter and marine influence within the coal-forming environment may all be important, marine influence, in particular, appears critical. However, understanding its actual impact on the Re-Os systematics of coaly rocks has been hindered by poor characterisation of both the degree and timing of marine influence. For example, floodplain coals and coaly shales of the Carboniferous Soldogg Formation (Finnmark Platform, southern Barents Sea) exhibit very low Re (0.06–0.63 ppb) and Os (8–104 ppt) concentrations and a ^{187}Re/^{188}Os vs ^{187}Os/^{188}Os relationship that lacks isochroneity (Goswami et al., 2018). These rocks were described as “purely terrestrial”, but no independent paleontological or geochemical paleosalinity indicator data were presented to verify the absence of marine influence. Such data may include the presence or absence of dinoflagellate cysts and mangrove pollen or coal sulfur concentrations. Jurassic coals and coaly shales from the Maghara area in Egypt similarly exhibit low average Re (0.85 ± 1.25 ppb) and Os (50 ± 30 ppt) concentrations and ^{187}Re/^{188}Os and ^{187}Os/^{188}Os ratios that do not correlate, albeit based on an analytical method that does not selectively extract hydrogenous Re and Os, and the use of different sample splits for Re and Os analyses (Baioumy et al., 2011). These coaly rocks have also been described as “terrestrial” (implying fully terrestrial; Baioumy et al., 2011; Tripathy et al., 2015; Goswami et al., 2018) despite Baioumy et al. (2011) stating that the depositional environments for these rocks were most likely brackish, grading to deltaic/paralic, but, again, without supporting paleontological or geochemical paleosalinity data.

In contrast, a study on the Carboniferous Matewan coal seam, central Appalachian Basin, USA (Tripathy et al., 2015) has shown that marine influence into peat-forming mires may result in significant enrichment of Re and Os in coals. The marine-influenced Matewan coals exhibit high Re (108 ± 16 ppb) and Os (516 ± 90 ppt) concentrations similar to those reported in many marine sediments, with Re-Os isotope ratios that yield a relatively precise and accurate depositional age (325 ± 14 Ma; Os_i = 0.86 ± 0.88; MSWD = 12). However, it remains unclear whether all marine-influenced coals are amenable to Re-Os geochronology and in particular, whether the degree (i.e., brackish versus fully marine conditions) and timing (syn- versus post-depositional) of marine transgression into peat-forming mires are critical for substantial sequestration and homogenisation of seawater-derived Re and Os.

In this study, Re and Os concentrations and Os isotopic compositions, bulk pyrolysis, and sulfur data are presented for geochemically well-characterized Late Cretaceous–Eocene coals and coaly mudstones from Taranaki Basin, New Zealand (Fig. 1), to investigate factors controlling Re-Os systematics and potential for geochronology in fully terrestrial and paralic sedimentary rocks. These coals and coaly mudstones exhibit varying degrees of marine influence and are from the Late Cretaceous Rakopi and North Cape formations, Paleocene Farewell Formation, and Eocene Mangahewa Formation. Samples from the Farewell Formation were obtained following recommended protocols for Re-Os geochronology, which includes use of core material and sampling from the smallest possible stratigraphic interval. The remaining samples were selected to target intervals with varying depositional settings, coal facies and degree of marine influence.

2. Geological setting

The Taranaki Basin is a mainly offshore Cretaceous–Cenozoic sedimentary basin located along the west coast of North Island, New Zealand (Fig. 1a). It also underlies the onshore Taranaki Peninsula and northwest Nelson region at the top of South Island (Fig. 1a). At present, the basin is defined by the Taranaki Fault to the east, the Challenger Plateau Basin to the southwest and extends northwest into the Deepwater Taranaki and New Caledonia basins (Uruski, 2008; Strogen et al., 2017). The basin was formed by rifting during the breakup of eastern Gondwana and opening of the Tasman Sea in the Cretaceous period (King and Thrasher, 1996). Syn-rift sediments were deposited within rift-controlled grabens and half-grabens, and are separated from the Median Batholith and metasedimentary basement rocks by a regional unconformity (King and Thrasher, 1996; Kroeger et al., 2013). A passive margin developed by the end of the Cretaceous which, together with changing sea level, allowed for deposition of Paleocene–Eocene sediments on coastal plains and an expansive shallow marine shelf (King, 2000).

The Late Cretaceous Rakopi and North Cape formations are terrestrial and marginal marine sedimentary units that were deposited in several isolated and inter-connected depocenters and sub-basins. These formations crop out onshore around the Whanganui Inlet and Puponga area of northwest Nelson (Fig. 1b). Apart from the locally developed Taniwha Formation, the Rakopi Formation is the lowest stratigraphic unit in the basin (Fig. 2) and consists mainly of sandstone-dominated coal measures, with interbedded coals, coaly mudstones and carbonaceous siltstones (Sykes et al., 2004). The formation was deposited in a low-gradient coastal plain environment crossed by a series of rivers and transgressed occasionally by marine incursions (Browne et al., 2008). The North Cape Formation conformably overlies and interfingers with the Rakopi Formation (Fig. 2). It is mainly distinguished from the latter by its greater marine depositional influence (King and Thrasher, 1996; Browne et al., 2008). Coal measures are less common in the North Cape Formation than in the Rakopi Formation but are the main facies of its Puponga and Wainui members.

The Paleocene Farewell Formation is a fluvio-deltaic unit consisting mainly of sandstones that are interbedded with coaly mudstones and minor coals. In the vicinity of the Kupe oil and gas field where the Paleocene samples of this study were taken from, the formation was deposited in a north-draining fluvial system that was controlled by the Manaia Fault, an active fault at the time of deposition (King and Thrasher, 1996). The Farewell Formation generally coarsens upwards in this area, indicating a broadly regressive depositional regime. However, the presence of fining-upwards, sandstone-dominated intervals within the formation suggests that there were also transgressive episodes (King and Thrasher, 1996).

The Middle–Late Eocene Mangahewa Formation consists of fully terrestrial to paralic coal measures and marginal marine, shoreline sediments (King and Thrasher, 1996; Sykes et al., 2014). The coal-rich intervals are intermittently developed throughout the formation and are best developed in the south-eastern part of the basin where samples of this study were obtained from, becoming thinner and more sporadic towards the northwest, coincident with a transition to a shallow marine depositional environment (Higgs et al., 2009; 2012). Coal seams are commonly thick and numerous in the upper section of the Eocene succession compared to the lower part, reflecting a change from transgressive to regressive depositional phases (Higgs et al., 2012).

3. Materials and methods

3.1 Samples

Eight outcrop samples from the Rakopi and North Cape formations and twenty core samples from the Farewell and Mangahewa formations were selected for this study. Coaly source rocks comprise a continuum of coaly lithologies with increasing TOC and decreasing mineral content from coaly mudstones to coals (Sykes and Snowdon, 2002). For practical purposes, this continuum can be divided into three broad lithologies using TOC thresholds: coaly mudstones with <20% TOC, shaly coals with 20–50% TOC, and coals with >50% TOC (Sykes and Raine, 2008). In the present study, almost all samples have either <20% TOC and can therefore be classed as coaly mudstones, or >50% TOC and can be classed as coals. Two of the samples are more strictly shaly coals with TOC values of 24.2% and 49.8% (Tables 1 and 2), but for simplicity are grouped with the coaly mudstones and coals, respectively.

3.1.1 Rakopi and North Cape Formation samples

Samples from the Rakopi and North Cape formations were obtained from a collection of archived outcrop samples held at GNS Science, Lower Hutt, previously collected from different outcrop locations in northwest Nelson (Fig. 1b). Prior to sampling, the outer 10–20 cm of the outcrop was removed using hand-held tools to mitigate for potential effects of weathering (Sykes et al., 2004; Sykes and Raine, 2008). The samples showed no visible signs of degradation from being in storage and had little to no veining or brecciation. Three of the Rakopi samples (PR/1, PR/6 and PR/10) are from a single outcrop on the west bank of the Paturau River (40°41'57.37" S, 172°28'27.98" E; Figs 1b, 3), approximately 100 m downstream from Thompson Creek (Sykes et al., 2004). The outcrop contains a series of 10 closely stacked, gently dipping, thin (<0.5 m) coal seams within a total thickness of ~5 m (Fig. 3). The coals contain bright vitrain (wood) lenses and have sharp, planar contacts with interbedded ~0.1 to 0.5 m thick dark brown coaly mudstone and grey-brown siltstone (Sykes et al., 2004). The fourth Rakopi sample (RF/4) is from an outcrop at a forestry block section, approximately 1 km south of Pakawau Bush Road (40°35'50.42" S, 172°34'12.36" E; location 2 in Fig. 1b). Combined spore-pollen and dinoflagellate cyst biostratigraphies for several Rakopi Formation outcrops in northwest Nelson suggest the formation here is no older than lower Zone PM2 (Upper Campanian, ~80 Ma) at its base and is probably middle Zone PM2 (early-late Maastrichtian, ~72 Ma) at its top (Fig. 2; Browne et al., 2008), based on the *Phyllocladidites mawsonii* Assemblage zonation of Raine (1984). The Paturau River outcrop samples studied here are stratigraphically close to the base of the formation (78 ± 2 Ma), whereas sample RF/4 is believed to represent the uppermost part of the formation (~72 Ma; Browne et al., 2008).

Three of the North Cape Formation samples (PM/3M, PM/3N and PM/3O) are from the base of a ~2 m thick coal seam exposed in the adit of the abandoned Puponga No. 1 coal mine (40°31'18.05'' S, 172°42'34.60'' E; Fig. 1b; Sykes and Raine, 2008). Based on the spore-pollen biostratigraphy of Raine (1984), this coal seam is estimated to be of upper PM2 Zone age (latest Maastrichtian, ~67 ± 1 Ma), very close to the top of the North Cape Formation (Fig. 2; Raine, 2004). The fourth North Cape sample (OP/1) is from a thin, 15 cm thick coal seam at Oyster Point (40°34'18.80'' S, 172°35'58.16'' E; Fig. 1b). Like the Puponga Mine samples, sample OP/1 is also estimated to be latest Maastrichtian in age (~67 ± 1 Ma).

3.1.2 Farewell Formation samples

The Farewell Formation samples were obtained from archived cores from the Kupe South-5 and -6 exploration wells, housed at the National Core Store in Featherston, New Zealand. Kupe South-5 (39°54'55.72'' S, 174°08'47.51'' E) and Kupe South-6 (39°51'09.63'' S, 174°07'11.09'' E) are located approximately 7 km apart in the Manaia sub-basin, offshore southern Taranaki Basin (Fig. 1a). Both cores were in good condition and the recommended protocols for selecting and sampling organic-rich sediments for precise Re-Os geochronology were followed (i.e., relatively large samples of >20 g, with no alteration or veining, were collected from a relatively small stratigraphic interval; Kendall et al., 2009; Stein and Hannah, 2014). For the Kupe South-5 core, seven samples were obtained from a 2.7 m interval from 2911.5 m to 2914.2 m (Fig. 4a). Five of these samples are closely spaced in a 0.5 m interval between 2912.8 m and 2913.3 m. The other two samples were selected to target a slight marine incursion at 2911.5 m (indicated by rare dinoflagellate cysts) and a 1 cm thick vitreous coal seam at 2914.2 m (Fig. 4a; Morgans and Pocknall, 1991; Flores et al., 1998; Crouch and Raine, 2012). The sampled interval largely comprises coaly mudstones and is interpreted to have been deposited in vegetated, low-lying swamps that were prone to influx of clastic sediments during fluvial floods (Flores et al., 1998). Palynological studies indicate that this interval is close to the top of Paleocene (Teurian) PM3a Zone and therefore, the Kupe South-5 samples are considered to be Late Paleocene in age (57 ± 1 Ma; Crouch and Raine, 2012). The Farewell Formation in Kupe South-6 comprises mainly sandstone with minor siltstone and mudstone interbeds. Five samples were obtained from a 0.8 m interval of core between 3167.2 m and 3168.0 m (Fig. 4b). This interval comprises coaly mudstones with megascopic plant remains, deposited in a more distal floodplain lake setting. It is also considered to be Late Paleocene in age (PM3a Zone, 57 ± 1 Ma) based on wireline logs and spore-pollen biostratigraphy (Constantine, 2008; Raine and Mildenhall, 2011).

3.1.3 Mangahewa Formation samples

Samples from the Mangahewa Formation were obtained from archived core held at GNS Science, previously obtained from three closely spaced coal seams (named seams 10, 11 and 12) from the Ohanga-2 exploration well (Fig. 5; Sykes et al., 1999). Ohanga-2 is located in northern onshore Taranaki Basin (39°01'43.43'' S, 174°21'07.32'' E; Fig. 1a). The three seams cover a total stratigraphic thickness of ~5 m, with seams 10 and 11 being 0.39 and 0.91 m thick, respectively. Seam 12 is estimated from electric logs to have a total thickness of 1 ± 0.15 m, however, only the upper 0.67 m were recovered because of jamming of the core barrel (Murray and McGregor, 1998; Sykes et al., 1999). The two upper coal seams (10 and 11) differ from the lower seam (12) in their chemical and petrographic compositions as a result of much stronger marine influence in the two upper seams (Fig. 5a; Sykes et al., 1999). In total, six coal samples from the three seams and two coaly mudstone samples from the roof and floor sediments of seam 10 were selected for this study (Fig. 5a). The selected Mangahewa Formation samples are stratigraphically located towards the top of the Mangahewa Formation and are estimated to be latest Eocene in age (*Myricipites harrisii* miospores zone 3 [MH3]; 37 ± 1 Ma; Raine, 1984; Murray and McGregor, 1998).

3.2 Analytical methods

3.2.1 Bulk pyrolysis and sulfur analyses

For most of the Rakopi, North Cape and Mangahewa samples, total organic carbon (TOC), bulk pyrolysis (Rock-Eval) and sulfur data had previously been obtained by GNS Science and are publicly available in a geochemical database and related reports (e.g., Sykes et al., 2012) on its Petroleum Basin Explorer (PBE) online data portal (https://data.gns.cri.nz/pbe/). The total sulfur (TS) data were used together with palynological information (Sykes et al., 1999; 2004; Browne et al., 2008) to target intervals within the three formations that have varying degrees of marine influence. TOC and Rock-Eval data for all Farewell Formation samples (except KS5/1a, b, c and d) were obtained in this study following protocols outlined in Naeher et al. (2019). TS content for all the Farewell Formation samples (except KS5/1d) and samples PM/3M, Oh2/MM10a and Oh2/MM10i were also obtained in this study by CRL Energy Ltd, following the same standard procedures (ASTM D4239; ASTM International, 2018) that were used previously for all other samples. Forms of sulfur (organic, pyritic and sulfate) were determined for the Mangahewa samples following standard procedures

(AS1038.11-2002; Standards Australia, 2002) to provide more information about the source and processes of sulfur incorporation in these samples.

3.2.2 Re-Os analysis

In preparation for Re-Os analysis, all samples were processed at Victoria University of Wellington following the protocols of Kendall et al. (2009). The samples were polished to remove cutting and drilling marks, dried in an oven overnight at 40 °C, broken into small chips with no metal contact, and crushed to a fine powder (~30 µm) using an agate mill. Re-Os analyses were carried out at the Laboratory for Source Rock and Sulfide Geochemistry and Geochronology, Durham University, UK. The Farewell Formation samples were digested and purified using established protocols for Re-Os geochronology in sedimentary rocks (e.g., Rooney et al., 2011; Jones et al., 2018; Rotich et al., 2020 and references therein). In brief, ~1 g of powdered rock was spiked with a known amount of ^{190}Os + ^{185}Re mixed tracer solution and digested with Cr^{VI}–H_2SO_4 in a sealed Carius tube at 220 °C for 48 h. Osmium was separated and purified using chloroform solvent extraction and HBr micro-distillation methods whereas Re was purified using NaOH-acetone solvent extraction and anion exchange chromatography. The Cr^{VI}–H_2SO_4 solution digestion method is preferred for Re-Os analysis of organic-rich sediments because it preferentially liberates hydrogenous Re and Os (Selby and Creaser, 2003; Kendall et al., 2004; Rooney et al., 2011). However, digestion with the Cr^{VI}–H_2SO_4 solution appeared to be incomplete for most of the samples from the Mangahewa, North Cape and Rakopi formations, based on the green colour of partially reduced Cr^{III} species in the digest, very weak analyte signal on the mass spectrometer and negative Os isotope compositions for some of the samples, which is a likely indicator of inadequate spike-sample equilibration. Increasing the acid to sample ratio by up to a factor of three (increasing 8 ml of acid to 24 ml for every 0.2 g sample) did not improve the digestion outcome, possibly due to high TOC content in the samples relative to the Farewell Formation samples. As a result, all samples from the Rakopi, North Cape and Mangahewa formations (except sample Oh2/MM10i) were digested using a stronger oxidizing solution, inverse *aqua-regia* (3 ml HCl: 6 ml HNO_3). It has been shown for moderately low TOC marine samples that the inverse *aqua-regia* digestion method can yield Re and Os concentrations, Re-Os ages and Os_i ratios that are identical within uncertainty to those produced using the Cr^{VI}–H_2SO_4 method, albeit with generally lower $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ ratios (15% and 9% lower, respectively) and lower precision in the resulting Re-Os ages, which has been attributed to incorporation of a detrital Os component (Selby and Creaser, 2003; Kendall et al., 2004; Rooney et al., 2011). Given that the Rakopi, North Cape and Mangahewa samples were not specifically selected for Re-Os geochronology and that the detrital (or mineral) component in these samples would likely be low due to their relatively high TOC content (average of 59.3%), we consider that any non-hydrogenous contribution to the Re-Os analysis by employing the inverse *aqua-regia* digestion method would have been minimal and would not affect the objectives of this study.

In the inverse *aqua-regia* method, ~200 mg of powdered rock was spiked with a known amount of ^{190}Os + ^{185}Re mixed tracer solution and digested with an inverse *aqua-regia* solution in a sealed Carius tube at 220 °C for 24 h. Digestion of larger amounts of sample powder (up to 1 g) for improved analytical precision was attempted, however, 200 mg proved to be the safe upper limit to avoid rupturing the Carius tube (30 cm body length) during digestion. Separation and purification of Re and Os followed similar procedures to those outlined for the Farewell Formation samples.

The purified Re and Os fractions from all samples were loaded onto nickel and platinum filaments, respectively (Selby, 2007). Rhenium and Os isotopic measurements were then obtained using a Thermo Scientific TRITON Negative Thermal Ionisation Mass Spectrometer housed at the Arthur Holmes Laboratory, Durham University. Rhenium measurements were obtained via static Faraday collection mode whereas ion-counting on a secondary electron multiplier (SEM) was used for Os measurements. Total procedural blanks for the Cr^{VI}–H_2SO_4 method were 15.2 ± 0.2 pg Re and 0.45 ± 0.01 pg Os, with an $^{187}Os/^{188}Os$ value of 0.23 ± 0.06 (n = 4). Total procedural blanks for the inverse *aqua-regia* method were 2.3 ± 0.02 pg Re and 0.19 ± 0.01 pg Os, with an $^{187}Os/^{188}Os$ value of 0.28 ± 0.17 (n = 4). Instrument reproducibility and data quality were monitored by repeated measurement of the Durham Romil Osmium Standard (DROsS) solution, which yielded an average $^{187}Os/^{188}Os$ of 0.16067 ± 0.00036 (n = 8), in good agreement with values reported by other laboratories (0.16078 ± 0.00024, Liu and Pearson, 2014; 0.16091 ± 0.00015, van Acken et al., 2019). Uncertainties for the reported $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ ratios were determined by error propagation of the uncertainties in spike and sample weights, mass spectrometer measurements, blank concentrations and isotopic compositions, and the reproducibility of standard Re and Os isotopic ratios.

3.3 Multivariate analysis

Principal component analysis (PCA) was used to assess statistical relationships between Re-Os data and bulk geochemical parameters. PCA was applied to 10 parameters from the entire sample set using the Pirouette® (Infometrix Inc.) statistical software. This analysis employed autoscale pre-processing in which the data for each parameter is mean centered and their variance scaled. This step standardises all parameters so that they exhibit an equal weighting in the chemometric analysis.

