

1 Terrestrial methane cycle perturbations during the onset of the  
2 Paleocene–Eocene Thermal Maximum

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24 **ABSTRACT**

25 Terrestrial methane (CH<sub>4</sub>) emissions could have increased during the Paleocene–Eocene Thermal  
26 Maximum (~ 56 million years ago; Ma) and promoted additional warming, especially in the high  
27 latitudes. Although there is evidence for increased CH<sub>4</sub> cycling in a single Northern Hemisphere  
28 site, whether enhanced methane cycling was globally widespread is unknown as there have been  
29 no subsequent investigations. The mechanism of CH<sub>4</sub> release is also unknown because a direct  
30 comparison between temperature and CH<sub>4</sub> cycling has so far not been possible. Here we use  
31 biomarkers to reconstruct temperature change and CH<sub>4</sub> cycling in a new PETM-aged succession  
32 in New Zealand. Our results indicate that the stable carbon isotopic composition ( $\delta^{13}\text{C}$ ) of bacterial  
33 hopanoids decreased to very low values (-60 ‰) during the onset of the PETM, indicating  
34 enhanced consumption of CH<sub>4</sub>. These values are much lower than found in modern wetlands and  
35 suggest a major perturbation of the CH<sub>4</sub> cycle during the onset of the PETM. Low hopanoid  $\delta^{13}\text{C}$   
36 values do not persist into the early Eocene, despite evidence for elevated temperatures. This  
37 indicates that the terrestrial CH<sub>4</sub> cycle operates differently during transient compared to gradual  
38 warming events. Enhanced CH<sub>4</sub> cycling during the PETM may help to resolve the temperature  
39 data-model mismatch in the high-latitudes and could yield higher estimates of Earth system  
40 sensitivity than expected from CO<sub>2</sub> alone.

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47 **INTRODUCTION**

48 The Paleocene-Eocene Thermal Maximum (PETM; ~56 Ma) is the most severe carbon cycle  
49 perturbation event of the Cenozoic. It is associated with ~5 °C of global warming (Dunkley Jones,  
50 2013; Inglis et al., 2020) and an enhanced hydrological cycle (see Carmichael et al., 2017 and ref.  
51 therein), which are hypothesized to increase terrestrial CH<sub>4</sub> emissions (Beerling et al., 2011).  
52 Although this may have acted as an important positive feedback mechanism (Zeebe et al., 2009),  
53 there are few data to support this hypothesis.

54 The stable carbon isotopic composition ( $\delta^{13}\text{C}$ ) of hopanoids (bacterial-derived biomarkers)  
55 can be used to reconstruct CH<sub>4</sub> cycling in peats (van Winden et al., 2012; Zheng et al., 2014) and  
56 lignites (Inglis et al., 2015; Pancost et al., 2007). Hopanoids are not exclusive to methanotrophs  
57 (Talbot and Farrimond, 2007), but can be linked to methanotrophy based on their  $\delta^{13}\text{C}$  value  
58 (Freeman et al., 1990; Inglis et al., 2019b). Previous work from a single lignite deposit (Cobham,  
59 UK) revealed a dramatic decrease in hopanoid  $\delta^{13}\text{C}$  values (minima: -75 ‰) during the onset of  
60 the PETM (Pancost et al., 2007). This suggested enhanced consumption of <sup>13</sup>C-depleted CH<sub>4</sub>  
61 during the onset of the PETM, potentially due to an increase in wetland methanogenesis and  
62 perhaps associated with an overall increase in CH<sub>4</sub> emissions. However, there have been no  
63 subsequent investigations of wetland CH<sub>4</sub> cycling during the PETM, in large part due to the paucity  
64 of such deposits. Moreover, the mechanism of CH<sub>4</sub> release remains uncertain because a direct  
65 comparison with temperature was not possible in the Cobham section (Inglis et al., 2019a).

