

1 *Palaeogeography, Palaeoclimatology, Palaeoecology*

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3 **Vascular plant biomarker distributions and stable carbon isotopic**  
4 **signatures from the Middle and Upper Jurassic (Callovian–Kimmeridgian)**  
5 **strata of Staffin Bay, Isle of Skye, northwest Scotland**

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25 **Abstract**

26 The molecular and stable carbon isotopic composition of higher plant biomarkers was  
27 investigated in Middle to Upper Jurassic strata of the Isle of Skye, northwest Scotland.  
28 Aromatic hydrocarbons diagnostic of vascular plants were detected in each of nineteen  
29 sedimentary rock samples from the Early Callovian to Early Kimmeridgian interval, a  
30 succession rich in fossil fauna including ammonites that define its constituent chronozones.  
31 The higher plant parameter (HPP) and higher plant fingerprint (HPF) calculated from the  
32 relative abundance of retene, cadalene and 6-isopropyl-1-isoheptyl-2-methylnaphthalene (ip-  
33 iHMN) exhibit several large fluctuations throughout the Skye succession studied. These  
34 molecular profiles contrast with both (1) the more uniform profiles previously observed in  
35 Jurassic successions, putatively of the same age, from other palaeogeographical settings,  
36 including the Carnarvon Basin, Western Australia and (2) the steady rise in global sea level  
37 during this interval. This suggests that the HPF profiles of Jurassic marine successions may  
38 not be reliable indicators of global climate change. Our results indicate that other factors such  
39 as local tectonism, resulting in changes to the relief and landscape of the hinterland, likely  
40 influenced the palaeovegetation and the mode of transport of its detritus into adjacent marine  
41 depocentres. However, the Skye succession showed similar  $\delta^{13}\text{C}$  profiles of total organic  
42 carbon (TOC; comprising mainly fossil wood), the vascular plant biomarker retene and a  
43 predominant phytoplanktonic derived biomarker (phytane). The apparent isotopic  
44 relationship between terrigenous and marine-derived biomarkers supports a strong coupling  
45 of the atmosphere and ocean. The maximum isotopic excursion occurs in the *Cardioceras*  
46 *cordatum* ammonite biozone of the Early to Middle Oxfordian, which may be indicative of  
47 changes in atmospheric and oceanic levels of  $\text{CO}_2$ .

48

49 **Keywords:** Jurassic, bitumen, GC-MS, stable carbon isotopes, biomarkers, higher plant  
50 parameters, global sea level, stable isotope stratigraphy, palynology, Scotland

51

## 52 **1. Introduction**

53 The sedimentary occurrence of bicyclic and tricyclic diterpenoid biomarkers with established  
54 plant source relationships (e.g. Thomas, 1969; Simoneit, 1977; 1985; Wakeham et al., 1980;  
55 Alexander et al., 1987; 1988; 1992; Ellis et al., 1996) are useful for palaeovegetation and  
56 palaeoclimate reconstructions (Jiang et al., 1998; van Aarssen et al., 2000; Grice et al., 2001;  
57 2005; 2009; Fleck et al., 2002; Hautevelle et al., 2006; Fenton et al., 2007; Dutta et al., 2009;  
58 Kuhn et al., 2010; Nabbefeld et al., 2010a). van Aarssen et al. (2000) proposed the higher  
59 plant parameter (HPP) and higher plant fingerprint (HPF) in which the relative abundances of  
60 retene, cadalene and 6-isopropyl-1-isoheptyl-2-methylnaphthalene (ip-iHMN) are used as  
61 proxies for the main types of vascular plant input to Jurassic sediments.

62 Retene has been attributed to all conifer families except *Taxaceae* (see Otto and Simoneit,  
63 2001; Otto and Wilde, 2001; Lu et al., 2013), although it can also be derived from algal  
64 sources (Wen et al., 2000) and plant combustion (Kuhn et al., 2010). It may also derive from  
65 the degradation of abietic acid, but this pathway also typically produces other compounds  
66 such as nor-abietane(s) that were not detected in our samples. Cadalene is a biomarker  
67 commonly detected in Quaternary sediments (e.g. Wang and Simoneit, 1990; Alexander et al.,  
68 1994; van Aarssen et al., 1996), and considered to be derived predominantly from cadinenes  
69 and cadinols, which occur ubiquitously in the resins of vascular plants (Simoneit, 1985).  
70 Indeed, cadalene has also been detected in fossil resins (Grantham and Douglas, 1980; van  
71 Aarssen et al., 1990) and essential oils (Simonsen and Barton, 1961). However, bryophytes  
72 and fungi are other potential sources of cadalene (Bordoloi et al., 1989). Although ip-iHMN  
73 is believed to be of vascular plant origin (Ellis et al., 1996), its actual biological precursor has

74 not yet been fully established. All three of these vascular plant biomarkers are often resistant  
75 to post-depositional alteration (i.e. diagenesis and catagenesis), meaning that their  
76 distributions in ancient sediments may therefore provide valuable information for use in  
77 reconstructions of palaeovegetation and palaeoclimate.