4. Results

Bulk pyrolysis, TS, sulfur species, and Re and Os data for all samples are provided in Tables 1 and 2. The bulk pyrolysis data are used to evaluate the thermal maturity and type of the organic matter present in the samples (Espitalié et al., 1977; Peters, 1986). The TOC content varies widely in samples from the four formations (Fig. 6a), reflecting mainly the two different lithologies present, i.e. coaly mudstone (<20 wt%) and coal (>50 wt%). Another feature of the TOC data is the very high TOC values of all six Mangahewa Formation coals, from 69.7 to 79.8 wt%. These high values reflect particularly low mineral matter contents, which is a feature of raised mire coals (see Section 5.2). Oxygen index (OI), which is a proxy for the amount of oxygen present in the kerogen (Peters, 1986), is very low in the Mangahewa Formation samples, ranging from 1–6 mg CO_2/g TOC compared to 9–87 mg CO_2/g TOC in samples from the other three formations (Fig. 6b). The OI values for the Kupe South-5 samples are overall, the highest in the sample set (49–87 mg CO_2/g TOC) and correlate positively with T_{max} values (except for KS5/1b, Fig. 6e). Hydrogen index (HI) varies widely in samples from the four formations (94–399 mg HC/g TOC; Fig. 6a), indicating variation in either the type or thermal maturity of the kerogen. Significant variation in thermal maturity can, however, be discounted given that the range in T_{max} values (418–440 °C) and inferred vitrinite reflectance values (mostly 0.5–0.7% R_o) indicate that all samples are immature to marginally mature (Fig. 6d, e). The Rock-Eval S2 vs TOC (Fig. 6c) and T_{max} vs HI (Fig. 6d) plots show that the Farewell Formation samples from Kupe South-5 contain mainly Type III kerogen whereas those from Kupe South-6, as well as those from the Rakopi, North Cape and Mangahewa formations contain a mixture of Type II and III kerogens. The low thermal maturity of these samples suggests that the observed kerogen types are representative of the initial organofacies composition.

The TS content of samples from the Rakopi, North Cape and Farewell formations ranges from 0.2 to 1.5% [dry, ash-free (daf); Fig. 6f], indicating entirely terrestrial to slightly marine-influenced depositional settings. In contrast, the TS content of samples from Mangahewa Formation ranges from 0.9 to very high values of 62.6% (daf; Fig. 6f), indicating slight to very strong marine influence. The two coaly mudstones in the Mangahewa Formation sample set (Oh2/MM10a and Oh2/MM10i) contain very high organic sulfur contents (10.9 and 57.3%, daf, respectively) relative to pyritic and sulfate sulfur contents, and are the cause of the extremely high TS contents in the sample set (Table 2; Fig. 6f).

Rhenium and Os concentrations in all samples range from 0.11 to 1.33 ppb and 14.2 to 66.2 ppt (5.3–26.7 ppt ^{192}Os), respectively (Fig. 7; Tables 1 and 2), comparable to those reported for the modern-day upper continental crust (UCC; 0.2–2 ppb Re and 30–50 ppt Os; Esser and Turekian, 1993; Peucker-Ehrenbrink and Jahn, 2001; Sun et al., 2003) and entirely terrestrial coals and shales (0.1–1.4 ppb Re and 8–104 ppt Os; Baioumy et al., 2011; Goswami et al., 2018). For all samples, there is no clear relationship between Re and ^{192}Os (Fig. 7a), but positive correlations exist between Re/TOC and Os/TOC for individual sample sets (Fig. 7b). Similarly, there is no relationship between TOC content and Re and ^{192}Os (an estimate of Os chelated at the time of deposition, i.e. without radiogenic ingrowth of ^{187}Os) concentrations across the entire sample set, but strong negative correlations exist between TOC and Re (R^2 = 0.94) and ^{192}Os (R^2 = 0.93) concentrations for the Mangahewa Formation samples (Fig. 7c, d). This is the opposite of what is expected for organophilic elements like Re and Os. However, it can be explained by differences in coal petrofacies and marine influence within the sample set (see sections 5.2 and 5.3).

Like TOC, there are no simple correlations between TS content and Re and ^{192}Os concentrations in samples from the Rakopi, North Cape and Farewell formations (Fig. 7e, f). However, the two Mangahewa Formation coaly mudstones with high TS contents [Oh2/MM10a (13.3%, daf) and Oh2/MM10i (62.6%, daf)] exhibit high Re (0.95 and 1.33 ppb, respectively) and ^{192}Os (15.1 and 25.9 ppt, respectively) concentrations (Fig. 7e, f).

The ^{187}Re/^{188}Os values for all samples are low (29.1–176.4; Tables 1 and 2), similar to published ^{187}Re/^{188}Os values for fully terrestrial Carboniferous and Jurassic coals (24–117; Baioumy et al., 2011; Goswami et al., 2018), but significantly lower than those reported for marine-influenced Carboniferous Matewan coals (^{187}Re/^{188}Os = 3299–5134; Tripathy et al., 2015). Samples of Farewell Formation from Kupe South-6 exhibit lower ^{187}Re/^{188}Os values (31.1–52.6) than those from Kupe South-5 (50.0–176.4). The present-day ^{187}Os/^{188}Os values for samples from North Cape, Farewell and Mangahewa formations are moderately radiogenic (0.35–0.57), whereas those from the Rakopi Formation are much more radiogenic (0.94–1.39).

Principal component analysis was undertaken to determine key environmental factors controlling the relationships between bulk geochemical parameters (TOC, HI, OI and TS) and Re and Os concentrations and ^{187}Re/^{188}Os ratios. The results show that PCA Factor 1 accounts for 45.0% of the total variance within the sample set whereas Factor 2 accounts for 30.4% (Fig. 8a, b). These two factors show a trend of changing redox conditions (defined by HI and OI) and marine influence (defined by TS content) within the complete sample set (Fig. 8). The PCA scores plot indicates that samples from the Farewell Formation were deposited in more oxidising conditions whereas samples from the Mangahewa Formation were deposited in generally more reducing conditions (Fig. 8a). Samples from the Rakopi and North Cape formations plot in between those of the Farewell and Mangahewa formations, with negative loadings on Factor 1, which suggests more reducing conditions. Rhenium and Os concentrations and ^{187}Re/^{188}Os ratios appear to be largely independent of these changing redox conditions, but exhibit a positive loading on Factor 1, which is mainly associated with TS content or the degree of marine influence (Fig. 8b).

5. Discussion

5.1 Sources of Os to the Taranaki coals and coaly mudstones

The Os_i values for organic-rich sedimentary rocks reflect the ^{187}Os/^{188}Os composition of a water body at the time of deposition (Peucker-Ehrenbrink and Ravizza, 2000; Selby and Creaser, 2003; Cohen, 2004), which in turn results from the balance of Os sourced from two end-members: 1) rivers that drain older continental strata contributing to the radiogenic end-member (^{187}Os/^{188}Os ≈ 1.4), and 2) magmatic activities, juvenile ocean crust and extra-terrestrial materials contributing to the non-radiogenic end-member ($^{187}Os/^{188}Os \approx 0.12$; Peucker-Ehrenbrink and Ravizza, 2000). The Os_i values for samples from the Mangahewa, Farewell and North Cape formations are all moderately radiogenic, ranging between 0.31 and 0.51 (Fig. 9a). In contrast, samples from the Rakopi Formation are characterized by distinctly more radiogenic Os_i values (0.81–1.24). Two possible explanations for the more radiogenic Os_i values of the Rakopi Formation compared to the younger formations are: 1) that seawater Os dominates for all formations but was more radiogenic in the Late Cretaceous than subsequent periods; or 2) the Os in this formation is dominated by Os derived from eroding continental strata rather than from seawater. Whilst the Late Cretaceous seawater was more radiogenic than during deposition of the younger formations (~0.6, compared with ~0.3–0.5), the Rakopi Formation Os_i values are significantly more radiogenic (0.81–1.24; Fig. 9b), suggesting that this formation was deposited in restricted mires where Os was largely sourced from weathering of the surrounding upper continental strata. Paleogeographic reconstructions of the Taranaki Basin at 75 Ma further indicate that the Rakopi Formation cropping out in the northwest Nelson region was deposited at a far greater distance from the shoreline than the younger formations (Fig. 10). However, with very low gradient coastal plains, freshwater-brackish water interfaces can extend several tens of kilometres inland from the coast, to impart elevated sulfur contents in peat mires (Bohacs and Suter, 1997; Sykes et al., 2014). Indeed, a slight marine influence is indicated in the Rakopi Formation by stratigraphic variations in coal sulfur content throughout the formation and presence of rare dinoflagellate cysts and glauconite grains in the upper interval (Wizevich, 1994; King and Thrasher, 1996; Sykes et al., 2004; Browne et al., 2008). Sample RF/4 from this upper interval exhibits an Os_i value (0.8) that is less radiogenic than those of the other samples from the lower intervals of the formation (1.1–1.2; Fig. 9a), suggesting there may have been mixing of Os from the radiogenic continental run-off and the less radiogenic contemporaneous seawater. A similar mixing of terrestrial- and marine-sourced Os has been observed in modern macroalgae living in coastal (brackish) waters of Iceland (Sproson et al., 2018; 2020).

The Os_i values for samples from the Farewell and Mangahewa formations are very similar to the $^{187}Os/^{188}Os$ composition of seawater at the time of their deposition (~0.35 and 0.50, respectively; Fig. 9b), suggesting likely derivation of the Os from seawater. These Os_i values also show very little variation over a wide range of Os concentrations (Fig. 9a), consistent with derivation of the Os from a single reservoir with well-mixed (homogeneous) $^{187}Os/^{188}Os$ composition, such as the open ocean. This interpretation is further supported by palynological and geochemical data that show variable but significant marine influence in these samples (Section 5.3).

The Os_i values (0.31–0.46) for the North Cape Formation samples are much lower than those of the Rakopi Formation samples deposited within the same epoch (Late Cretaceous), and slightly lower than the $^{187}Os/^{188}Os$ composition of seawater at the time of deposition (67 Ma; ~0.50; Fig. 9). However, given the age uncertainty of these samples (± 1 Ma), calculated Os_i values at 66 Ma would overlap with the $^{187}Os/^{188}Os$ composition of contemporaneous seawater, suggesting likely derivation of Os from the open ocean (Fig. 9). If the North Cape Formation samples are indeed older (>66 Ma), then their Os_i composition would suggest that there was a significant change in the nature of detrital sediment flux. This change may have resulted from the eruption of a large (60 km across) subaerial volcanic centre (Vulcan/Hestia) at the present-day

Taranaki slope between 78 and 72 Ma, after the deposition of Rakopi Formation (Fig. 2; Uruski, 2020). Seismic imaging of the geometry and stratigraphy of this volcanic centre shows a flat crest which has been interpreted to indicate that it was at least partially subaerial and eroding in the latest Cretaceous, contributing sediments to the surrounding region for about 10 Myr (Uruski, 2020). The composition of the extrusive units from the Vulcan/Hestia volcanic centre is currently unknown, but is likely to be broadly similar to mafic rocks extruded at about the same time to the northwest in the Deepwater Taranaki Basin (Romney volcano; Rad, 2015; Uruski, 2020). Weathering of such newly erupted mafic rocks has previously been shown to lower the ^{187}Os/^{188}Os composition of sediments deposited in close vicinity, either directly as a sediment source or by lowering the Os composition of surrounding localised seawater (e.g., Rooney et al., 2016; Liu et al., 2019; Schröder-Adams et al., 2019). The presence of dinoflagellates, moderate to high total coal sulfur content and marine sedimentological structures such as mud drapes, burrows and bimodal ripples in sediments from the North Cape Formation suggest that brackish conditions were common throughout the deposition of this formation (Wizevich et al., 1992; King and Thrasher, 1996; Sykes and Dow, 2000). Therefore, it is likely that weathering of the mafic rocks lowered the ^{187}Os/^{188}Os composition of the series of complex waterways that characterised the southern part of the Taranaki Basin at ~67 Ma (Fig. 10c), which in turn influenced the deposition of the North Cape Formation coals and coaly mudstones.

5.2 Effects of coal petrofacies on Re-Os systematics

There are two main types of coal seam facies represented amongst New Zealand humic coaly rocks: 1) planar mire coals and coaly mudstones, and (2) raised mire coals

(Sykes et al., 2014 and references therein). Planar mire coals are thin and commonly formed from peats that accumulated under relatively high rates of accommodation space increase in syn-rift settings. Groundwater levels within these mires were consistently high and the vegetation was well fed with nutrients from the underlying mineral substrate and frequent inundation of clastics during flooding (Edbrooke et al., 1994; Sykes et al., 2004). These mires are therefore eutrophic (nutrient-rich) and rheotrophic (flow-fed). Although coal petrofacies investigations were not undertaken specifically for this study, the sampled Rakopi, North Cape and Farewell coals and coaly mudstones are all considered to be planar mire facies.

In contrast, raised mire coals, which are represented by the Mangahewa Formation coals in this study, typically form in passive margin settings under more moderate rates of accommodation space increase and under an ever-wet climate that allow for the development of thick coal seams (Edbrooke et al., 1994; Sykes et al., 2004). The upper surface of thick raised mire deposits is generally elevated above normal river flood levels and vegetation roots no longer have access to the underlying mineral substrate. The only nutrients are therefore from rainwater. These peat mires are thus oligotrophic (nutrient-poor) and ombrotrophic (rain-fed). The resulting coal facies is typically low in mineral matter and trace elements (hence the high TOC values of 69.7–79.8 wt% for the Mangahewa Formation coal samples), reflecting both the lack of mineral input and the leaching that occurs when rainwater drains down through raised mire peats (Cameron et al., 1989; Cohen and Stack, 1996).

These differences in coal petrofacies might, therefore, explain the lower Re concentrations in four Mangahewa Formation coals compared with the majority of the

Rakopi, North Cape and Farewell Formation coals (Fig. 7c). The leaching of elements in ombrotrophic coals may also partly explain why the Mangahewa Formation coals are low in Re and Os, while the Mangahewa Formation coaly mudstones have higher concentrations of these elements leading to negative correlations of the elements with TOC (Fig. 7c, d). An alternative explanation for this is that the Mangahewa Formation coaly mudstones are from the base and roof of seam 10, where marine influence is greatest (Sykes et al., 1999; Section 5.3).

5.3 Effects of marine influence on Re-Os systematics of fluvio-deltaic sediments

Total sulfur content is a sensitive indicator of marine influence in fluvio-deltaic sediments, with coals and coaly mudstones having elevated TS content commonly occurring immediately below marine roof sediments (Williams and Keith, 1963; Banerjee and Goodarzi, 1990; Diessel, 1992; Gayer et al., 1999; Shao et al., 2003; Chou, 2012; Dai et al., 2015), and in marine transgressive and regressive regimes (Sykes et al., 1999; 2004; 2014; Chou, 2012; Dai et al., 2020 and references therein). The high TS content in marine-influenced coals and coaly mudstones originates from bacterial reduction of seawater sulfate to elemental S, H_2S and polysulfides, which then react with either ferrous iron or organic matter to produce pyrite and organic S compounds, respectively (Calkins, 1994; Chou, 2012). The TS content in coaly rocks generally varies considerably, and there is no universally accepted maximum value for coaly rocks deposited in fully terrestrial environments. However, based on extensive analyses of New Zealand coals, 0.5% TS (daf) is taken as the approximate upper limit for coals deposited in entirely terrestrial environments (e.g., Suggate, 1959; Edbrooke et al., 1994; Sykes et al., 1999; 2004; 2014; Sykes, 2001; Browne et al., 2008; Higgs et al., 2012). Accordingly, samples exhibiting 0.5–1.5% (daf) TS content are classified as slightly marine-influenced and those with TS content >1.5% (daf) are classified as strongly marine-influenced (Sykes, 2001; Sykes et al., 2004; 2014). In this study, we also adopt these classifications and consider all samples with TS content above 0.5% (daf) to indicate at least some degree of marine influence (Fig. 6f).

The TS content for samples from the Rakopi, North Cape and Farewell formations range from 0.2 to 1.5% (daf), indicating entirely terrestrial to moderately marine-influenced depositional conditions. Marine influence has been suggested to cause significant enrichment of Re and Os in coals (up to two orders of magnitude higher than freshwater coals; Tripathy et al., 2015). However, none of the samples from these three formations are significantly enriched in Re and Os, with concentrations levels that are comparable to those of fully terrestrial fluvio-deltaic coals and coaly mudstones (Baioumy et al., 2011; Goswami et al., 2018). In the Farewell Formation samples from Kupe South-5 core, Os concentrations increase stratigraphically upwards (except sample KS5/1b), reaching the highest concentration (46 ppt) in sample KS5/1a, which contains rare dinoflagellate cysts (Fig. 4a; Table 1; Morgans and Pocknall, 1991; Flores et al., 1998). This may indicate a progressive increase in the degree of brackishness of the mire and subsequently, the amount of Os derived from seawater. However, this increase in Os concentrations is not commensurate with variations in Re concentrations and shows no relationship with TS (Table 1). Therefore, the observed trend in Os content is unlikely to have directly resulted from the increasing marine influence in these samples. There are two likely explanations for the lack of significant Re and Os enrichment in samples from the Rakopi, North Cape and Farewell formations: 1) the documented marine influence may have been too slight or too late (post-depositional) to enable substantial sequestration of these elements from the seawater or 2) the prevailing depositional conditions were not suitable for chelation of the elements to the organic matter.

The Mangahewa Formation samples offer an opportunity to evaluate the impact of strong syn-sedimentary marine influence on Re-Os systematics of fluvio-deltaic sediments. In these samples, TS content ranges from 0.9 to 62.6% (daf), indicating slight to very strong marine influence (Sykes et al., 1999). This is consistent with common occurrences of dinoflagellate cysts, *Ophiomorpha* burrows and mangrove pollen at the base and roof of the sampled seams, and interpretations of a tidally-influenced, brackish coastal plain to marginal marine depositional setting (Figs 5a, 10a; Sykes et al., 1999; Flores, 2004; Higgs et al., 2006; Sykes et al., 2014). Other conspicuous signs of marine influence within the Mangahewa coals include suppressed vitrinite reflectance, enhanced vitrinite fluorescence and stratigraphic correlations between HI and TS content (Sykes et al., 1999; 2014). The marine influence within the Mangahewa coals has been shown to be syn-sedimentary based on moderately strong, positive correlations between TS and aromatic sulfur compounds such as benzothiophenes (Volk et al., 2008). Despite the strong syn-sedimentary marine influence, none of the Mangahewa Formation samples is significantly enriched in Re and Os, with concentrations ranging from 0.1 to 1.3 ppb and 14.2 to 66.2 ppt, respectively (Fig. 7). These concentrations are up to two orders of magnitude lower than the average Re (108 ppb) and Os (520 ppt) concentrations in the marine-influenced Matewan coals, despite apparent comparable levels of marine influence (Geboy et al., 2015; Tripathy et al., 2015). This suggests that depositional conditions may not have been favourable for chelation of Re and Os in the Mangahewa Formation coals and coaly mudstones.

The factors controlling Re and Os chelation in organic-rich sedimentary rocks are currently not well understood, making it difficult to establish the specific conditions that may have limited the uptake of Re and Os in the Mangahewa Formation samples. However, it is unlikely to relate to redox conditions of the water column (e.g., Crusius et al., 1996; Crusius and Thomson, 2000; Yamashita et al., 2007) because Re and Os concentrations in the Mangahewa Formation samples do not show any significant correlation with HI and OI (Fig. 8b). Moreover, the average OI values of the Mangahewa Formation coal samples (4 mg CO_2/g TOC) are essentially just as low as those of the Matewan coal samples (2 mg CO_2/g TOC; Tripathy et al., 2015), indicating similar oxygen-poor depositional conditions; possibly sulfidic, as indicated by high TS and abundant pyrite in both sets of samples. It is also considered unlikely that differences in coaly organic matter type have limited the organic-chelation of Re and Os because the organic matter type in the Mangahewa Formation samples appears comparable to that in the Matewan coals. The average HI (321 mg HC/g TOC) and maceral group composition (86.6 vol% vitrinite, 9.3 vol% inertinite and 4.0 vol% liptinite) for the Mangahewa Formation coal samples are very similar to those of the Matewan coal samples reported by Geboy et al. (2015) and Tripathy et al. (2015): HI of 278 mg HC/g TOC, 79.1 vol% vitrinite, 14.7 vol% inertinite and 6.2 vol.% liptinite.

Restricted basin conditions with limited seawater renewal is another potential cause of relatively low Re and Os concentrations in marine-influenced peat-forming mires (Turgeon et al., 2007; McArthur et al., 2008). However, these factors are unlikely to have caused the low Re and Os concentrations in the Mangahewa coals because the Os_i values (0.43–0.51; $\bar{x} = 0.48$) for these samples overlap with Os isotope composition of seawater at the time of deposition (~0.5; Fig. 9). Such overlap suggests that either (1) the Mangahewa peat mires were hydrologically connected to the global ocean or (2) the isotopic composition of Os flux into the mires from the weathering of the surrounding continental mass was extremely similar. The latter is highly unlikely because the radiogenic samples from the Rakopi Formation (mean Os_i value of 1.1) imply that the New Zealand continental mass must have been contributing radiogenic Os flux and there are no major Late Eocene igneous extrusions in the Taranaki Basin that could lower this value.