66 Here we use biomarker data to reconstruct changes in temperature (branched glycerol  
67 dialkyl glycerol tetraethers; brGDGTs) and methanotrophy (hopanoid  $\delta^{13}\text{C}$ ) from a new PETM-  
68 aged succession in Otaio River, New Zealand (~48°S paleolatitude). This novel dataset allows us

69 to explore: i) the relationship between temperature and CH<sub>4</sub> cycling and, ii) whether enhanced CH<sub>4</sub>  
70 cycling was widespread during the PETM.

71

## 72 **MATERIALS AND METHODS**

### 73 **Depositional Setting**

74 The Broken River Formation exposed in Otaio River (New Zealand; Fig. 1) consists of mixed  
75 sandstone, mudstone, and lignite facies (Fig. 2) and is overlain by the early Eocene Kauru  
76 Formation (Forsyth et al., 2001; Naafs et al., 2018; Pancost et al., 2013). The ~55m sequence  
77 sampled at Otaio River represents deposition in a low-energy, estuarine or deltaic setting with a  
78 change to marine deposition at ~41.5 m (Fig. 2). This marks the boundary between the Broken  
79 River and Kauru formations, as indicated by intense bioturbation, the presence of glauconite and  
80 abundant marine fauna (e.g. bivalves; Field and Browne, 1986; Marwick, 1960). The Broken River  
81 Formation also contains thin lignite seams (~10-50 cm thickness) which reflect a coastal wetland  
82 environment.

83 The sequence is thermally immature and characterised by high organic carbon content  
84 (~5%, but >30% in the lignites), high BIT indices (~0.6-1.0; Appendix 1), abundant terrestrial  
85 palynomorphs (Pancost et al., 2013) and abundant leaf wax biomarkers. Scattered leaf fossils also  
86 occur in mudstones from the lower part of the Broken River Formation exposure (Pancost et al.,  
87 2013). Collectively, this indicates a dominant input of terrestrial OM through the section.

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### 89 **Age Control**

90 Sediments of the Broken River Formation are late Paleocene (NZ Teurian stage) to early Eocene  
91 (NZ Waipawan–Mangaorapan stages) age (~59 to 49.3 Ma) and encompass the PETM (5.5 m to

92 ~17.5m; Fig. 2) (Naafs et al., 2018; Pancost et al., 2013). Identification of the PETM is based on:  
93 (i) a negative carbon isotope excursion (CIE) in bulk OM (Fig. 2a) and leaf wax biomarkers (Fig.  
94 2b), (ii) a change from Paleocene (New Zealand pollen zone PM3a) to earliest Eocene (pollen zone  
95 PM3b) palynofloral indicators, including the appearance of thermophilic taxa (Fig. 2; Naafs et al.,  
96 2018), (iii) a marine incursion immediately following the onset of the CIE, and (iv) the dominance  
97 of the dinoflagellate cyst genus *Apectodinium* (Pancost et al., 2013; Fig. 2) between 9.50 and  
98 11.70m depth. The occurrence of dinoflagellate cyst *Rhombodinium subtile* – previously only  
99 found in samples dated as calcareous nannoplankton Zone NP10 (Crouch et al., 2001; Crouch et  
100 al., 2020) suggests a post-PETM deposition by 17.45m depth (Fig. 2).

101

## 102 **Analytical Methods**

103 We analysed 24 samples including both lignite and shallow marine interbeds. Approximately 1-  
104 10g of sediment was extracted via Soxhlet apparatus for 24 hours using dichloromethane  
105 (DCM):methanol (MeOH) (2:1 v/v). The total lipid extract was separated over alumina into apolar  
106 and polar fractions using hexane:DCM (9:1 v/v) and DCM:MeOH (1:2 v/v), respectively. Urea  
107 adduction was performed upon the apolar fraction to separate non-adduct and adduct fractions  
108 (Pancost et al., 2008). Both fractions were analysed using a Thermo ISQ Single Quadrupole gas  
109 chromatography-mass spectrometer (GC-MS) and an Isoprime 100 GC-combustion-isotope ratio-  
110 MS system (Appendix 1). The polar fraction was dissolved in hexane/isopropanol (99:1, v/v),  
111 passed through 0.45µm PTFE filters and analysed by HPLC/APCI-MS using the methods of  
112 Hopmans et al. (2016).