78 van Aarssen et al. (2000) reported a close correlation between the varying abundances of  
79 these key plant biomarkers with previously defined palaeoclimate fluctuations and second  
80 order cycles in the global sea level. The HPP profile of four sequences covering the entire  
81 Jurassic Period, since there is no complete sequence, reflected three major 10 Ma cycles that  
82 the authors considered to be temporally similar to four climatic cycles identified in the  
83 Jurassic succession of northwest Australia (Parrish et al., 1996). The variations in HPP were  
84 attributed to changes in the relative abundance of the major plant sources. The similar nature  
85 of these molecular records obtained from petroleum exploration wells up to 1,500 km apart  
86 suggested a regional uniformity of palaeovegetation over geographically extensive regions,  
87 while the consistent deviations in biomarker distributions indicated widespread impacts on  
88 palaeovegetation. For instance, the increase in retene through the Oxfordian of all successions  
89 was attributed to a marked expansion of conifer forests throughout this interval (van Aarssen  
90 et al. 2000). These Jurassic HPP profiles showed second order (> 10,000 yr) cycles that  
91 correlate closely with global sea level (Haq et al., 1987) and, more generally, four distinct  
92 climatic periods (Parrish et al., 1996), all indicative of global forcing by rising atmospheric  
93 CO<sub>2</sub> concentrations and temperatures.

94 A similar palaeo-climatic scenario was also suggested by Hautevelle et al. (2006) when  
95 attributing an increasing retene/cadalene ratio in the Callovian–Oxfordian succession of the  
96 Paris Basin to a progressively higher proportion of *Pinaceae* conifers in response to  
97 aridification of the climate. The abundance of retene in these European sediments was  
98 observed to increase in a similar fashion to the rising levels of this biomarker through the

99 Oxfordian of Western Australia (van Aarssen et al., 2000), lending further support to the  
100 hypothesis that sedimentary distributions of biomarkers representative of different plant types  
101 may reflect the response of terrestrial flora to global climate change, such as a worldwide  
102 increase in aridity during the latest Early Oxfordian (Hautevelle et al., 2006).

103 In contrast, Fleck et al. (2002) found that the HPP values of Cretaceous sedimentary rocks  
104 from southeast France do not correlate with the transgressive/regressive sea level cycle that  
105 occurred during this interval. This observation suggests that global climate cannot be the sole  
106 influence on sea level, as any alteration to the climate would also affect the composition of  
107 the palaeovegetation. Other factors such as local uplift and subsidence may have led to  
108 increased sedimentation rates (Fleck et al., 2002), and therefore higher deposition of biomass  
109 from specific floras. Furthermore, in a study of Triassic-Jurassic fluvio-deltaic sediments  
110 from NW Australia, Grice et al. (2005) reported higher abundances of retene in facies,  
111 reflecting a strong influence of local depositional conditions on the concentration of this  
112 biomarker.

113 Here we investigate the combined use of molecular and stable carbon isotopic composition of  
114 vascular plant biomarkers as indicators of environmental and climate change in the Staffin  
115 Bay and Staffin Shale formations of Skye, northwest Scotland. We examine to what extent  
116 Jurassic vascular plant biomarkers reflect responses to global events such as climate change  
117 and related changes in sea level or increasing aridity. Specifically, stable isotopic dynamics of  
118 vascular plant biomarkers prevalent in Jurassic sedimentary rocks may provide valuable  
119 evidence of atmospheric CO<sub>2</sub> dynamics and regional or global climatic events.  $\delta^{13}\text{C}$  values of  
120 fossilised organic matter (OM) are particularly sensitive to palaeodepositional factors, most  
121 notably the concentration of CO<sub>2</sub> (Hayes et al., 1989; Andrusевич et al., 1998; Nunn et al.,  
122 2009). Furthermore, the  $\delta^{13}\text{C}$  signature of individual biomarkers can provide specific  
123 information such as the identity of their precursor biota, the mode and biosynthetic pathway

124 of CO<sub>2</sub> fixation, and changes in atmospheric and oceanic levels of CO<sub>2</sub>. However, we also  
125 consider the impact of local factors such as heterogenic landscapes, water availability as well  
126 as site-specific transport and accumulation characteristics that may largely affect vascular  
127 plant distributions and thus complicate the interpretation of the palaeoenvironmental and  
128 palaeoclimatic significance of their biomarkers.