The key difference between the Matewan and Mangehewa coals, and indeed the other coal formations that have been analysed for Re and Os (Baioumy et al., 2011; Goswami et al., 2018), is that the Matewan coal seam is directly overlain by a marine shale (Betsie Shale Member; Geboy et al., 2015; Tripathy et al., 2015). This may have allowed Re- and Os-rich seawater to percolate down and be fixed by reduction into the Matewan coals. Mangahewa Formation seams 10 and 11 show increases in total and pyritic sulfur towards their tops and bases, culminating with the presence of dinoflagellate cysts and mangrove pollen in the roof and floor sediments, as well as an *Ophiomorpha* burrow in the roof of seam 10 (Sykes et al., 1999). These features indicate brackish but not fully marine conditions and thus, represent lowstand deposits at the turnaround of short regressive-transgressive cycles within an overall transgressive regime. A similar upward decreasing then increasing trend of sulfur content is seen across the Rakopi coal seams in the Paturau River section (Sykes et al., 2004), which again indicates a change in shoreline retreat to advance, but in this case at a far greater distance from the shoreline. In both depositional environments, the conditions were brackish rather than fully marine, and this may explain the relatively limited enrichment and homogenisation of Re and Os in the Mangahewa and Rakopi coals. Enrichment and homogenisation of Re and Os in coals might occur only in the rare situation where precursor peat mires are drowned directly by fully marine seawater, as in the case of the organic-rich Betsie marine shale directly overlying the Matewan coal seam (Tripathy et al., 2015). Elevated Re (up to ppm levels) and Os concentrations have also been reported in Late Carboniferous–Late Permian high-sulfur coals overlain by marine carbonate and mudstone successions from China (Dai et al., 2015; 2017; Liu et al., 2015; Zhao et al., 2017; Liu et al., 2019; Zhao et al., 2019). A depth profile through one of the major coal seams overlain by a marine limestone in Jincheng Coalfield, northern China shows that Re enrichment is confined to the top of the coal seam rather than distributed evenly through the vertical profile (Zhao et al., 2019). This was suggested to indicate derivation of Re from seawater percolating through the peat in the early diagenetic stage (Zhao et al., 2019).

5.4 Re-Os geochronology in fluvio-deltaic coals and coaly mudstones

The Farewell Formation samples from Kupe South-5 and -6 were analysed in an attempt to constrain their Re-Os depositional age. However, regression of the ^{187}Re/^{188}Os and ^{187}Os/^{188}Os ratios for these samples shows significant scatter with no discernible linear trend (Fig. 11). The only previous attempt at producing Re-Os depositional ages for fluvio-deltaic sediments also reported large scatter in ^{187}Re/^{188}Os and ^{187}Os/^{188}Os ratios for entirely non-marine coals and shales from the Carboniferous Soldogg Formation, southern Barents Sea (Goswami et al., 2018). The lack of an isochron fit in the Soldogg Formation sediments was attributed to heterogeneity in the Os_i compositions, which varied by 0.5 units. However, unlike the Soldogg Formation sediments, samples from the Farewell Formation exhibit Os_i values that vary by only 0.1 units (Table 1). Published Re-Os data for several marine and terrestrial sample suites also show more variability in the Os_i values than both the Farewell and Soldogg Formation samples, but still yield reliable Re-Os depositional ages. For example, comparably aged Douglas Creek Member shales of the lacustrine Green River Formation, USA, exhibit Os_i values that vary by ~0.2 units, but produce an accurate, albeit imprecise, depositional age of 49.8 ± 4.8 Ma (Cumming et al., 2012). Similarly, the marine-influenced Carboniferous Matewan coals, USA, and Mesoproterozoic marine shales of the Kaimur Group, central India, yield accurate but imprecise Re-Os depositional ages (325 ± 14 Ma and 1210 ± 52 Ma, respectively) despite having Os_i values that vary by 0.7 and 1.1 units, respectively (Tripathy et al., 2015; Tripathy and Singh, 2015). The Douglas Creek Member shales, Matewan coals and Kaimur shales may have developed reliable isochrons despite significant variation in Os_i ratios because of their significantly large variations in the $^{187}Re/^{188}Os$ ratios (ranges of ~1500, 2400 and 850 units, respectively) compared to those in the Soldogg and Farewell Formation samples (93 and 145 units, respectively). However, sample suites with similarly limited variations in $^{187}Re/^{188}Os$ have produced reliable isochrons (e.g., Selby et al., 2009; Rooney et al., 2014; Sperling et al., 2014). For example, the Aptian-Albian boundary interval in northwest Germany exhibits $^{187}Re/^{188}Os$ values that vary by only ~70 units, but yields a Re-Os age (108.9 ± 6.2 Ma) that is within uncertainty of the Geological Time Scale (GTS2016) determination (Selby et al., 2009; Ogg et al., 2016). The Os_i values in this interval, however, vary by only 0.002 units, thereby enabling an isochron fit despite the low spread in $^{187}Re/^{188}Os$ ratios. We therefore suggest that either very low Os_i variability or large ranges in $^{187}Re/^{188}Os$ values are required to produce meaningful Re-Os isochrons, but not necessarily both. The Farewell Formation samples lack both these features, preventing the development of an isochron.

Many instances of low spread in $^{187}Re/^{188}Os$ ratios have been reported for both marine and terrestrial sediments (e.g., Turgeon et al., 2007; Selby et al., 2009; Zhu et al., 2013; Rooney et al., 2014; Sperling et al., 2014; Liu et al., 2018). The Re-Os isotope data for the Farewell Formation samples from Kupe South-5 and -6 cores support previous findings that variability of depositional conditions exert some control on Re-Os fractionation (Cumming et al., 2012; Harris et al., 2013; Liu et al., 2020). The Kupe South-5 samples exhibit a six times larger spread in $^{187}Re/^{188}Os$ ratios (126 units) than those from Kupe South-6 (21 units) which, although not a large difference, may have resulted from differences in depositional conditions. The Kupe South-5 samples are interpreted as paleosols, deposited in low-lying swamps that were proximal to an active channel (Flores et al., 1998) and thus, generally susceptible to fluctuating high and low energy clastic sedimentation during fluvial floods. These samples contain abundant but variable vitrain (wood) lenses and streaks, leaves and macerated plant fragments (Flores et al., 1998), which may have provided variable chelating surfaces for complexation of Re and Os, leading to increased $^{187}Re/^{188}Os$ fractionation (Cumming et al., 2012). In contrast, the sampled interval in Kupe South-6 lacks coarse sediments and paleosols, and exhibits thickening upward linsen lamination that is characteristic of sediments deposited in a distal floodplain lake setting (Constantine, 2008). This more stable depositional setting may have favoured more homogeneous uptake of Re and Os leading to the lower spread in ^{187}Re/^{188}Os ratios of the Kupe South-6 samples.

Although there have been only a few case studies, fluvio-deltaic sediments appear to rarely attain the levels of Os_i homogeneity commonly seen in marine shales. There are two likely explanations, which are not mutually exclusive: 1) the source materials for these sediments (primarily detrital silicates and plant debris) are typically heterogeneous, or 2) these sediments were deposited in restricted basins, preventing complete mixing and homogenisation of the Os signature before sequestration. Of the fluvio-deltaic sample suites studied here, the coals and coaly mudstones of the Mangahewa Formation exhibit the most marine influence (Section 5.3; Sykes et al., 1999). These samples have Os_i values that are identical to that of seawater at the time of deposition, indicating that the Mangahewa paleomires and the open ocean were hydrologically connected (Fig. 9b). Such connection may have allowed essentially complete homogenisation of the Os signature in the Mangahewa Formation samples, as seen in the Matewan coals (Tripathy et al., 2015). It is, therefore, unsurprising that six of the eight samples from this formation exhibit Os_i values that vary by only 0.03 units (Table 2) and appear to form a linear trend on an isochron diagram (Fig. 12a). The isochron age of 28 ± 16 Ma [Mean Square of Weighted Deviates (MSWD) = 1.5; Os_i = 0.50 ± 0.03] produced by these samples is, however, imprecise and younger than, albeit within uncertainty of, the estimated biostratigraphic age (37 ± 1 Ma) for the samples (Fig. 12a). A 37 Ma reference line with an assumed Os_i value of 0.48 passes through all the data points (Fig. 12a), implying that uncertainties in the measured Re-Os data largely contributed to the imprecision of the Re-Os age. A Monte Carlo simulation of the uncertainties (Fig. 12b; Li et al., 2019) shows that 69% of total uncertainties can be attributed to uncertainties in the analytical measurements, likely arising from the low Re and Os concentrations in the Mangahewa Formation samples and small amounts of rock powder (0.2 g) used for analysis (Section 3.2). The relatively wide stratigraphic interval (~5 m) represented by the Mangahewa Formation samples may have also introduced variation in Os_i values. Two of the eight samples have Os_i values of 0.43 and 0.44, significantly outside the narrow range of 0.48–0.51 displayed by the other six samples (Table 2). As with the Farewell Formation samples, a lack of spread in $^{187}Re/^{188}Os$ ratios (97 units) and relatively young geological age are also factors likely to have contributed to the imprecise Re-Os age.

Conclusions

This study presented Re-Os, S and bulk pyrolysis data for variably marine-influenced, fluvio-deltaic Late Cretaceous–Eocene coals and coaly mudstones from Taranaki Basin, New Zealand. Rhenium (0.1–1.3 ppb) and Os (14.2–66.2 ppt) concentrations in these coaly rocks are low, even in strongly marine-influenced, high-sulfur samples. These concentration ranges are up to two orders of magnitude lower than values reported for similarly marine-influenced coals from the Matewan coal seam, USA. Notably, the Matewan coal seam is directly overlain by a marine shale, leading to a suggestion that direct—or at least very close—juxtaposition of depositional environments may be required for enhanced Re and Os enrichment in coaly rocks.

Samples from the Late Cretaceous Rakopi Formation exhibit radiogenic Os_i values ranging from 0.8 to 1.2, as expected for fully terrestrial coals deposited in restricted mires in which Os is mainly sourced from weathering of surrounding UCC. In contrast, samples from the progressively younger North Cape, Farewell and Mangahewa formations record non-radiogenic Os_i values (0.3–0.5), which are attributed to variable proportions of Os derived from seawater (Farewell and Mangehewa) and contributions from nearby freshly erupted mafic extrusives (North Cape).

The results of this study also show that strong marine influence improves Re-Os isochroneity in coaly rocks even where overall concentrations are not greatly increased. The strongly marine-influenced coals and coaly mudstones of the Mangahewa Formation exhibit $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ compositions that form a linear trend on an isochron diagram, producing an age of 28 ± 16 Ma. Although this age is highly imprecise, it is consistent with the assigned biostratigraphic age of the samples (37 ± 1 Ma). In contrast, the essentially freshwater to slightly marine-influenced samples from the Farewell Formation display $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ compositions that are significantly scattered without any linear relationship, which is attributed mainly to heterogeneity in Os_i compositions. Nonetheless, it appears that Os_i values are not intrinsically too heterogeneous to preclude Re-Os dating in marine-influenced coaly samples, provided sufficient spread in $^{187}Re/^{188}Os$ can be obtained. Further evaluation of how Re and Os may be fractionated in these settings may allow the geochronometer to be more widely applied to such units.

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Figures

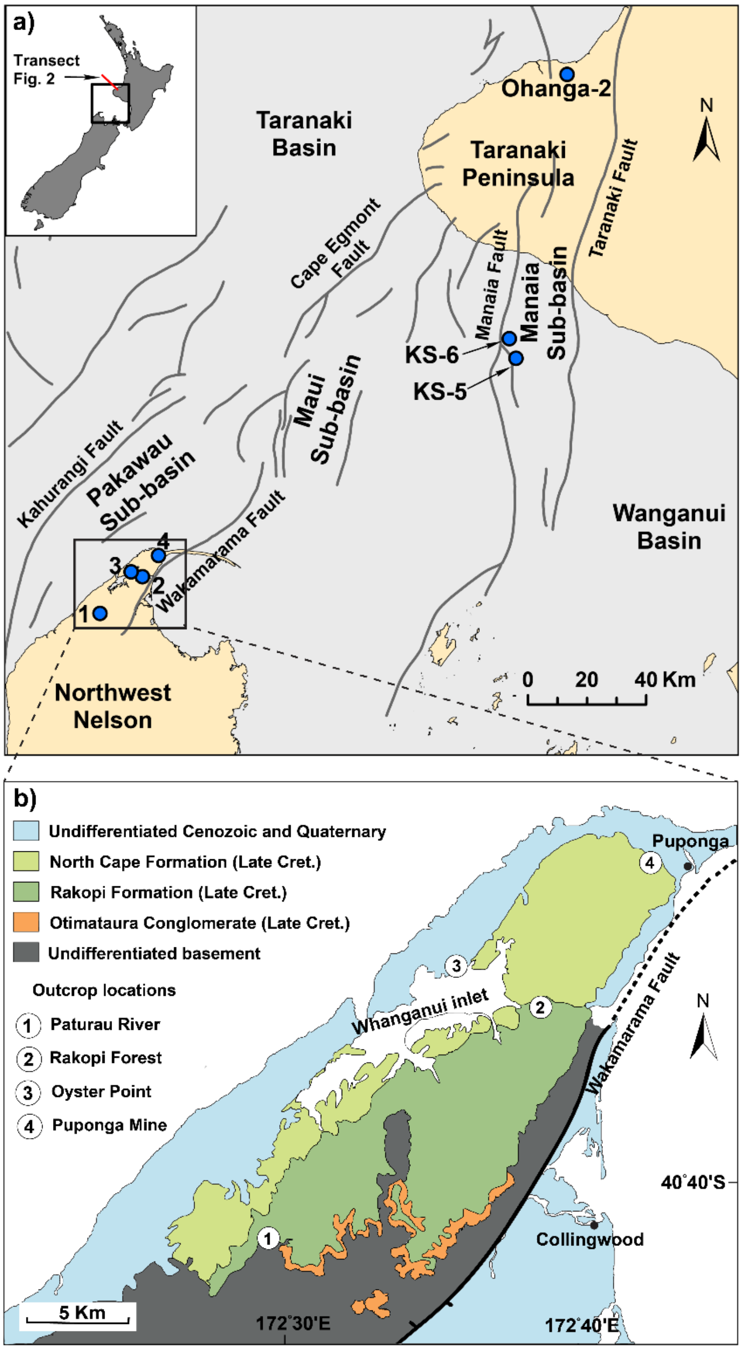

Fig. 1. a) Map of Taranaki Basin showing the main structural features and location of the samples studied. KS-5 and -6 = wells Kupe South-5 and -6. b) Simplified geological map of the northwest Nelson region (modified after Browne et al., 2008). In a), labels 1–4 refers to outcrop locations named in b).

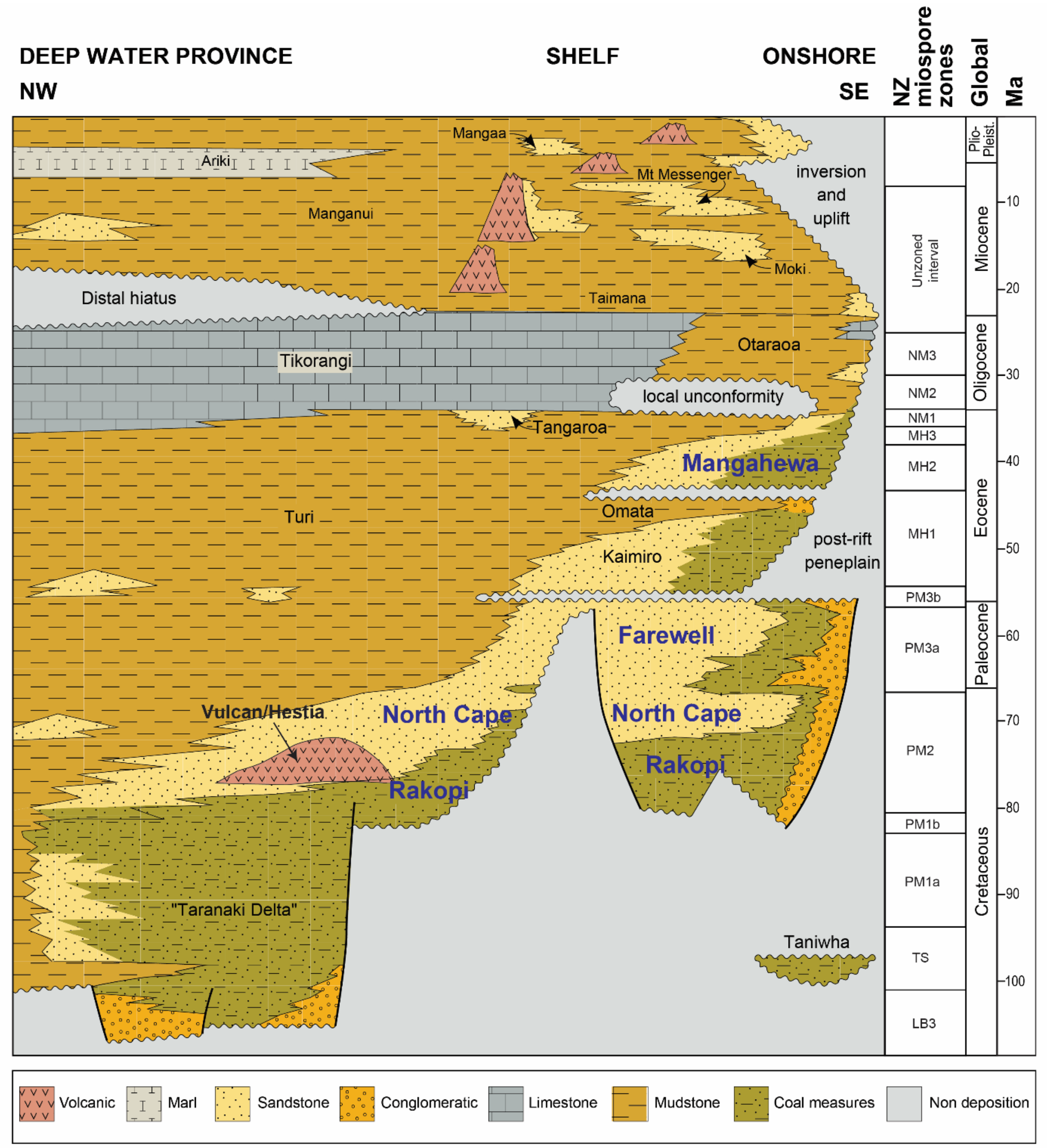

Fig. 2. Generalized chronostratigraphic panel for Taranaki Basin across a northwest-southeast transect (see inset, Fig. 1a, for approximate location). Sampled formations are highlighted by bold blue font. The approximate stratigraphic location of the Vulcan/Hestia volcano is from Uruski (2020). Modified from New Zealand Petroleum and Minerals (2014).

Fig. 3. Outcrop of thin, planar mire coal seams and intervening coaly mudstone-siltstone beds within the Rakopi Formation exposed in the upper reaches of the Paturau River (see Fig. 1 for location). Seam 6, containing distinctive thin mudstone laminae, and from which sample PR/6 was collected is labelled. Seams 1 and 10 from which samples PR/1 and 10 were collected are out of the field of view. Yellow scale bar is approximately 1 m long.