113

## 114 **RESULTS**

### 115 **Carbon cycling during the PETM**

116 Bulk OM (Fig. 2a) and long-chain *n*-alkanes (Fig. 2b) exhibit a negative CIE during the onset of  
117 the PETM (ca. -2 and -3‰, respectively) and remain low throughout the early Eocene. The *n*-  
118 alkane CIE is similar to other terrestrial sites (e.g. Baczynski et al., 2019). There is no clear return  
119 to pre-PETM values, implying a hiatus between the PETM and early Eocene sediments (Fig. 2).  
120 This could be explained by low sample resolution and/or missing exposure between ~13 and 18m  
121 (Fig. 2).  $\delta^{13}\text{C}$  values were also obtained for a range of hopanoids (i.e.  $\text{C}_{30}$  hop-17(21)-ene,  $\text{C}_{29}$   $\beta\beta$   
122 hopane, and  $\text{C}_{31}$   $\alpha\beta$  hopane). During the PETM, hop-17(21)-ene  $\delta^{13}\text{C}$  values decrease from -31 to  
123 -61‰ (Fig. 2c). These values are lower than those observed in any modern peatland (-20 to -45‰;  
124 Inglis et al., 2019b).  $\text{C}_{29}$   $\beta\beta$  hopane  $\delta^{13}\text{C}$  values exhibit similar temporal trends (Fig. 2c) and  
125 decrease from -35‰ to values as low as -43‰.  $\text{C}_{31}$   $\alpha\beta$  hopane  $\delta^{13}\text{C}$  values remain relatively  
126 invariant throughout the record, ranging between -25 and -32‰ (Fig. 2c). This is consistent with  
127 modern observational evidence, which indicates that  $\text{C}_{31}$  hopanoids are less sensitive tracers for  
128 methanotrophy (Inglis et al., 2019b).

129

### 130 **Temperature change during the PETM**

131 For lignites (TOC >20%) and coastal marine interbeds (TOC <5%), we translate brGDGT  
132 distributions into mean annual air temperature (MAAT) using a Bayesian calibration model  
133 (BayMBT<sub>0</sub>; Crampton-Flood et al., 2020) (Appendix 1). During the body of the PETM, MAAT  
134 estimates from the marine interbeds increase from ~12 to 17 °C (Fig. 2e), consistent with the first  
135 occurrence of thermophilic taxa during the PETM. There is also an increase in MAAT estimates  
136 within the lignite beds from ~22 to 25°C (Fig. 2f), although only one lignite bed was recovered  
137 during the PETM. As such, the magnitude of warming (ca. 3°C) is a minimum estimate. The onset  
138 of warming in the marine interbeds occurs ~2m after the onset of the CIE. This could arise from

139 our relatively low sample resolution. Alternatively, it could arise from caveats associated with the  
140 brGDGT paleothermometer. For instance, recent work demonstrates that brGDGTs typically  
141 underestimate terrestrial temperatures within coastal marine settings (e.g. Inglis et al., 2017; Hollis  
142 et al., 2019). MAAT estimates from the marine interbeds and lignites yield different absolute  
143 values. This is attributed to changes in brGDGT provenance, as documented elsewhere (Inglis et  
144 al., 2017). Despite this, MAAT estimates from the lignites and marine interbeds yield a similar  
145 magnitude of warming (~3 to 5 °C) during the PETM (Fig. 2e-f). Following the PETM, MAAT  
146 estimates remain relatively high and stable (Fig. 2e-f).

