Palaeogeography, Palaeoclimatology, Palaeoecology

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

Kliti Grice [1,*], Clinton B. Foster [2], James B. Riding [3], Sebastian Naeher [1], Paul F. Greenwood [1,4]

[1] *WA Organic and Isotope Geochemistry Centre, The Institute for Geoscience Research, Department of Chemistry, Curtin University, GPO Box U1987 Perth, WA 6845, Australia*

[2] *Geoscience Australia, GPO Box 378, Canberra, ACT, 2601, Australia*

[3] *British Geological Survey, Environmental Science Centre, Keyworth, Nottingham NG12 5GG, United Kingdom*

[4] *Centre for Exploration Targeting and WA Biogeochemistry Centre (M090), The University of Western Australia, 35 Stirling Highway, Crawley, WA, 6009, Australia*

* Corresponding author. Tel.: +61 8 9266 2474; Fax: +61 8 9266 2300

E-mail address: K.Grice@curtin.edu.au (K. Grice)

Abstract

The molecular and stable carbon isotopic composition of higher plant biomarkers was investigated in Middle to Upper Jurassic strata of the Isle of Skye, northwest Scotland. Aromatic hydrocarbons diagnostic of vascular plants were detected in each of nineteen sedimentary rock samples from the Early Callovian to Early Kimmeridgian interval, a succession rich in fossil fauna including ammonites that define its constituent chronozones. The higher plant parameter (HPP) and higher plant fingerprint (HPF) calculated from the relative abundance of retene, cadalene and 6-isopropyl-1-isohexyl-2-methylnaphthalene (ip-iHMN) exhibit several large fluctuations throughout the Skye succession studied. These molecular profiles contrast with both (1) the more uniform profiles previously observed in Jurassic successions, putatively of the same age, from other palaeogeographical settings, including the Carnavon Basin, Western Australia and (2) the steady rise in global sea level during this interval. This suggests that the HPF profiles of Jurassic marine successions may not be reliable indicators of global climate change. Our results indicate that other factors such as local tectonism, resulting in changes to the relief and landscape of the hinterland, likely influenced the palaeovegetation and the mode of transport of its detritus into adjacent marine depocentres.However, the Skye succession showed similar $\delta^{13}C$ profiles of total organic carbon (TOC; comprising mainly fossil wood), the vascular plant biomarker retene and a predominant phytoplanktonic derived biomarker (phytane). The apparent isotopic relationship between terrigenous and marine-derived biomarkers supports a strong coupling of the atmosphere and ocean. The maximum isotopic excursion occurs in the *Cardioceras cordatum* ammonite biozone of the Early to Middle Oxfordian, which may be indicative of changes in atmospheric and oceanic levels of CO_2.

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

1. Introduction

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

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

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

van Aarssen et al. (2000) reported a close correlation between the varying abundances of these key plant biomarkers with previously defined palaeoclimate fluctuations and second order cycles in the global sea level. The HPP profile of four sequences covering the entire Jurassic Period, since there is no complete sequence, reflected three major 10 Ma cycles that the authors considered to be temporally similar to four climatic cycles identified in the Jurassic succession of northwest Australia (Parrish et al., 1996). The variations in HPP were attributed to changes in the relative abundance of the major plant sources. The similar nature of these molecular records obtained from petroleum exploration wells up to 1,500 km apart suggested a regional uniformity of palaeovegetation over geographically extensive regions, while the consistent deviations in biomarker distributions indicated widespread impacts on palaeovegetation. For instance, the increase in retene through the Oxfordian of all successions was attributed to a marked expansion of conifer forests throughout this interval (van Aarssen et al. 2000). These Jurassic HPP profiles showed second order (> 10,000 yr) cycles that correlate closely with global sea level (Haq et al., 1987) and, more generally, four distinct climatic periods (Parrish et al., 1996), all indicative of global forcing by rising atmospheric CO_2 concentrations and temperatures.

A similar palaeo-climatic scenario was also suggested by Hautevelle et al. (2006) when attributing an increasing retene/cadalene ratio in the Callovian–Oxfordian succession of the Paris Basin to a progressively higher proportion of *Pinaceae* conifers in response to aridification of the climate. The abundance of retene in these European sediments was 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_2 dynamics and regional or global climatic events. $\delta^{13}C$ values of
120 fossilised organic matter (OM) are particularly sensitive to palaeodepositional factors, most
121 notably the concentration of CO_2 (Hayes et al., 1989; Andrusevich et al., 1998; Nunn et al.,
122 2009). Furthermore, the $\delta^{13}C$ signature of individual biomarkers can provide specific
123 information such as the identity of their precursor biota, the mode and biosynthetic pathway

of CO_2 fixation, and changes in atmospheric and oceanic levels of CO_2. However, we also consider the impact of local factors such as heterogenic landscapes, water availability as well as site-specific transport and accumulation characteristics that may largely affect vascular plant distributions and thus complicate the interpretation of the palaeoenvironmental and palaeoclimatic significance of their biomarkers.