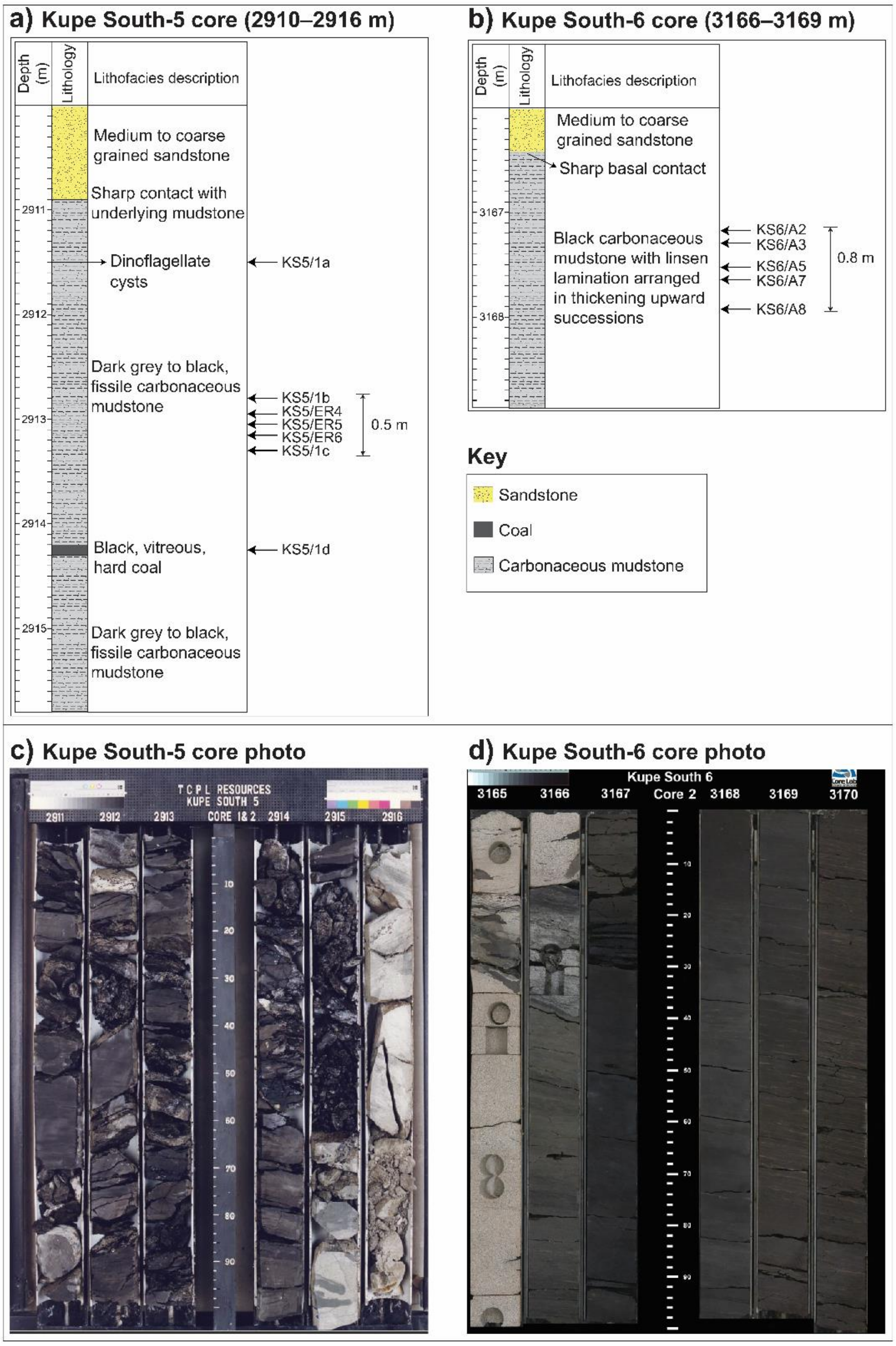

Fig. 4. Core description (a, b) and photographs (c, d) of the sampled intervals of the Farewell Formation in Kupe South-5 and -6, respectively. The photos show that the sampled interval of the Kupe South-5 core is more coaly (carbonaceous) than the sampled interval in Kupe South-6, which is more laminated and slightly coarser-grained.

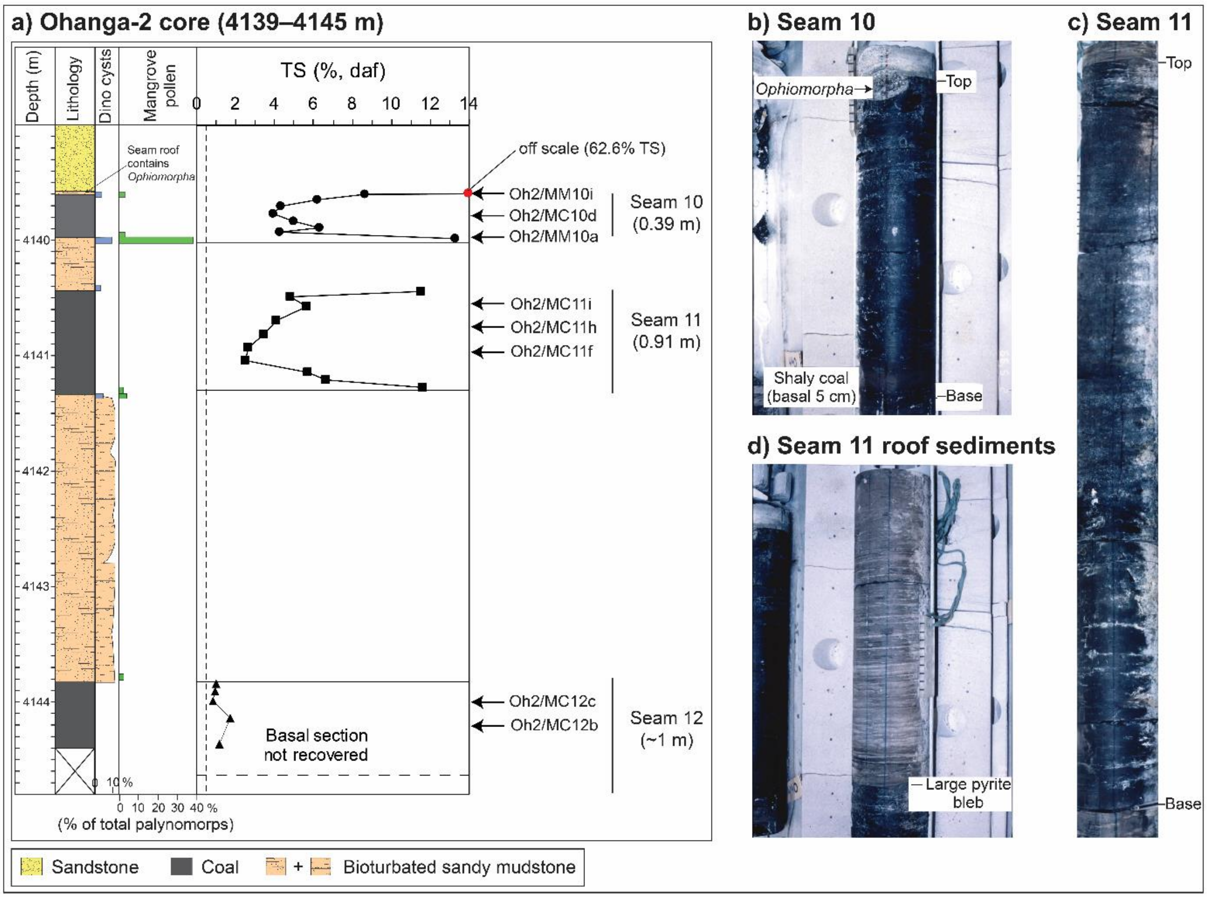

Fig. 5. a) Core description of the sampled interval of the Mangahewa Formation in Ohanga-2 well showing coal seams 10, 11 and 12 (modified after Sykes et al., 1999). High total sulfur (TS) concentrations are recorded in intervals containing dinoflagellate cysts and mangrove pollen, indicating early rather than late diagenetic emplacement of sulfur as a result of marine influence. The vertical dashed line in the sulfur panel is at 0.5% total sulfur (daf), which is the inferred approximate upper limit for entirely freshwater coals (e.g., Sykes et al., 2004; 2014). Also shown are photographs of b) coal seam 10, c) coal seam 11 and d) the roof sediments of seam 11. An *Ophiomorpha* burrow in the roof of seam 10, a large pyrite bleb at the top of seam 11 and inferred tidal-laminated sediments directly overlying seam 11 are clear evidence of marine influence in the coal-forming environment.

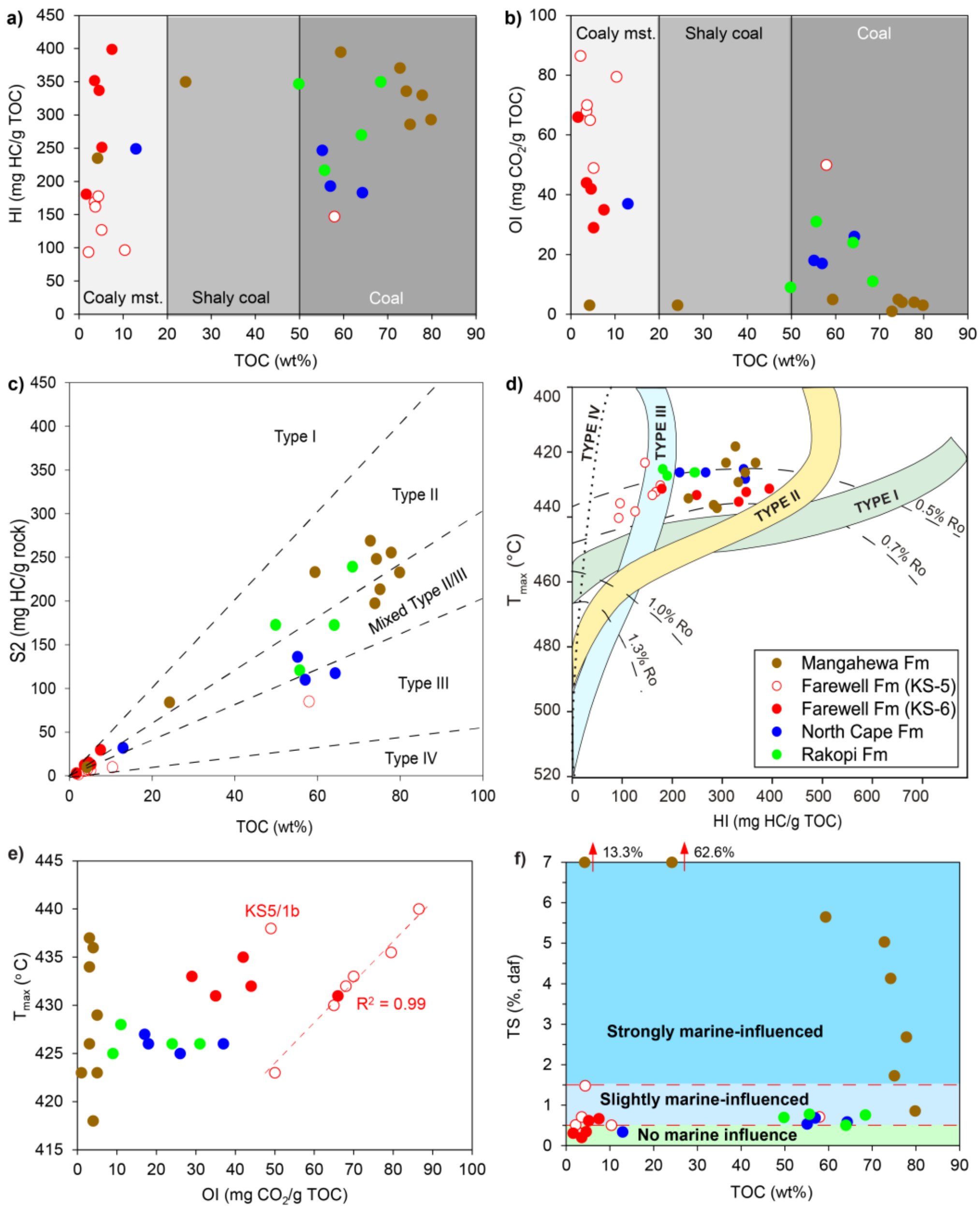

Fig. 6. Cross-plots of a) HI vs TOC, b) OI vs TOC, c) S2 vs TOC, d) T$_{max}$ vs HI, e) T$_{max}$ vs OI, and f) TS vs TOC, for coaly rocks in the sampled formations. KS-5 and -6 = wells Kupe South-5 and -6. TOC thresholds for coaly lithologies are from Sykes and Raine (2008). TS (dry, ash-free) thresholds for the degree of marine influence are from Sykes (2004). In d), the trends in vitrinite reflectance (R$_o$) and kerogen types are from Peters (1986) and the p:IGI programme (IGI Ltd). In f), samples Oh2/MM10a (13.3% TS) and Oh2/MM10i (62.6% TS) are off scale. The legend in d) is used for all plots.

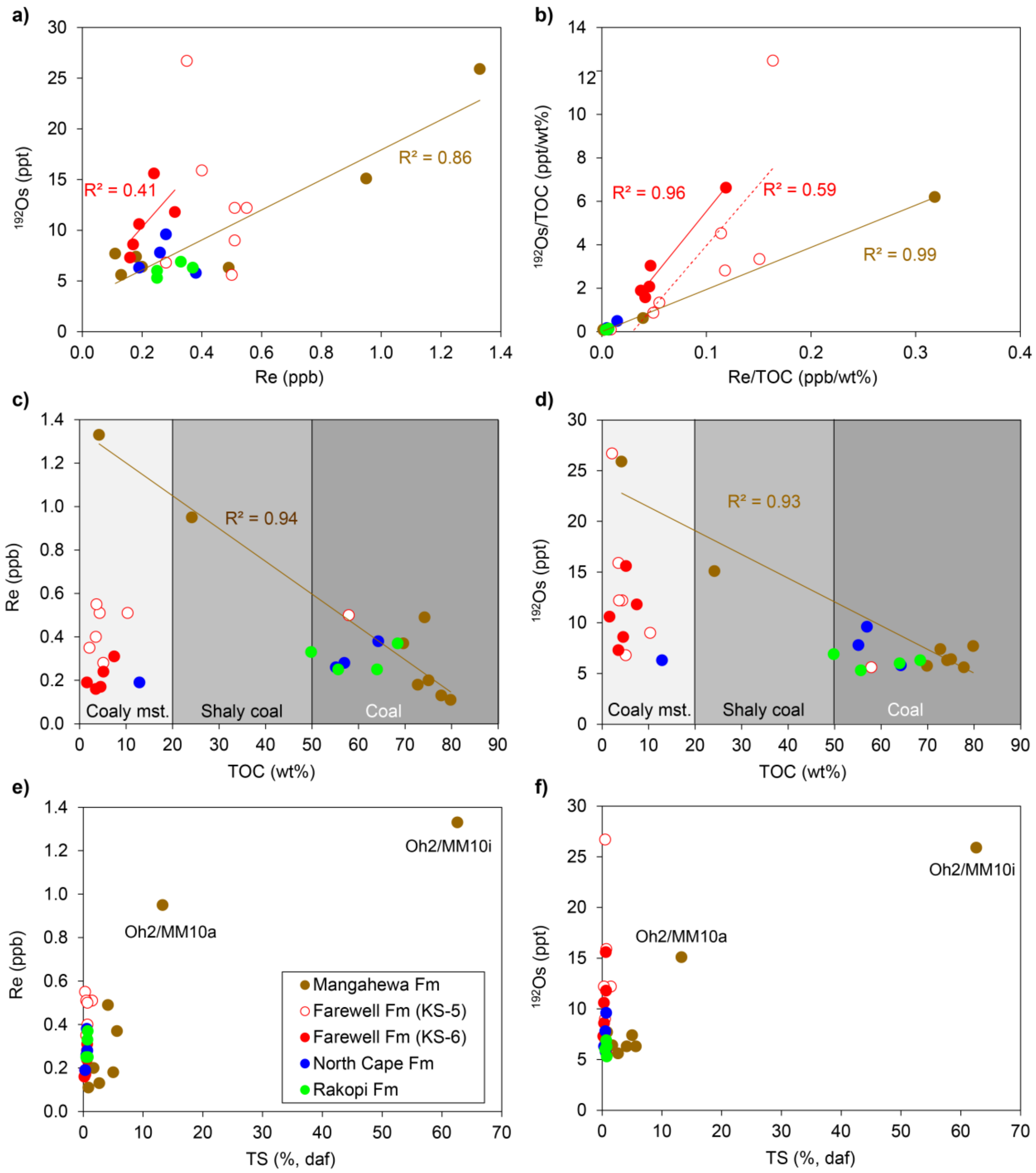

Fig. 7. Cross-plots of a) ^{192}Os vs Re, b) ^{192}Os/TOC vs Re/TOC, c) Re vs TOC, d) ^{192}Os vs TOC, e) Re vs TS and f) ^{192}Os vs TS for coaly rocks in the sampled formations. KS-5 and -6 = wells Kupe South-5 and -6. In c) and d), the TOC thresholds for coaly lithologies are from Sykes and Raine (2008).

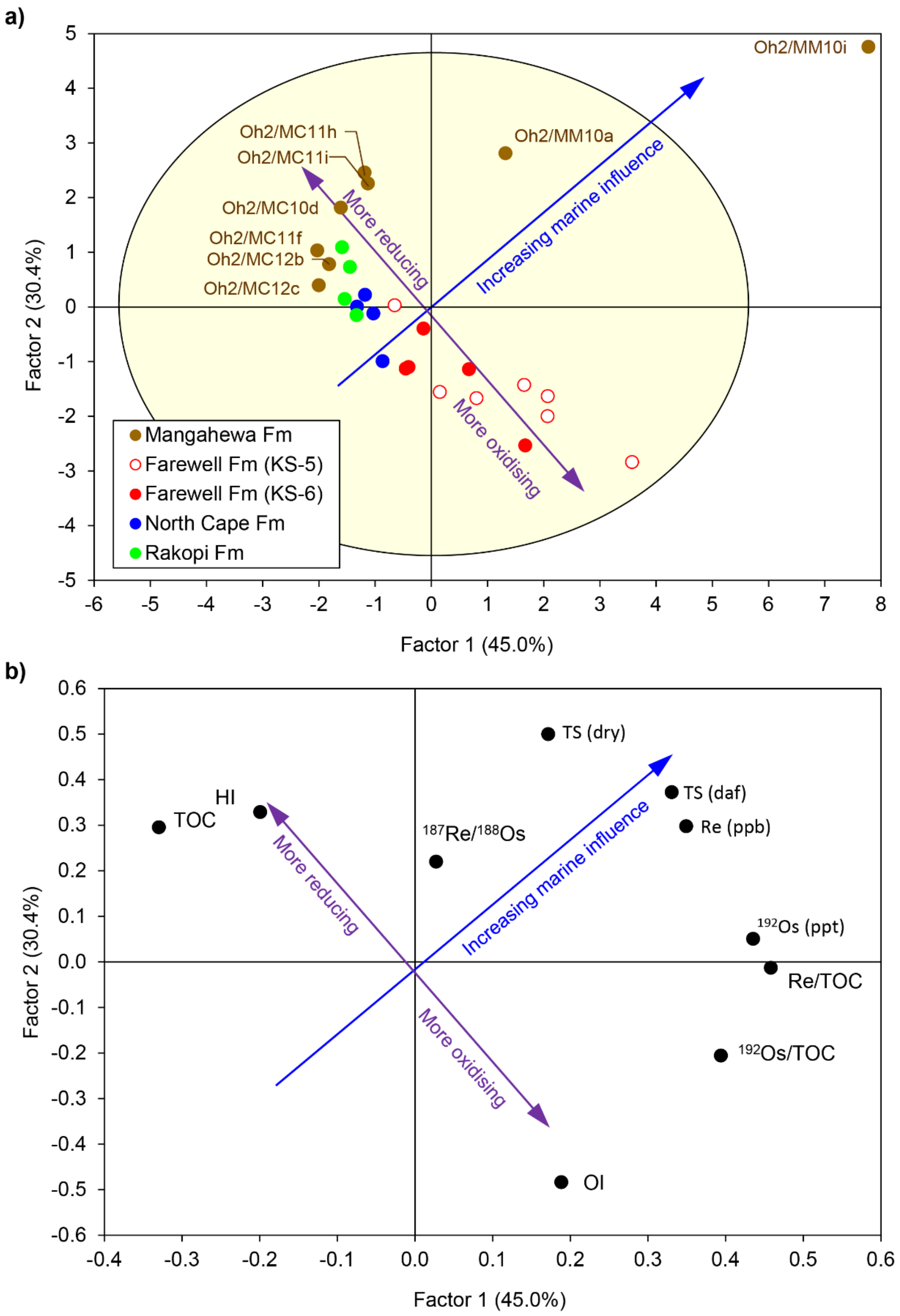

Fig. 8. a) Sample scores and b) parameter loadings on principal components 1 and 2 for the sample set. In a), the shaded ellipse represents the 95% confidence limit. KS-5 and -6 = wells Kupe South-5 and -6.