147

## 148 **DISCUSSION**

### 149 **Enhanced CH<sub>4</sub> cycling during the PETM at Otaio River**

150 The  $\Delta^{13}\text{C}_{\text{hop-alk}}$  index ( $= \delta^{13}\text{C}_{\text{hopanoid}} - \delta^{13}\text{C}_{\text{alkane}}$ ; following Inglis et al. 2019b) has been developed  
151 to assess past variations in the CH<sub>4</sub> cycle. In modern wetlands,  $\Delta^{13}\text{C}_{\text{hop-alk}}$  values range between  
152 +10 and -10‰. Here we calculate  $\Delta^{13}\text{C}_{\text{hop-alk}}$  values using the C<sub>29</sub> *n*-alkane, but similar results are  
153 obtained with other long-chain *n*-alkanes. Prior to the PETM, values in Otaio River (Fig. 2d) are  
154 similar to those observed in modern wetlands (Inglis et al., 2019b) and indicate a bacterial  
155 community largely consuming <sup>13</sup>C-enriched plant biomass. However,  $\Delta^{13}\text{C}_{\text{hop-alk}}$  values (-15 to -  
156 30‰; Fig. 2d) during the onset of the PETM are far below the modern range (+10 to -10‰).  
157 Enhanced consumption of <sup>13</sup>C-depleted substrates (e.g. lipids, lignin) by heterotrophic bacteria  
158 could yield lower  $\Delta^{13}\text{C}_{\text{hop-alk}}$  values during the onset of the PETM (Hobbie and Werner, 2004).  
159 However, in modern settings, the  $\delta^{13}\text{C}$  value of the aforementioned substrates is rarely < -40 ‰  
160 (Inglis et al., 2019). This implies that very low  $\Delta^{13}\text{C}_{\text{hop-alk}}$  can only be explained by invoking the  
161 consumption of lighter substrates (i.e. CH<sub>4</sub>). Within the body of the PETM (~9 to 17.5m; Fig. 2d),

162  $\Delta^{13}\text{C}_{\text{hop-alk}}$  values gradually return to pre-PETM values. These values persist into the early Eocene  
163 (~17.5m to 36m; Fig. 2d), despite persistently high MAATs and indicate that perturbations to the  
164  $\text{CH}_4$  cycle were limited to the onset of the PETM, similar to that observed at Cobham (Pancost et  
165 al., 2007).

166

### 167 **Decoupling between physical climate and the $\text{CH}_4$ cycle during the PETM**

168 Earth system model (ESM) simulations indicate coupling of physical climate processes (e.g.  
169 temperature, hydrology) under increasing  $\text{CO}_2$  (e.g. Carmichael et al., 2016). However,  
170 perturbations in physical climate can trigger a cascade of biogeochemical feedbacks (e.g. enhanced  
171 runoff can increase the delivery of freshwater, nutrients and terrigenous materials to continental  
172 shelves with associated impacts on marine biogeochemistry; Carmichael et al., 2017). In our study,  
173 decoupling between physical climate (brGDGT-based MAAT) and the  $\text{CH}_4$  cycle ( $\delta^{13}\text{C}_{\text{hopanoid}}$ )  
174 could arise from a range of factors. An increase in  $\text{CO}_2$  could stimulate  $\text{CH}_4$  emissions by  
175 increasing primary productivity (Beerling et al. 2011) and/or modifying substrate supply for  
176 methanogenesis (Yvon-Durocher et al., 2014). Although the PETM is characterized by higher  $\text{CO}_2$   
177 estimates compared to the EECO and late Paleocene (Hollis et al, 2019),  $\text{CO}_2$  estimates from all  
178 three intervals remain poorly constrained. Alternatively, hopanoid  $\delta^{13}\text{C}$  values and temperature  
179 could be related (e.g. Pancost et al., 2007), with higher temperatures leading to higher rates of  
180 methanogenesis (Yvon-Durocher et al., 2014) and therefore a larger methanotroph community and  
181 lower hopanoid  $\delta^{13}\text{C}$  values. High temperatures ( $>20^\circ\text{C}$ ; Fig. 2e-f) and thermophilic taxa persist  
182 throughout the PETM and early Eocene. However, depleted hopanoid  $\delta^{13}\text{C}$  values are limited to  
183 the PETM onset (Fig. 2c-d). The onset of warming (Fig. 2e-f) also appears to occur after the initial  
184 decline in hopanoid  $\delta^{13}\text{C}$ . Collectively, this indicates that temperature is not the primary control

