

1 Re-Os geochronology and isotope systematics, and organic and sulfur
2 geochemistry of the middle–late Paleocene Waipawa Formation, New Zealand:
3 Insights into early Paleogene seawater Os isotope composition

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23 Abstract

24 In the middle–late Paleocene, a marine, organic-rich sedimentary unit (Waipawa
25 Formation [Fm]) in which the organic matter was derived mainly from terrestrial plants
26 was deposited in many of New Zealand’s sedimentary basins. The unique
27 organofacies of this formation has not been identified in any other time interval within
28 the geological history of the Southwest Pacific, indicating that unusual climatic and
29 oceanographic conditions likely prevailed during this time. It has, therefore, attracted
30 wide scientific interest due to its significance for regional and global reconstruction of
31 the early Paleogene transitional climate as well as potential for oil and gas
32 production. Scarcity of age-diagnostic fossils, presence of unconformities and lack of
33 volcanic interbeds have, however, hindered precise dating and correlations of all the
34 known occurrences of the formation. Here, rhenium-osmium (Re-Os) geochronology
35 has yielded the first radiometric age for the formation (57.5 ± 3.5 Ma), which is
36 consistent with available biostratigraphic age determinations (59.4–58.7 Ma). Further,
37 a comparison of Re-Os, bulk pyrolysis, sulfur and palynofacies data for the Waipawa
38 Fm with those of more typical marine sediments such as the underlying Whangai Fm
39 supports the interpretation that the chelating precursors or fundamental binding sites
40 responsible for uptake of Re and Os are present in all types of organic matter, and
41 that these elements have a greater affinity for organic chelating sites than for
42 sulfides. The results also indicate that sedimentation rate may not play a dominant
43 role in enhanced uptake of Re and Os by organic-rich sedimentary rocks.

44 The initial $^{187}\text{Os}/^{188}\text{Os}$ values for the Waipawa (~ 0.28) and Whangai (~ 0.36)
45 formations are broadly similar to those reported for coeval pelagic sediments from
46 the central Pacific Ocean, further constraining the low-resolution marine $^{187}\text{Os}/^{188}\text{Os}$
47 record of the Paleocene. We present a compilation of $^{187}\text{Os}/^{188}\text{Os}$ values from

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organic-rich sedimentary rocks spanning the period between 70 and 50 Ma which shows that seawater Os gradually became less radiogenic from the latest Cretaceous, reaching a minimum value in the earliest late Paleocene (~59 Ma) during the deposition of Waipawa Fm, and then increased through the later Paleocene and into the early Eocene. The composite Os isotope record broadly correlates with global temperature ($\delta^{18}\text{O}$ and TEX_{86}) and carbon isotope ($\delta^{13}\text{C}$) records from the middle Paleocene to early Eocene, which is inferred to reflect climate-modulated changes in continental weathering patterns.

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57 *Keywords:*

58 Re-Os geochronology; Waipawa Formation; New Zealand; Paleocene; seawater Os curve

60 **1. Introduction**

61 Marine organic-rich sediments are important archives of past climatic, oceanographic
62 and geodynamic events. The Waipawa Fm is one such organic-rich sedimentary unit
63 that has attracted considerable attention due to its significance for the early
64 Paleogene climate reconstructions of the Southwest Pacific (e.g., Killops et al., 2000;
65 Hollis et al., 2012; 2014; Hines et al., 2019), as well as its potential as a petroleum
66 source rock (Moore, 1988; 1989; Killops et al., 1997; 2000; Schiøler et al., 2010;
67 Field et al., 2018; Naeher et al., 2019). The formation contains a distinctive
68 organofacies, termed the 'Waipawa organofacies', that is dominated by woody
69 phytoclasts despite also showing a high abundance of marine C_{30} steranes and a
70 heavy carbon isotope ($\delta^{13}\text{C}$) signature (values of -24 to -16‰) (Killops et al., 2000;
71 Schiøler et al., 2010; Hollis et al., 2014; Field et al., 2018; Naeher et al., 2019). The

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72 formation was deposited over a wide geographic extent covering multiple
73 sedimentary basins around New Zealand and reaching as far west as the eastern
74 margin of Tasmania (Fig. 1a; Schiøler et al., 2010; Hollis et al., 2014). The
75 widespread deposition of such an unusual organic-rich sediment could only have
76 resulted from a perturbation in Earth's oceanographic and climatic system (Killops et
77 al., 2000; Schiøler et al., 2010; Hollis et al., 2014; Hines et al., 2019). However, it has
78 not been established whether all known occurrences of Waipawa organofacies are
79 coeval. This is because precise dating of the formation through biostratigraphy has
80 so far been complicated by several factors, such as the presence of unconformities,
81 scarcity of age-diagnostic fossils, poor age control for dinoflagellate datums, varying
82 geochemical signatures between sections, and lack of reliable paleomagnetic data
83 (Hollis et al., 2014). The Waipawa Fm and correlated units also lack interbedded
84 volcanic beds that could potentially be used for radiometric dating. Available
85 biostratigraphy and magnetostratigraphy from the East Coast Basin, New Zealand,
86 place the timing of deposition of the formation in the late middle to early late
87 Paleocene, spanning the Selandian–Thanetian boundary (Crouch et al., 2014; Hollis
88 et al., 2014). Here, we investigate the potential of using the Re-Os isotope system to
89 independently verify this age range and establish whether correlative units from other
90 sedimentary basins are coeval.

91 Rhenium and Os are organophilic trace metals that become enriched in organic-rich
92 sedimentary rocks (e.g., Ravizza and Turekian, 1989; Cohen et al., 1999; Selby and
93 Creaser, 2003 and references therein). The resulting combination of high and
94 variable Re and Os concentrations with variations in $^{187}\text{Re}/^{188}\text{Os}$ positively correlating
95 with $^{187}\text{Os}/^{188}\text{Os}$ values means that the Re-Os isotope system can be used to directly
96 obtain precise (in some cases, <1% uncertainty) and accurate ages of a wide variety

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97 of organic-rich rocks including: marine shales (e.g., Ravizza and Turekian, 1989;
98 Cohen et al., 1999; Selby and Creaser, 2005b; Kendall et al., 2006; Selby, 2007;
99 Kendall et al., 2009b; Xu et al., 2009; Georgiev et al., 2011; Georgiev et al., 2017;
100 Tripathy et al., 2018), lacustrine mudstones (Creaser et al., 2008; Poirier and Hillaire-
101 Marcel, 2011; Cumming et al., 2012; Xu et al., 2017), and marine-influenced coals
102 (Tripathy et al., 2015). Previous studies have also shown that post-depositional
103 processes such as greenschist metamorphism and flash pyrolysis associated with
104 igneous intrusions do not appreciably disturb the Re-Os isotope system (Creaser et
105 al., 2002; Kendall et al., 2004; Yang et al., 2009; Rooney et al., 2011; Bertoni et al.,
106 2014). In addition, the Re-Os isotope system remains closed during thermal
107 maturation of organic matter and hydrocarbon generation (Creaser et al., 2002; Selby
108 and Creaser, 2003). Based on these points, the Re-Os system represents an ideal
109 geochronological tool to constrain the age of the Waipawa Fm. However, our current
110 understanding of the exact mechanisms that control enrichment and fractionation of
111 Re and Os in organic-rich sediments remains limited. For instance, despite the strong
112 geochemical affinity that the elements have for organic matter, direct relationships
113 between total organic carbon (TOC) content and Re and Os concentrations are not
114 always evident; some sediments with high TOC may have low Re and Os
115 concentrations and vice versa (Cohen et al., 1999; Kendall et al., 2004; Selby et al.,
116 2009; Rooney et al., 2010). In addition, limited fractionation between Re and Os, and
117 thus similar $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ compositions, has resulted in the production
118 of imprecise ages (e.g., Turgeon et al., 2007; Selby et al., 2009; Rooney et al., 2011;
119 Cumming et al., 2012; Bertoni et al., 2014). To further understand some of the factors
120 controlling uptake and fractionation of Re and Os in sedimentary rocks, we have
121 included the underlying Whangai Fm in our analyses because its organic matter

122 composition and depositional conditions appreciably differ from those of the Waipawa
1 123 Fm.

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5 124 In addition to geochronology, the Os isotope composition ($^{187}\text{Os}/^{188}\text{Os}$) of organic-
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8 125 rich sediments provide useful information about past climatic and oceanographic
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10 126 conditions (Ravizza et al., 2001; Schmitz et al., 2004; Peucker-Ehrenbrink and
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13 127 Ravizza, 2012; Du Vivier et al., 2014; Dickson et al., 2015). The Waipawa Fm was
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15 128 deposited during a prolonged temperature minimum in the mid-Paleocene (~60–58
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17 129 Ma) prior to the start of progressive warming into the early Eocene. This trend is
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20 130 evident in both high-resolution deep-sea oxygen and carbon isotope records
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22 131 (Westerhold et al., 2011; Littler et al., 2014; Barnet et al., 2019) as well as regional
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25 132 sea surface temperatures (58–53 Ma; Bijl et al., 2009; Hollis et al., 2012, 2014). The
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27 133 deposition of the formation also corresponds with the first phase of a positive $\delta^{13}\text{C}$
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30 134 excursion (~59–57 Ma; Westerhold et al., 2011; Littler et al., 2014; Barnet et al.,
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32 135 2019), which is interpreted to reflect a time of enhanced carbon burial, either as
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35 136 marine (Corfield and Cartlidge, 1992) or terrestrial organic matter (Kurtz et al., 2003).
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37 137 Shifts in $\delta^{13}\text{C}$ of marine organic-rich rocks have also been linked to changes in the
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40 138 rate of oxidative weathering of organic matter buried in continents (Ravizza, 1993;
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42 139 Ravizza and Esser, 1993; Ravizza et al., 2001; Percival et al., 2016; Them et al.,
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45 140 2017; De Lena et al., 2019). The marine Os isotope record can track globally-
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47 141 averaged variations in continental weathering fluxes because at any point in time, the
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50 142 record reflects the balance between radiogenic Os weathered from the continent
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52 143 ($^{187}\text{Os}/^{188}\text{Os} = \sim 1.4$) and non-radiogenic Os from hydrothermal activities and extra-
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54 144 terrestrial materials ($^{187}\text{Os}/^{188}\text{Os} = 0.12$) (Peucker-Ehrenbrink and Ravizza, 2000;
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57 145 Cohen, 2004). The residence time of Os in the water column (10–50 ka range,
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59 146 sometimes <10 ka) is also short enough to respond to short-term variations in input
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147 but sufficiently long to allow homogenization of the Os signature in the global ocean
148 (Burton et al., 1999; Cohen, 2004; Du Vivier et al., 2014; 2015; Rooney et al., 2016).
149 The seawater Os record for much of the Paleocene, however, remains poorly
150 resolved (Peucker-Ehrenbrink and Ravizza, 2012). The few available $^{187}\text{Os}/^{188}\text{Os}$
151 data for this period are also based on analyses of pelagic clay sequences (Pegram
152 and Turekian, 1999) and Fe-Mn crusts (Klemm et al., 2005) which have numerical
153 age models that are not easily correlated with those of marine organic-rich
154 sedimentary rocks because they are based on coarse resolution ichthyolith
155 biostratigraphy and empirical growth rates of hydrogenous cobalt (Peucker-
156 Ehrenbrink and Ravizza, 2012). These analyses are also based on a leaching
157 method that may not have preferentially isolated the hydrogenous component of Os,
158 possibly recording inaccurate seawater Os composition due to the potential presence
159 of detrital Os (Pegram and Turekian, 1999; Peucker-Ehrenbrink and Ravizza, 2012).
160 Nonetheless, the pelagic clay record hints at seawater Os with low $^{187}\text{Os}/^{188}\text{Os}$
161 values of around 0.26–0.32 from around 57–61 Ma, but the extent and cause of
162 these non-radiogenic $^{187}\text{Os}/^{188}\text{Os}$ values remain unclear due to the low resolution of
163 the record (Pegram and Turekian, 1999; Peucker-Ehrenbrink and Ravizza, 2012).

164 Here, we present Re-Os elemental and isotope compositions and bulk pyrolysis and
165 sulfur data for the Waipawa and Whangai formations from the Wairarapa and
166 Hawke's Bay region of the East Coast Basin, New Zealand (Fig. 1a). One additional
167 Waipawa Fm sample from the North Slope Basin was included to assess Re-Os
168 abundance and isotopic composition of Waipawa organofacies beyond the East
169 Coast Basin (Fig. 1a). These data allow us to constrain the depositional age of the
170 Waipawa Fm and contribute to further understanding of mechanistic controls of Re-
171 Os systematics in organic-rich sedimentary rocks. In addition, the Os isotope data of

172 the Waipawa and Whangai formations are included in a compilation of initial
173 $^{187}\text{Os}/^{188}\text{Os}$ (Os_i) ratios for sedimentary rocks that span the latest Cretaceous to early
174 Eocene (70–50 Ma), enabling us to evaluate temporal trends in Os geochemical
175 cycle during this period.

176 **2. Geological setting**

177 The focus of this study is on the Waipawa and Whangai formations from the East
178 Coast Basin, New Zealand, which extends from East Cape in North Island to the
179 Kaikoura Peninsula in South Island, and about half of which is offshore (Fig. 1a). The
180 basin occupied a site on the Pacific subduction margin of Gondwana during the
181 Triassic to early Cretaceous time when rocks of Torlesse Terrane (greywacke) were
182 accreted to form the now weakly metamorphosed and deformed mudstone and
183 sandstone basement (Field et al., 1997; King, 2000). From the mid-Cretaceous, the
184 basin transitioned into a northward-prograding, passive continental margin (Fig. 1b)
185 that allowed thick units of Late Cretaceous to Paleogene sediments, eroded from
186 axial ranges, to be deposited onto the continental shelf and slope (King, 2000). The
187 propagation of the modern plate boundary in the early Miocene transformed the
188 setting of the basin from a passive margin to a convergent forearc basin (King, 2000).
189 The additional one sample (Blacks Quarry) from Northland is from an allochthonous
190 sequence, which is inferred to have originated in the North Slope Basin (Fig. 1a, b;
191 Hollis et al., 2006).

192 The Waipawa Fm is a poorly bedded, brownish black, organic-rich marine
193 sedimentary unit that ranges in thickness from ~2 to 80 m (Moore, 1988; Hollis et al.,
194 2014; Field et al., 2018; Naeher et al., 2019). Foraminiferal paleobathymetry
195 indicates that the formation was deposited in an upper- to mid-slope setting (Field et

196 al., 2018; Naeher et al., 2019). Palynological and palynofacies data suggest that the
197 Waipawa Fm and correlated units were deposited during a sea-level fall (Schjøler et
198 al., 2010; Hollis et al., 2014 and references therein) within a relatively short period of
199 time in the late Paleocene (ca. 0.7 My; Fig. 2; Hollis et al., 2014). The fall in sea-level
200 is thought to have resulted in increased delivery of terrestrial organic matter to
201 continental slope settings as the exposed nearshore and shelfal areas were largely
202 bypassed (Hines et al., 2019; Naeher et al., 2019). Oscillations in key geochemical
203 parameters (e.g., TOC, hydrogen index [HI], oxygen index [OI], $\delta^{13}\text{C}$ and
204 palynofacies) through the formation indicate that influxes of terrestrial organic matter
205 occurred episodically (Naeher et al., 2019). For the most part, the Waipawa Fm
206 conformably overlies the Whangai Fm and the transition into Waipawa organofacies
207 is gradational (Moore, 1989; Naeher et al., 2019). There is, however, an unconformity
208 in some sections where the Waipawa Fm is condensed (Wilson and Moore, 1988;
209 Hollis et al., 2014). The top of the formation is commonly marked by an unconformity
210 (Schjøler et al., 2010; Hollis et al., 2014).