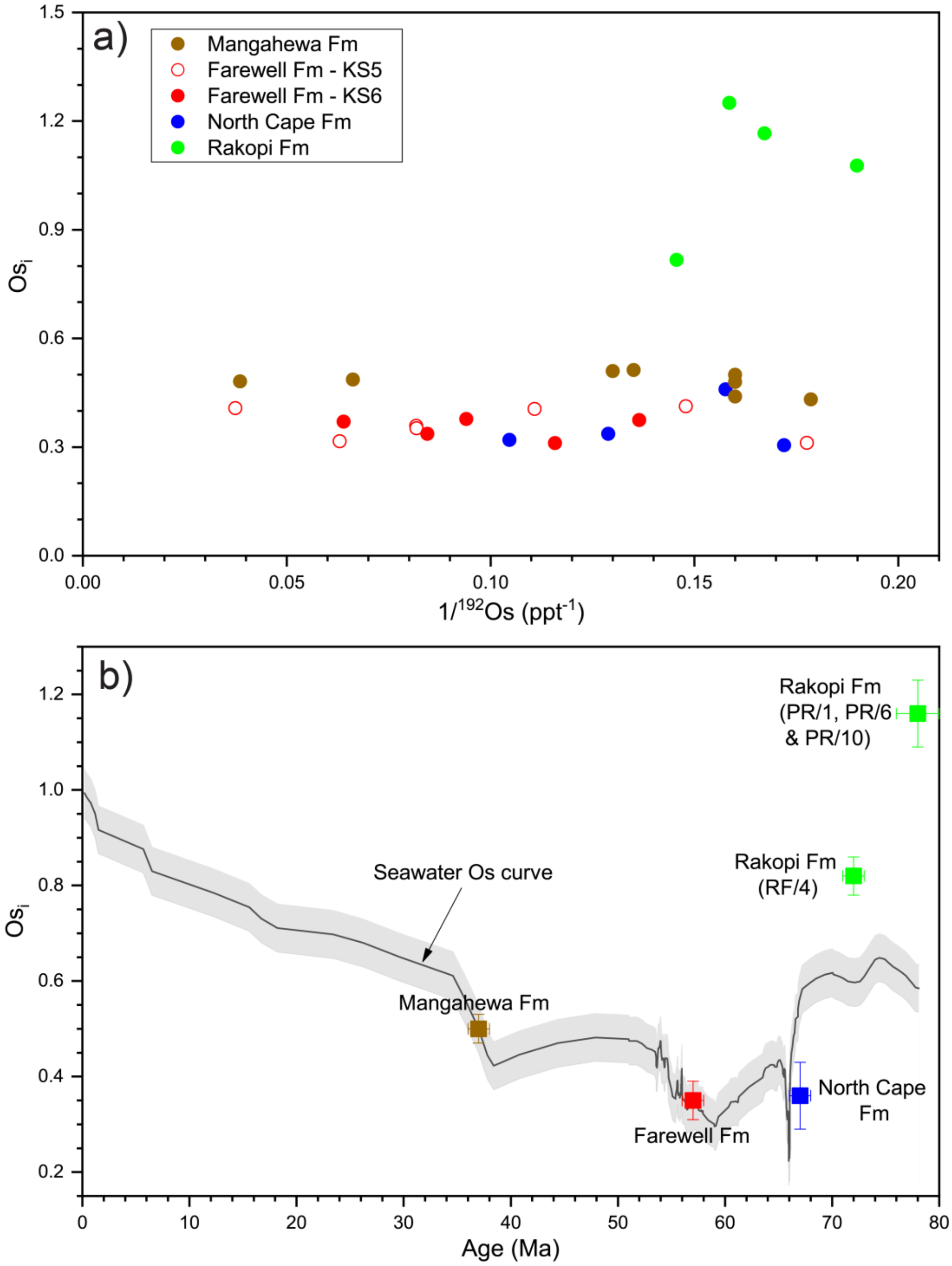

Fig. 9. a) Cross-plot of initial ^{187}Os/^{188}Os composition (Os$_i$) versus 1/^{192}Os for samples from the Mangahewa, Farewell, North Cape and Rakopi formations. b) The Os$_i$ for the Mangahewa, Farewell, North Cape and Rakopi formations plotted on the seawater Os curve for the past 80 Myr (Peucker-Ehrenbrink and Ravizza, 2012). The shaded region represents a standard deviation of 0.1 in the Os curve.

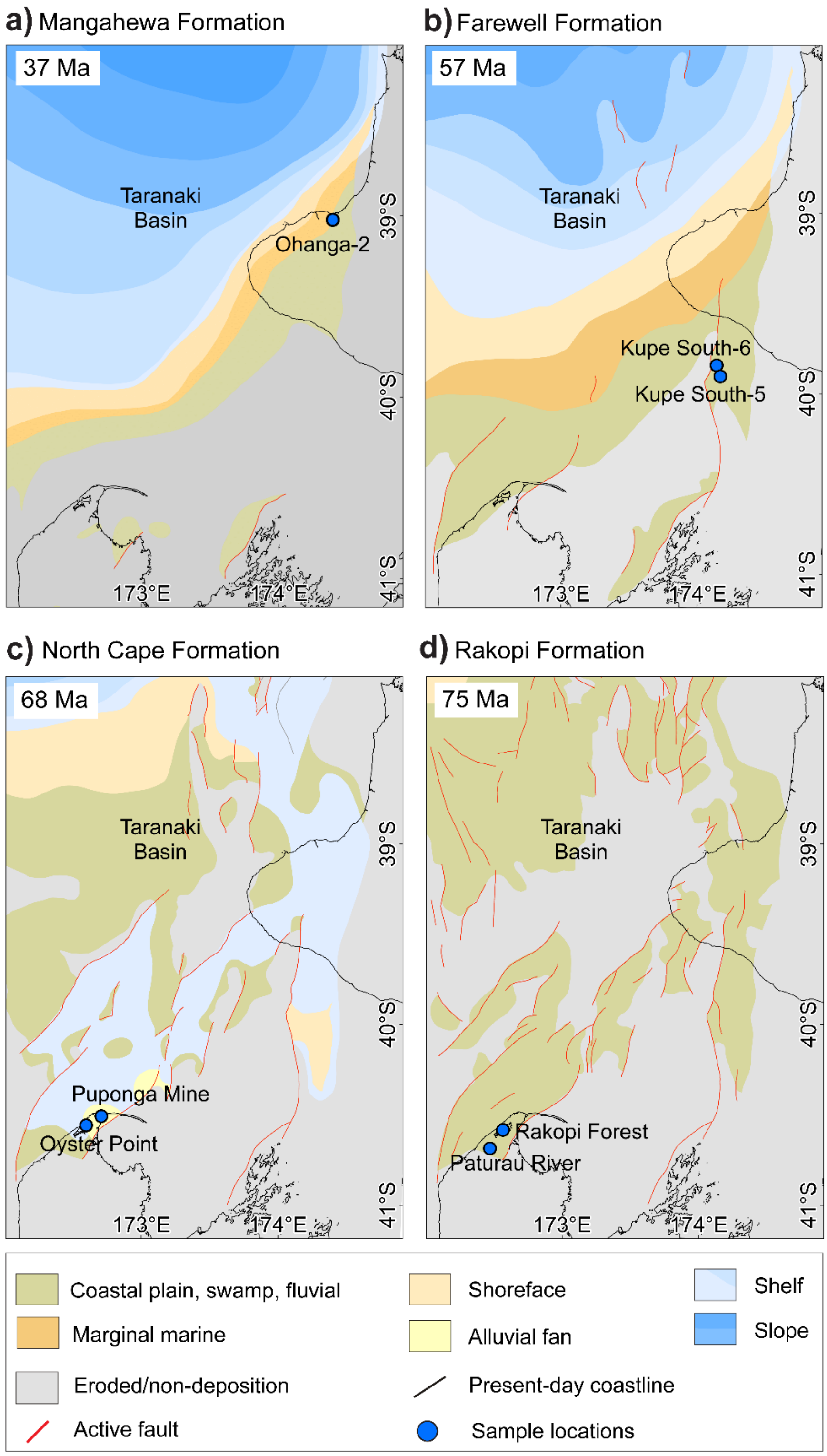

Fig. 10. Paleogeographic reconstructions of Taranaki Basin during the deposition of the a) Mangahewa, b) Farewell, c) North Cape and d) Rakopi formations. Modified after Strogen (2011).

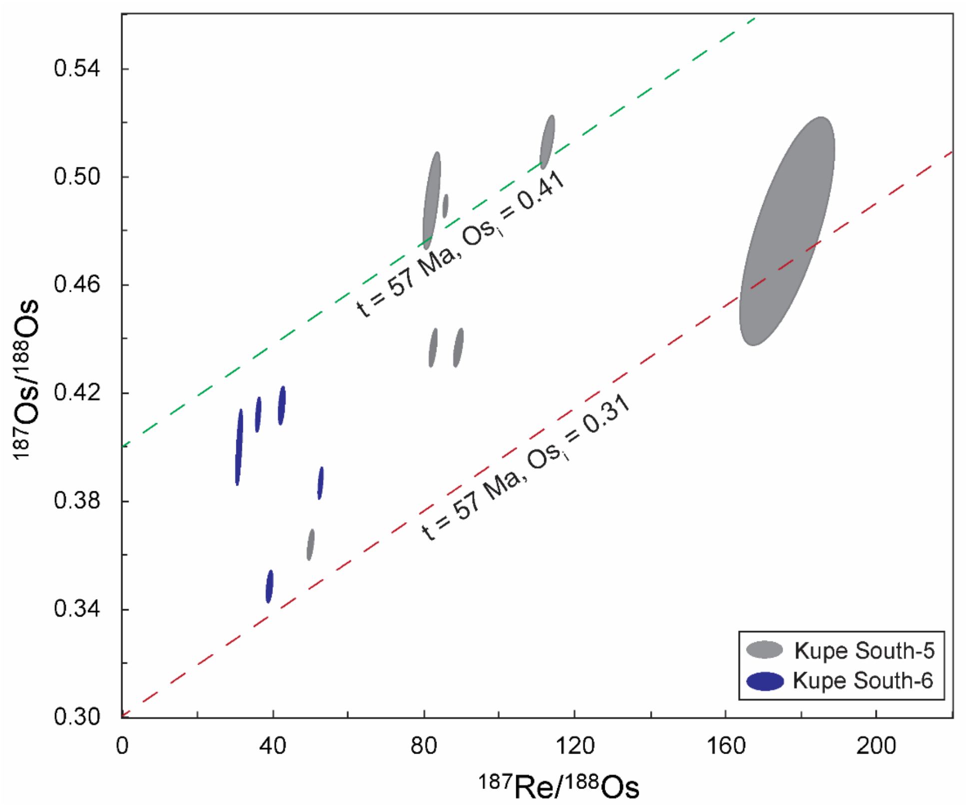

Fig. 11. Re-Os isochron diagram for Farewell Formation samples from Kupe South-5 and -6. Reference lines with slopes equivalent to the approximate biostratigraphic age of the samples (57 Ma; Crouch and Raine, 2012) and Os_i values of 0.31 and 0.41 (minimum and maximum values) are shown by the red and green dashed lines, respectively.

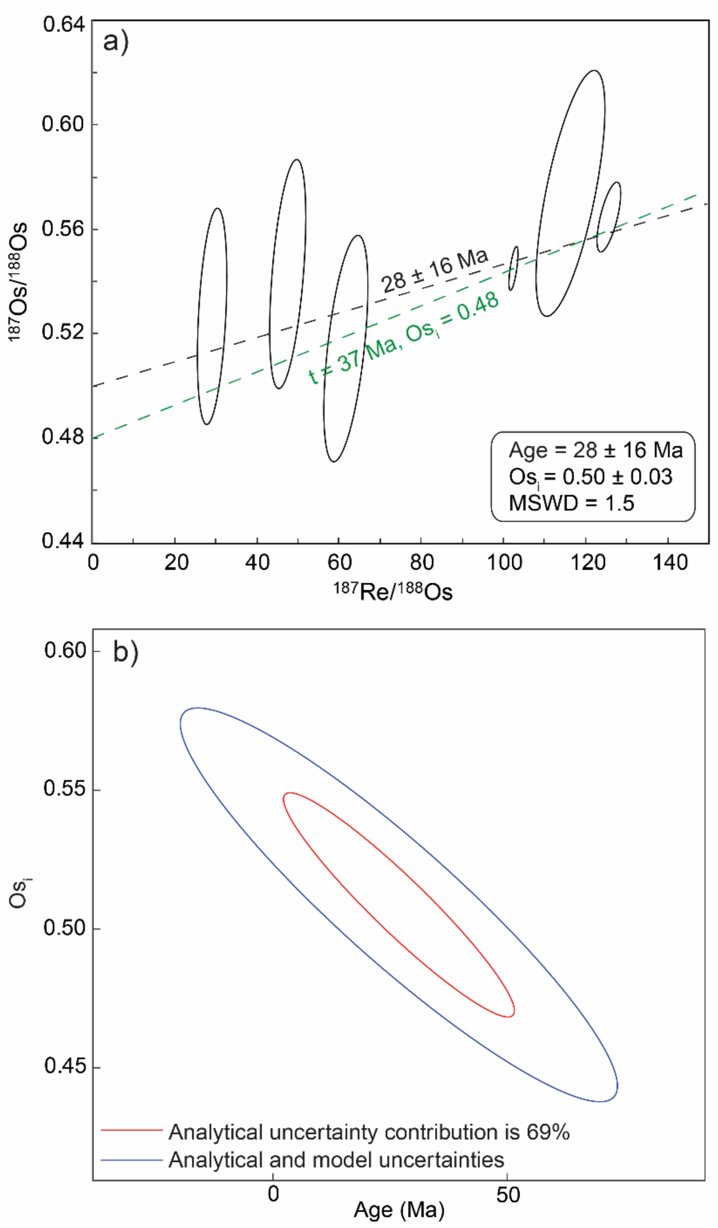

Fig. 12. a) Re-Os isochron diagram for six Mangahewa Formation samples with Os_i values between 0.48 and 0.51. The data appear to form an isochron (black dashed line), but the age produced is highly imprecise (28 ± 16 Ma). A reference line with a slope equivalent to the biostratigraphic age of the samples (37 Ma) and an Os_i value of 0.48 is shown by the green dashed line. b) Monte Carlo simulation of uncertainties in the Os_i value and age of the six Mangahewa Formation samples shown in a).

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Table 1: Re and Os concentrations and isotope compositions, TS and bulk pyrolysis data for samples from the Rakopi, North Cape and Farewell formations

Sample	Depth (m)	Lithology	TOC (wt%)	Re (ppb)	Os (ppt)	^{192}Os (ppt)	^{187}Re/^{188}Os	^{187}Os/^{188}Os	rho	Os$_i$ [a]	HI	OI	T$_{max}$ (ºC)	TS (%, dry)	TS (%, daf)
Farewell Formation - Kupe South-5															
KS5/1a	2911.50	coaly mst.	2.1	0.35 ± 0.004	46.1 ± 0.3	26.7 ± 0.2	85.7 ± 0.4	0.49 ± 0.01	0.438	0.41	94	87	440	0.06	0.52
KS5/1b	2912.80	coaly mst.	5.1	0.28 ± 0.002	17.2 ± 0.2	6.8 ± 0.1	82.1 ± 1.9	0.49 ± 0.02	0.675	0.41	127	49	438	0.09	0.62
KS5/ER4	2912.92	coaly mst.	3.5	0.40 ± 0.002	39.6 ± 0.2	15.9 ± 0.1	50.0 ± 0.5	0.36 ± 0.01	0.605	0.32	169	68	432	0.11	0.71
KS5/ER5	2913.02	coaly mst.	4.3	0.51 ± 0.002	30.8 ± 0.2	12.2 ± 0.1	82.4 ± 0.9	0.44 ± 0.01	0.644	0.36	178	65	430	0.25	1.48
KS5/ER6	2913.15	coaly mst.	3.7	0.55 ± 0.002	31.4 ± 0.2	12.2 ± 0.1	89.1 ± 0.9	0.44 ± 0.01	0.651	0.35	162	70	433	0.05	0.31
KS5/1c	2913.30	coaly mst.	10.3	0.51 ± 0.002	23.0 ± 0.2	9.0 ± 0.1	112.7 ± 1.4	0.51 ± 0.01	0.670	0.41	97	80	436	0.09	0.51
KS5/1d	2914.20	coal	57.9	0.50 ± 0.010	14.3 ± 0.4	5.6 ± 0.3	176.4 ± 10.3	0.48 ± 0.03	0.720	0.31	147	50	423	0.61	0.71
Farewell Formation - Kupe South-6															
KS6/A2	3167.21	coaly mst.	3.5	0.16 ± 0.002	18.4 ± 0.1	7.3 ± 0.1	42.4 ± 0.7	0.42 ± 0.01	0.456	0.38	352	44	432	0.03	0.21
KS6/A3	3167.33	coaly mst.	4.6	0.17 ± 0.002	21.5 ± 0.1	8.6 ± 0.1	39.2 ± 0.6	0.35 ± 0.01	0.459	0.31	337	42	435	0.06	0.35
KS6/A5	3167.54	coaly mst.	7.5	0.31 ± 0.002	29.6 ± 0.2	11.8 ± 0.1	52.6 ± 0.6	0.39 ± 0.01	0.580	0.34	399	35	431	0.14	0.67
KS6/A7	3167.60	coaly mst.	5.1	0.24 ± 0.002	39.2 ± 0.4	15.6 ± 0.3	31.1 ± 0.7	0.40 ± 0.01	0.653	0.37	252	29	433	0.10	0.62
KS6/A8	3167.98	coaly mst.	1.6	0.19 ± 0.002	26.7 ± 0.1	10.6 ± 0.1	36.2 ± 0.5	0.41 ± 0.01	0.482	0.38	181	66	431	0.04	0.31
North Cape Formation															
PM/3M	–	coaly mst.	12.9	0.19 ± 0.01	16.2 ± 0.4	6.3 ± 0.3	60.9 ± 4.5	0.53 ± 0.04	0.545	0.46	249	37	426	0.06	0.34
PM/3N	–	coal	64.2	0.38 ± 0.01	14.7 ± 0.4	5.8 ± 0.3	128.3 ± 7.7	0.45 ± 0.03	0.683	0.31	183	26	425	0.54	0.59
PM/3O	–	coal	55.1	0.26 ± 0.01	19.5 ± 0.4	7.8 ± 0.4	67.2 ± 4.1	0.41 ± 0.03	0.583	0.34	247	18	426	0.42	0.54
OP/1	–	coal	57.0	0.28 ± 0.01	23.9 ± 0.5	9.6 ± 0.4	58.8 ± 3.4	0.39 ± 0.02	0.577	0.32	193	17	427	0.58	0.69
Rakopi Formation															
RF/4	–	coal	49.8	0.33 ± 0.01	18.4 ± 0.4	6.9 ± 0.3	96.1 ± 5.6	0.94 ± 0.06	0.665	0.82	347	9	425	0.47	0.70
PR/1	–	coal	55.6	0.25 ± 0.01	14.5 ± 0.4	5.3 ± 0.3	95.9 ± 6.6	1.20 ± 0.08	0.661	1.07	217	31	426	0.60	0.78
PR/6	–	coal	64.0	0.25 ± 0.01	16.6 ± 0.4	6.0 ± 0.3	84.4 ± 5.6	1.27 ± 0.09	0.636	1.16	270	24	426	0.44	0.51
PR/10	–	coal	68.4	0.37 ± 0.01	17.8 ± 0.4	6.3 ± 0.3	115.0 ± 6.8	1.39 ± 0.09	0.696	1.24	350	11	428	0.68	0.76

All uncertainties are stated at 2σ. Rho is the associated error correlation

[a] Initial ^{187}Os/^{188}Os values calculated at 57 Ma for the Farewell Formation, 67 Ma for the North Cape Formation and 78 Ma for the Rakopi Formation using the ^{187}Re decay constant of 1.666 $\times 10^{-11}$ a^{-1} (Smoliar et al., 1996)

coaly mst. = coaly mudstone; TS = total sulfur; daf = dry, ash free basis; HI units = mg HC/g TOC; OI units = mg CO_2/g TOC

Table 2: Re and Os concentrations and isotope compositions, S and bulk pyrolysis data for samples from the Mangahewa Formation

Sample	Depth	Lithology	TOC	Re	Os	^{192}Os	$^{187}Re/^{188}Os$	$^{187}Os/^{188}Os$	rho	Os_i [a]	HI	OI	T_{max}	TS	TS	Ssul	Spyr	Sorg
	(m)		(wt%)	(ppb)	(ppt)	(ppt)				(37 Ma)			(°C)	(%, dry)	(%, daf)	(%, daf)		
Oh2/MM10i	4139.58	coaly mst.	4.2	1.33 ± 0.00	66.2 ± 0.4	25.9 ± 0.2	102.5 ± 1.0	0.55 ± 0.01	0.671	0.48	235	3	434	9.3	62.6	3.5	1.8	57.3
Oh2/MC10d	4139.87	coal	72.8	0.18 ± 0.01	18.9 ± 0.4	7.4 ± 0.4	47.4 ± 3.6	0.54 ± 0.04	0.495	0.51	371	1	423	4.6	5.0	0.1	3.2	1.7
Oh2/MM10a	4140.02	coaly mst.	24.2	0.95 ± 0.01	38.7 ± 0.3	15.1 ± 0.2	125.7 ± 2.4	0.57 ± 0.01	0.680	0.49	350	3	426	4.4	13.3	1.9	0.4	10.9
Oh2/MC11i	4140.63	coal	69.7	0.37 ± 0.01	16.3 ± 0.4	6.3 ± 0.3	116.3 ± 6.8	0.57 ± 0.03	0.687	0.50	311	6	423	5.2	5.6	0.1	3.4	2.2
Oh2/MC11h	4140.76	coal	74.2	0.49 ± 0.01	16.0 ± 0.4	6.3 ± 0.3	156.7 ± 8.8	0.53 ± 0.04	0.720	0.44	336	5	429	3.9	4.1	0.1	2.2	1.8
Oh2/MC11f	4140.99	coal	77.8	0.13 ± 0.01	14.2 ± 0.4	5.6 ± 0.3	45.5 ± 4.3	0.46 ± 0.04	0.419	0.43	330	4	418	2.6	2.7	0.1	1.0	1.6
Oh2/MC12c	4144.01	coal	79.8	0.11 ± 0.01	19.7 ± 0.4	7.7 ± 0.4	29.1 ± 2.9	0.53 ± 0.03	0.366	0.51	293	3	437	0.8	0.9	0.0	0.1	0.7
Oh2/MC12b	4144.16	coal	75.1	0.20 ± 0.01	16.3 ± 0.4	6.4 ± 0.3	61.6 ± 4.4	0.51 ± 0.04	0.548	0.48	286	4	436	1.6	1.7	0.2	0.8	0.7

All uncertainties are stated at 2σ. Rho is the associated error correlation

[a] Initial $^{187}Os/^{188}Os$ values calculated at 37 Ma for the Mangahewa Formation using the ^{187}Re decay constant of 1.666×10^{-11} a^{-1} (Smoliar et al., 1996)

coaly mst. = coaly mudstone; TS = total sulfur; Ssul = sulfate sulfur; Spyr = pyritic sulfur; Sorg = organic sulfur

HI units = mg HC/g TOC; OI units = mg CO_2/g TOC; daf = dry, ash-free basis.