129

## 130 **2. Materials and methods**

131

### 132 *2.1. Geological setting*

133 The Staffin Bay and Staffin Shale formations, of Trotternish, northeast Skye, northwest  
134 Scotland (Figs. 1, 2) represent an important Middle–Upper Jurassic reference section, with  
135 abundant ammonite faunas (Sykes, 1975; Morton and Hudson 1995; Cox and Sumblar, 2002)  
136 that define the Boreal Middle and Upper Oxfordian ammonite zones and subzones (Fig. 3,  
137 Table 1) established by Sykes and Callomon (1979). The Staffin Shale Formation is of  
138 international significance because it includes the reference sections for the Oxfordian  
139 *Cardioceras cordatum* to *Amoeboceras rosenkrantzi* ammonite biozones (Fig. 3, Table 1;  
140 Sykes and Callomon, 1979), and is one of the most complete Oxfordian successions in  
141 Europe (Nunn et al., 2009). The section was also proposed as a Global Stratotype Section and  
142 Point (GSSP) for the Oxfordian/Kimmeridgian boundary (Wierzbowski et al., 2006). The  
143 mudstone-dominated succession has yielded abundant palynofloras, rich in both marine and  
144 terrestrially-derived palynomorph groups (Riding, 1992; Riding and Thomas, 1997).  
145 Nineteen samples were selected for detailed palynological and geochemical analysis in order  
146 to investigate the types and rates of organic input during the Middle and Late Jurassic.  
147 Sample localities and stratigraphical data are illustrated in Figs. 1 and 3.

148 The Callovian to Kimmeridgian succession studied was deposited in the Sea of the Hebrides  
149 Basin (Fig. 2). This depocentre is separated by the Central Skye Palaeo High from the smaller  
150 Inner Hebrides Basin to the southeast (Binns et al., 1975). The Sea of the Hebrides and the  
151 Inner Hebrides basins are collectively termed the Hebrides Basin (Morton et al., 1987). The  
152 Hebrides Basin is a northeast-southwest trending half graben 65 to 90 km wide, and is located  
153 between the Outer Hebrides and Scottish landmasses (Fig. 2). Throughout most of the  
154 Jurassic, basin subsidence *via* the Minch Fault was relatively gentle due to the presence of  
155 laterally persistent strata. The Callovian to Kimmeridgian Staffin Bay and Staffin Shale  
156 formations represent virtually continuous open marine sedimentation. This mudstone-  
157 dominated succession is highly fossiliferous and rich in marine biotas with wide geographical  
158 extents (Fig. 3, Table 1). The ammonite faunas in particular are of international significance  
159 for correlation and are a standard for the Boreal province (Turner, 1966; Wright, 1973; 1989;  
160 Sykes and Callomon, 1979; Riding and Thomas, 1997). These rich molluscan assemblages  
161 provide a critical link between Greenland in the north to the Alps in the south.  
162 In a wider palaeogeographical context, the Hebrides Basin is located within the Viking  
163 Corridor. This is a relatively wide intra-Laurasian seaway which linked the Boreal Ocean in  
164 the north with the western Tethys in the south (Fig. 2). The Viking Corridor represented a  
165 relatively extensive north-south marine connection north of western Gondwana. This means  
166 that the geochemistry of the Callovian to Kimmeridgian succession of the Hebrides Basin is  
167 of global significance.

168

## 169 2.2. Palynology

170 The results from palynological analyses of the 19 samples (Table 1) are adapted from a  
171 database which was used during the preparation of Riding and Thomas (1997). The samples

172 were stored in annealed glass containers in a dark cold room at Geoscience Australia,  
173 Canberra, ACT, Australia.

174

### 175 *2.3. Total Organic Carbon (TOC) and Rock-Eval determinations*

176 Total organic carbon (TOC) content,  $T_{\max}$  value and hydrogen index (HI) of each sample  
177 (Table A.1) were measured by Rock-Eval pyrolysis (RockEval 6 Turbo; Vinci Technologies).

178

### 179 *2.4. Extraction and fractionation*

180 Between 10 and 20 g of crushed, dry rock was extracted with a dichloromethane (DCM):  
181 methanol (MeOH) mixture (4:1) using a Dionex ASE 200 Accelerated Solvent Extractor  
182 (Dionex Corporation, Sunnyvale, CA, USA). An aliquot of the extractable organic matter (5–  
183 10 mg) was then separated into aliphatic, aromatic and polar fractions by column  
184 chromatography on an activated silica gel packed Pasteur pipette (4 cm) with successive  
185 elutions of *n*-hexane (1.8 ml), *n*-hexane: DCM (8:2, 2 mL) and methanol: DCM (1:1, 2 mL),  
186 respectively. Aliphatic and aromatic hydrocarbon fractions were analysed by GC-MS.  
187 For compound specific isotope analysis (CSIA), aromatic hydrocarbon fractions (containing  
188 the vascular plant biomarkers of specific interest) were separated by alumina thin layer  
189 chromatography (TLC) into monoaromatic, diaromatic, triaromatic and tetraaromatic  
190 hydrocarbon fractions as described by Ellis et al. (1994). Aliquots of aliphatic hydrocarbon  
191 fractions were separated by 5 Å molecular sieving as outlined in Grice et al. (2008) using  
192 hydrofluoric acid to digest the 5 Å sieve.