211 The Whangai Fm is a thick (typically 300–500 m), poorly bedded, variably calcareous
212 and regionally extensive mudstone that consists of the Upper Calcareous, Rakauroa,
213 Te Uri, Porangahau and Kirks Breccia members (Moore, 1988; Field et al., 1997).
214 The Whangai Fm samples analysed in this study are all from the Upper Calcareous
215 Member, which commonly underlies the Waipawa Fm in the East Coast Basin.

216 **3. Samples and analytical methodology**

217 *3.1 Samples and sample preparation*

218 Waipawa Fm samples were collected from the Orui-1A drill core, housed at the New
219 Zealand National Core Store in Featherston, and archived outcrop samples from

220 Taylor White section and Blacks Quarry held at GNS Science. The Orui-1A
221 stratigraphic drill hole was drilled in 2011 to a total depth of 117.3 m near Riversdale,
222 coastal Wairarapa (41° 3' 54.36" S, 176° 5' 16.44" E; Fig. 1a; Field et al., 2018).
223 Taylor White section is a road-side section exposed on Angora Road (40°27'46.9" S,
224 176°28'24.9" E), near the small settlement of Wimbledon, southern Hawke's Bay
225 (Fig. 1a; Bland et al., 2014). This section was freshly exposed when road
226 construction was undertaken to widen the Angora Road, allowing for fresh samples
227 to be collected after several meters of rock had been removed (Bland et al., 2014;
228 Naeher et al., 2019). Blacks Quarry is located in the Doubtless Bay, in the Northland
229 region of North Island (34° 58' 40.62" S, 173° 23' 54.24" E, Fig. 1a). Whangai Fm
230 samples were obtained from a collection of archived outcrop samples held at GNS
231 Science, previously collected from the lower part of Angora Road (40°27'43.2" S,
232 176°28'42.2" E; Tayler, 2011; Hollis et al., 2014), termed the 'Angora Road section' in
233 the present study. Stratigraphically, the Whangai Fm samples are located ca. 17–35
234 m below the base of Waipawa Fm (Tayler, 2011; Hollis et al., 2014). The Orui-1A
235 samples were obtained from a 3.2 m stratigraphic interval between the depths of 48.4
236 and 51.6 m, with sample spacing ranging from 13 to 72 cm and each sample
237 representing a stratigraphic interval of approximately 3 to 5 cm. Care was taken to
238 avoid zones of faulting, brecciation and calcite veining that were present in the core.
239 By contrast, the Taylor White samples are from a much thicker stratigraphic interval
240 of approximately 50 m and were not collected specifically for Re-Os geochronology
241 which requires that sampling to be done over a small stratigraphic interval to
242 minimize possible variation in initial $^{187}\text{Os}/^{188}\text{Os}$ ratios (Cohen et al., 1999; Selby and
243 Creaser, 2003; Kendall et al., 2009b). The Taylor White samples were included to
244 examine how varying depositional conditions within the Waipawa Fm, as shown by

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5 245 stratigraphic oscillations in key geochemical parameters (Naeher et al., 2019), may
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8 246 have affected the Re-Os systematics. A total of 23 samples are examined in this
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13 247 study; 18 from the Waipawa Fm and 5 from Whangai Fm.

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15 248 Sample processing was undertaken in the rock crushing facility at Victoria University
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18 249 of Wellington (VUW). Rock samples (80–100 g) were polished to remove any
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22 250 surface contamination and drilling marks from the core material following the
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25 251 protocols of Kendall et al. (2009a). The samples were then dried in an oven overnight
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28 252 at 40 °C, broken into small pieces without direct metal contact, and powdered using
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31 253 an agate mill.

32 254 *3.2 Bulk pyrolysis and sulfur analyses*

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34 255 Bulk pyrolysis and sulfur data obtained by this study were used in conjunction with
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37 256 published geochemical and palynofacies datasets (Naeher et al., 2019) to assess the
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41 257 variation in organic matter type and depositional conditions within the Waipawa and
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44 258 Whangai formations. Bulk pyrolysis analyses for the Orui-1A and Angora Road
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47 259 samples were undertaken at GNS Science following published methods (Naeher et
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50 260 al., 2019). In brief, powdered samples were analysed using a Weatherford
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53 261 Laboratories TOC/TPH Source Rock Analyser (SRA) to obtain key geochemical
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56 262 parameters that include TOC, total volatile (S1) and pyrolysable (S2) hydrocarbons,
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59 263 temperature of maximum pyrolysis yield (T_{max}), HI and OI. The temperature
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62 264 programme used was 300 °C isothermal for 3 min, then increased at a rate of 25 °C
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65 265 min^{-1} to 650 °C (isothermal at 650 °C for 1 min) to pyrolyse the kerogen, followed by
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68 266 oxidation at 630 °C for 20 min. A standard (Institut Français du Pétrole [IFP] standard
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71 267 160000) was run at the start and finish of each sample sequence, and after every 8
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74 268 samples to check for data quality. Bulk pyrolysis data for the Taylor White samples

269 were obtained from Naeher et al. (2019). Bulk pyrolysis data for the Blacks Quarry
270 sample were obtained previously from the Geological Survey of Canada, Calgary,
271 using a Rock-Eval 6 instrument.

272 Analyses of total sulfur content (S_{tot}) and forms of sulfur for the Orui-1A, Angora
273 Road and Blacks Quarry samples were undertaken by CRL Energy Ltd in Lower
274 Hutt, New Zealand, using standard procedures (Naeher et al., 2019). In brief, S_{tot} was
275 determined by high-temperature (1350 °C) tube furnace combustion, based on the
276 ASTM Standard D4239 technique, using a Leco Truspec Sulfur Analyser model 630-
277 100-700 (Naeher et al., 2019). The different forms of sulfur were determined
278 according to Australian Standard AS1038.11-2002 where sulfate sulfur (S_{sul}) is
279 extracted by 10% HCl and determined gravimetrically after purification and
280 precipitation. The HCl extracted residue is then decomposed with nitric acid and
281 oxidised using H_2O_2 to obtain pyritic iron. The pyritic iron is measured by atomic
282 absorption spectroscopy and used to calculate pyritic sulfur (S_{pyr}). Organic sulfur
283 (S_{org}) is obtained by subtracting the sum of S_{sul} and S_{pyr} from S_{tot} . Sulfur data for the
284 Taylor White samples were available from Naeher et al. (2019) and were also
285 analysed by CRL Energy Ltd using the same procedures and instrumentation.

286 *3.3 Re-Os analyses*

287 To enable optimisation for isotope dilution analyses, Re concentrations were first
288 determined at the VUW geochemistry laboratory following protocols from Durham
289 University as described in the supplementary online material (e.g., Jones et al.,
290 2018). Full Re-Os isotope analyses of the samples were carried out at Durham
291 University's laboratory for source rock and sulfide geochronology and geochemistry
292 following previously published protocols for isolation, purification and measurement

293 by isotope dilution - negative thermal ionization mass spectrometry (e.g., Cumming et
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2 294 al., 2012; Jones et al., 2018). In brief, a known amount of rock powder (300–500 mg)
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4 295 was spiked with a known amount of $^{190}\text{Os} + ^{185}\text{Re}$ mixed tracer solution and digested
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7 296 using $\text{Cr}^{\text{VI}}\text{-H}_2\text{SO}_4$ solution in a sealed carius tube at 220 °C for 48 h. Osmium was
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10 297 separated and purified from the solution using solvent extraction and micro-distillation
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12 298 methods. The residual Re bearing solution was evaporated to dryness at 80 °C and
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14 299 purified by NaOH-acetone solvent extraction and further purified using HCl-HNO₃
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17 300 anion exchange chromatography.

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20 301 The resulting Re and Os fractions were loaded onto Nickel and Platinum wire
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22 302 filaments, respectively, and their isotopic compositions measured on a Thermo
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25 303 Scientific TRITON Negative Thermal Ionisation Mass Spectrometer housed at the
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27 304 Arthur Holmes Laboratory, Durham University. Rhenium isotopic composition was
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30 305 measured via static collection mode in Faraday cups, with Os measured via ion-
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32 306 counting through a secondary electron multiplier (SEM) in a peak-hopping mode.
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35 307 Total procedural blanks during this study were 14.6 ± 0.16 pg Re and 50 ± 0.01 fg
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37 308 Os, with an $^{187}\text{Os}/^{188}\text{Os}$ value of 0.22 ± 0.08 ($n = 4$). In-house standards for both Re
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40 309 (Restd; Selby, 2007) and Os (DROsS; Nowell et al., 2008) were run with every batch
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42 310 of samples to monitor instrument reproducibility and ensure data quality. The Re
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44 311 standard solution yields an average $^{185}\text{Re}/^{187}\text{Re}$ ratio of 0.59843 ± 0.00193 ($n = 7$)
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47 312 that is similar to the established natural $^{185}\text{Re}/^{187}\text{Re}$ ratio of 0.59739 ± 0.00039
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50 313 (Gramlich et al., 1973), and was used to correct for mass fractionation in the
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52 314 measured Re data. The average $^{187}\text{Os}/^{188}\text{Os}$ ratio of the in-house Durham Romil
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54 315 Osmium Standard (DROsS) was 0.16089 ± 0.00056 ($n = 7$), consistent with values
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57 316 reported in previous studies from the same lab (e.g., Cumming et al., 2012; Liu and
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59 317 Selby, 2018, and references therein), and also in excellent agreement with values

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318 reported by other laboratories (0.16078 ± 0.00024 , Liu and Pearson, 2014;
319 0.16091 ± 0.00015 , van Acken et al., 2019). The Re-Os isotopic data, calculated 2σ
320 uncertainties for $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ and the associated error correlation
321 function (rho; Ludwig, 1980), were regressed using the beta version of the Isochron
322 program (Li et al., 2019) which incorporates the benchmark Isoplot algorithm
323 (Ludwig, 2012) and a new approach that employs the Monte Carlo sampling method
324 for error propagation. In the Isoplot program, a Model 1 age assumes that the
325 assigned 2σ uncertainties and calculated error correlations are the only reason the
326 data-points scatter from the regression line whereas a Model 3 age assumes that the
327 scatter about the isochron line may be linked to both the assigned analytical errors
328 and other geological factors that produce variation in the initial $^{187}\text{Os}/^{188}\text{Os}$ values
329 (Ludwig, 2012). The Isoplot program separates the two scenarios based on the
330 probability of how well the data fit the regression line. By contrast, the Monte Carlo
331 method makes no prior assumption about the possible causes of scatter in the
332 geochronological results and propagates uncertainties (2σ) from both analytical
333 measurements and model assumptions in a consistent manner irrespective of the
334 probability of fit (Li et al., 2019).

42 335 **4. Results and discussion**

43 44 45 336 *4.1 Kerogen type and maturity*

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48 337 The bulk pyrolysis data for the Orui-1A, Taylor White and Angora Road samples
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50 338 (Table 1; Fig. 3) are consistent with published results for the Waipawa and Whangai
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53 339 formations in the East Coast Basin (Tayler, 2011; Field et al., 2018; Naeher et al.,
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55 340 2019). The TOC within the Waipawa Fm in the Orui-1A core and Taylor White
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58 341 section is highly variable, generally ranging from 0.4–5 wt.% with a mean of 2.2 wt.%
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342 (Fig. 3a; Naeher et al., 2019). TOC is very high (~10 wt.%) in the Blacks Quarry
343 sample from the North Slope Basin (Fig. 3a). By contrast, the Whangai Fm at Angora
344 Road exhibits low TOC content (mostly <1 wt.%, Fig. 3a). All samples presented here
345 are thermally immature as indicated by T_{\max} values ranging from 396–428 °C (Fig.
346 3b; Tissot and Welte, 1984), and thus, the observed kerogen types within the two
347 formations are representative of the initial kerogen types which, based on the
348 modified van Krevelen diagram (Fig. 3c), varies from Type II to Type III. The wide
349 variations in T_{\max} , HI and OI values displayed by the Waipawa Fm samples in the
350 complete Taylor White sample set in Fig. 3b and c are a result of stratigraphic
351 variations in kerogen type, in part resulting from changing redox conditions within the
352 depositional environment, rather than to variations in maturity or sample weathering
353 (Field et al., 2018; Naeher et al., 2019). Similar stratigraphic variations in kerogen
354 type also occur within the Waipawa Fm in the Orui-1A core (Field et al., 2018), but
355 are not reflected amongst the Orui-1A samples because these were selected from a
356 thin (3.2 m) stratigraphic interval with relatively uniform T_{\max} , HI and OI values. In
357 both the Taylor White Section and Orui-1A core, OI is consistently low (≤ 50 mg
358 $\text{CO}_2/\text{g TOC}$) in the upper part of the Waipawa Fm despite high variability in TOC, S_2 ,
359 and HI (Field et al., 2018; Naeher et al., 2019). Palynofacies analyses indicate that
360 the organic matter in the Waipawa Fm is mainly terrestrial woody plant matter
361 whereas marine-sourced amorphous organic matter dominates in the Whangai Fm
362 (Field et al., 2018; Naeher et al., 2019).

4.2 Re and Os concentrations

364 The Waipawa Fm samples from Orui-1A core, Taylor White section and Blacks
365 Quarry are all enriched in both Re (22.5–85.9 ppb) and Os (397.9–598.6 ppt [^{192}Os
366 153.8–254.9]; Table 2) relative to the average concentrations of these elements in

367 the upper continental crust (0.2–2 ppb Re and 30–50 ppt Os; Esser and Turekian,
368 1993; Sun et al., 2003). The Whangai Fm samples from the Angora Road section are
369 only slightly enriched in Re (3.6–11.8 ppb) and Os (141.8–228.1 ppt [^{192}Os 55.4–
370 89.0]) compared to the upper continental crust. Three Waipawa Fm samples from the
371 Taylor White section are particularly enriched in Re (TW-17 = 85.9 ppb, TW-29 =
372 72.9 ppb and TW-51 = 56.3 ppb). The high and variable Re concentrations in the
373 Waipawa Fm, especially in the Taylor White samples (Table 2), may indicate some
374 form of water mass restriction with varying degrees of replenishment of the water
375 column by Re-rich water from the open ocean (McArthur et al., 2008; van Acken et
376 al., 2019). This is supported by biomarker evidence which suggests that there was
377 persistent water column stratification during the deposition of the formation in the
378 East Coast Basin (Naeher et al., 2019), as well as suggestions of restricted shallow
379 marine depositional setting for Waipawa organofacies in other sedimentary basins
380 such as the Great South and Canterbury basins (Schjøler et al., 2010). Sample TW-
381 17 and TW-29 show elevated OI values of 131 mg CO₂/g TOC and 68 mg CO₂/g
382 TOC, respectively, compared to the other Taylor White samples studied here, which
383 are very consistent between 25 and 29 mg CO₂/g TOC (Table 1, Fig. 3c). This
384 suggests that these two samples either contain different types of organic matter or
385 they have been affected by oxidative weathering. The latter appears more likely since
386 Re-Os isotope data for the two samples also yield negative initial $^{187}\text{Os}/^{188}\text{Os}$ (Os_i)
387 values (Table 2), which has been suggested to indicate disturbance to the Re-Os
388 system through oxidative weathering (Jaffe et al., 2002; Georgiev et al., 2012). We
389 therefore treat these two samples as outliers and exclude them from further
390 discussion.