Fig. 1

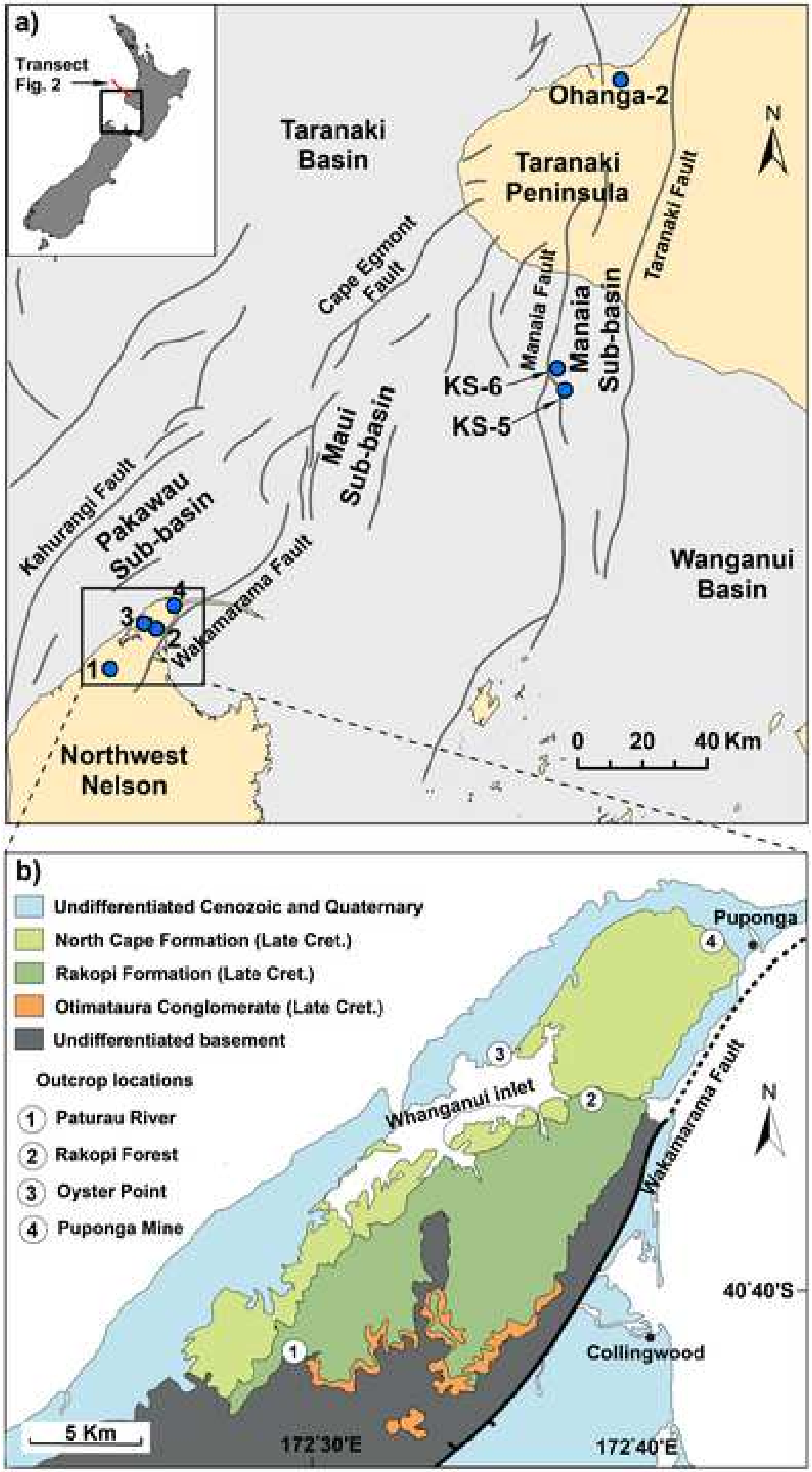

a)
Transect
Fig. 2
Taranaki
Basin
Ohanga-2
Taranaki
Peninsula
N
Taranaki Fault
Cape Egmont
Fault
Manaia Fault
Manaia
Sub-basin
KS-6
KS-5
Maui
Sub-basin
Kahurangi Fault
Pakawau
Sub-basin
Wakamarama Fault
Wanganui
Basin
1
2
3
4
Northwest
Nelson
0
20
40 Km
b)
Undifferentiated Cenozoic and Quaternary
North Cape Formation (Late Cret.)
Rakopi Formation (Late Cret.)
Otimataura Conglomerate (Late Cret.)
Undifferentiated basement
Outcrop locations
1 Paturau River
2 Rakopi Forest
3 Oyster Point
4 Puponga Mine
Puponga
Whanganui Inlet
Wakamarama Fault
N
40˚40'S
Collingwood
5 Km
172˚30'E
172˚40'E

Fig. 2

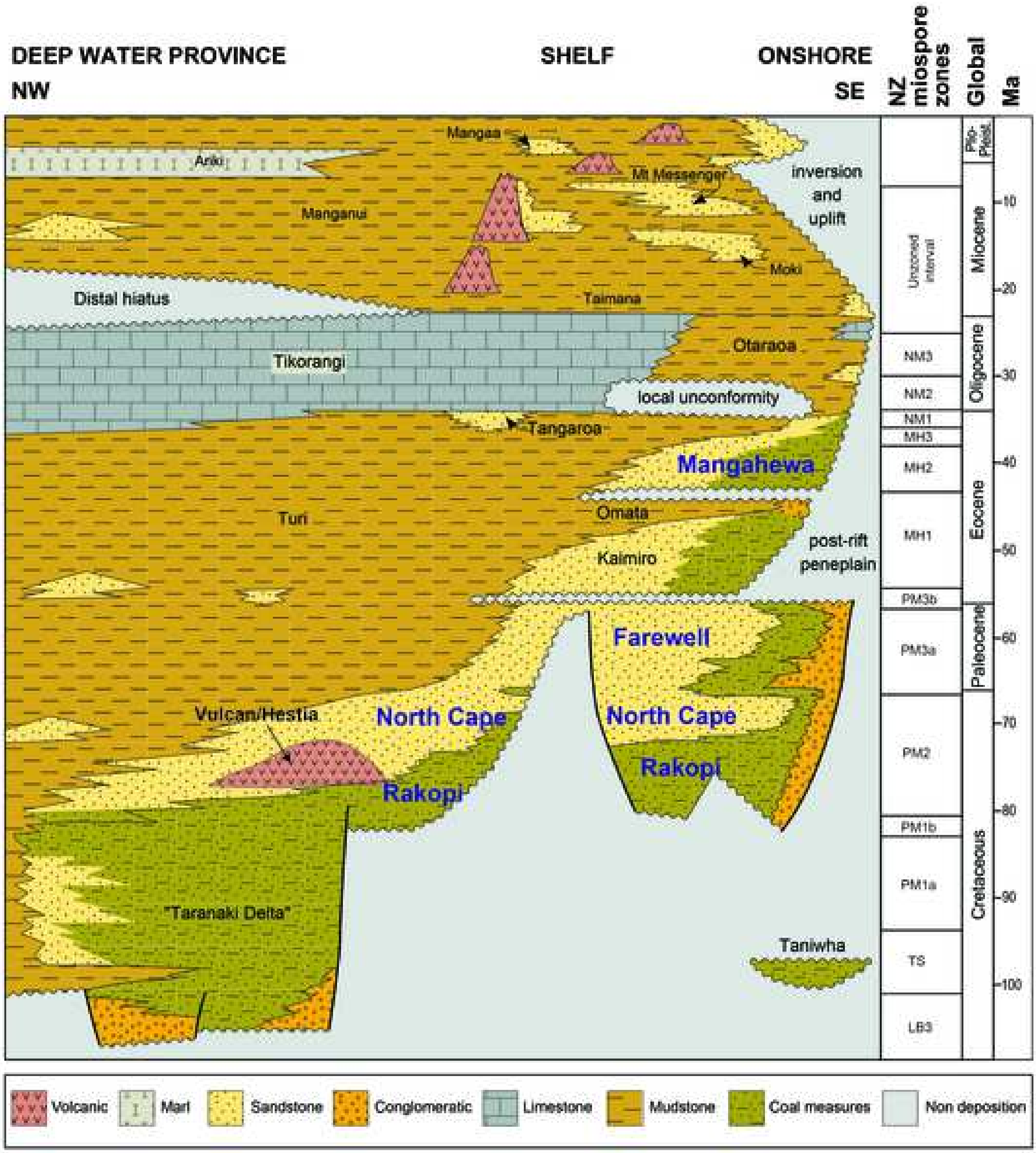

DEEP WATER PROVINCE
SHELF
ONSHORE
NW
SE
NZ miospore zones
Global
Ma
Mangaa
Ariki
Mt Messenger
inversion and uplift
Manganui
Moki
Distal hiatus
Taimana
Tikorangi
Otaraoa
local unconformity
Tangaroa
Mangahewa
Omata
Turi
Kaimiro
post-rift peneplain
Farewell
Vulcan/Hestia
North Cape
North Cape
Rakopi
Rakopi
"Taranaki Delta"
Taniwha
Unzoned interval
NM3
NM2
NM1
MH3
MH2
MH1
PM3b
PM3a
PM2
PM1b
PM1a
TS
LB3
Plio-Pleist.
Miocene
Oligocene
Eocene
Paleocene
Cretaceous
10
20
30
40
50
60
70
80
90
100
Volcanic
Marl
Sandstone
Conglomeratic
Limestone
Mudstone
Coal measures
Non deposition

Fig. 3

Fig. 4

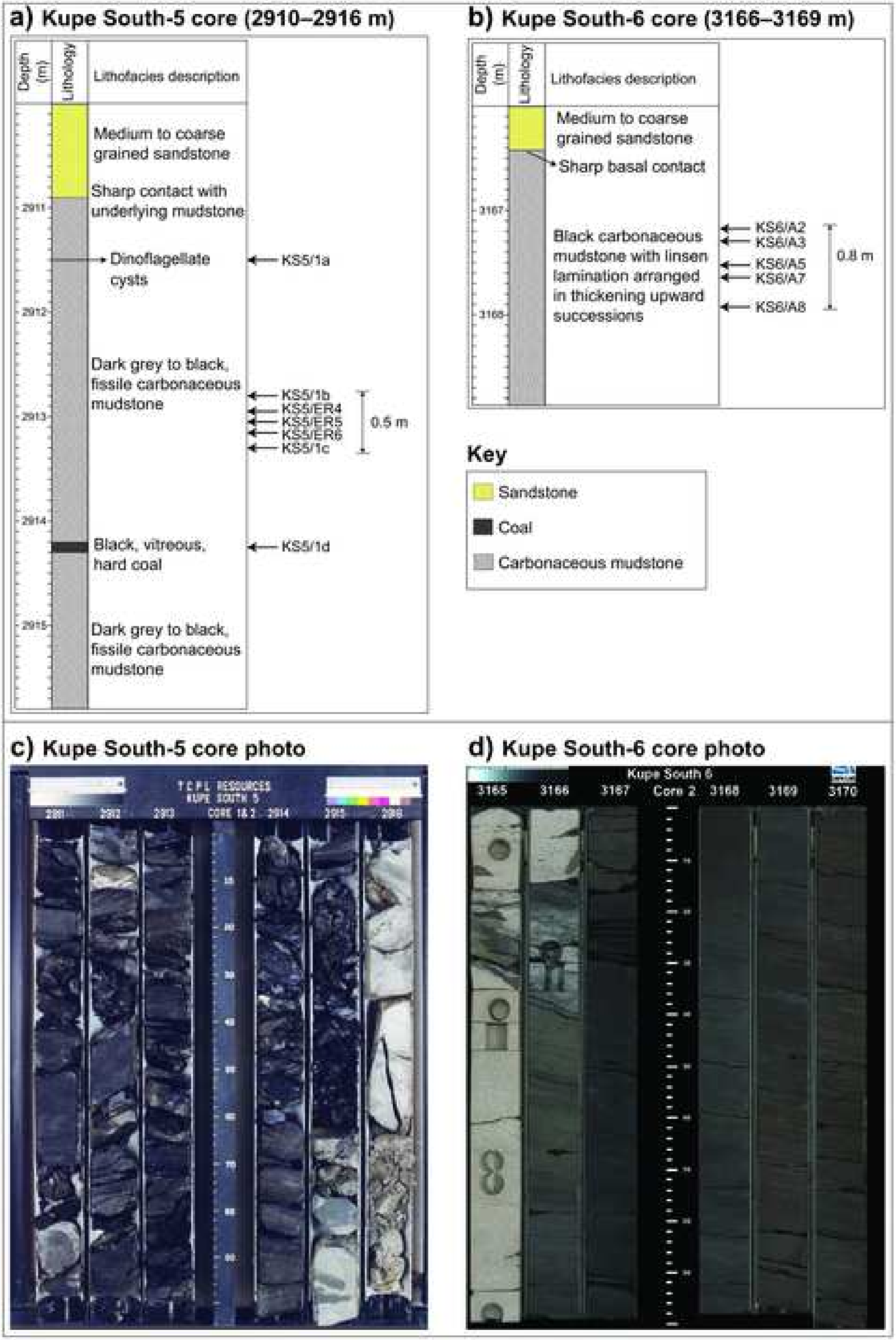

a) Kupe South-5 core (2910–2916 m)
Depth (m)
Lithology
Lithofacies description
Medium to coarse grained sandstone
Sharp contact with underlying mudstone
Dinoflagellate cysts
KS5/1a
2911
2912
2913
2914
2915
Dark grey to black, fissile carbonaceous mudstone
KS5/1b
KS5/ER4
KS5/ER5
KS5/ER6
KS5/1c
0.5 m
Black, vitreous, hard coal
KS5/1d
Dark grey to black, fissile carbonaceous mudstone
b) Kupe South-6 core (3166–3169 m)
Depth (m)
Lithology
Lithofacies description
Medium to coarse grained sandstone
Sharp basal contact
3167
3168
Black carbonaceous mudstone with linsen lamination arranged in thickening upward successions
KS6/A2
KS6/A3
KS6/A5
KS6/A7
KS6/A8
0.8 m
Key
Sandstone
Coal
Carbonaceous mudstone
c) Kupe South-5 core photo
TCPL RESOURCES
KUPE SOUTH 5
CORE 1&2
2911
2912
2913
2914
2915
2916
d) Kupe South-6 core photo
Kupe South 6
3165
3166
3167
Core 2
3168
3169
3170

Fig. 5

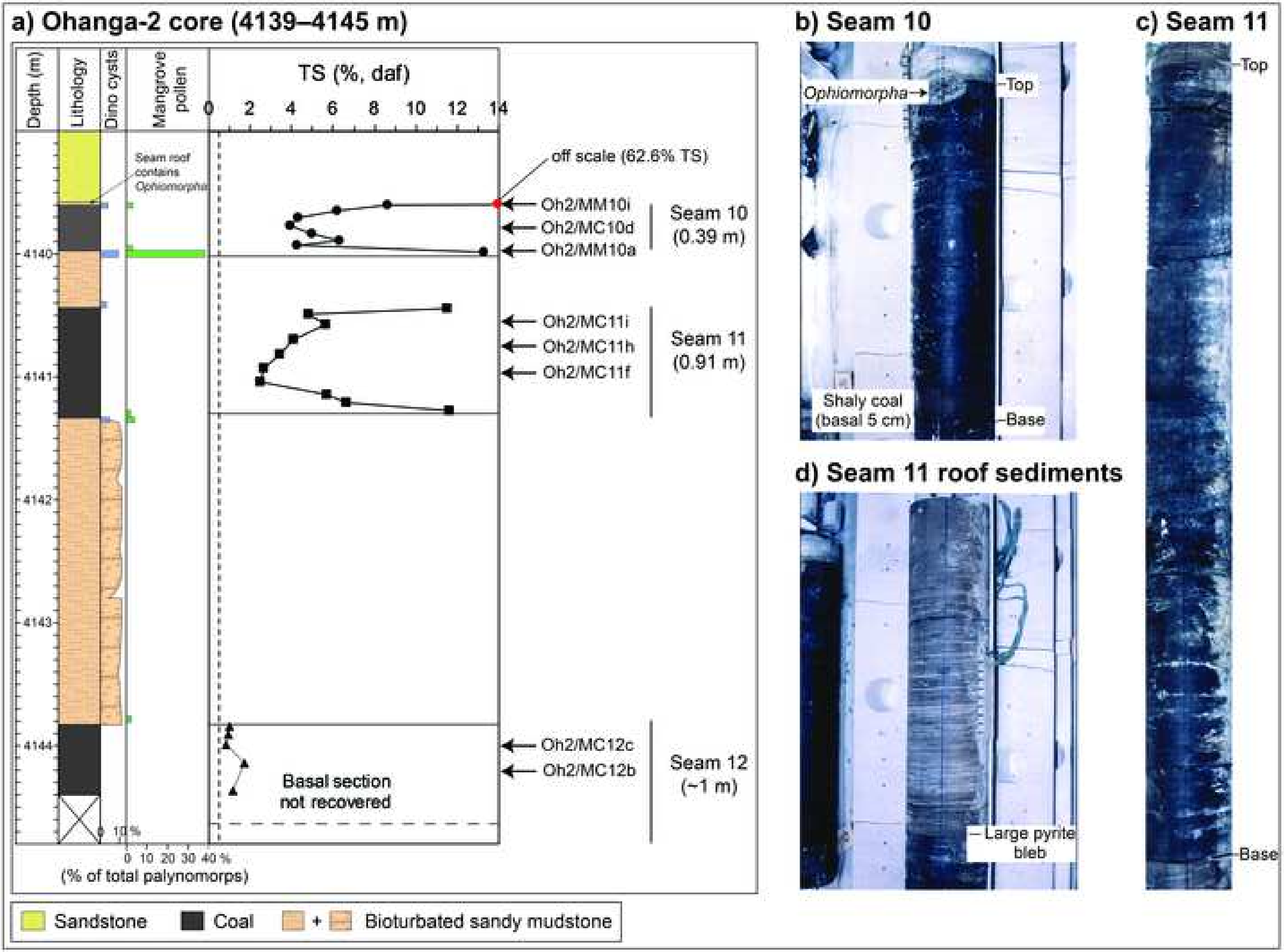

a) Ohanga-2 core (4139–4145 m)
Depth (m)
Lithology
Dino cysts
Mangrove pollen
TS (%, daf)
0
2
4
6
8
10
12
14
4140
4141
4142
4143
4144
Seam roof contains Ophiomorpha
off scale (62.6% TS)
Oh2/MM10i
Oh2/MC10d
Oh2/MM10a
Seam 10 (0.39 m)
Oh2/MC11i
Oh2/MC11h
Oh2/MC11f
Seam 11 (0.91 m)
Oh2/MC12c
Oh2/MC12b
Seam 12 (~1 m)
Basal section not recovered
10 %
0 10 20 30 40 %
(% of total palynomorps)
Sandstone
Coal
+
Bioturbated sandy mudstone
b) Seam 10
Ophiomorpha
Top
Shaly coal (basal 5 cm)
Base
c) Seam 11
Top
Base
d) Seam 11 roof sediments
Large pyrite bleb