193

### 194 *2.5. Gas chromatography-mass spectrometry (GC-MS)*

195 The saturate and aromatic hydrocarbon fractions were analysed using a HP 5890 Series II gas  
196 chromatograph (GC) interfaced to a 5971A mass selective detector (MSD). A 60 m x 0.25



197 mm inner diameter column containing a DB-1 phase with a 0.25  $\mu\text{m}$  film thickness (J&W  
198 Scientific) was used. The GC oven was programmed from 40–300  $^{\circ}\text{C}$  at 3  $^{\circ}\text{C}/\text{min}$  and held  
199 isothermally at 300  $^{\circ}\text{C}$  for 30 min. Samples were separately analysed in the full scan and  
200 single ion recording (SIR;  $m/z$  128, 142, 154, 156, 168, 170, 178, 182, 183, 184, 192, 197,  
201 198, 206, 219, 234, 237, 248, 251, 252, 266 and 268) modes.

202 The saturate fractions were additionally analysed for trace terpenoid biomarkers by SIR ( $m/z$   
203 217, 191, 123, 149, 151, and 205) using an Agilent 6890GC/5973-MSD. A HP-5 fused silica  
204 capillary column (50 m x 0.2 mm x 0.11  $\mu\text{m}$ ) was used with a helium carrier and the GC oven  
205 was temperature programmed to increase at 2  $^{\circ}\text{C}/\text{min}$  from an initial 150  $^{\circ}\text{C}$  to final 300  $^{\circ}\text{C}$   
206 (held for 12 min). Mass spectral parameters included an ionisation energy of 70 eV and a  
207 source temperature of 250  $^{\circ}\text{C}$ . The selected ion data were used to directly compare key  
208 biomarker parameters to those previously obtained with this methodology from archived oils  
209 (AGSO and GeoMark Research Inc., 1996; Summons et al., 1998).

210

## 211 *2.6. Stable isotope analysis*

212 Compound specific isotope analyses (CSIA) were performed on a Micromass IsoPrime  
213 isotope ratio monitoring (irm)-GCMS mass spectrometer. All samples were dissolved in  
214 hexane and analysed using a HP 6890 gas chromatograph equipped with an autosampler and  
215 a split/splitless injector and helium was used as a carrier gas at a constant 1ml/min flow rate.  
216 A 60 m x 0.25 mm i.d. column containing a DB-1 phase (0.25  $\mu\text{m}$  film thickness) was used  
217 and the sample was injected using pulsed splitless mode (injection holding for 30 seconds at  
218 15 psi above the head pressure of the column and the purge time of 35 seconds). The GC  
219 oven was programmed from 40  $^{\circ}\text{C}$  (held for 2 min) to 300  $^{\circ}\text{C}$  (held for 30 min) at 3  $^{\circ}\text{C}/\text{min}$   
220 and after GC separation products were combusted (CuO quartz packed tube, 850  $^{\circ}\text{C}$ ) to  
221 produce  $\text{CO}_2$ . Their isotopic composition was then measured by integration of the  $m/z$  44, 45

222 and 46 ion currents of product peaks. The analyte compositions are reported relative to CO<sub>2</sub>  
223 of known <sup>13</sup>C content which was pulsed into the mass spectrometer. Average values and  
224 standard deviations of at least two analytical runs were reported in the delta notation (δ<sup>13</sup>C)  
225 relative to the VPDB carbonate standard.

226 Decarbonated samples for δ<sup>13</sup>C analysis of bulk organic matter (δ<sup>13</sup>C<sub>TOC</sub>) were measured  
227 using a Micromass IsoPrime isotope ratio mass spectrometer interfaced to a EuroVector  
228 EuroEA3000 elemental analyser following the method described by Grice et al. (2007).

229

### 230 *2.7. Definition of higher plant parameter and higher plant fingerprint*

231 The higher plant parameter (HPP) was defined by van Aarssen et al. (2000) as the abundance  
232 of retene relative to the sum of retene and cadalene as measured from the *m/z* 219 and 183  
233 GC-MS chromatograms. The same authors defined the higher plant fingerprint (HPF) as the  
234 relative abundance of retene, cadalene and *ip-iHMN*, calculated from their respective peak  
235 areas in the *m/z* 219, 183 and 197 mass chromatograms and expressed as a percentage of their  
236 sum.

237

## 238 **3. Results and discussion**

### 239 *3.1. Biostratigraphy and palynofloras*

240 The mudstone-dominated Skye succession is rich in marine dinoflagellate cysts and  
241 terrestrially-derived pollen/spores (Riding, 1992; Riding and Thomas, 1997). The rich  
242 ammonite faunas also present in these strata allowed a reliable correlation with the standard  
243 ammonite zonation (Fig. 3, Table 1; Sykes and Callomon, 1979). The dinoflagellate cysts  
244 were used biostratigraphically to constrain the ages of the host strata (e.g. Riding and  
245 Thomas, 1997). Palynological data from Riding and Thomas (1997) are summarised in Table  
246 1. Pteridophytic fern spores were most abundant in the Lower Callovian (up to 13%) with

247 higher gymnosperm pollen abundances in the overlying Middle Callovian (~~Table 1~~);  
248 [Sebastian – you should delete “Table 1” on line 247 because I have not differentiated spores  
249 and pollen in Table 1] indicating either a slight change in palaeovegetation or differential  
250 transport and deposition of fern spores *versus* pollen in the section studied. Pollen and spores  
251 were generally more abundant than marine palynomorphs, consistent with the common  
252 presence of wood fragments (Table 1) and suggesting a high terrestrial supply of plant  
253 material. Furthermore, Pearce et al. (2005) observed the prevalence of conifers of the genus  
254 *Cupressinoxylon* in the Staffin Bay section.