392 4.3 Re and Os uptake and fractionation in the Waipawa and Whangai formations

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3 393 The association of Re and Os with TOC and sulfur may provide useful information on
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5 394 the depositional conditions that enhance the uptake of these elements into organic-
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8 395 rich sediments (Cohen et al., 1999; Cumming et al., 2012; Georgiev et al., 2012;
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10 396 Rooney et al., 2012). Strong positive correlations exist between TOC and Re ($R^2 =$
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12 397 0.91) and ^{192}Os ($R^2 = 0.73$) in the Orui-1A samples (Fig. 4a, b), suggesting an uptake
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15 398 mechanism that is linked to the abundance of organic matter (e.g., Georgiev et al.,
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17 399 2012; Rooney et al., 2012 and references therein). The ^{192}Os isotope is plotted to
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19 400 avoid the effects of radiogenic in-growth of ^{187}Os , allowing for direct comparison of
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22 401 hydrogenous Os concentrations in the different samples. Samples from the Taylor
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24 402 White section show no significant correlation between TOC and Re ($R^2 = -0.04$) and
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26 403 ^{192}Os ($R^2 = 0.08$) (Fig. 4a, b), which may indicate possible effects of surficial
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28 404 weathering in these outcrop samples. The apparent correlations between TOC and
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30 405 Re and Os concentrations in the Angora Road samples may be spurious because
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32 406 they rely on one sample that plots away from the other clustered samples (Fig. 4a,
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34 407 b). In general, the Waipawa Fm, with higher TOC content, exhibits higher
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36 408 concentrations of Re and Os than the Whangai Fm (Fig. 4a, b). The large proportion
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38 409 of terrestrial organic matter (66 to 98% degraded phytoclasts) in the Waipawa Fm
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40 410 (Schjøler et al., 2010; Hollis et al., 2014; Field et al., 2018; Naeher et al., 2019) does
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42 411 not appear to have impacted the uptake of Re and Os, supporting previous
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44 412 interpretations that chelating precursors or fundamental binding sites responsible for
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46 413 the uptake of Re and Os are present in all types of organic matter (Cumming et al.,
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48 414 2012; Harris et al., 2013; Du Vivier et al., 2015). The difference in concentrations of
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50 415 Re and Os in the two formations might also be a factor of the abundance, variability
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52 416 and preservation of organisms such as macroalgae that are components of
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417 sedimentary organic matter and which have recently been shown to accumulate Re
418 (up to several hundreds of ppb) and Os (Racionero-Gómez et al., 2016; Rooney et
419 al., 2016; Racionero-Gómez et al., 2017; Ownsworth et al., 2019). The accumulation
420 of Re by macroalgae has been shown to be syn-life and unidirectional i.e. once the
421 living macroalgae absorb Re, it does not release it back to the water (Racionero-
422 Gómez et al., 2016). However, the study also suggests that Re may be released
423 back to the water column once the macroalgae die and break down, and that
424 depositional conditions which prevent or lower the rate of macroalgal degradation
425 (such as anoxia and low temperature) may be required for much of the accumulated
426 Re to be incorporated into sediments (Racionero-Gómez et al., 2016). The hypoxic
427 conditions during the deposition of the Waipawa Fm, compared to the oxic conditions
428 in the Whangai Fm (Naeher et al., 2019), might therefore be the reason for its higher
429 Re and Os concentrations.

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430 The Waipawa Fm is enriched in S_{tot} (1.25–2.31 wt.%) compared to the Whangai Fm
431 (0.72–0.85 wt.%) (Fig. 5a, b), suggesting deposition under less oxic conditions (Didyk
432 et al., 1978; Georgiev et al., 2012; Naeher et al., 2019). S_{tot} is also positively
433 correlated with the abundance of Re ($R^2 = 0.84$) and ^{192}Os ($R^2 = 0.72$), as well as the
434 $^{187}\text{Re}/^{188}\text{Os}$ ratio ($R^2 = 0.66$) in samples from this study (Fig. 5a, b, c). This may
435 suggest that the uptake and fractionation of Re and Os are linked to the redox
436 conditions of the depositional environment (Colodner et al., 1993; Crusius et al.,
437 1996; Cohen et al., 1999; Morford and Emerson, 1999; Crusius and Thomson, 2000;
438 Yamashita et al., 2007; Georgiev et al., 2011). However, no simple correlation can be
439 established between Re and Os concentrations and other indicators of redox
440 conditions such as HI and OI (Table 1). The sulfur speciation data [normalised to S_{tot}
441 as there is a high variation in S_{tot} within the Waipawa Fm (Naeher et al., 2019)] also

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2 443 show that only organic sulfur ($S_{\text{org}}/S_{\text{tot}}$) exhibits strong positive correlations with Re
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4 444 ($R^2 = 0.75$; Fig. 6a) and ^{192}Os ($R^2 = 0.77$; Fig. 6b) concentrations compared to pyritic
5 445 sulfur ($S_{\text{pyr}}/S_{\text{tot}}$) and sulfate sulfur ($S_{\text{sul}}/S_{\text{tot}}$), which exhibit negative (Re $R^2 = -0.68$;
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7 446 ^{192}Os $R^2 = -0.80$; Fig. 6c, d) and weak-positive (Re $R^2 = 0.25$; ^{192}Os $R^2 = 0.39$; Fig.
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9 447 6e, f) correlations, respectively. This supports previous findings that suggested that
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11 448 Re and Os have a greater affinity for organic chelating sites than sulfides (Cohen et
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13 al., 1999; Rooney et al., 2012).

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17 449 Slow sedimentation, which increases the time of exposure of organic matter to the
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19 450 sediment-water interface, is another factor that has been considered to play an
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21 451 important role in enhanced uptake of Re and Os in organic-rich sedimentary rocks
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23 452 (Lewan and Maynard, 1982; Selby et al., 2009; Cumming et al., 2012; Rooney et al.,
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25 453 2012). The average sedimentation rate for the Waipawa Fm (~10.6 cm/ky) is almost
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27 454 an order of magnitude higher than that of the Whangai Fm (~1.1 cm/ky) (Naeher et
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29 455 al., 2019), and also significantly higher than those of several other marine organic-
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31 456 rich rocks previously dated with the Re-Os isotope system (<2 cm/ky) (e.g., Kendall
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33 457 et al., 2009b; Georgiev et al., 2017; Tripathy et al., 2018). Therefore, if slow
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35 458 sedimentation rate plays a primary control in Re and Os uptake in organic-rich
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37 459 sediments, then the Waipawa Fm would be expected to record low levels of Re and
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39 460 Os. Instead, the average concentrations of Re (38.9 ppb) and ^{192}Os (192.6 ppt) in the
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41 461 Waipawa Fm are approximately 6 and 3 times higher, respectively, than those of
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43 462 Whangai Fm (Re = 6.6 ppb; ^{192}Os = 65.6 ppt), indicating that, in this instance, slower
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45 463 sedimentation rates have not had a significant impact on sequestration of Re and Os.
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47 464 The relatively low levels of Re and Os in the Whangai Fm, compared to the Waipawa
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49 465 Fm, may simply be a factor of its low TOC content and different depositional
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51 466 conditions. However, the Re and Os concentrations in the Waipawa Fm are
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467 comparable to those reported for other marine shales with similar geochemical
468 characteristics, albeit with much lower sedimentation rates. For example, the Upper
469 Jurassic Hekkingen Fm with TOC of 3.08–10.9 wt.%, Type II/III kerogen, anoxic
470 depositional conditions and a sedimentation rate of 1.83 cm/ky has average Re and
471 ^{192}Os abundances of 46 ppb and 158.4 ppt, respectively, similar to those of the
472 Waipawa Fm (Langrock and Stein, 2004; Georgiev et al., 2017; Tripathy et al., 2018).
473 Therefore, based on these results, it appears that a slow sedimentation rate does not
474 play a significant role in Re and Os enrichment in organic-rich sediments, at least in
475 the range from 1.1 cm/ky to 10.6 cm/ky. This argument is supported by previous
476 studies which suggested that the oxidation effects brought about by a slow
477 sedimentation rate lead to poor preservation of organic matter (Ingall and Cappellen,
478 1990) and subsequent re-immobilization (precipitation) of Re (Crusius and Thomson,
479 2000).

480 *4.4 Re-Os geochronology of the Waipawa Formation*

481 The $^{187}\text{Re}/^{188}\text{Os}$ values of samples from the Orui-1A core range from 256.4 to 345.1
482 and are positively correlated to the $^{187}\text{Os}/^{188}\text{Os}$ values, which range from 0.527 to
483 0.612 (Fig. 7a). Regression of the isotope data using the Isoplot algorithm yields a
484 Model 3 isochron age of 58.1 ± 3.9 Ma ($n = 9$; Mean Square of Weighted Deviates
485 [MSWD] = 4.1), with an Os_i of 0.28 ± 0.02 (Fig. 7a). When the Monte Carlo method is
486 used, the age (58.1 ± 4.4 Ma) and Os_i (0.28 ± 0.02) are the same as those of the
487 Isoplot method, except that the age uncertainty is slightly greater in the Monte Carlo
488 method due to a higher percentage of the uncertainties (61%) being related to the
489 model age calculation (Li et al., 2019; Fig. 7b). Precise Re-Os dating of sedimentary
490 rocks requires that: 1) the initial $^{187}\text{Os}/^{188}\text{Os}$ ratios (Os_i) are identical, 2) there is a
491 sufficient spread in $^{187}\text{Re}/^{188}\text{Os}$ ratios of at least a few hundred units, and 3) the Re-

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492 Os system remains undisturbed (Cohen et al., 1999; Selby and Creaser, 2005a). The
493 obtained Os_i values for Orui-1A samples are all nearly identical, ranging from 0.277–
494 0.286, with a mean of 0.280 ± 0.002 (1SD; Table 2). Only sample Orui-11e shows a
495 slightly larger deviation from the mean Os_i (0.006) and as a result, exhibits the largest
496 standard error of prediction (0.92%) from the line of best-fit through the data (Fig.
497 7a). Analytical uncertainties, variation in the composition of Os during deposition and
498 post-depositional processes such as brecciation and calcite veining that were present
499 in the core are some of the possible reasons for the variance in the Os_i of sample
500 Orui-11e. Regression of the Re-Os data without this sample (Orui-11e) using the
501 Isoplot program yields a more precise Model 1 age of 57.4 ± 1.7 Ma ($Os_i = 0.28 \pm$
502 0.01 , $n = 8$, $MSWD = 1.5$; Fig. 7c). In comparison, the Monte Carlo method yields an
503 age of 57.5 ± 3.5 Ma ($Os_i = 0.28 \pm 0.02$; Fig. 7d), which indicates that the Model 1
504 scenario of the Isoplot program underestimated the age uncertainties by ~50%. We
505 suggest that the larger uncertainties in the obtained Re-Os age may be a result of the
506 limited spread in both $^{187}Re/^{188}Os$ (80 units) and $^{187}Os/^{188}Os$ (0.085 units) displayed
507 by the Orui-1A samples, in addition to uncertainties from analytical measurements
508 (Selby et al., 2009; Rooney et al., 2017; Li et al., 2019). Small ranges in Re-Os ratios
509 have also been reported for other marine and lacustrine organic-rich rocks (Turgeon
510 et al., 2007; Selby et al., 2009; Finlay et al., 2010; Cumming et al., 2012; Zhu et al.,
511 2013; Tripathy et al., 2018) where a lack of variability in organic matter type coupled
512 with a relatively homogenous depositional environment (Cumming et al., 2012) and
513 redox conditions that drawdown Re relative to Os (Turgeon et al., 2007) were
514 suggested as the main reasons for the low spread in Re-Os ratios. A lack of
515 variability in organic matter type is a feature of the Waipawa Fm, especially in the

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516 Orui-1A samples, possibly explaining the observed similarity in the Re-Os ratios of
517 these samples.

518 The $^{187}\text{Re}/^{188}\text{Os}$ ratios of samples from the Taylor White section range from 283.7 to
519 498.9 (excluding the two outliers discussed in Section 4.2) and are positively
520 correlated with their corresponding $^{187}\text{Os}/^{188}\text{Os}$ values, which range from 0.551 to
521 0.767 (Fig. 8a). Regression of the isotope data yields a Re-Os date of 58.3 ± 7.7 Ma
522 ($\text{Os}_i = 0.29 \pm 0.05$; MSWD = 28.8) using the Isoplot algorithm and 58.3 ± 6.5 Ma (Os_i
523 = 0.29 ± 0.04 ; $n = 6$) using the Monte Carlo method (Fig. 8a, b). These Re-Os dates
524 agree well with those derived from the Orui-1A samples, but with larger uncertainties.
525 The high MSWD value associated with the Re-Os date from the Isoplot program,
526 relative to the ideal value of ~ 1 , indicates that the final age uncertainty is controlled
527 by both analytical and geological uncertainties (Ludwig, 2012). This might be
528 expected given the large stratigraphic interval that the samples represent. However,
529 the whole ~ 80 m of Waipawa Fm in the Taylor White section is estimated to have
530 been deposited within a relatively short period of time (~ 700 ky; Hollis et al., 2014;
531 Naeher et al., 2019) and thus, temporal variation in Os_i is deemed unlikely to fully
532 explain the uncertainty in the obtained Re-Os date. An alternative explanation is that
533 the episodic influxes of large amounts of terrestrial material during deposition of the
534 formation in the Taylor White section (Naeher et al., 2019) may have supplied high
535 loads of continental-derived Os that introduced localised variation in seawater Os_i .
536 Further, the oxidative weathering that affected the Re-Os systematics of the two
537 outlier samples discussed above (Section 4.2) may have also caused subtle effects
538 in the other Taylor White samples.

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540 *4.5 Comparison of the Waipawa Formation Re-Os and biostratigraphic ages*

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3 541 Dating the Waipawa Fm through biostratigraphy has been challenging mainly due to
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5 542 poor preservation and scarcity of age-diagnostic fossils. For example, the boundaries
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8 543 of dinoflagellate (NZDP) or calcareous nannofossil (NP) zones were not precisely
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10 544 located in the Orui-1A core due to the scarcity of fossils (Field et al., 2018). The
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12 545 interval of the Orui-1A core sampled in the present study (48.4 to 51.6 m) is also
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14
15 546 barren of nannofossils and thus, lacks precise age constraints. However, the base of
16
17 547 the overlying Wanstead Fm, at 36.84 m, is assigned to Zones NZDP8 and NP8 while
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20 548 the top of Zone NZDP7 is placed at 75.88 m (Fig. 2), which indicates that the Orui-1A
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22 549 samples studied here are of earliest late Paleocene age (~59 Ma). Dinocyst
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25 550 assemblages from several sections in eastern New Zealand indicate that the
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27 551 Waipawa Fm can be correlated with an interval that extends from upper Zone NZDP7
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30 552 to lower NZDP8 (Crouch et al., 2014; Hollis et al., 2014). Nannofossil biostratigraphy
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32 553 for the Angora Road section also indicates that the Waipawa Fm is correlated with an
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35 554 interval that spans lowermost Zone NP6 to upper Zone NP7 (Fig. 2; Hollis et al.,
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37 555 2014). This biostratigraphy was combined with age control from other sections to
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40 556 infer that the Waipawa Fm was deposited over a short period of time (~700 ky)
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42 557 during the late middle to early late Paleocene (59.4 to 58.7 Ma; Hollis et al., 2014).
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44 558 The Re-Os depositional age for the Waipawa Fm obtained from the Orui-1A samples
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46
47 559 (57.5 ± 3.5 Ma) overlaps with this biostratigraphic age, effectively providing the first
48
49 560 direct radiometric age constraint for this formation.