185 regulating hopanoid  $\delta^{13}\text{C}$  values at Otaio River. This is consistent with published studies that failed  
186 to detect low hopanoid  $\delta^{13}\text{C}$  values in Paleocene or early Eocene lignites, deposited under  
187 greenhouse conditions (Diefendorf et al., 2015; Inglis et al., 2015; Fig. 3). Wetter and/or drier  
188 conditions can also be associated with low hopanoid  $\delta^{13}\text{C}$  values (Zheng et al., 2014). Although  
189 the response of the hydrological cycle at Otaio River remains uncertain, nearby records indicate  
190 an unstable hydrological cycle characterised by wet/dry cycles (Handley et al., 2011; Pole, 2010)  
191 which could also have perturbed the wetland  $\text{CH}_4$  cycle. Regardless of the primary forcing, the  
192 striking observation from both Cobham and Otaio River is that the  $\text{CH}_4$  cycle response was  
193 dramatic but transient.

194

#### 195 **Significance of enhanced $\text{CH}_4$ cycling in warm climates**

196 ESMs that include climate-chemistry feedbacks indicate that enhanced  $\text{CH}_4$  emissions can  
197 contribute ~20% of additional warming for a PETM-type event (i.e. a doubling of  $\text{CO}_2$ ; Beerling  
198 et al., 2011). Due to polar amplification, this may be even greater in the high-latitudes (Beerling  
199 et al., 2011) and can reduce the high latitude temperature data-model mismatch (Hollis et al.,  
200 2019). The inclusion of climate-chemistry feedbacks in an Eocene ESM (Beerling et al., 2011)  
201 also leads to higher estimates of Earth system sensitivity ( $4.0^\circ\text{C}$ ) (i.e. the temperature rise resulting  
202 from a doubling in  $\text{CO}_2$  incorporating ‘slow’ and ‘fast’ feedbacks) than expected from  $\text{CO}_2$  forcing  
203 alone ( $3.2^\circ\text{C}$ ; Beerling et al., 2011). ESMs that do not account for  $\text{CH}_4$  emissions may therefore  
204 underestimate Earth system sensitivity during the geological record.

205 We find no evidence for wetland  $\text{CH}_4$  cycle perturbations during gradual warming events  
206 (e.g. the early Eocene), implying that enhanced  $\text{CH}_4$  emissions could be driven by the wider  
207 geographical distribution of wetland environments (Beerling et al., 2011). This is consistent with

208 a two- to threefold increase in model-predicted wetland extent during the early Eocene (Wilton et  
209 al., 2019). Instead, perturbations in the terrestrial CH<sub>4</sub> cycle (Pancost et al., 2007; *this study*) appear  
210 to occur exclusively during climate transitions (e.g. the onset of the PETM). After the initial  
211 perturbation, the Earth system appears to stabilize (i.e. the body of the PETM), resulting in a  
212 climate regime that no longer favors CH<sub>4</sub> cycling. This demonstrates that the response of the CH<sub>4</sub>  
213 cycle is different for transient vs gradual warming events, and highlights the limitations of ESMs  
214 that simulate ‘equilibrium’ or steady state conditions (e.g. Beerling et al., 2011; Carmichael et al.,  
215 2016; Inglis et al., 2019a).

216

## 217 **CONCLUSIONS**

218 Here we reconstruct temperature change and CH<sub>4</sub> cycling in a new PETM-aged succession in Otaio  
219 River, New Zealand. Hopanoid  $\delta^{13}\text{C}$  values during the onset of the PETM are much lower than  
220 observed today and indicate enhanced consumption of <sup>13</sup>C-depleted CH<sub>4</sub>. These results indicate  
221 that a global perturbation of the CH<sub>4</sub> cycle occurred at the onset of the PETM. Low hopanoid  $\delta^{13}\text{C}$   
222 values do not persist into the early Eocene despite continuous high MAAT, indicating partial  
223 decoupling between physical climate and the CH<sub>4</sub> cycle. Enhanced CH<sub>4</sub> cycling during the PETM  
224 could help to resolve the temperature data-model mismatch in the high-latitudes and could yield  
225 higher estimates of Earth system sensitivity than expected from CO<sub>2</sub> alone. The dramatic but  
226 transient responses observed here could also foreshadow changes that the CH<sub>4</sub> cycle will  
227 experience in the future due to anthropogenic emissions.