255

### 256 3.2. Rock-Eval parameters

257 The TOC contents of the rock samples varied between 0.2 and 7.6% (Fig. 3, Table A.1).  
258 These values were generally similar to those reported by Nunn et al. (2009), but both datasets  
259 do not closely correlate, with higher TOC values in the Lower and Middle Callovian obtained  
260 in the present study. This may be due to a higher rate of burial of OM and/or a high degree of  
261 heterogeneity in this part of the succession.  $T_{\max}$  values within the range 413 - 431 °C (Table  
262 A.1) reflect OM at a low level of thermal maturity, but show no obvious trends throughout  
263 the sequence. These results agree with previous observations that, unlike other successions in  
264 the Hebrides Basin, the Skye section is not especially thermally mature (Pearce et al., 2005  
265 and references therein). Hydrogen indices were low (< 115 mg HC/g TOC; Fig. 3; Table A.1),  
266 which is consistent with the generally high inertinite maceral composition of these deposits  
267 (Riding and Thomas, 1997). The kerogen was mainly Type III, reflecting its derivation from  
268 predominantly terrigenous OM., Higher values (173–269 mg HC/g TOC; Fig. 3; Table A.1)  
269 in the Callovian samples correspond to the TOC spike and reflect the presence of marine OM  
270 represented by Type II kerogen (Pearce et al., 2005; Nunn et al., 2009). Amorphous OM  
271 characterizes the palynofacies of two of these samples (Table 1).

272 3.3. *Molecular distributions*

273 3.3.1. *Aliphatic fraction*

274 Homologous series of *n*-alkanes and isoprenoids were the major components of the saturated  
275 hydrocarbon fraction (unpublished data). The  $>C_{23}$  *n*-alkanes exhibited an odd/even  
276 predominance consistent with terrigenous lipid input (Eglinton and Hamilton, 1963; Meyers  
277 and Ishiwatari, 1993). The ratio of the acyclic isoprenoid hydrocarbons pristane (Pr) and  
278 phytane (Ph) ranged from 0.7 to 1.6 with an average of 1.1 (Table A.2). These values are  
279 consistent with marine carbonate/shale facies and low levels of oxygen in the water column.  
280 Sedimentary Pr/Ph values are believed to reflect specific lithologies and depositional  
281 environments with values  $<1$  generally ascribed to marine carbonates or hypersaline  
282 environments, whereas values of 1 to 3 have been attributed to marine shales and  $>3$  to non-  
283 marine shales and coals (Hughes et al., 1995; Peters et al., 2005).  
284 Hopanes and steranes were detected in trace amounts in all samples (Table A.2). The similar  
285 proportions of  $C_{27}$  and  $C_{29}$  steranes (typically 20–40% of each) throughout the succession  
286 reflect significant inputs of both marine and terrestrial OM (Table A.2). Diasterane/sterane  
287 ratios (e.g.  $C_{27}$  diasterane/ $C_{27}$  sterane) were below 0.31, except in the Upper Callovian and  
288 Lower Oxfordian where values of 0.72 and 1.06 were measured in samples DUN 39 and  
289 DUN 36, respectively (Table A.2). Diasterane/sterane ratios can be influenced by the relative  
290 proportions of clay and organic matter in the host rock (i.e. clay/TOC ratios: van Kaam-  
291 Peters et al., 1998; Nabbefeld et al., 2010b). Thus the greater extent of diasterane diagenesis  
292 in these two samples may indicate higher clay/TOC ratios in this part of the Dunans Clay  
293 Member (Fig. 3). The relatively high  $C_{29}$  hopane/ $C_{30}$  hopane ratio (0.7–1.9) concomitant with  
294 generally low abundances of diasteranes ( $C_{27}$  diasterane/ $C_{27}$  regular sterane typically  $< 0.1$ ;  
295 Table A.2) can be attributed to carbonate-rich deposits with low clay contents (e.g. Peters et  
296 al., 2005), consistent with the Pr/Ph ratios measured. **Comment from reviewer: The naive**

297 interpretation in this sentence is completely at odds with the shale/claystone lithofacies of  
298 most of the samples (see Fig. 3), and the previous discussion. For example, a maximum  
299 diaster/ster = 0.31 is a lot different to “typically <0.1”. Another reason for showing the reader  
300 your biomarker data in a table. Rewrite.