561 *4.6 Re-Os depositional age of the Whangai Formation*

562 The $^{187}\text{Re}/^{188}\text{Os}$ ratios in the Whangai Fm samples from the Angora Road section
563 range from 121.1 to 264.7 and correlate positively with the $^{187}\text{Os}/^{188}\text{Os}$ ratios, which

564 range from 0.484 to 0.633 (Fig. 8c). Regression of the isotope data yields imprecise
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2 565 Re-Os date of 61.9 ± 17.8 Ma ($Os_i = 0.36 \pm 0.06$; $n = 5$; $MSWD = 79.7$) using the
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4 566 Isoplot algorithm (Fig. 8c) and 61.9 ± 13.5 Ma ($Os_i = 0.36 \pm 0.05$) using the Monte
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6
7 567 Carlo method (Fig. 8d). The large uncertainties in the Re-Os date for these samples
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9 568 reflect the likely variations in Os_i over the relatively large time period (~ 2 Ma)
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11 569 represented by the ~ 17 m stratigraphic thickness covered by the Angora Road
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13 570 samples (Kendall et al., 2009b). Over this interval, Os_i varies from 0.343–0.369 and
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15 571 tends to become lower up-section, consistent with an overall decreasing trend in Os_i
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17 572 from the lowest Whangai Fm sample (0.369) to the highest Waipawa Fm sample in
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19 573 the Taylor White section (0.285). Despite the Re-Os date for the Angora Road
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21 574 samples being imprecise, the mean value of 61.9 Ma is in good agreement with the
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23 575 published age model for the section (Hollis et al., 2014), which combines both
24
25 576 calcareous nannofossil and dinoflagellate biostratigraphy (Crouch et al., 2014;
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27 577 Kulhanek et al., 2015), to infer an age range of ~ 62 to 61 Ma for the sampled interval.
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34 578 *4.7 Middle–late Paleocene seawater Os isotope composition*

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38 579 The Os_i ratio derived from regression of Re-Os data is interpreted to record the Os
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40 580 isotope composition of the seawater at the time of deposition (Ravizza and Turekian,
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42 581 1989; Cohen et al., 1999; Selby and Creaser, 2003; Selby et al., 2009). The
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44 582 isochron-derived Os_i values for the Waipawa Fm in Orui-1A (0.28 ± 0.02) and Taylor
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46 583 White (0.29 ± 0.04) samples, and the Whangai Fm in Angora Road samples ($0.36 \pm$
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48 584 0.05) are non-radiogenic, and significantly lower than the present-day seawater
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50 585 $^{187}Os/^{188}Os$ value of ~ 1.02 to 1.06 (Woodhouse et al., 1999; Peucker-Ehrenbrink and
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52 586 Ravizza, 2000; Gannoun and Burton, 2014). The Os_i value (calculated at 58 Ma) for
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54 587 the one additional Waipawa Fm sample from Blacks Quarry in North Slope Basin
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56 588 ($\sim 0.24 \pm 0.01$; Table 2) is also non-radiogenic but lower than those of the Waipawa
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589 Fm samples from the Orui-1A and Taylor White sections in the East Coast Basin
590 (~0.28–0.29). If this sample represents a closed Re-Os system that has not been
591 affected by post-depositional processes, then it would suggest that the Waipawa Fm
592 in the North Slope Basin is either slightly younger or was deposited in a more open
593 marine setting with less radiogenic Os_i . The latter appears more likely because the
594 sample is from an allochthonous sequence that was emplaced from an everted
595 marine basin with oceanic volcanic basement, at least 350 km north of its present
596 location (Ballance and Spörli, 1979; Hollis et al., 2006). The Os_i values for the
597 Waipawa Fm samples from the East Coast Basin are broadly similar to those of time
598 correlative units from the central Pacific Ocean (0.26–0.33; Fig. 9a), suggesting that
599 the basin was mixing with, at least, the wider Pacific Ocean. In addition, the observed
600 Os_i values may be indicative of the global seawater $^{187}Os/^{188}Os$ values at the time
601 given that paleo-ocean circulation patterns show that the Pacific, Atlantic and Indian
602 oceans were all connected 59 Ma ago (Fig. 9a; Haq, 1981; Barron and Peterson,
1991; Thomas et al., 2003; Batenburg et al., 2018).

604 A composite record of $^{187}Os/^{188}Os$ values from sedimentary rocks spanning the
605 period between 70 and 50 Ma and including the $^{187}Os/^{188}Os$ values for the Waipawa
606 and Whangai formations in the present study (Fig. 9b), provides a broader temporal
607 context in which the source of the non-radiogenic Os in the Paleocene can be
608 examined. The $^{187}Os/^{188}Os$ value for the Waipawa Fm is based on the mean Os_i
609 values [calculated at 59 Ma – the established biostratigraphic age (Hollis et al.,
2014); Table 2] for the Orui-1A samples which, unlike the Taylor White samples,
611 demonstrate an isochronous Re-Os relationship (Fig. 7). The obtained composite
612 record highlights a progressive shift to low $^{187}Os/^{188}Os$ ratios from a value of ~0.61 in
613 the latest Cretaceous (~68 Ma) to ~0.28 in late Paleocene (Fig. 9b). In particular, the

614 $^{187}\text{Os}/^{188}\text{Os}$ value of ~ 0.28 at ca. 59 Ma during the deposition of the Waipawa Fm
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2 615 coincides with the minimum before the marine $^{187}\text{Os}/^{188}\text{Os}$ trend increases leading up
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4 616 to the Paleocene-Eocene boundary. Superimposed upon the overall decreasing
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6 617 trend in $^{187}\text{Os}/^{188}\text{Os}$ values from the latest Cretaceous to the late Paleocene is the
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8
9 618 abrupt negative excursion at ca. 66 Ma associated with the Cretaceous-Paleogene
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11 619 (K-Pg) impact event (Fig. 9b; Pegram and Turekian, 1999; Ravizza and VonderHaar,
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13 620 2012). Extra-terrestrial impact events are distinguished in the marine Os record by
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15 621 abrupt shifts to low $^{187}\text{Os}/^{188}\text{Os}$ values (resulting from a sudden influx of non-
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17 622 radiogenic Os), followed by recovery to pre-impact values over a short duration of
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19 623 time (Paquay et al., 2008; Ravizza and VonderHaar, 2012). By contrast, the gradual
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21 624 nature of the long-term decline in $^{187}\text{Os}/^{188}\text{Os}$ values from the latest Cretaceous to
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23 625 late Paleocene indicates either a progressive increase in the supply of non-
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25 626 radiogenic Os or diminished supply of radiogenic Os from continental weathering.
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32 627 A number of events have been proposed as potential sources of the non-radiogenic
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34 628 Os during this period. These include emplacement of large igneous provinces such
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36 629 as the Deccan Traps (Ravizza and Peucker-Ehrenbrink, 2003; Robinson et al., 2009)
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38 630 and the first eruptive phase of the North Atlantic Igneous Province (Peucker-
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40 631 Ehrenbrink and Ravizza, 2012), as well as weathering of exhumed large ophiolites
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42 632 such as the Papuan Ultramafic Belt (Fig. 9b; Lus et al., 2004; Peucker-Ehrenbrink
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44 633 and Ravizza, 2012). It is unclear, however, how much these events contributed to the
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46 634 $^{187}\text{Os}/^{188}\text{Os}$ decline given the significant time gaps between them and the long
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48 635 duration of the decline. Interestingly, though, the $^{187}\text{Os}/^{188}\text{Os}$ record is correlated with
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50 636 global temperature proxies ($\delta^{18}\text{O}$, TEX_{86}) and the carbon isotope ($\delta^{13}\text{C}$) record for
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52 637 much of the Paleocene and into the early Eocene (Figs 9b, 10). The temperature
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54 638 records indicate moderate cooling between 64 and 58 Ma followed by a more
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639 pronounced warming trend (by ~10 °C) to around 53 Ma (Bijl et al., 2009; Hollis et al.,
640 2012; Hollis et al., 2014; Westerhold et al., 2018). The temperature minimum at
641 around 58.7 Ma coincides with the $^{187}\text{Os}/^{188}\text{Os}$ minimum and deposition of the
642 Waipawa Fm (Fig. 10b, c). The simplest interpretation for these observations is that
643 the gradual shift to low $^{187}\text{Os}/^{188}\text{Os}$ values in the middle–late Paleocene relates to a
644 reduction in global rates of continental weathering as temperature (and thus, the
645 hydrological cycle) decreased, whereas the positive shift from the late Paleocene to
646 early Eocene relates to increased rates of continental weathering in response to
647 rising temperatures and an accelerated hydrological cycle (Zachos et al., 2008). This
648 interpretation, although based on an assumption that fluxes of non-radiogenic Os to
649 the ocean remain relatively constant during this period, is supported by previous
650 findings that attributed the positive excursion in the $^{187}\text{Os}/^{188}\text{Os}$ ratios at the
651 Paleocene-Eocene Thermal Maximum (PETM) to increased chemical weathering
652 from an accelerated hydrological cycle, albeit on a much shorter time scale and a
653 more severe climatic perturbation (Ravizza et al., 2001; Wieczorek et al., 2013;
654 Dickson et al., 2015).

655 The $\delta^{13}\text{C}$ record follows a similar trend to those of the $\delta^{18}\text{O}$ and TEX_{86} records, but
656 with a maximum at around 58 Ma, ~1 my later than the temperature and $^{187}\text{Os}/^{188}\text{Os}$
657 minimum (Fig. 10a). Temporal variations in the stable carbon isotope composition
658 have been attributed to many factors, the discussion of which is beyond the scope of
659 this paper. However, the broad correlation of $^{187}\text{Os}/^{188}\text{Os}$ with $\delta^{13}\text{C}$ is consistent with
660 the inference that continental weathering patterns may have contributed significantly
661 to the observed middle Paleocene to early Eocene $^{187}\text{Os}/^{188}\text{Os}$ record. This is
662 because enhanced weathering of isotopically evolved (ancient) organic-rich rocks
663 would have driven the seawater $^{187}\text{Os}/^{188}\text{Os}$ ratios to more radiogenic values and

664 shifted the carbon isotope composition to lighter values (Ravizza and Esser, 1993).
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2 665 This explanation, however, requires that there was an exposure of large amounts of
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5 666 significantly older organic-rich rocks. It has been suggested that large quantities of
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7 667 neo-Tethyan (Triassic to Cretaceous) marine sediments were exhumed, oxidised and
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10 668 eroded during the initial stages of Indian-Asian collision causing the late Paleocene
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12 669 to early Eocene shift to lighter $\delta^{13}\text{C}$ values and the coeval global warming via the
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15 670 greenhouse effect (Beck et al., 1995). Using an estimated average $^{187}\text{Re}/^{188}\text{Os}$ value
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17 671 of 517 for organic-rich shales (bootstrapped 95% confidence interval of 468 to 582;
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20 672 calculated from a geochemical database of organic-rich sediments from 42 different
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22 673 sources; Dubin and Peucker-Ehrenbrink, 2015) and seawater $^{187}\text{Os}/^{188}\text{Os}$ values
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24 674 ranging from ~0.2 to 0.9 for the Triassic to Cretaceous period (100–250 Ma; Cohen
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26
27 675 and Coe, 2007; Porter et al., 2013; Dubin and Peucker-Ehrenbrink, 2015; Them et
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29 676 al., 2017; van Acken et al., 2019), these exhumed marine sediments would have
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32 677 contained $^{187}\text{Os}/^{188}\text{Os}$ values ranging from 1.1 to 3.1, with an average of 2.1,
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34 678 significantly more radiogenic than the average $^{187}\text{Os}/^{188}\text{Os}$ value of 1.4 for the upper
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37 679 continental crust. Further, the high abundance of Re and Os in organic-rich
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39 680 sediments coupled with the propensity of the Os hosted in these sediments to be
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42 681 readily mobilized during chemical weathering compared to the Os in typical granitic
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44 682 upper continental crust (Peucker-Ehrenbrink and Hannigan, 2000; Jaffe et al., 2002;
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46 683 Pierson-Wickmann et al., 2002; Georgiev et al., 2012; Dubin and Peucker-
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48
49 684 Ehrenbrink, 2015) supports the interpretation that exposure of the neo-Tethyan
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51 685 organic-rich sediments in the late Paleocene may have had potential to
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54 686 disproportionately drive seawater $^{187}\text{Os}/^{188}\text{Os}$ to more radiogenic values.
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689 5. Conclusions

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3 690 The Re-Os geochronology of the Waipawa Fm has yielded ages of 57.5 ± 3.5 Ma
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5 691 from the Orui-1A drill hole and 58.3 ± 6.5 Ma from the Taylor White section that are in
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7
8 692 close agreement with the available biostratigraphic age range for the formation (59.4
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10 693 to 58.7 Ma; Hollis et al., 2014). These are the first radiometric ages for this formation
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13 694 and demonstrate the potential of the Re-Os method for future dating of correlative
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15 695 units identified in other sedimentary basins across the Southwest Pacific. However,
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17 696 the large uncertainties in the Re-Os dates make it difficult to refine the age control
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20 697 and establish whether all known occurrences of the Waipawa Fm are coeval. Future
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22 698 Re-Os studies on the formation should target intervals where the spread in Re-Os
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25 699 ratios is likely to be larger based on variation in organic matter type and other
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27 700 geochemical features, especially in the upper part of the formation. The results from
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30 701 the Taylor White section also highlight the benefit of using fresh core material for
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32 702 such work given the apparent high susceptibility of the Waipawa Fm to oxidative
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35 703 weathering that may disturb the Re-Os system.

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38 704 The initial $^{187}\text{Os}/^{188}\text{Os}$ values for the Waipawa (~ 0.28) and Whangai (~ 0.36)
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40 705 formations are non-radiogenic and broadly similar to $^{187}\text{Os}/^{188}\text{Os}$ values from coeval
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43 706 pelagic sediments, further constraining the low-resolution marine Os record for the
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45 707 Paleocene. The broad correlation between the $^{187}\text{Os}/^{188}\text{Os}$ record and the global
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48 708 temperature proxies ($\delta^{18}\text{O}$, TEX_{86}) and carbon isotope ($\delta^{13}\text{C}$) records from the middle
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50 709 Paleocene to early Eocene suggests that changes in global weathering patterns may
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53 710 have been the main driver of the Os geochemical cycle during this time.

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24
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31 **Figure captions**

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35 726 **Fig. 1.** a) Map of the study area showing sample locations and distribution of
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37 727 Waipawa organofacies in the Southwest Pacific. Geological data extracted from
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40 728 QMAP 1:250K data set (Heron, 2014). Abbreviations: R-NB = Reinga-Northland
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42 729 Basin; NSB = North Slope Basin; DTB = Deepwater Taranaki Basin; TB = Taranaki
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45 730 Basin; ECB = East Coast Basin; WCB = West Coast Basin; CB = Canterbury Basin;
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47 731 GSB = Great South Basin. b) Paleogeographic reconstruction of the New Zealand
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50 732 region in the late Paleocene (58 Ma), adapted after King (2000), Killops et al. (2000)
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52 733 and Hollis et al. (2014).
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735 **Fig. 2.** Chronostratigraphic column of the East Coast Basin from the Late Cretaceous
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2 736 to early Eocene (after King, 2000; Hollis et al., 2014). Nannofossil assemblages are
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4 737 correlated to the biostratigraphic zonation scheme of Martini (1971), with absolute
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6 738 ages for events from Gradstein et al. (2012). Calcareous nannofossils zonation
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9 739 (CNZ) after Crouch et al. (2014). IUGS = International Union of Geological Sciences;
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12 740 UCM = Upper Calcareous Member.
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18 742 **Fig. 3.** Cross-plots of bulk pyrolysis data identifying the type and maturity of organic
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20 743 matter present in the Waipawa and Whangai formations. a) TOC vs HI, with the oil-
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22 744 (1) and gas-prone (2) trends of Naeher et al. (2019). b) OI vs T_{max} . c) Modified van
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25 745 Krevelen diagram showing the general maturation pathways for the main types of
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27 746 organic matter (after Hunt, 1995).
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34 748 **Fig. 4.** Cross-plots of TOC vs Re (a) and ^{192}Os (b) concentrations in the Waipawa
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36 749 and Whangai formations. Separate trendlines and correlation coefficients are shown
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39 750 by locality. Outlier samples TW-17 and TW-29 (unfilled red squares) are excluded
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41 751 from the trendlines (see text for discussion).
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47 753 **Fig. 5.** Cross-plots of total sulfur vs a) Re concentrations, b) ^{192}Os concentrations
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49 754 and c) $^{187}\text{Re}/^{188}\text{Os}$ for the Waipawa and Whangai formations samples. Outlier
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52 755 samples TW-17 and TW-29 are excluded from these plots.
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757 **Fig. 6.** Cross-plots of normalised forms of sulfur and Re and ^{192}Os concentrations.
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2 758 Organic sulfur ($S_{\text{org}}/S_{\text{tot}}$) vs Re (a) and ^{192}Os (b); pyritic sulfur ($S_{\text{pyr}}/S_{\text{tot}}$) vs Re (c) and
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4 759 ^{192}Os (d); sulphate sulfur ($S_{\text{sul}}/S_{\text{tot}}$) vs Re (e) and ^{192}Os (f). Outlier samples TW-17
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7 760 and TW-29 are excluded from these plots. The legend shown in Fig. 6f is used for all
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9 761 plots.