Fig. 6

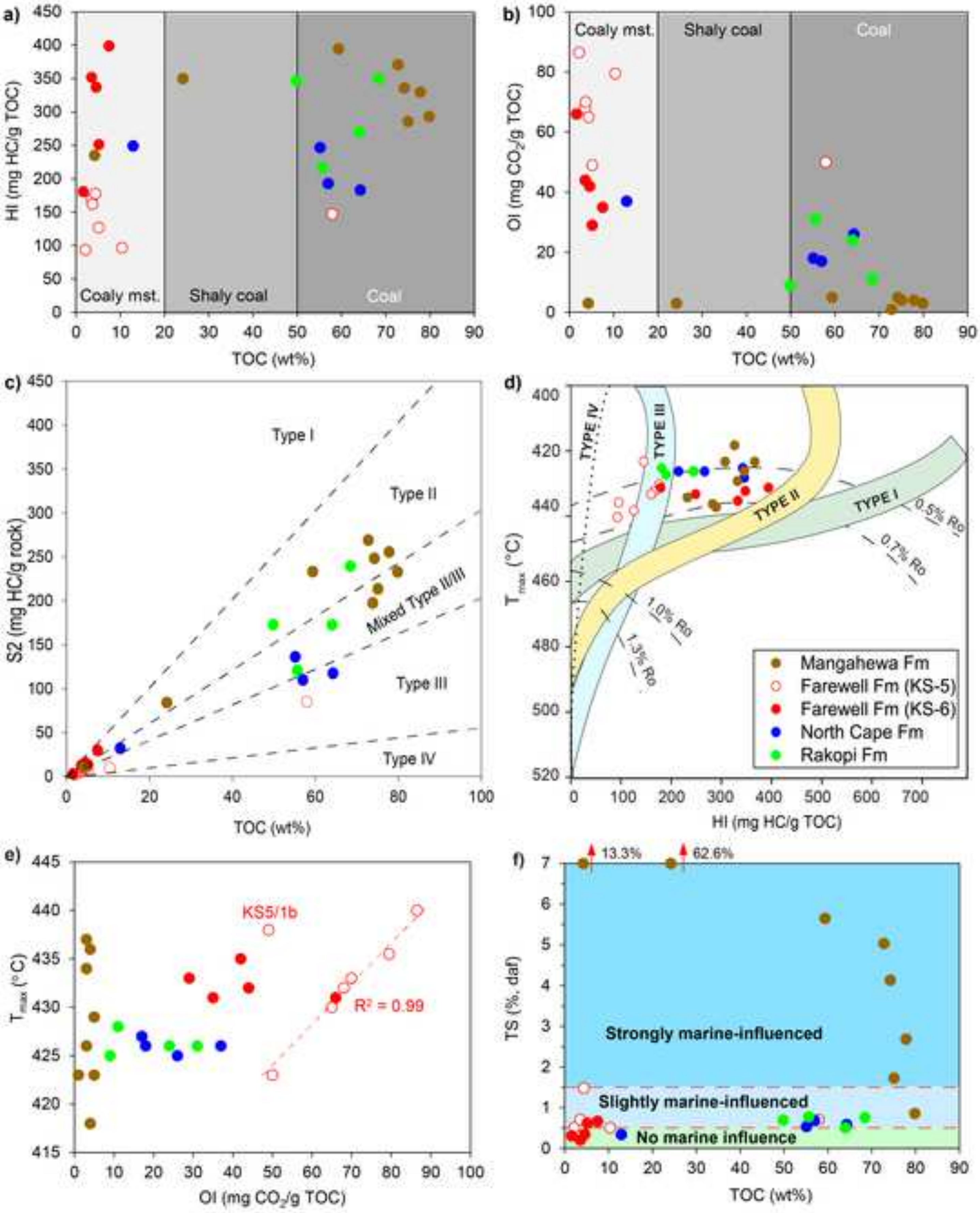

a)
HI (mg HC/g TOC)
TOC (wt%)
Coaly mst.
Shaly coal
Coal
0
50
100
150
200
250
300
350
400
450
0
10
20
30
40
50
60
70
80
90
b)
OI (mg CO$_2$/g TOC)
TOC (wt%)
Coaly mst.
Shaly coal
Coal
0
20
40
60
80
100
c)
S2 (mg HC/g rock)
TOC (wt%)
Type I
Type II
Mixed Type II/III
Type III
Type IV
0
20
40
60
80
100
d)
T$_{max}$ (°C)
HI (mg HC/g TOC)
TYPE IV
TYPE III
TYPE II
TYPE I
0.5% Ro
0.7% Ro
1.0% Ro
1.3% Ro
400
420
440
460
480
500
520
0
100
200
300
400
500
600
700
● Mangahewa Fm
○ Farewell Fm (KS-5)
● Farewell Fm (KS-6)
● North Cape Fm
● Rakopi Fm
e)
T$_{max}$ (°C)
OI (mg CO$_2$/g TOC)
KS5/1b
R² = 0.99
415
420
425
430
435
440
445
0
10
20
30
40
50
60
70
80
90
100
f)
TS (%, daf)
TOC (wt%)
13.3%
62.6%
Strongly marine-influenced
Slightly marine-influenced
No marine influence
0
1
2
3
4
5
6
7
0
10
20
30
40
50
60
70
80
90

Fig. 7

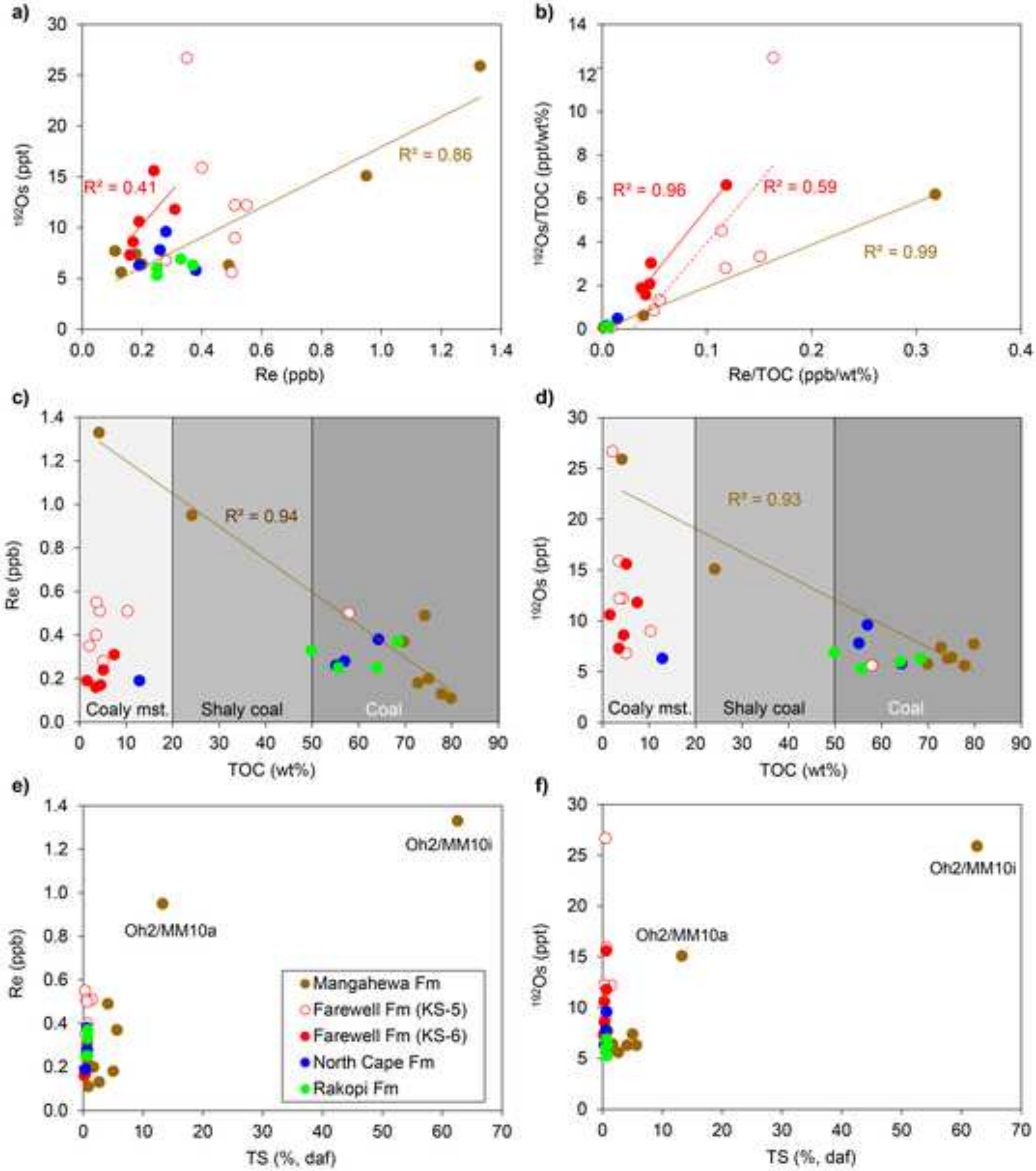
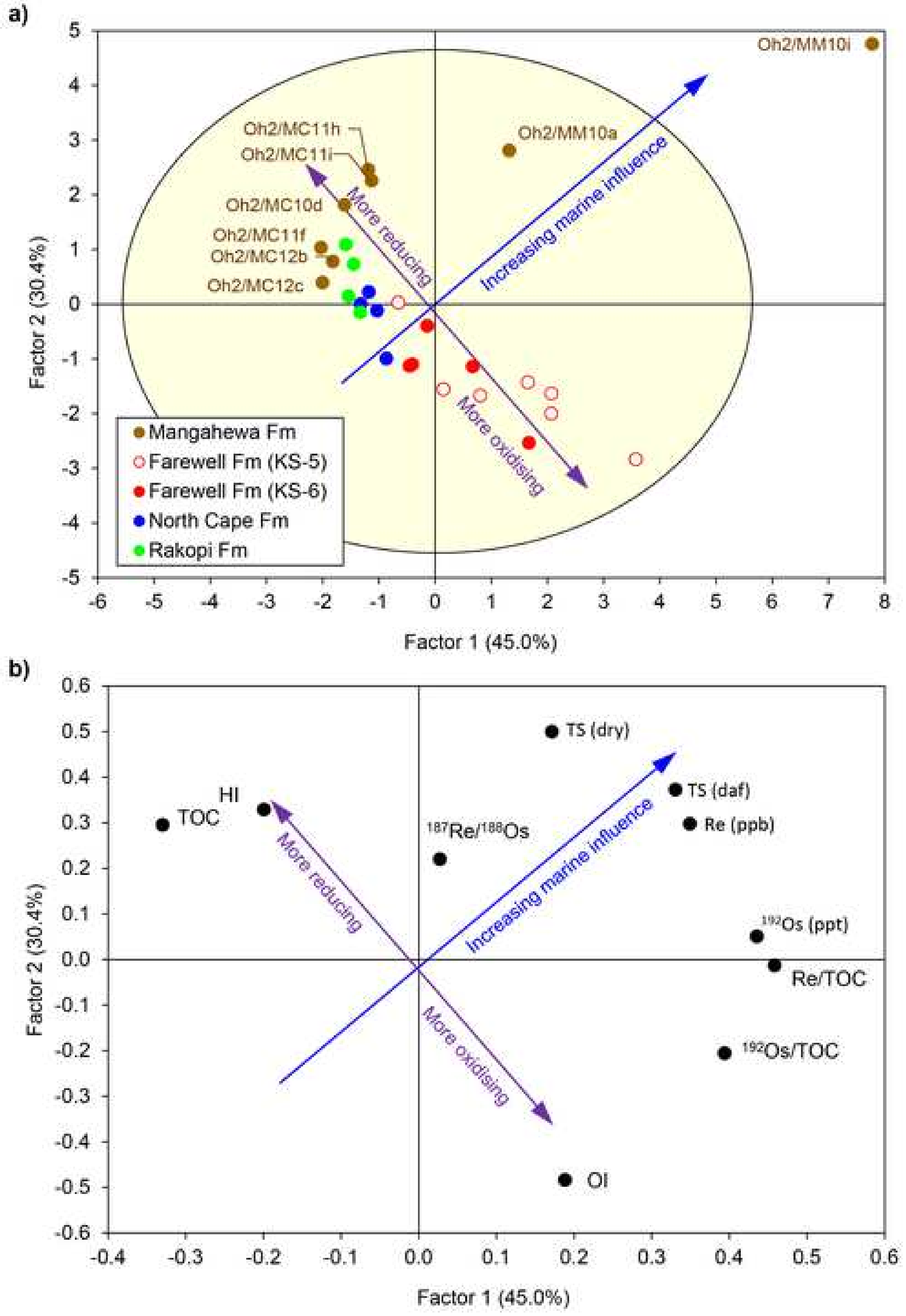

a)
^{192}Os (ppt)
Re (ppb)
0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4
0 5 10 15 20 25 30
R² = 0.41
R² = 0.86
b)
^{192}Os/TOC (ppt/wt%)
Re/TOC (ppb/wt%)
0.0 0.1 0.2 0.3 0.4
0 2 4 6 8 10 12 14
R² = 0.96
R² = 0.59
R² = 0.99
c)
Re (ppb)
TOC (wt%)
0 10 20 30 40 50 60 70 80 90
0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4
R² = 0.94
Coaly mst.
Shaly coal
Coal
d)
^{192}Os (ppt)
TOC (wt%)
0 10 20 30 40 50 60 70 80 90
0 5 10 15 20 25 30
R² = 0.93
Coaly mst.
Shaly coal
Coal
e)
Re (ppb)
TS (%, daf)
0 10 20 30 40 50 60 70
0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4
Oh2/MM10i
Oh2/MM10a
● Mangahewa Fm
○ Farewell Fm (KS-5)
● Farewell Fm (KS-6)
● North Cape Fm
● Rakopi Fm
f)
^{192}Os (ppt)
TS (%, daf)
0 10 20 30 40 50 60 70
0 5 10 15 20 25 30
Oh2/MM10i
Oh2/MM10a

Fig. 8


a)
Oh2/MM10i
Oh2/MC11h
Oh2/MC11i
Oh2/MM10a
Oh2/MC10d
Oh2/MC11f
Oh2/MC12b
Oh2/MC12c
More reducing
Increasing marine influence
More oxidising
● Mangahewa Fm
○ Farewell Fm (KS-5)
● Farewell Fm (KS-6)
● North Cape Fm
● Rakopi Fm
Factor 2 (30.4%)
Factor 1 (45.0%)
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-5
-4
-3
-2
-1
0
1
2
3
4
5
6
7
8
b)
TS (dry)
TS (daf)
Re (ppb)
HI
TOC
^{187}Re/^{188}Os
^{192}Os (ppt)
Re/TOC
^{192}Os/TOC
OI
More reducing
Increasing marine influence
More oxidising
Factor 2 (30.4%)
Factor 1 (45.0%)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.4
-0.3
-0.2
-0.1
0.0
0.1
0.2
0.3
0.4
0.5
0.6

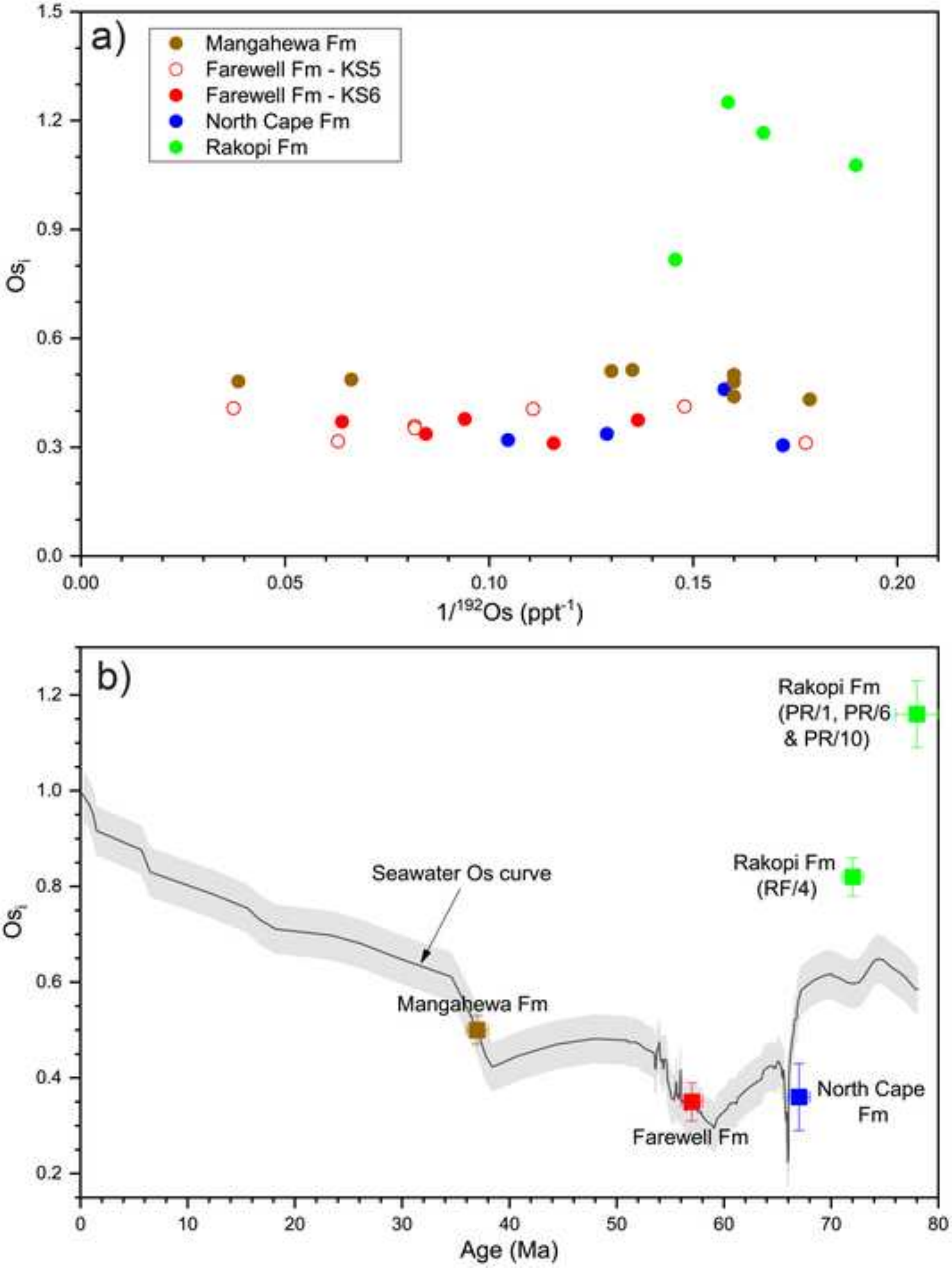

a)
Mangahewa Fm
Farewell Fm - KS5
Farewell Fm - KS6
North Cape Fm
Rakopi Fm
Os_i
1.5
1.2
0.9
0.6
0.3
0.0
0.00
0.05
0.10
0.15
0.20
$1/^{192}Os$ (ppt^{-1})
b)
Rakopi Fm (PR/1, PR/6 & PR/10)
Rakopi Fm (RF/4)
Seawater Os curve
Mangahewa Fm
Farewell Fm
North Cape Fm
Os_i
1.2
1.0
0.8
0.6
0.4
0.2
0
10
20
30
40
50
60
70
80
Age (Ma)