301

### 302 3.3.2. *Aromatic fraction*

303 GC-MS analysis of the aromatic fraction identified several distinctive vascular plant  
304 biomarkers, several of which are highlighted in the selected ion chromatograms shown in  
305 Figure 4. The stratigraphic variation of HPP (retene/[retene+cadalene]) and HPF (relative %  
306 retene, cadalene and ip-iHMN) is shown in Figures 3 and 5, respectively. The relative  
307 abundance of ip-iHMN was consistently very low (<3%) in all but one sample (DUN 32:  
308 6.1%). Retene abundance was mostly <25 %, although in a few samples (FLOD 32, DUN 51,  
309 32 and 20) it is much higher (Table A.2). Although gymnosperm pollen (Table 1) were  
310 prevalent throughout the section (typically > 95% compared to fern spores), there was no  
311 strong correlation with % retene.

312 The cadalene and retene profiles of the HPF (Fig. 5; Table A.2) show that they were  
313 consistently more abundant than ip-iHMN and present in generally constant concentrations  
314 throughout the successions, apart from several sporadic fluctuations of significant magnitude  
315 in the Callovian and Lower Oxfordian. This irregular behaviour contrasts with the relatively  
316 smooth HPF and HPP profiles reported in Jurassic successions of northwest Australia (van  
317 Aarssen et al., 2000). In the latter study, retene was reported to increase from <20% to ~90%  
318 from the Callovian to the Upper Oxfordian Western Australian sections, whilst cadalene  
319 correspondingly decreased from >50% to ~10%. The retene/cadalene ratio likewise increased  
320 through Bathonian–Oxfordian sections of the Paris Basin, France (Hauteville et al., 2006),  
321 albeit with frequent variations. These smooth secular trends in vascular plant biomarker

322 abundance were reported to strongly correlate with sea level (van Aarssen et al., 2000) or  
323 aridity (Hauteville et al., 2006) gradients, prompting the idea that these may be molecular  
324 indicators of global climate change events.

325 Various studies of the Scottish region have also revealed a gradual transgressive-regressive  
326 sea level cycle over the Callovian–Oxfordian interval (Fig. 5d), with maximum sea level  
327 close to the boundary of these two intervals (e.g. Norris and Hallam, 1995). **Comment from**  
328 **reviewer: This figure shows a continuous rise in global sea level (from the Lower Callovian**  
329 **to the Lower Kimmeridgean). This does not equate to ‘a gradual transgressive-regressive**  
330 **cycle, with a maximum at the Callovian-Oxfordian boundary’.** However, the poor correlation  
331 of the HPP and HPF profiles with sea level in the Skye succession and other formations,  
332 including the relatively close Paris Basin (Hauteville et al., 2006), is not consistent with a  
333 sole global control on **gradual transgressive-regressive sea level** cycle over the Callovian–  
334 Oxfordian interval and the distribution of the biomarkers represented by HPF.

335 Furthermore, palaeotemperatures based on the stable oxygen isotopic composition ( $\delta^{18}\text{O}$ ) of  
336 belemnites varied between 6.7 and 20.6 °C (average of 12.4 °C), and increased slightly  
337 through the section studied (despite considerable scatter), in agreement with values obtained  
338 in other studies (Nunn et al., 2009 and references therein). Indeed, from the Upper Callovian  
339 to Lower Oxfordian (*Quenstedtoceras mariae* ammonite biozone) was likely to have been  
340 characterised by severe cooling, whereas the Kimmeridgian (*Pictonia baylei* ammonite  
341 biozone) was characterised by higher temperatures (Frakes, 1979; Dromart et al., 2003; Nunn  
342 et al., 2009; Riding, 2012; Riding and Michoux, 2013). Although the HPP was higher in the  
343 lower part of the profile, corresponding to a colder and more arid climate, it displays no  
344 correlation with palaeotemperature. However, palaeoclimate may have not been the only  
345 control on global sea level variations; geodynamics (e.g. subsidence, eustasy) can also drive  
346 sea level change, especially on the depositional timescales of deposition of the succession

347 studied (Fig. 3). Furthermore, local factors including the relief of the hinterland and other  
348 landscape characteristics affect the abundance and distribution of land plants, which may in  
349 turn also lead to changes in the transport and deposition of their remains. This may explain  
350 the fluctuating biomarker distributions in the Skye and Paris Basin sections, which contrast  
351 with those obtained by van Aarssen et al. (2000) for the Jurassic of Western Australia. The  
352 latter study was carried out on sediments deposited at a palaeolatitude of ca. 40°S in a setting  
353 without a direct connection to the Proto-Atlantic, whereas the Skye and Paris Basin sections  
354 were situated at ca. 40°N during the Jurassic Period. Notwithstanding the relative proximity  
355 of the Skye and Paris Basin depocentres, spatial differences in the climate may have resulted  
356 in the poor correlation between their respective HPF profiles and sea level change.