228

## 229 **ACKNOWLEDGMENTS**

230 We thank three anonymous reviewers for constructive and helpful feedback. This research is  
231 funded via the ERC (340923) and NERC (NE\J008591\1). RDP acknowledges a Royal Society  
232 Wolfson Research Merit Award. GNI acknowledges a Royal Society Dorothy Hodgkin Fellowship  
233 (DHF\R1\191178). BDAN acknowledges a Royal Society Tata University Research Fellowship.  
234 GNI thanks H. Whelton and NEIF for analytical support and E. Dearing Crampton-Flood for  
235 generating BayMBT values. EMK, JIR, EMC and DPS were supported by the ‘Global Change  
236 Through Time’ programme at GNS Science.

237

238 **Figure 1:** Map of New Zealand showing the location of Otaio River (star).

239

240 **Figure 2:** CH<sub>4</sub> cycle perturbations at Otaio River during the PETM. 2a) bulk OM  $\delta^{13}\text{C}$  values, 2b)  
241 C<sub>29</sub> (black) and C<sub>31</sub> (dark grey) *n*-alkane  $\delta^{13}\text{C}$  values, 2c) C<sub>30</sub> hop-17(21)-ene (black square), C<sub>29</sub>  
242  $\beta\beta$  hopane (dark grey diamond) and C<sub>31</sub>  $\alpha\beta$  hopane (light grey triangle)  $\delta^{13}\text{C}$  values, 2d) C<sub>30</sub> hop-  
243 17(21)-ene (black square), C<sub>29</sub>  $\beta\beta$  hopane (dark grey diamond) and C<sub>31</sub>  $\alpha\beta$  hopane (light grey  
244 triangle)  $\Delta^{13}\text{C}_{\text{hop-alk}}$  values, 2e) MAAT estimates in marine interbeds, and 2f) MAAT estimates in  
245 lignite seams. The shaded region in (2e) and (2f) indicates the  $1\sigma$  error. Key biostratigraphic  
246 markers also shown (Pancost et al., 2013; Naafs et al., 2018).

247

248 **Figure 3:**  $\Delta^{13}\text{C}_{\text{hop-alk}}$  values in a) mid-to-late Paleocene (63-56 Ma; Diefendorf et al., 2015; this  
249 paper), b) PETM (56 Ma; Pancost et al., 2007; this paper) and c) early Eocene (56-48 Ma;  
250 Diefendorf et al., 2015; Inglis et al., 2015; this paper) lignite and siliciclastic sediments.

251

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371 <sup>1</sup>GSA Data Repository item xxxx (i.e. bulk and compound-specific isotope data, biomarker  
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373 [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