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16 763 **Fig. 7.** Re-Os geochronological results for the Waipawa Fm samples from Orui-1A
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18 764 core. All samples are plotted in (a) and (b) whereas sample Orui-11e is excluded in
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21 765 (c) and (d). Regression of the Re-Os isotope data together with the 2σ uncertainties
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23 766 in the isotope ratios and the associated error correlation functions (ρ) were done
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25 767 using the beta version of Isochron program (Li et al., 2019), which incorporates the
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28 768 Isoplot algorithm (a and c) (Ludwig, 2012) and the Monte Carlo method (b and d).
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31 769 The Re-Os dates and Os_i composition are very similar in both methods, except that
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33 770 the uncertainties from the Monte Carlo method are higher, especially for the Model 1
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35 771 scenario of the Isoplot program (c) (Li et al., 2019). See text for discussion. The
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38 772 bracketed age uncertainty includes the uncertainty in the ^{187}Re decay constant (λ),
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40 773 where $\lambda = 1.666 \pm 0.0031 \times 10^{-11} \text{ yr}^{-1}$ (Smoliar et al., 1996; Selby et al., 2007).

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46 775 **Fig. 8.** Re-Os geochronological results for the Waipawa Fm samples from the Taylor
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49 776 White section (a and b) and Whangai Fm samples from the Angora Road section (c
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51 777 and d). The data were regressed using the beta version of the Isochron program (Li
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54 778 et al., 2019) as described in Fig. 7 and in the text. Outlier samples TW-17 and TW-29
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56 779 are not included in the regression. Note that the uncertainties from the Monte Carlo
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59 780 method are lower than those of the Model 3 scenario of the Isoplot method. See text

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781 for discussion. The bracketed age uncertainty includes the uncertainty in the ^{187}Re
782 decay constant (λ), where $\lambda = 1.666 \pm 0.0031 \times 10^{-11} \text{ yr}^{-1}$ (Smoliar et al., 1996; Selby
783 et al., 2007).

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Fig. 9. a) A GPlates global paleogeographic reconstruction of the late Paleocene (59
785 Ma) using the relative finite rotations, continental polygons and coastlines from
786 Matthews et al. (2016), placed in the global paleomagnetic reference frame of
787 Torsvik et al. (2012). Ocean circulation patterns are inferred from Haq (1981), Barron
788 and Peterson (1991), Thomas et al. (2003) and Batenburg et al. (2018). b) composite
789 $^{187}\text{Os}/^{188}\text{Os}$ record of the latest Cretaceous to early Eocene period (70–50 Ma). The
790 $^{187}\text{Os}/^{188}\text{Os}$ value for the Waipawa Fm is based on mean Os_i ratios (calculated at 59
791 Ma) from Orui-1A samples (see text for discussion) whereas that of the Whangai Fm
792 is derived from the Angora Road samples isochron. The benthic foraminiferal oxygen
793 isotope ($\delta^{18}\text{O}$) record from ODP site 1209 is shown for the period between 66 and 50
794 Ma (Westerhold et al., 2017; 2018). Os isotope data sources: LL44-GPC3 = Pegram
795 and Turekian (1999); DSDP 549 = Ravizza et al. (2001); CD29-2 = Klemm et al.
796 (2005); ODP 886C = Ravizza (2007); ODP 690C and ODP 1262B = Ravizza and
797 VonderHaar (2012) and ODP 865 = Rolewicz (2013). Not shown are initial
798 $^{187}\text{Os}/^{188}\text{Os}$ ratios for late Maastrichtian (65.5 to 68.5 Ma) sediments from ODP 690,
800 DSDP 577 and DSDP 525 (Robinson et al., 2009) that agree well with the data from
801 Ravizza (2007) and Ravizza and VonderHaar (2012). NAIP = North Atlantic Igneous
802 Province; Papuan UMB = Papuan Ultramafic Belt; PETM = Paleocene-Eocene
803 Thermal Maximum.

805 **Fig. 10.** Trends in benthic stable carbon isotope values ($\delta^{13}\text{C}$) (a), benthic oxygen
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3 806 isotope values ($\delta^{18}\text{O}$) (b) and TEX_{86} values (c), overlain by a smoothing of the
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5 807 composite $^{187}\text{Os}/^{188}\text{Os}$ data from Fig. 9 (brown line). Data were smoothed using
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7 808 Origin Pro 2018 v9.5.1 software, employing the 5-point adjacent averaging method.
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10 809 TEX_{86} data are from Hollis et al. (2014); benthic foraminiferal $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records
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12 810 are from ODP sites 1209, 1262 and 1263 (Westerhold et al., 2017, 2018), calibrated
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15 811 to the age model of Westerhold et al. (2017). The $^{187}\text{Os}/^{188}\text{Os}$ data points for
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17 812 Waipawa and Whangai formations are shown by the purple and blue squares,
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20 813 respectively, with the legends shown applying to all plots.
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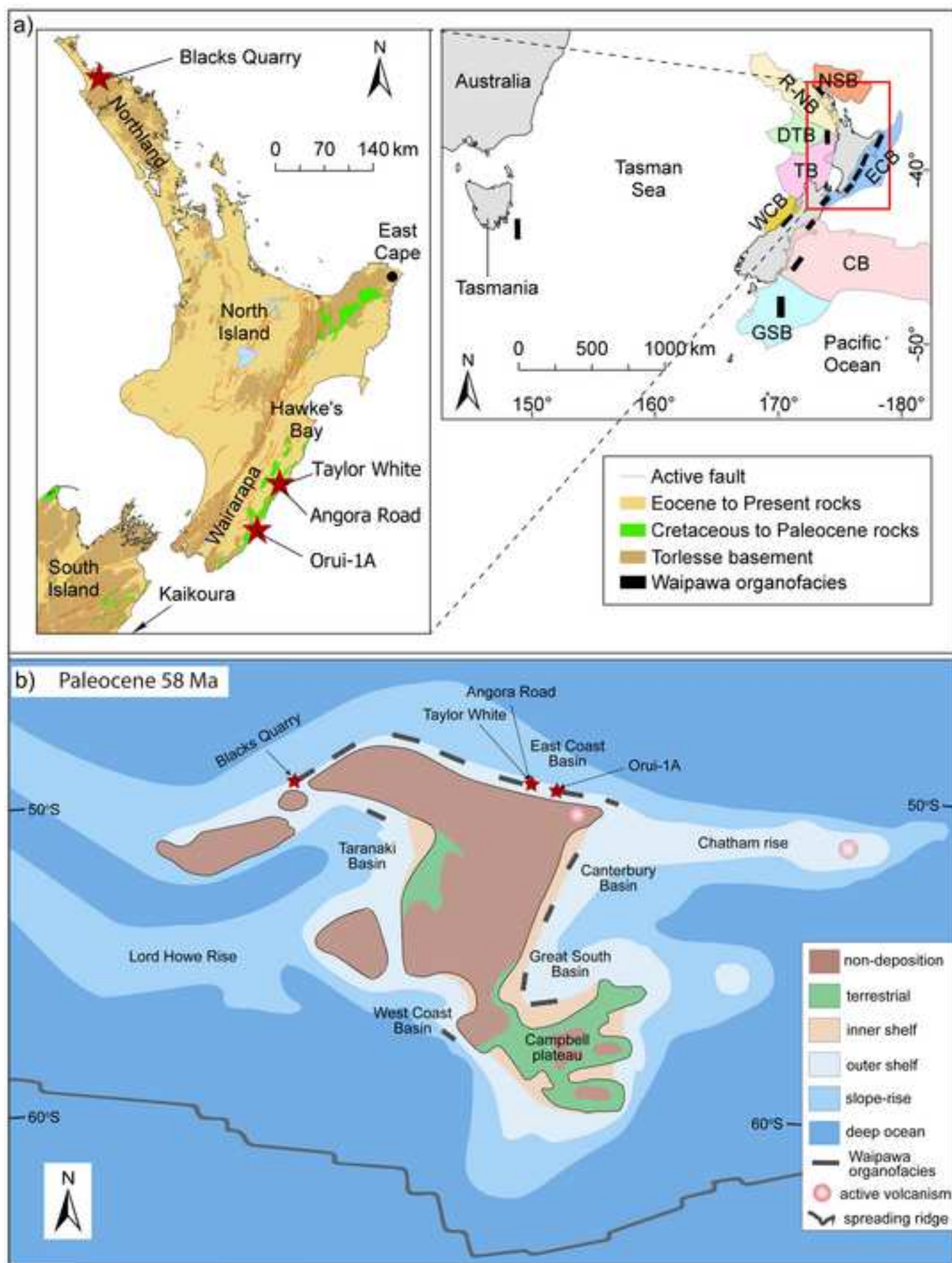


Fig. 2

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Ma	Epoch	IUGS Stage	NZ Stage	CNZ	Dinocyst zone (NZ)	Formation	
51	Eocene	Ypresian	Mangao- rapan (Dm)	NP13	NZE4	Wanstead	
52			Waipawan (Dw)	NP12			
53				NP11			NZE3
54				NP10			NZE2
55	Paleocene	Thanetian	Teurian (Dt)	NP9	NZE1		
56				NZDP8	Waipawa		
57			NP8				
58			NP7 NP6	NZDP7			
59		Selandian	Teurian (Dt)	NP5	NZDP6		
60				NZDP5	Whangai (UCM)		
61						NP4	
62				NZDP4			
63	NP3	NZDP3					
64	Danian	Teurian (Dt)	NP2	NZDP2			
65			NP1	NZDP1			
66	Late Cretaceous	Maastrichtian	Haumurian (Mh)	CC26			
67				CC25			
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Fig. 3

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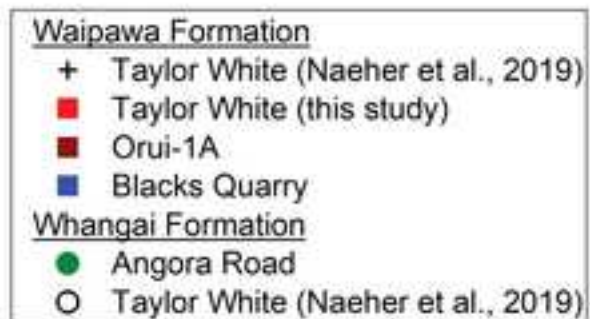
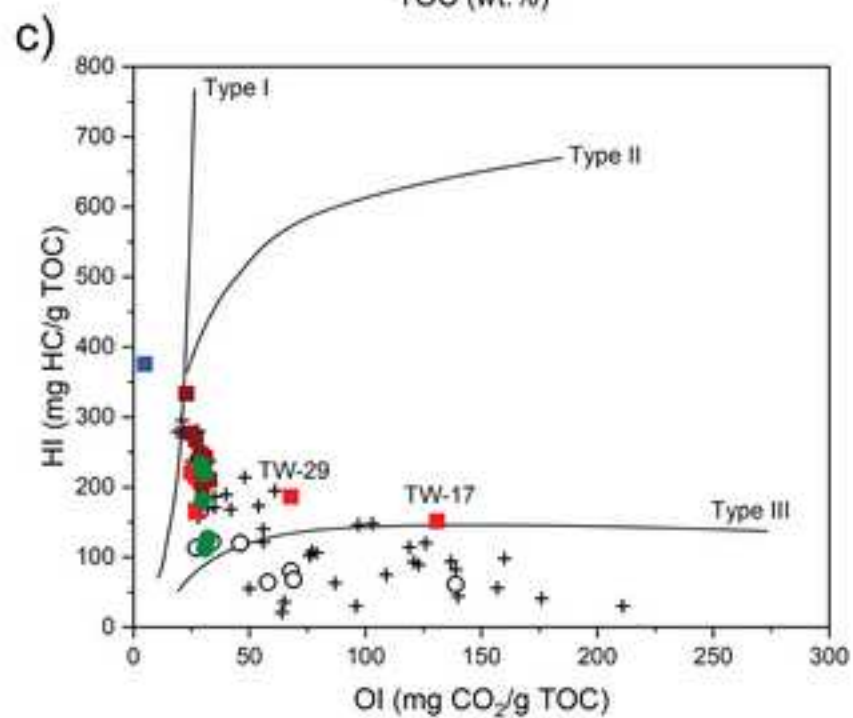
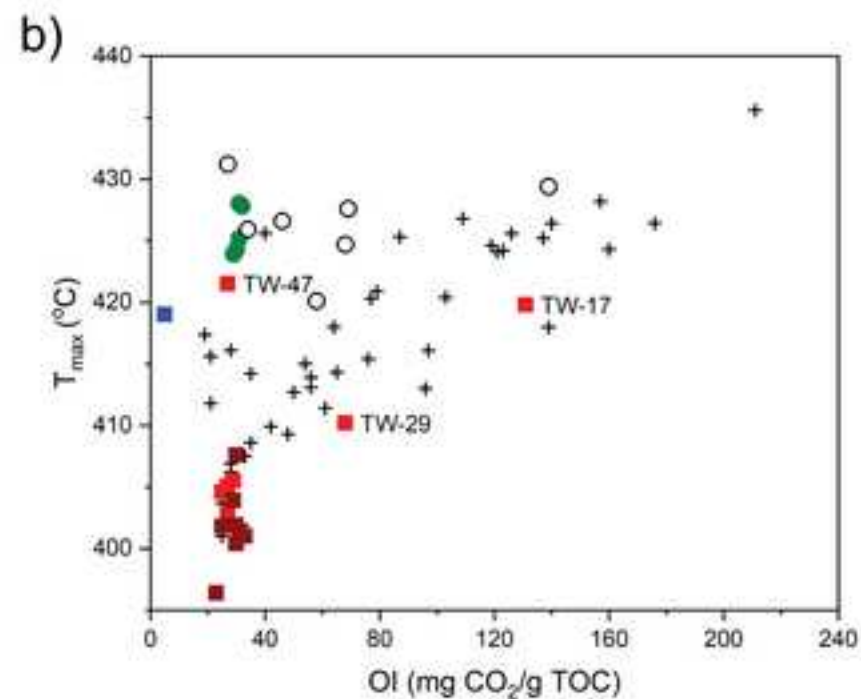
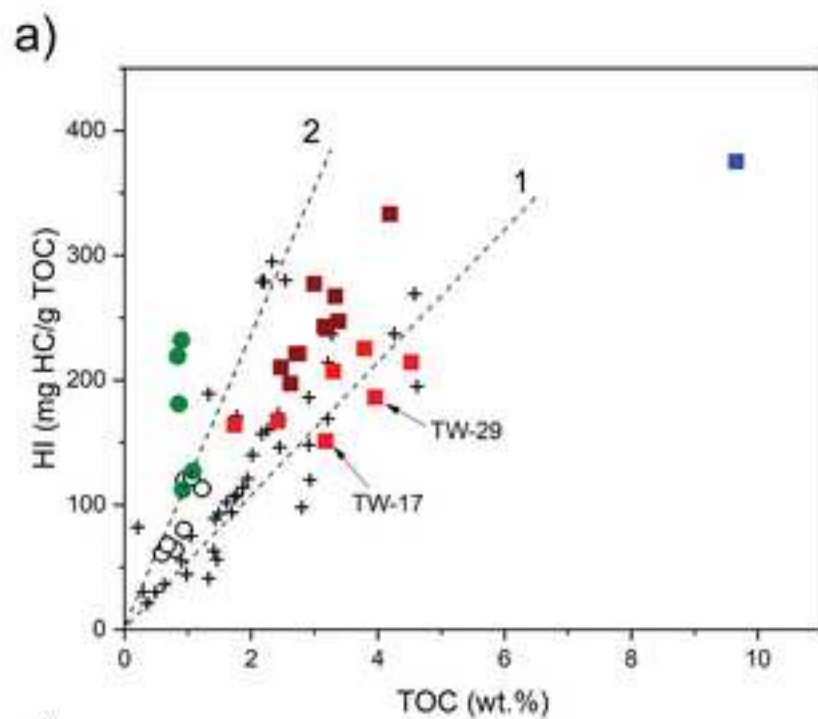