Fig. 10

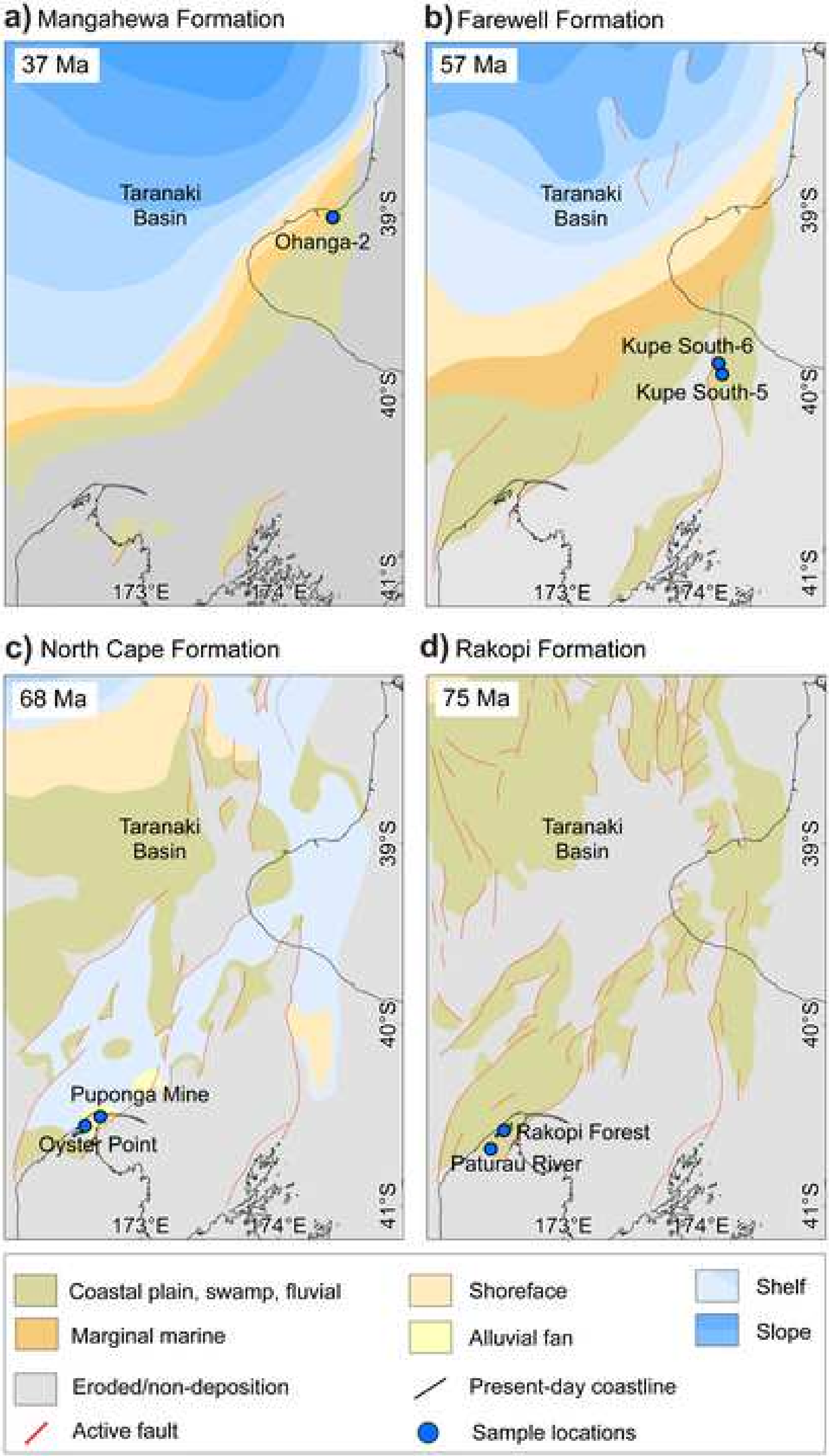

a) Mangahewa Formation
37 Ma
Taranaki Basin
Ohanga-2
39°S
40°S
41°S
173°E
174°E
b) Farewell Formation
57 Ma
Taranaki Basin
Kupe South-6
Kupe South-5
39°S
40°S
41°S
173°E
174°E
c) North Cape Formation
68 Ma
Taranaki Basin
Puponga Mine
Oyster Point
39°S
40°S
41°S
173°E
174°E
d) Rakopi Formation
75 Ma
Taranaki Basin
Rakopi Forest
Paturau River
39°S
40°S
41°S
173°E
174°E
Coastal plain, swamp, fluvial
Marginal marine
Eroded/non-deposition
Active fault
Shoreface
Alluvial fan
Present-day coastline
Sample locations
Shelf
Slope

Fig. 11

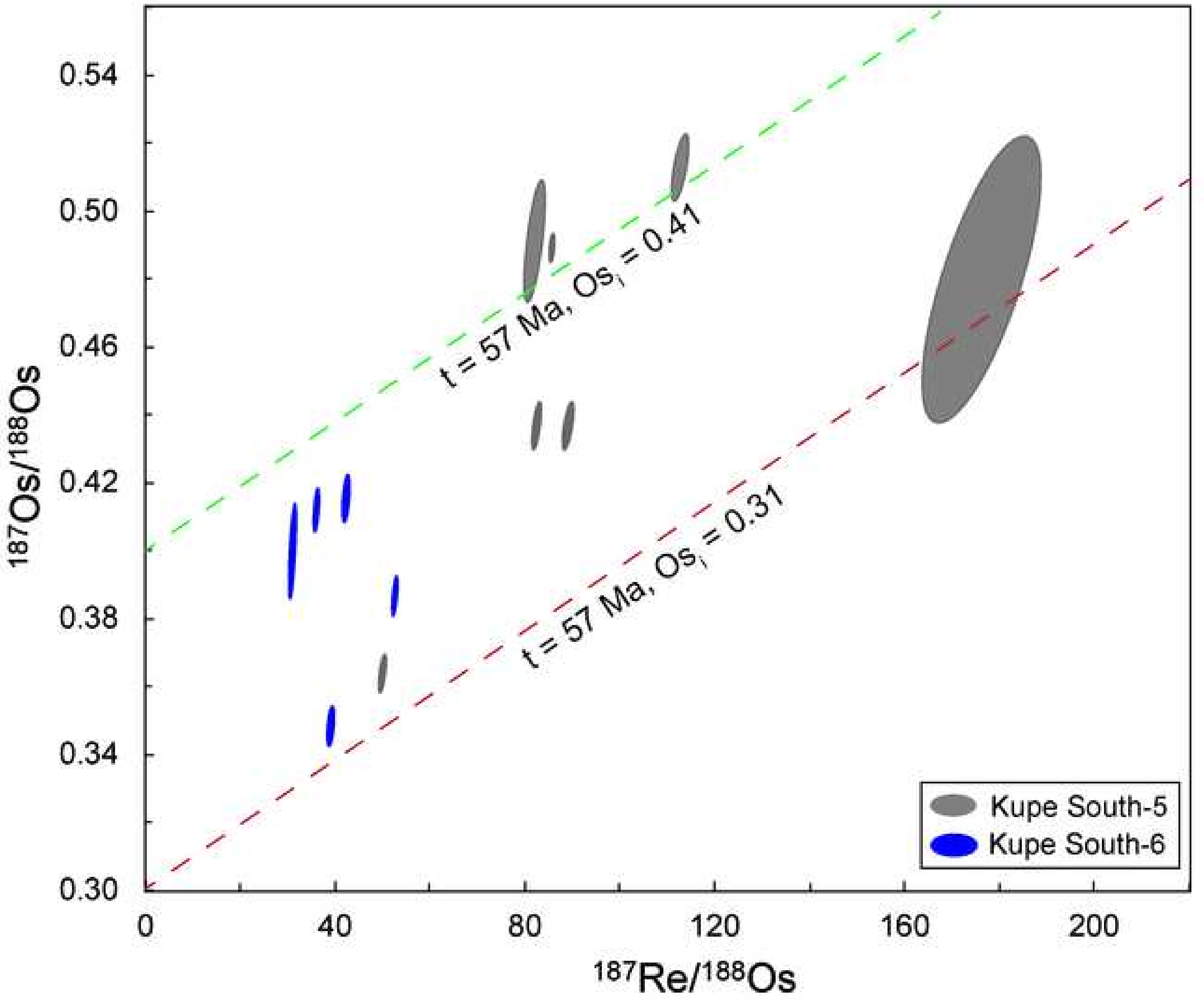

0.54
0.50
0.46
0.42
0.38
0.34
0.30
0
40
80
120
160
200
$^{187}Os/^{188}Os$
$^{187}Re/^{188}Os$
t = 57 Ma, Os_i = 0.41
t = 57 Ma, Os_i = 0.31
Kupe South-5
Kupe South-6

Fig. 12

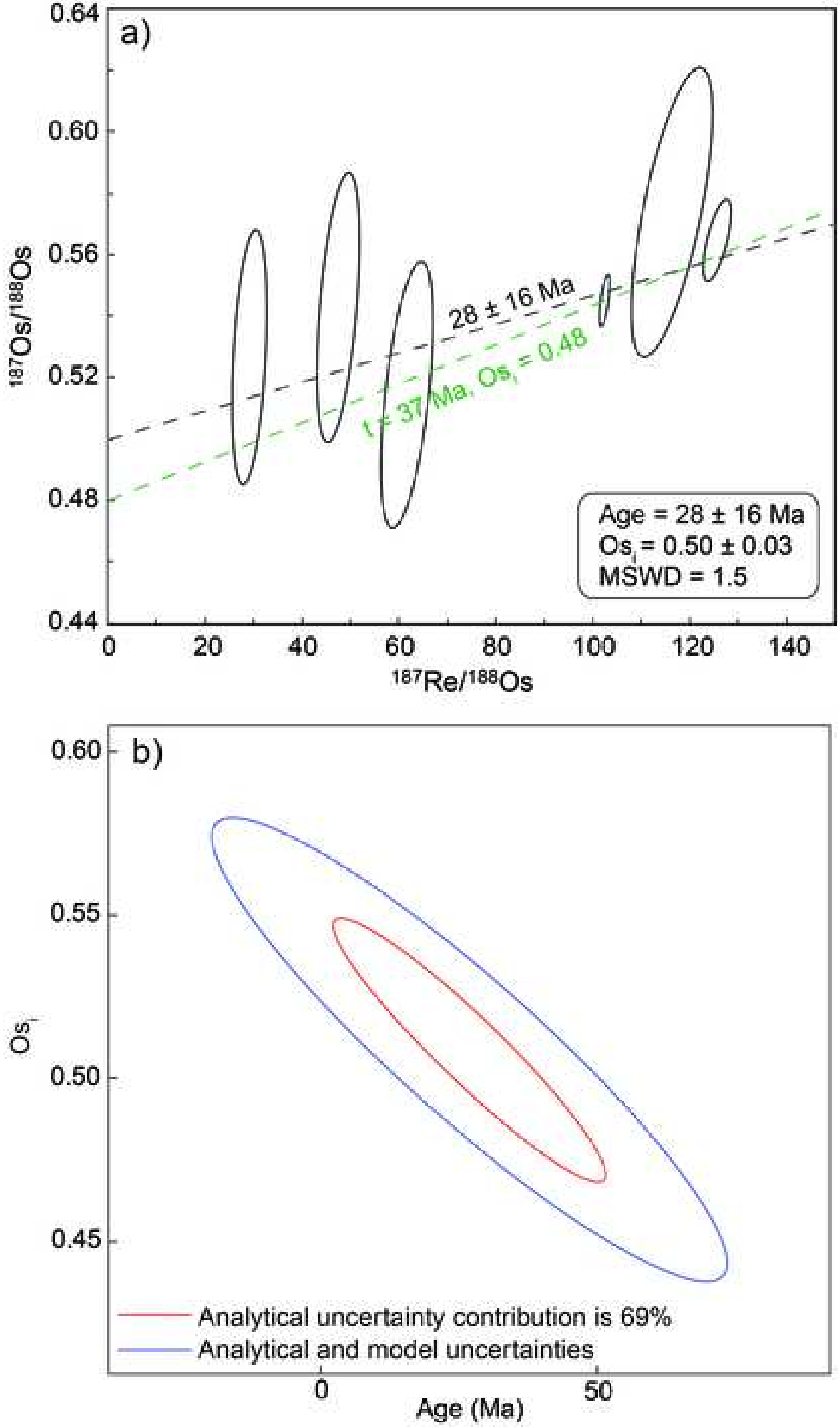

a)
0.64
0.60
0.56
0.52
0.48
0.44
$^{187}Os/^{188}Os$
0
20
40
60
80
100
120
140
$^{187}Re/^{188}Os$
28 ± 16 Ma
t = 37 Ma, Os_i = 0.48
Age = 28 ± 16 Ma
Os_i = 0.50 ± 0.03
MSWD = 1.5
b)
0.60
0.55
0.50
0.45
Os_i
0
50
Age (Ma)
Analytical uncertainty contribution is 69%
Analytical and model uncertainties

Table 1: Re and Os concentrations and isotope compositions, TS and bulk pyrolysis data for samples from the Rakopi, North Cape and Farewell formations

Sample	Depth (m)	Lithology	TOC (wt.%)	Re (ppb)	Os (ppt)	^{192}Os (ppt)	^{187}Re/^{188}Os	^{187}Os/^{188}Os	rho	Os$_i$ [a]	HI	OI	T$_{max}$ (^{o}C)	TS (%, dry)	TS (%, daf)
Farewell Formation - Kupe South-5															
KS5/1a	2911.50	coaly mst.	2.1	0.35 ± 0.004	46.1 ± 0.3	26.7 ± 0.2	85.7 ± 0.4	0.49 ± 0.01	0.438	0.41	94	87	440	0.06	0.52
KS5/1b	2912.80	coaly mst.	5.1	0.28 ± 0.002	17.2 ± 0.2	6.8 ± 0.1	82.1 ± 1.9	0.49 ± 0.02	0.675	0.41	127	49	438	0.09	0.62
KS5/ER4	2912.92	coaly mst.	3.5	0.40 ± 0.002	39.6 ± 0.2	15.9 ± 0.1	50.0 ± 0.5	0.36 ± 0.01	0.605	0.32	169	68	432	0.11	0.71
KS5/ER5	2913.02	coaly mst.	4.3	0.51 ± 0.002	30.8 ± 0.2	12.2 ± 0.1	82.4 ± 0.9	0.44 ± 0.01	0.644	0.36	178	65	430	0.25	1.48
KS5/ER6	2913.15	coaly mst.	3.7	0.55 ± 0.002	31.4 ± 0.2	12.2 ± 0.1	89.1 ± 0.9	0.44 ± 0.01	0.651	0.35	162	70	433	0.05	0.31
KS5/1c	2913.30	coaly mst.	10.3	0.51 ± 0.002	23.0 ± 0.2	9.0 ± 0.1	112.7 ± 1.4	0.51 ± 0.01	0.670	0.41	97	80	436	0.09	0.51
KS5/1d	2914.20	coal	57.9	0.50 ± 0.010	14.3 ± 0.4	5.6 ± 0.3	176.4 ± 10.3	0.48 ± 0.03	0.720	0.31	147	50	423	0.61	0.71
Farewell Formation - Kupe South-6															
KS6/A2	3167.21	coaly mst.	3.5	0.16 ± 0.002	18.4 ± 0.1	7.3 ± 0.1	42.4 ± 0.7	0.42 ± 0.01	0.456	0.38	352	44	432	0.03	0.21
KS6/A3	3167.33	coaly mst.	4.6	0.17 ± 0.002	21.5 ± 0.1	8.6 ± 0.1	39.2 ± 0.6	0.35 ± 0.01	0.459	0.31	337	42	435	0.06	0.35
KS6/A5	3167.54	coaly mst.	7.5	0.31 ± 0.002	29.6 ± 0.2	11.8 ± 0.1	52.6 ± 0.6	0.39 ± 0.01	0.580	0.34	399	35	431	0.14	0.67
KS6/A7	3167.60	coaly mst.	5.1	0.24 ± 0.002	39.2 ± 0.4	15.6 ± 0.3	31.1 ± 0.7	0.40 ± 0.01	0.653	0.37	252	29	433	0.10	0.62
KS6/A8	3167.98	coaly mst.	1.6	0.19 ± 0.002	26.7 ± 0.1	10.6 ± 0.1	36.2 ± 0.5	0.41 ± 0.01	0.482	0.38	181	66	431	0.04	0.31
North Cape Formation															
PM/3M	—	coaly mst.	12.9	0.19 ± 0.01	16.2 ± 0.4	6.3 ± 0.3	60.9 ± 4.5	0.53 ± 0.04	0.545	0.46	249	37	426	0.06	0.34
PM/3N	—	coal	64.2	0.38 ± 0.01	14.7 ± 0.4	5.8 ± 0.3	128.3 ± 7.7	0.45 ± 0.03	0.683	0.31	183	26	425	0.54	0.59
PM/3O	—	coal	55.1	0.26 ± 0.01	19.5 ± 0.4	7.8 ± 0.4	67.2 ± 4.1	0.41 ± 0.03	0.583	0.34	247	18	426	0.42	0.54
OP/1	—	coal	57.0	0.28 ± 0.01	23.9 ± 0.5	9.6 ± 0.4	58.8 ± 3.4	0.39 ± 0.02	0.577	0.32	193	17	427	0.58	0.69
Rakopi Formation															
RF/4	—	coal	49.8	0.33 ± 0.01	18.4 ± 0.4	6.9 ± 0.3	96.1 ± 5.6	0.94 ± 0.06	0.665	0.82	347	9	425	0.47	0.70
PR/1	—	coal	55.6	0.25 ± 0.01	14.5 ± 0.4	5.3 ± 0.3	95.9 ± 6.6	1.20 ± 0.08	0.661	1.07	217	31	426	0.60	0.78
PR/6	—	coal	64.0	0.25 ± 0.01	16.6 ± 0.4	6.0 ± 0.3	84.4 ± 5.6	1.27 ± 0.09	0.636	1.16	270	24	426	0.44	0.51
PR/10	—	coal	68.4	0.37 ± 0.01	17.8 ± 0.4	6.3 ± 0.3	115.0 ± 6.8	1.39 ± 0.09	0.696	1.24	350	11	428	0.68	0.76

All uncertainties are stated at 2σ. Rho is the associated error correlation

[a] Initial ^{187}Os/^{188}Os values calculated at 57 Ma for the Farewell Formation, 67 Ma for the North Cape Formation and 78 Ma for the Rakopi Formation using the ^{187}Re decay constant of 1.666 $\times 10^{-11}$ a^{-1} (Smoliar et al., 1996)

coaly mst. = coaly mudstone; TS = total sulfur; daf = dry, ash free basis; HI units = mg HC/g TOC; OI units = mg CO$_2$/g TOC

Table 2: Re and Os concentrations and isotope compositions, S and bulk pyrolysis data for samples from the Mangahewa Formation

Sample	Depth	Lithology	TOC	Re	Os	^{192}Os	^{187}Re/^{188}Os	^{187}Os/^{188}Os	rho	Os$_i$ [a]	HI	OI	T$_{max}$	TS	TS	Ssul	Spyr	Sorg
	(m)		(wt%)	(ppb)	(ppt)	(ppt)				(37 Ma)			(^{o}C)	(%, dry)	(%, daf)		(%, daf)	
Oh2/MM10i	4139.58	coaly mst.	4.2	1.33 ± 0.00	66.2 ± 0.4	25.9 ± 0.2	102.5 ± 1.0	0.55 ± 0.01	0.671	0.48	235	3	434	9.3	62.6	3.5	1.8	57.3
Oh2/MC10d	4139.87	coal	72.8	0.18 ± 0.01	18.9 ± 0.4	7.4 ± 0.4	47.4 ± 3.6	0.54 ± 0.04	0.495	0.51	371	1	423	4.6	5.0	0.1	3.2	1.7
Oh2/MM10a	4140.02	coaly mst.	24.2	0.95 ± 0.01	38.7 ± 0.3	15.1 ± 0.2	125.7 ± 2.4	0.57 ± 0.01	0.680	0.49	350	3	426	4.4	13.3	1.9	0.4	10.9
Oh2/MC11i	4140.63	coal	69.7	0.37 ± 0.01	16.3 ± 0.4	6.3 ± 0.3	116.3 ± 6.8	0.57 ± 0.03	0.687	0.50	311	6	423	5.2	5.6	0.1	3.4	2.2
Oh2/MC11h	4140.76	coal	74.2	0.49 ± 0.01	16.0 ± 0.4	6.3 ± 0.3	156.7 ± 8.8	0.53 ± 0.04	0.720	0.44	336	5	429	3.9	4.1	0.1	2.2	1.8
Oh2/MC11f	4140.99	coal	77.8	0.13 ± 0.01	14.2 ± 0.4	5.6 ± 0.3	45.5 ± 4.3	0.46 ± 0.04	0.419	0.43	330	4	418	2.6	2.7	0.1	1.0	1.6
Oh2/MC12c	4144.01	coal	79.8	0.11 ± 0.01	19.7 ± 0.4	7.7 ± 0.4	29.1 ± 2.9	0.53 ± 0.03	0.366	0.51	293	3	437	0.8	0.9	0.0	0.1	0.7
Oh2/MC12b	4144.16	coal	75.1	0.20 ± 0.01	16.3 ± 0.4	6.4 ± 0.3	61.6 ± 4.4	0.51 ± 0.04	0.548	0.48	286	4	436	1.6	1.7	0.2	0.8	0.7

All uncertainties are stated at 2σ. Rho is the associated error correlation

[a] Initial ^{187}Os/^{188}Os values calculated at 37 Ma for the Mangahewa Formation, using the ^{187}Re decay constant of 1.666×10^{-11} a^{-1} (Smoliar et al., 1996)

coaly mst. = coaly mudstone; TS = total sulfur; Ssul = sulfate sulfur; Spyr = pyritic sulfur; Sorg = organic sulfur

HI units = mg HC/g TOC; OI units = mg CO_2/g TOC; daf = dry, ash-free basis