357

### 358 3.3. Stable carbon isotopic composition of vascular plant biomarkers

359 Bulk and compound-specific stable carbon isotopic values ( $\delta^{13}\text{C}$ ) are plotted in Figure 3.  
360  $\delta^{13}\text{C}_{\text{TOC}}$  values closely correlate with the  $\delta^{13}\text{C}$  signature of retene (Fig. 6) and the  
361 phytoplankton biomarker phytane. TOC and retene in lower and middle Oxfordian sediments  
362 were on average 2‰ less depleted in  $^{13}\text{C}$  than in the youngest and oldest deposits of the  
363 sequence (Fig. 3). This offset is smaller than the carbon isotopic shifts of ca. 4‰ in fossil  
364 wood (Pearce et al., 2005) and ca. 5‰ in TOC (Nunn et al., 2009), reported for the same  
365 period. Significantly, these  $\delta^{13}\text{C}_{\text{TOC}}$  and  $\delta^{13}\text{C}_{\text{retene}}$  profiles resemble quite closely the  $\delta^{13}\text{C}_{\text{carb}}$   
366 profile of Nunn et al. (2009) derived from Middle to Upper Jurassic belemnites. One notable  
367 difference is the lower  $\delta^{13}\text{C}_{\text{TOC}}$  values in the Dunans Shale Member and lower Dunans Clay  
368 Member that coincide with higher TOC values. Both datasets show a positive excursion  
369 within the *Cardioceras cordatum* ammonite biozone of the Lower Oxfordian, with the  
370 exception of one aberrant sample (DUN 55) **Reviewer comment: What is the significance of**  
371 **this sample???** The excursion maximum occurs in the *Cardioceras cordatum* ammonite

372 biozone, although high  $\delta^{13}\text{C}$  values continue into the *Cardioceras tenuiserratum* ammonite  
373 biozone. A minimum in the  $\delta^{13}\text{C}$  profiles of TOC, phytane and selected plant biomarkers (viz.  
374 pristane and 1,2-DMN) occurs in the *Amoeboceras regulare* ammonite biozone of the upper  
375 Oxfordian. Various negative carbon isotope excursions observed in other Jurassic sections  
376 (Padden et al., 2001; Jenkyns et al., 2002) have been attributed to the dissociation of methane  
377 hydrates and the consequent release of light carbon into the ocean–atmosphere system. This  
378 could also account for the negative excursions of the algal and higher plant biomarkers  
379 detected in the Staffin Bay succession. However, Pearce et al. (2005) and Nunn et al. (2009)  
380 did not observe any negative carbon isotope excursions in the Middle Oxfordian so they  
381 cannot be the result of global release of methane from hydrates.  
382 Interestingly, the  $\delta^{13}\text{C}$  of retene shows no relationship with its relative abundance, as was  
383 previously observed in the Delambre-1 well located on the NW Shelf of Australia where it  
384 was linked to a higher plant source in the distal hinterland of a deltaic setting (Grice et al.,  
385 2005). This disconnect may be due to significant local influences (eg. stresses arising from  
386 aridity, water composition, light exposure, temperature, nutrient availability: Tappert et al.,  
387 2013) on the carbon isotopic composition of the plant biomarkers, in addition to changes in  
388 the abundance and isotopic composition of atmospheric  $\text{CO}_2$ .

389

#### 390 **4. Conclusions**

391 The Mid-Late Jurassic marine shales of the Isle of Skye contain OM with a significant  
392 terrigenous contribution (abundant vascular plant biomarkers and a  $\text{C}_{29}$ -dominant sterane  
393 signature). The irregular secular profiles of HPP and HPF behaviour of the Staffin Bay  
394 Formation and Staffin Bay Shale Formation do not compare with those of Australian  
395 deposits, putatively of the same age, which were previously interpreted to reflect rising global  
396 sea levels. The absence of a similar trend in the Scottish deposits suggests that local controls,



397 such as changing transport of plant detritus in the Sea of Hebrides Basin due to eustatic  
398 changes in the relief and landscape of its hinterland, were potentially more significant than  
399 climate for the Jurassic vegetation at this palaeolatitude. The vascular plant signatures  
400 recorded in the Skye deposits could also have been influenced by additional non-climatic  
401 parameters (e.g. organic facies). Thus it may be that individual biomarkers can contribute to  
402 modelling the flora of simple vegetative environments, but are less reliable for this purpose in  
403 more complex environments impacted by multiple sources of OM or local tectonism. On the  
404 other hand, the  $\delta^{13}\text{C}$  profiles of TOC and selected vascular plant and algal biomarkers do  
405 define a single positive excursion peaking in the lower-mid Oxfordian, which may be  
406 indicative of global changes in atmospheric and oceanic  $\text{CO}_2$  levels.

407

#### 408 **Acknowledgements**

409 K.G. acknowledges the ARC for a QEII Discovery grant supporting this work on Triassic and  
410 Jurassic sedimentary sections. S.N. acknowledges additional funding from DFG Research  
411 Fellowship NA 1172/1-1 from the German Research Council. C.B.F. publishes with the  
412 permission of the CEO Geoscience Australia. J.B.R. publishes with the approval of the  
413 Executive Director, British Geological Survey (NERC).