Fig. 4

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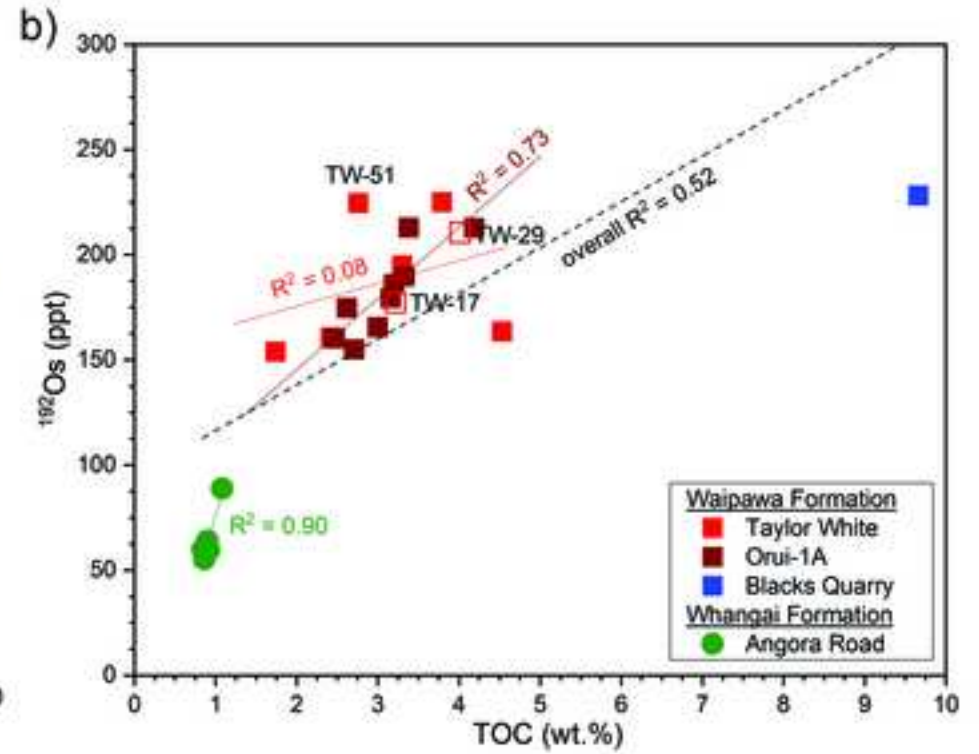
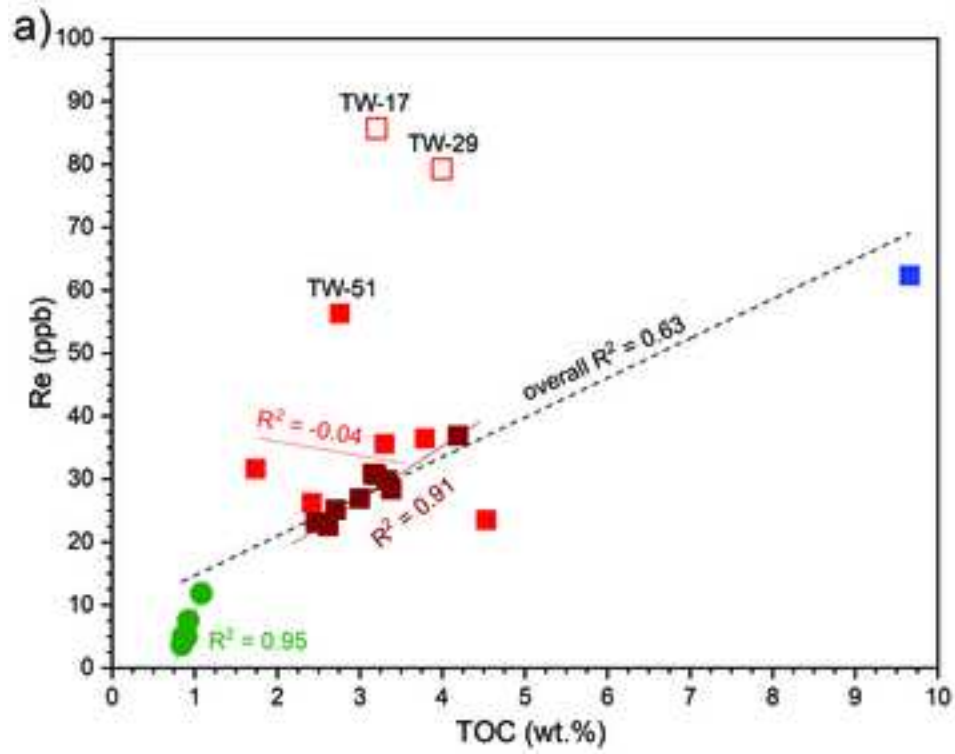
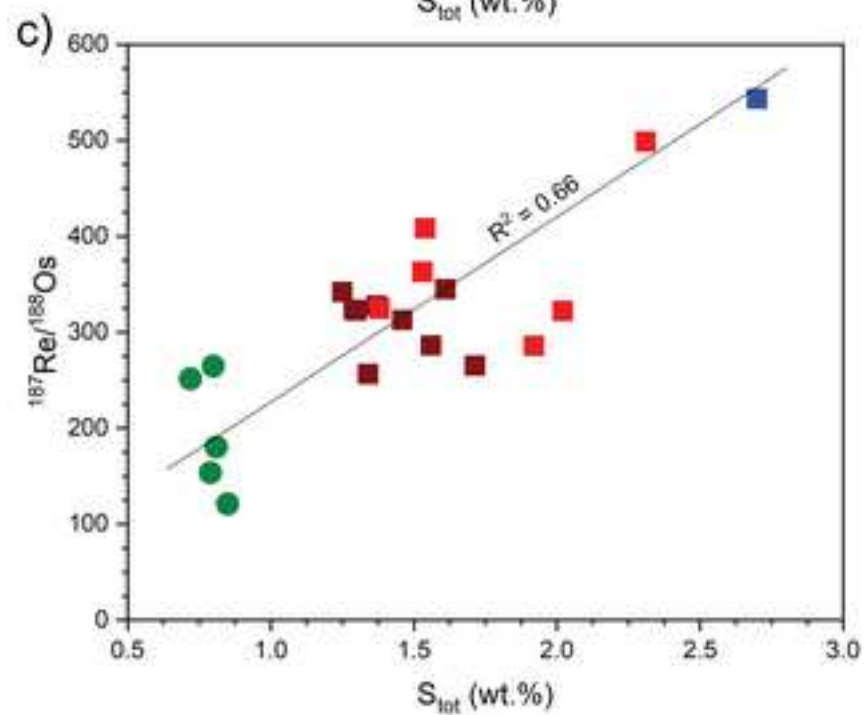
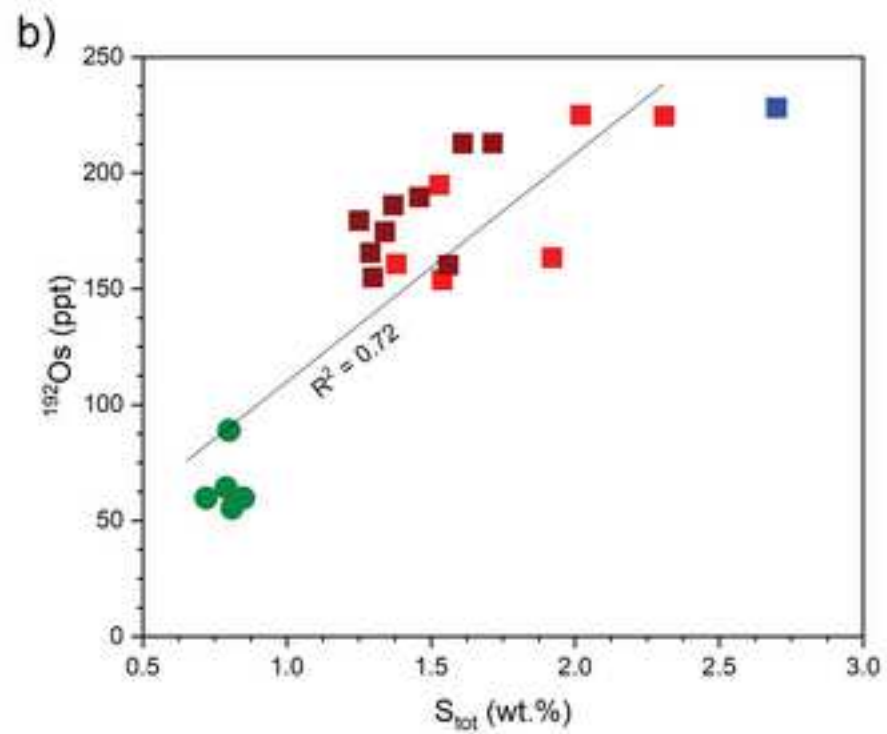
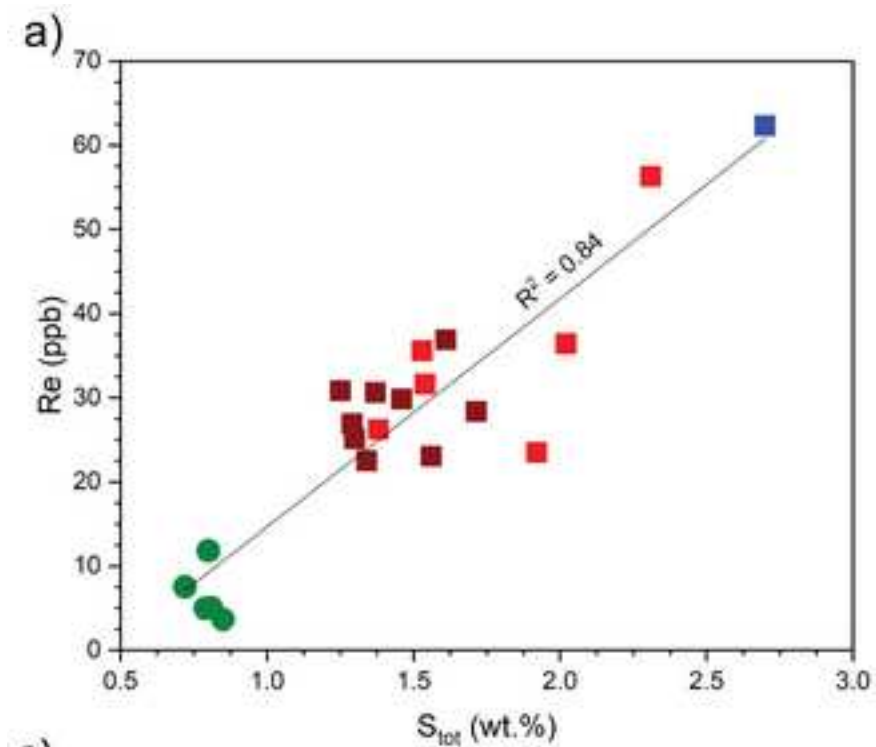


Fig. 5

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Waipawa Formation

■ Taylor White

■ Orui-1A

■ Blacks Quarry

Whangai Formation

● Angora Road

Fig. 6
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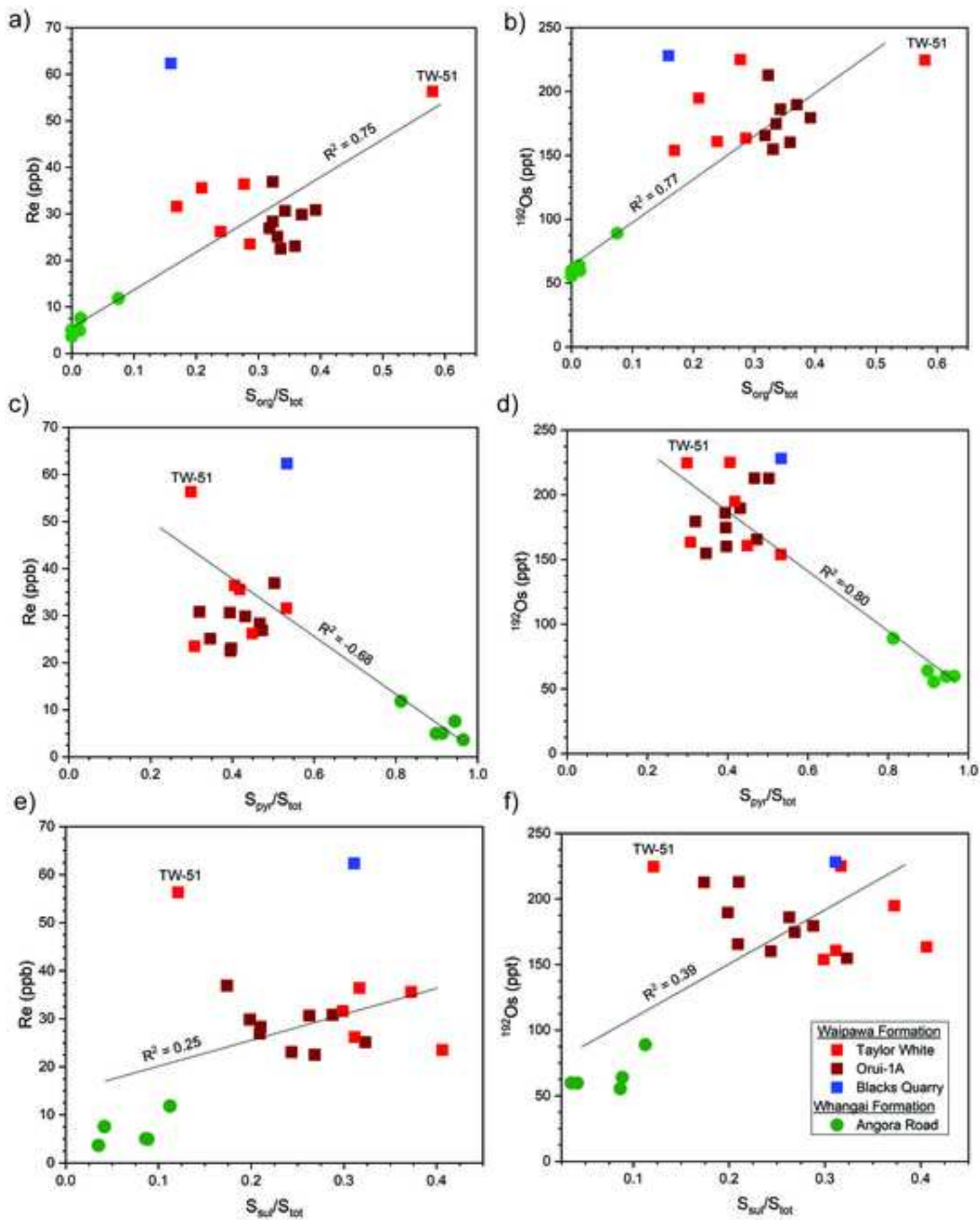