2. Materials and methods

2.1. Geological setting

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

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

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

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

2.4. Extraction and fractionation

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

2.5. Gas chromatography-mass spectrometry (GC-MS)

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

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

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

2.6. Stable isotope analysis

Compound specific isotope analyses (CSIA) were performed on a Micromass IsoPrime isotope ratio monitoring (irm)-GCMS mass spectrometer. All samples were dissolved in hexane and analysed using a HP 6890 gas chromatograph equipped with an autosampler and a split/splitless injector and helium was used as a carrier gas at a constant 1ml/min flow rate. A 60 m x 0.25 mm i.d. column containing a DB-1 phase (0.25 μm film thickness) was used and the sample was injected using pulsed splitless mode (injection holding for 30 seconds at 15 psi above the head pressure of the column and the purge time of 35 seconds). The GC oven was programmed from 40 ºC (held for 2 min) to 300 ºC (held for 30 min) at 3 ºC/min and after GC separation products were combusted (CuO quartz packed tube, 850 °C) to produce CO_2. Their isotopic composition was then measured by integration of the *m/z* 44, 45

and 46 ion currents of product peaks. The analyte compositions are reported relative to CO_2 of known ^{13}C content which was pulsed into the mass spectrometer. Average values and standard deviations of at least two analytical runs were reported in the delta notation ($\delta^{13}C$) relative to the VPDB carbonate standard.

Decarbonated samples for $\delta^{13}C$ analysis of bulk organic matter ($\delta^{13}C_{TOC}$) were measured using a Micromass IsoPrime isotope ratio mass spectrometer interfaced to a EuroVector EuroEA3000 elemental analyser following the method described by Grice et al. (2007).

2.7. Definition of higher plant parameter and higher plant fingerprint

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

3. Results and discussion

3.1. Biostratigraphy and palynofloras

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

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

3.2. Rock-Eval parameters

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

3.3. Molecular distributions

3.3.1. Aliphatic fraction

Homologous series of *n*-alkanes and isoprenoids were the major components of the saturated hydrocarbon fraction (unpublished data). The >C_{23} *n*-alkanes exhibited an odd/even predominance consistent with terrigenous lipid input (Eglinton and Hamilton, 1963; Meyers and Ishiwatari, 1993). The ratio of the acyclic isoprenoid hydrocarbons pristane (Pr) and phytane (Ph) ranged from 0.7 to 1.6 with an average of 1.1 (Table A.2). These values are consistent with marine carbonate/shale facies and low levels of oxygen in the water column. Sedimentary Pr/Ph values are believed to reflect specific lithologies and depositional environments with values <1 generally ascribed to marine carbonates or hypersaline environments, whereas values of 1 to 3 have been attributed to marine shales and >3 to non-marine shales and coals (Hughes et al., 1995; Peters et al., 2005).

Hopanes and steranes were detected in trace amounts in all samples (Table A.2). The similar proportions of C_{27} and C_{29} steranes (typically 20–40% of each) throughout the succession reflect significant inputs of both marine and terrestrial OM (Table A.2). Diasterane/sterane ratios (e.g. C_{27} diasterane/C_{27} sterane) were below 0.31, except in the Upper Callovian and Lower Oxfordian where values of 0.72 and 1.06 were measured in samples DUN 39 and DUN 36, respectively (Table A.2). Diasterane/sterane ratios can be influenced by the relative proportions of clay and organic matter in the host rock (i.e. clay/TOC ratios: van Kaam-Peters et al., 1998; Nabbefeld et al., 2010b). Thus the greater extent of diasterane diagenesis in these two samples may indicate higher clay/TOC ratios in this part of the Dunans Clay Member (Fig. 3). The relatively high C_{29} hopane/C_{30} hopane ratio (0.7–1.9) concomitant with generally low abundances of diasteranes (C_{27} diasterane/C_{27} regular sterane typically < 0.1; Table A.2) can be attributed to carbonate-rich deposits with low clay contents (e.g. Peters et 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 (Hautevelle et al., 2006),
321 albeit with frequent variations. These smooth secular trends in vascular plant biomarker

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

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

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

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

3.3. Stable carbon isotopic composition of vascular plant biomarkers

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

372 biozone, although high $\delta^{13}C$ values continue into the *Cardioceras tenuiserratum* ammonite
373 biozone. A minimum in the $\delta^{13}C$ 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 $\delta^{13}C$ 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 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 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,

such as changing transport of plant detritus in the Sea of Hebrides Basin due to eustatic changes in the relief and landscape of its hinterland, were potentially more significant than climate for the Jurassic vegetation at this palaeolatitude. The vascular plant signatures recorded in the Skye deposits could also have been influenced by additional non-climatic parameters (e.g. organic facies). Thus it may be that individual biomarkers can contribute to modelling the flora of simple vegetative environments, but are less reliable for this purpose in more complex environments impacted by multiple sources of OM or local tectonism. On the other hand, the $\delta^{13}C$ profiles of TOC and selected vascular plant and algal biomarkers do define a single positive excursion peaking in the lower-mid Oxfordian, which may be indicative of global changes in atmospheric and oceanic CO_2 levels.

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Figure captions:

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

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

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

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

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

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

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

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

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

Supplementary online material

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

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