414

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627

628 **Figure captions:**

629

630 **Fig. 1:** The location of the nineteen samples in this study. The main map (A)  
631 illustrates the foreshore outcrops at Staffin Bay, northeast Skye. The thirteen  
632 samples in the range DUN 2 to DUN 59 are from Dunans, which is designated  
633 as locality 1. The single sample DIGG 3 is from Digg, which is designated as  
634 locality 2. The five samples in the range FLOD 1 to FLOD 32 are from  
635 Flodigarry, which is designated as locality 3. The numbers on the northern and  
636 eastern margins of the main map (A) are National Grid Reference coordinates.  
637 The inset map (B) illustrates the location of the Staffin Bay area in northeast  
638 Skye.

639

640 **Fig. 2:** The Triassic and Jurassic palaeogeography and geological structure of the  
641 Hebrides Basin, northwest Scotland based on Steel (1977), Hudson (1983) and  
642 Riding et al. (1991). The thick lines represent major faults, with ticks on the  
643 downthrown side where known. The major palaeoslopes are indicated by the  
644 large arrows and the horizontally-ruled areas depict emergent landmasses,  
645 which are sediment sources. The numbers on the western and southern  
646 margins of the main map (A) are National Grid Reference coordinates.

647

648 **Fig. 3:** (a) The lithostratigraphy and ammonite biostratigraphy of the Callovian to  
649 Kimmeridgian succession at Staffin Bay based on Riding and Thomas (1997)  
650 and Nunn et al. (2009). Note that sample DUN 24 is within the *Kosmoceras*  
651 (*Gulielmites*) *medea* ammonite subbiozone of the *Kosmoceras* (*Gulielmites*)  
652 *jason* ammonite biozone, sample DUN 27 is within the *Kosmoceras*

653 *(Gulielmites) jason* ammonite subbiozone of the *Kosmoceras (Gulielmites)*  
654 *jason* ammonite subzone and sample DUN 38 is within the *Quenstedtoceras*  
655 *henrici* ammonite subbiozone of the *Quenstedtoceras lamberti* ammonite  
656 biozone. The scale is the height above the base of this composite section in  
657 metres. (b) TOC (wt%) from this study (red circles) and TOC (wt%) from a  
658 dataset adapted from Nunn et al. (2009) (grey circles). (c)  $\delta^{13}\text{C}$  data of  
659 selected biomarkers, (d) higher plant parameters (HPP) and (e) hydrogen  
660 indices (HI).

661

662 **Fig. 4:** Partial reconstructed ion chromatograms showing vascular plant biomarkers  
663 from the sample DIGG 3. C=cadalene; S=simonellite; ip-iHMN=6-isopropyl-  
664 1-isohexyl-2-methylnaphthalene; iHMN=1-isohexyl-2-methylnaphthalene.

665

666 **Fig. 5:** Relative abundances (%) of (a) retene, (b) cadalene and (c) 6-isopropyl-1-  
667 isohexyl-2-methylnaphthalene (ip-iHMN) in the Callovian–Kimmeridgian, of  
668 Staffin Bay. (d) Global sea-level adapted from Haq et al. (1987) and van  
669 Aarssen et al. (2000), plotted in metres relative to the present level.

670

671 **Fig. 6:** Correlation between  $\delta^{13}\text{C}$  values for TOC ( $\delta^{13}\text{C}_{\text{TOC}}$ ) and retene ( $\delta^{13}\text{C}_{\text{retene}}$ ) with  
672 correlation coefficient ( $R^2$  value).

673

674 Table 1: A listing of the 19 samples from the Isle of Skye which were studied herein  
675 with their correlation to the ammonite biozones (column 2) and a variety of  
676 relevant palynological data (columns 3–7). The dinoflagellate cyst species  
677 richness (or species diversity) is given in column 3. Semiquantitative

678 assessments of disseminated woody tissues are listed in column 4. Column 5  
679 gives the most dominant kerogen maceral(s). Columns 6 and 7 depict the  
680 percentages of indigenous marine and terrestrially-derived palynomorphs (i.e.  
681 pollen and spores) respectively. The indigenous marine palynomorphs are  
682 dominantly dinoflagellate cysts. Sample DUN 24 proved palynologically  
683 sparse and consequently palynomorph counts were not undertaken. All the  
684 information herein is from the database used during the preparation of Riding  
685 and Thomas (1997).

686

687 Supplementary online material

688

689 Table A.1: Rock-Eval pyrolysis data of samples analysed in this study, with calculated  
690 maximum temperatures (Tmax), S1, S2 and S3 values, calculated total organic  
691 carbon content (TOC), hydrogen (HI) and oxygen (OI) indices and  
692 TPI????????????

693 Table A.2: Parameters determined in the samples of this study comprising  
694 pristine/phytane ratios, values of the higher plant index (HPI) and higher plant  
695 parameter (HPP) with R=retene, C=cadalene and ip-iHMN=6-isopropyl-1-  
696 isohexyl-2-methylnaphthalene, relative abundances of C<sub>27</sub>, C<sub>28</sub> and C<sub>29</sub>  
697 steranes, ratios of diasteranes to regular steranes (S<sub>Dia</sub>/S<sub>Reg</sub>), ratios of C<sub>29</sub> to C<sub>30</sub>  
698 hopanes (C<sub>29</sub>H/C<sub>30</sub>H) and sterane to hopane ratios (S/H).

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