Fig. 7

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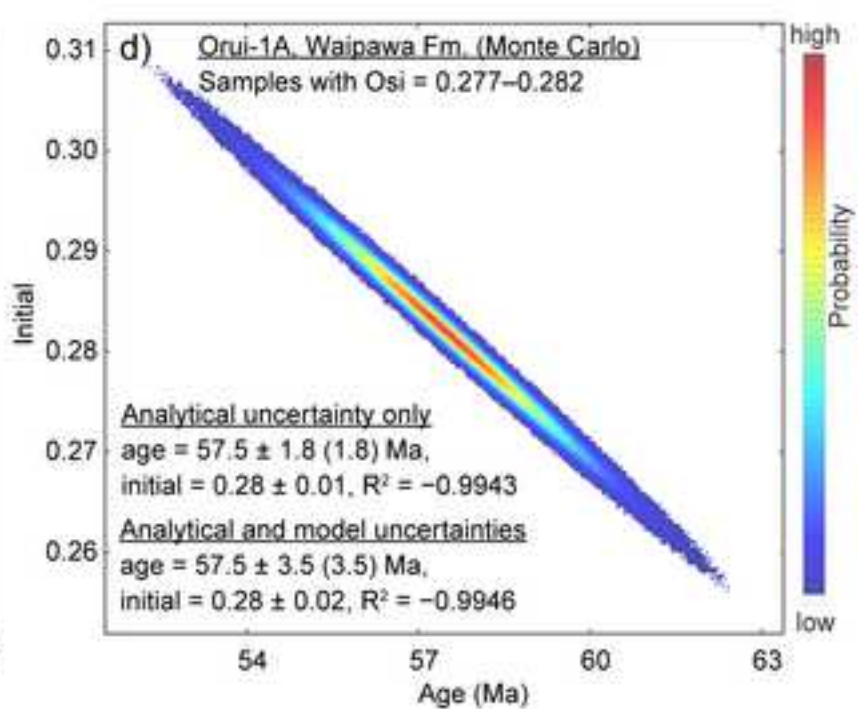
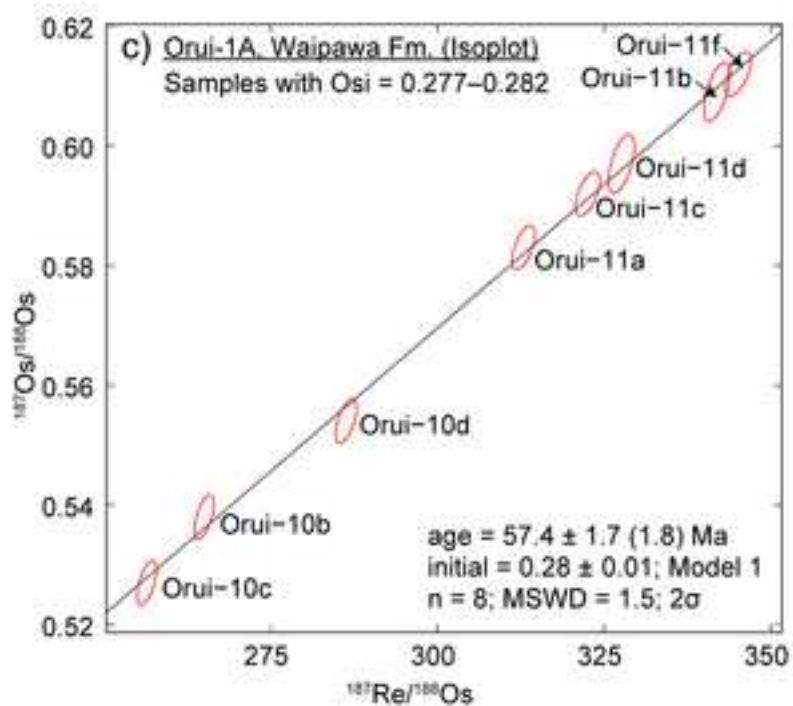
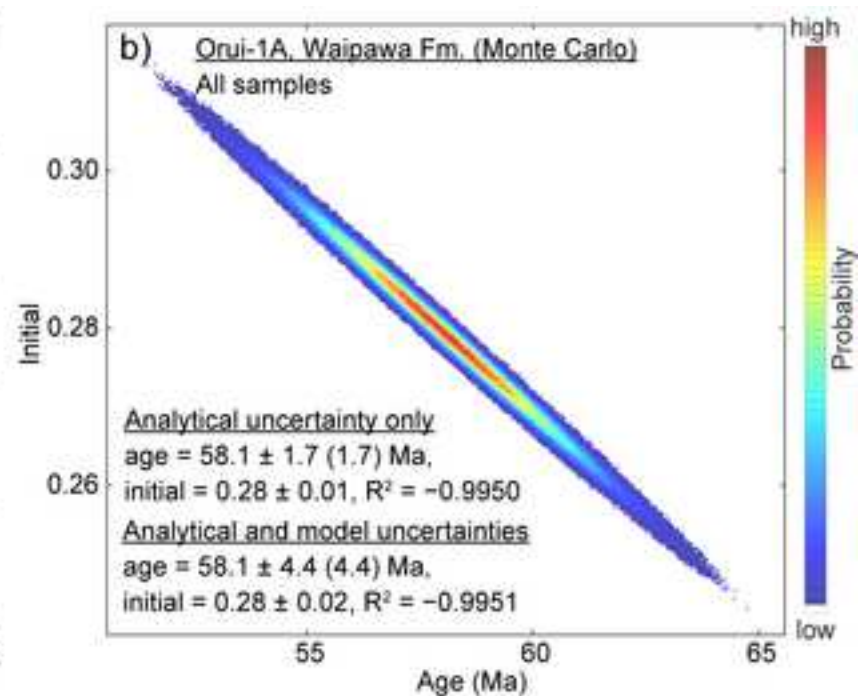
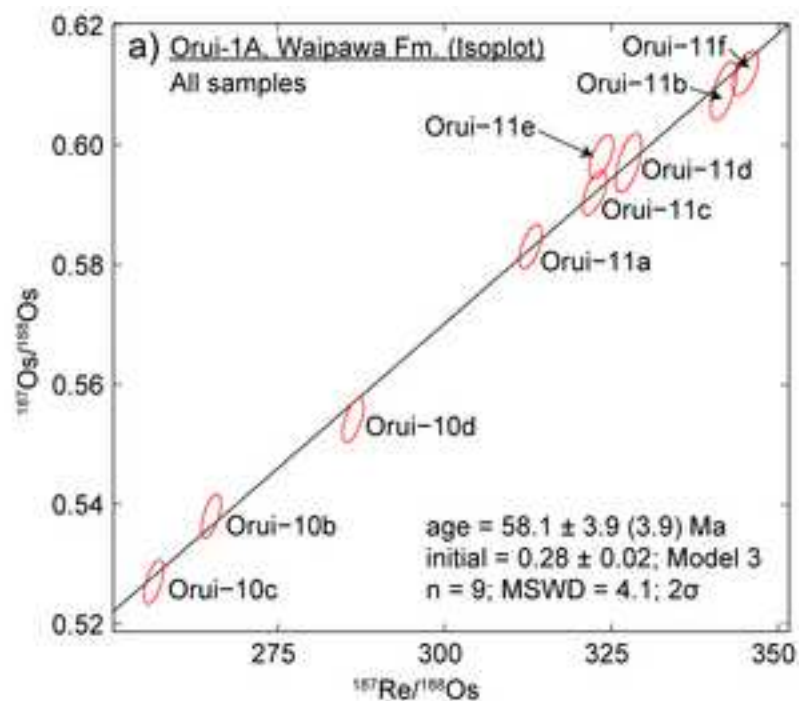


Fig. 8

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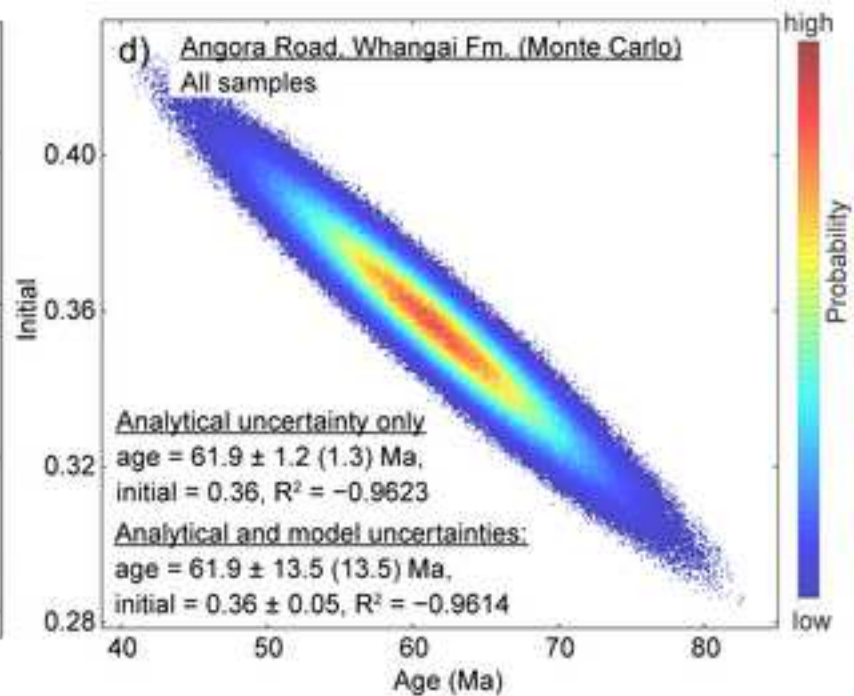
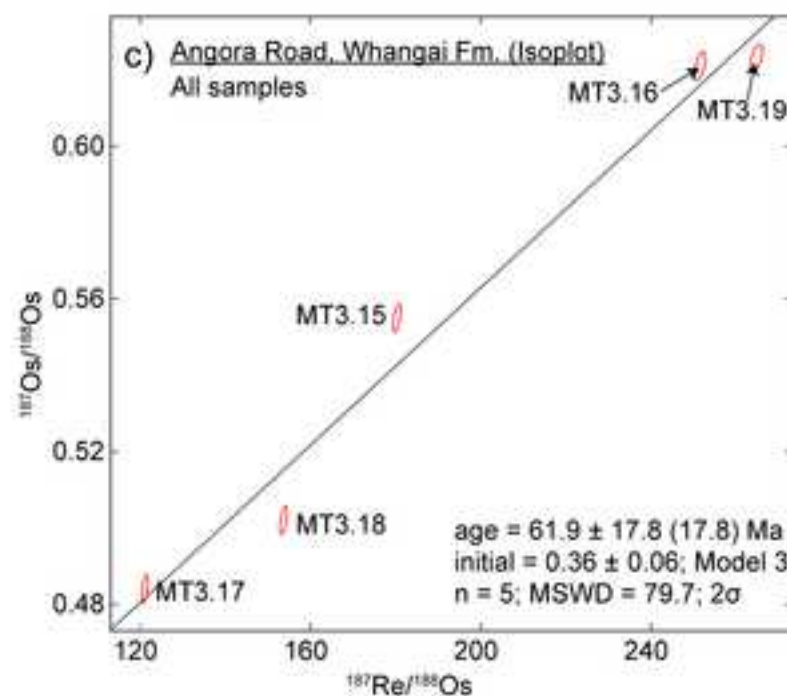
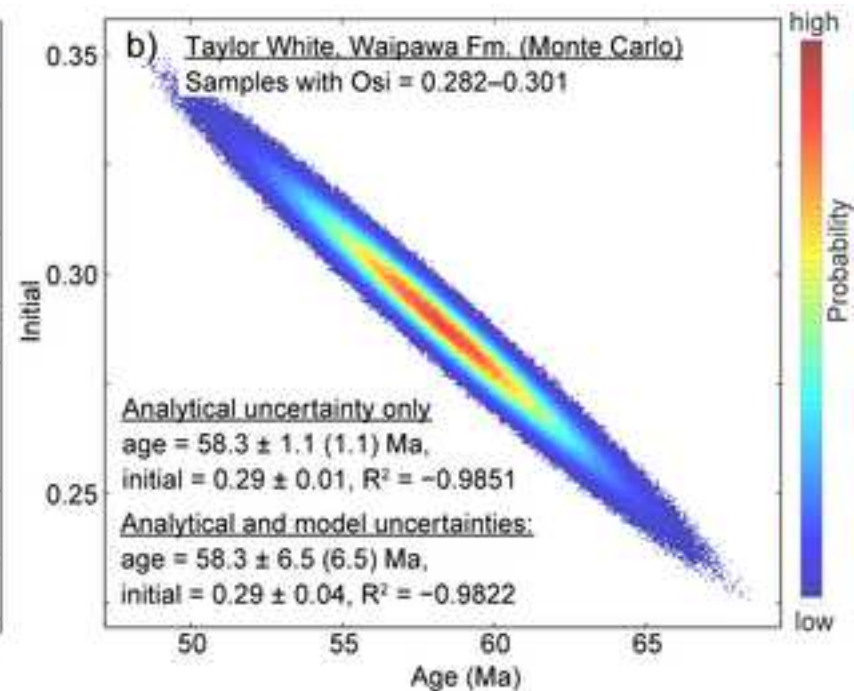
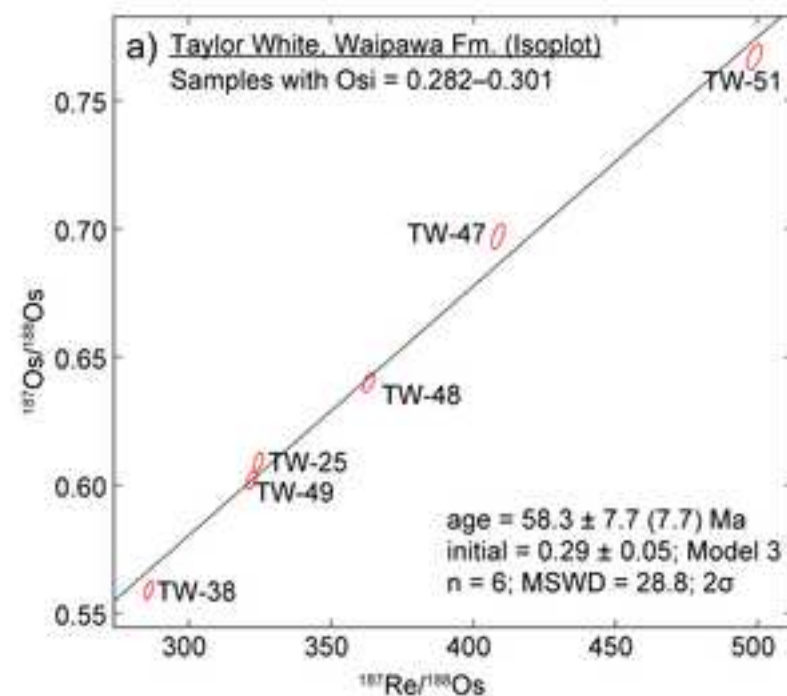