374

Figure 1

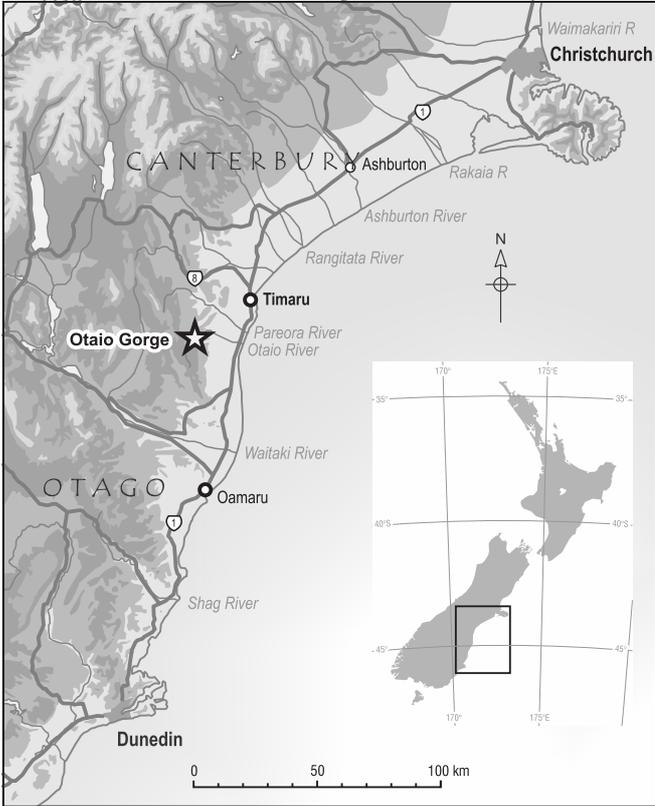


Figure 2

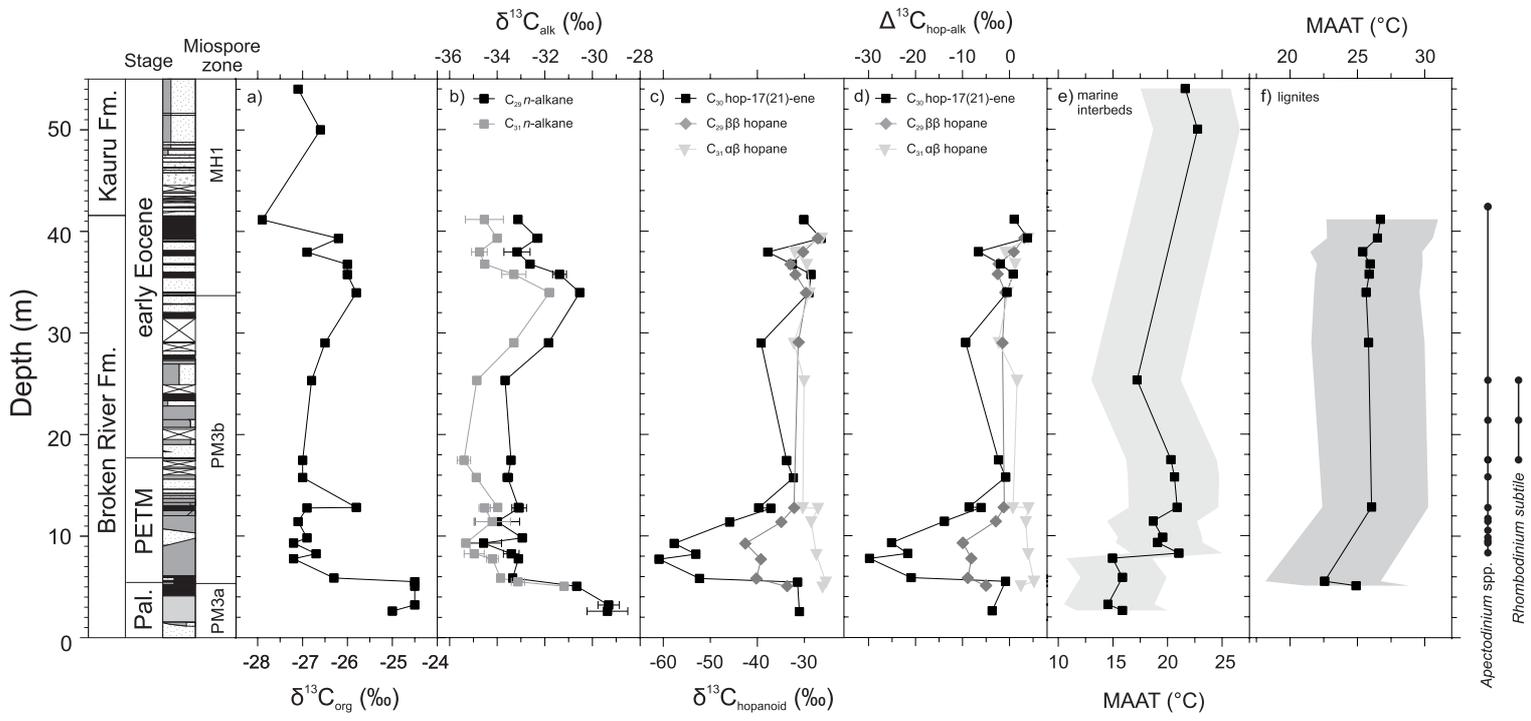


Figure 3