Fig. 9

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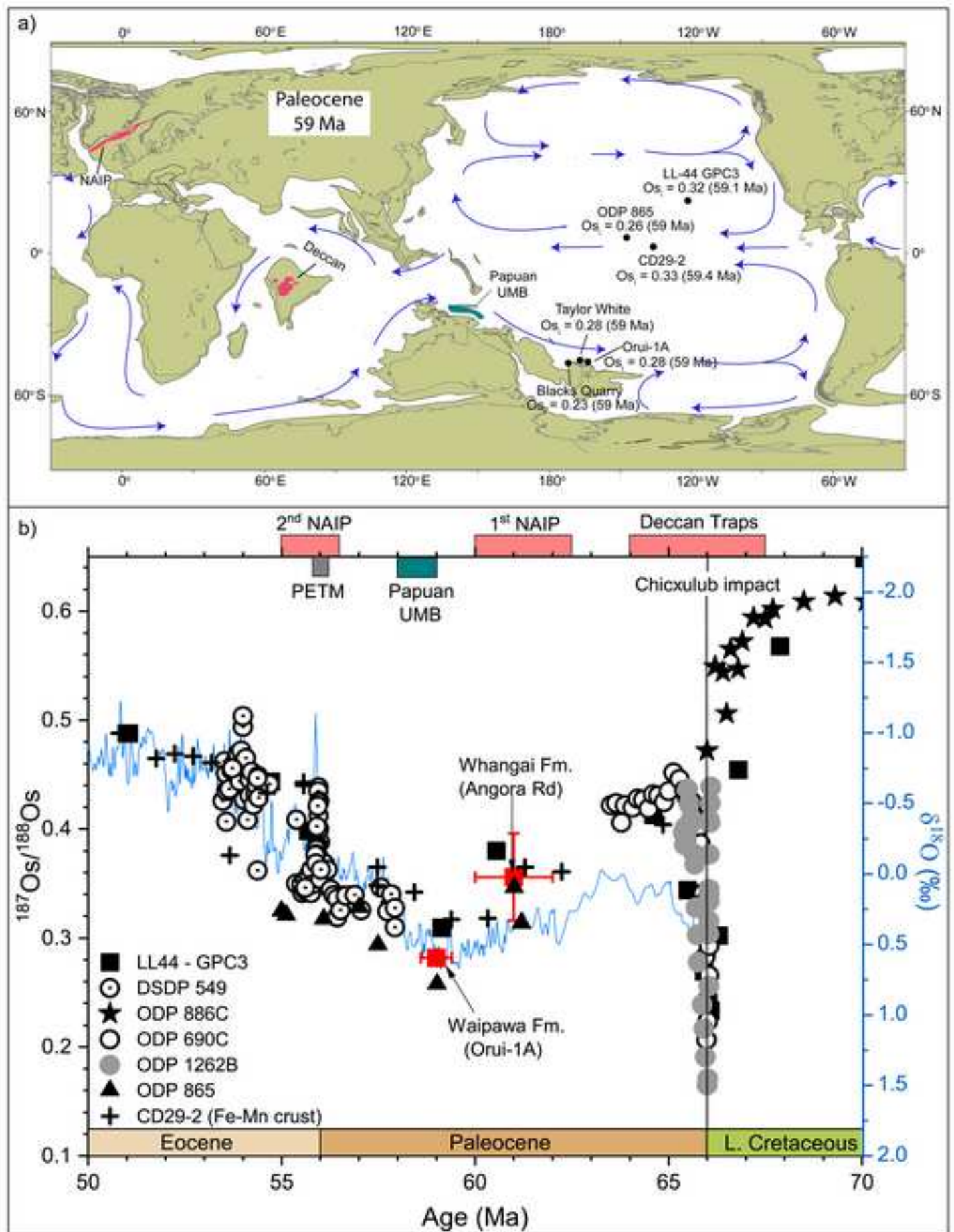


Fig. 10

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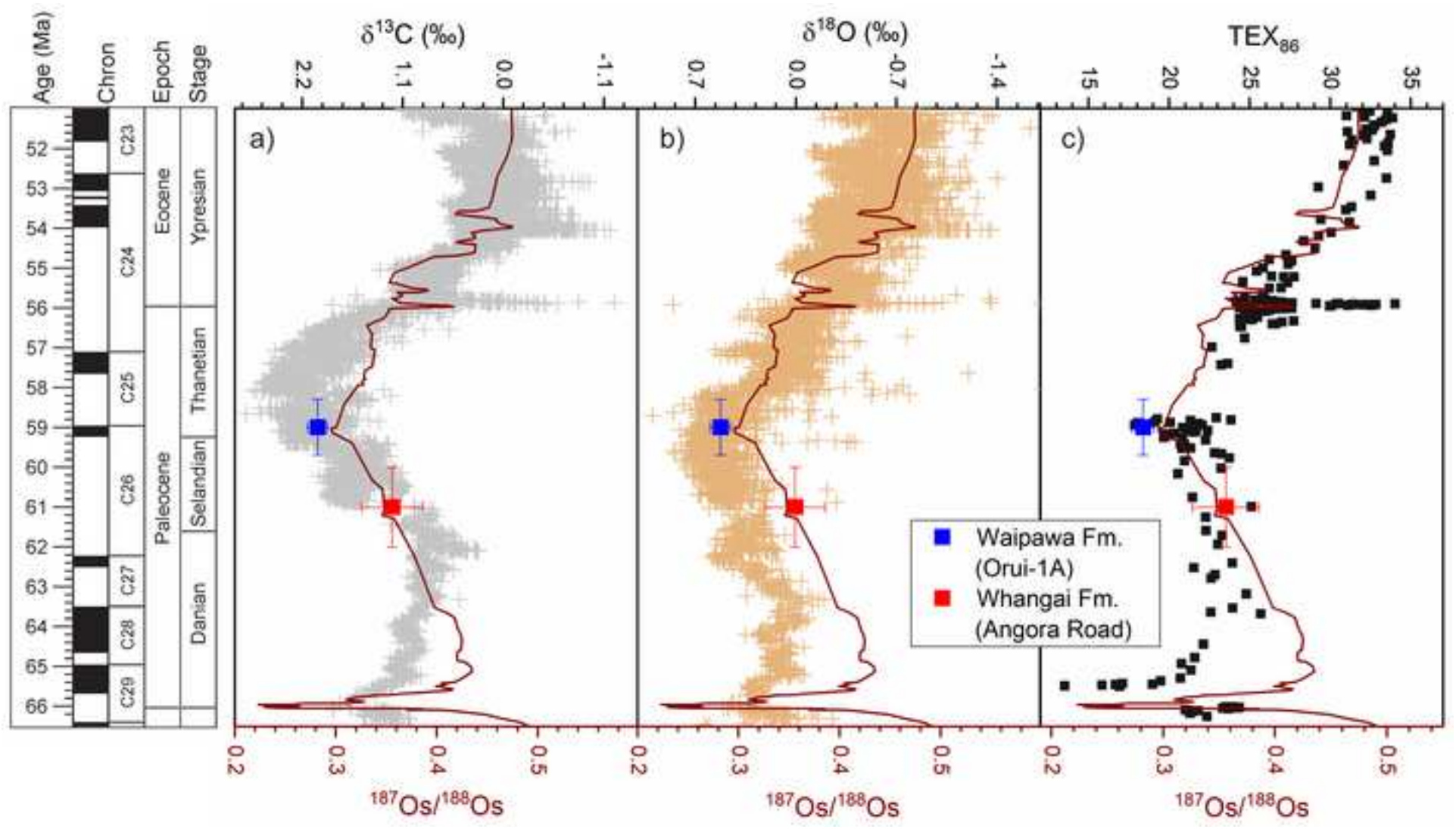


Table 1: Bulk pyrolysis and sulphur data for the Waipawa and Whangai formation samples.

Sample ID	*Height/depth (m)	TOC (wt.%)	T _{max} (°C)	S1	S2	HI (mg HC/ g TOC)	OI (mg CO ₂ / g TOC)	S _{tot}	S _{sul}	S _{pyr}	S _{org}	S _{sul} /S _{tot}	S _{pyr} /S _{tot}	S _{org} /S _{tot}
				(mg HC/g rock)				(wt.%)						
<u>Orui-1A core – Waipawa Fm.</u>														
Orui-10b	48.4	3.4	404	0.16	8.4	247	29	1.71	0.36	0.80	0.55	0.21	0.47	0.32
Orui-10c	48.8	2.6	408	0.14	5.2	197	30	1.34	0.36	0.53	0.45	0.27	0.40	0.34
Orui-10d	49.5	2.5	401	0.15	5.2	210	33	1.56	0.38	0.62	0.56	0.24	0.40	0.36
Orui-11a	49.9	3.3	402	0.21	8.9	267	27	1.46	0.29	0.63	0.54	0.20	0.43	0.37
Orui-11b	50.2	3.2	402	0.25	7.7	243	30	1.25	0.36	0.40	0.49	0.29	0.32	0.39
Orui-11c	50.4	2.7	400	0.16	6.0	221	30	1.30	0.42	0.45	0.43	0.32	0.35	0.33
Orui-11d	50.9	3.2	401	0.19	7.7	241	31	1.37	0.36	0.54	0.47	0.26	0.39	0.34
Orui-11e	51.1	3.0	402	0.15	8.3	277	25	1.29	0.27	0.61	0.41	0.21	0.47	0.32
Orui-11f	51.6	4.2	396	0.28	13.9	333	23	1.61	0.28	0.81	0.52	0.17	0.50	0.32
<u>Taylor White section – Waipawa Fm.</u>														
TW-51	138.0	2.8	405	0.14	6.1	221	25	2.31	0.28	0.69	1.34	0.12	0.30	0.58
TW-49	135.5	3.8	405	0.13	8.5	225	27	2.02	0.64	0.82	0.56	0.32	0.41	0.28
TW-48	134.0	3.3	406	0.07	6.8	207	29	1.53	0.57	0.64	0.32	0.37	0.42	0.21
TW-47	132.5	1.7	422	0.04	2.9	164	27	1.54	0.46	0.82	0.26	0.30	0.53	0.17
TW-38	119.0	4.5	405	0.16	9.7	214	27	1.92	0.78	0.59	0.55	0.41	0.31	0.29
TW-29	105.5	4.0	410	0.11	7.4	186	68	1.21	0.27	0.60	0.34	0.22	0.50	0.28
TW-25	99.5	2.4	403	0.10	4.0	167	27	1.38	0.43	0.62	0.33	0.31	0.45	0.24
TW-17	87.5	3.2	420	0.17	4.8	151	131	0.28	0.10	0.09	0.09	0.36	0.32	0.32
<u>Blacks Quarry – Waipawa Fm.</u>														
BQ02	–	9.7	419	3.35	36.3	375	5	2.70	0.84	1.44	0.43	0.31	0.53	0.16
<u>Angora Road – Whangai Fm.</u>														
MT3.19	34.6	1.1	428	0.01	1.4	127	32	0.80	0.09	0.65	0.06	0.11	0.81	0.08
MT3.18	29.0	0.9	424	0.02	2.1	232	29	0.79	0.07	0.71	0.01	0.09	0.90	0.01
MT3.17	25.4	0.8	425	0.01	1.9	219	31	0.85	0.03	0.82	0.00	0.04	0.96	0.00
MT3.16	21.8	0.9	428	0.01	1.0	112	31	0.72	0.03	0.68	0.01	0.04	0.94	0.01
MT3.15	17.8	0.9	424	0.01	1.6	181	30	0.81	0.07	0.74	0.00	0.09	0.91	0.00

* Stratigraphic height for outcrop samples and drill-hole depth for the core samples.

Table 2

[Click here to download Table: Table 2 - Re-Os abundance and isotope data.doc](#)

Table 2: Re and Os concentrations and isotope data for the Waipawa and Whangai formation samples.

Sample ID	*Height/depth (m)	Re (ppb)	±	Os (ppt)	±	¹⁹² Os (ppt)	±	¹⁸⁷ Re/ ¹⁸⁸ Os	±	¹⁸⁷ Os/ ¹⁸⁸ Os	±	rho	Os _i ^a (58 Ma)	Os _i ^b (59 Ma)
<u>Orui-1A - Waipawa Fm.</u>														
Orui-10b	48.4	28.35	0.07	543.1	1.7	212.8	0.8	265.0	1.2	0.538	0.003	0.598	0.282	0.278
Orui-10c	48.8	22.51	0.06	445.1	1.4	174.7	0.7	256.4	1.2	0.527	0.003	0.600	0.279	0.275
Orui-10d	49.5	23.07	0.06	409.8	1.3	160.2	0.6	286.3	1.3	0.554	0.003	0.600	0.277	0.272
Orui-11a	49.9	29.83	0.07	486.7	1.6	189.7	0.7	312.9	1.4	0.583	0.003	0.601	0.281	0.276
Orui-11b	50.2	30.84	0.08	461.9	1.6	179.4	0.7	341.9	1.6	0.609	0.004	0.593	0.279	0.273
Orui-11c	50.4	25.11	0.06	397.9	1.3	154.9	0.6	322.5	1.5	0.592	0.003	0.601	0.280	0.275
Orui-11d	50.9	30.64	0.08	478.2	1.6	186.0	0.8	327.6	1.6	0.597	0.004	0.583	0.281	0.275
Orui-11e	51.1	26.91	0.07	425.5	1.4	165.5	0.7	323.5	1.5	0.598	0.003	0.599	0.286	0.280
Orui-11f	51.6	36.89	0.09	547.8	1.8	212.7	0.8	345.1	1.6	0.612	0.003	0.596	0.279	0.273
<u>Taylor White - Waipawa Fm.</u>														
TW-51	138.0	56.31	0.14	589.3	1.9	224.5	0.8	498.9	2.1	0.767	0.004	0.574	0.285	0.276
TW-51 (rpt)	138.0	56.26	0.14	587.2	1.9	223.2	0.8	496.7	2.0	0.764	0.004	0.571	0.284	0.276
TW-49	135.5	36.42	0.09	578.7	1.8	225.0	0.8	322.1	1.4	0.602	0.003	0.570	0.291	0.285
TW-49 (rpt)	135.5	36.35	0.09	651.1	1.9	254.9	0.9	283.7	1.2	0.545	0.003	0.564	0.271	0.266
TW-48	134.0	35.58	0.09	503.6	1.6	194.9	0.7	363.2	1.6	0.640	0.003	0.586	0.289	0.283
TW-47	132.5	31.60	0.08	400.2	1.3	153.8	0.6	408.7	1.8	0.697	0.004	0.584	0.301	0.295
TW-38	119.0	23.51	0.06	418.3	1.3	163.5	0.6	286.0	1.2	0.559	0.003	0.571	0.282	0.278
TW-29	105.5	72.92	0.18	538.7	1.6	210.7	0.7	688.4	2.9	0.551	0.003	0.570	-0.114	-0.126
TW-25	99.5	26.21	0.06	413.7	1.3	160.7	0.6	324.5	1.4	0.609	0.003	0.582	0.296	0.290
TW-17	87.5	85.86	0.21	455.4	1.4	177.3	0.6	963.2	4.0	0.588	0.003	0.571	-0.343	-0.359
<u>Blacks Quarry – Waipawa Fm.</u>														
BQ02	—	62.32	0.15	598.6	2.1	228.2	0.8	543.4	2.4	0.764	0.004	0.572	0.239	0.230
<u>Angora Road - Whangai Fm.</u>														
													(62 Ma)	
MT3.19	34.6	11.83	0.03	228.1	0.7	89.0	0.3	264.7	1.2	0.623	0.003	0.584	0.349	
MT3.18	29.0	4.95	0.01	162.9	0.5	64.1	0.3	153.7	0.7	0.502	0.003	0.599	0.343	
MT3.17	25.4	3.64	0.01	151.7	0.5	59.8	0.3	121.1	0.6	0.484	0.003	0.609	0.359	
MT3.16	21.8	7.55	0.02	153.9	0.5	59.7	0.2	251.5	1.1	0.621	0.003	0.593	0.361	
MT3.15	17.8	5.02	0.01	141.8	0.5	55.4	0.2	180.3	0.8	0.555	0.003	0.597	0.369	

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

rpt = replicate analysis on sample splits of the same sample powder

*Stratigraphic height for outcrop samples and drill-hole depth for the core samples

^aInitial $^{187}\text{Os}/^{188}\text{Os}$ values calculated at 58 Ma for the Waipawa Formation and 62 Ma for the Whangai Formation using the ^{187}Re decay constant of $1.666 \times 10^{-11} \text{ a}^{-1}$ (Smoliar et al., 1996)

^bInitial $^{187}\text{Os}/^{188}\text{Os}$ values calculated at 59 Ma for the Waipawa Formation

Supplementary online material

[Click here to download Background dataset for online publication only: Supplementary information.doc](#)

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: