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1 **An organic record of terrestrial ecosystem collapse and recovery at the**  
2 **Triassic–Jurassic boundary in East Greenland**

3  
4 Kenneth H. Williford<sup>1\*†</sup>, Kliti Grice<sup>1\*</sup>, Alexander Holman<sup>1</sup>, Jennifer C. McElwain<sup>2</sup>

5  
6 <sup>1</sup>Western Australian Organic and Isotope Geochemistry Centre, Department of  
7 Chemistry, Curtin University of Technology, Perth, WA 6845 Australia

8 <sup>2</sup>School of Biology and Environmental Science, University College Dublin, Belfield,  
9 Dublin 4, Ireland

10  
11 \*Authors to whom correspondence may be addressed: [kenneth.h.williford@jpl.nasa.gov](mailto:kenneth.h.williford@jpl.nasa.gov),  
12 [k.grice@curtin.edu.au](mailto:k.grice@curtin.edu.au)

13  
14 <sup>†</sup>Present address: Jet Propulsion Laboratory, California Institute of Technology, M/S 183-  
15 301, Pasadena, CA 91104 USA

16  
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18  
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20 **specific isotope analysis**

21

22 **Abstract**

23

24 **Terrestrial ecosystem collapse at the end of the Triassic Period coincided with a**  
25 **major mass extinction in the marine realm and has been linked to increasing**  
26 **atmospheric carbon dioxide, global warming, and fire activity. Extractable**  
27 **hydrocarbons in samples from the fluvial Triassic–Jurassic boundary section at**  
28 **Astartekløft, East Greenland were analyzed to investigate the molecular and**  
29 **isotopic organic record of biotic and environmental change during this event.**  
30 **Carbon isotopic compositions of individual plant wax lipids show a >4‰ negative**  
31 **excursion coinciding with peak extinction and a further decrease of 2‰ coinciding**  
32 **with peak  $p\text{CO}_2$  as estimated from the stomatal indices of fossil Ginkgoales. An**  
33 **increase of ~30‰ in the hydrogen isotopic compositions of the same plant wax lipids**  
34 **coincides with ecosystem collapse, suggesting that the biotic crisis was accompanied**  
35 **by strong hydrologic change. Concentrations of polycyclic aromatic hydrocarbons**  
36 **related to combustion also increase together with abrupt plant diversity loss and**  
37 **peak with fossil charcoal abundance and maximum plant turnover, supporting the**  
38 **role of fire in terrestrial extinctions. Anomalously high concentrations of a**  
39 **monoaromatic diterpenoid related to gymnosperm resin derivatives (and similar to**  
40 **dehydroabietane) occur uniquely in samples from the boundary bed, indicating that**  
41 **environmental stress factors leading to peak plant extinction stimulated increased**  
42 **resin production, and that plant resin derivatives may be effective biomarkers of**  
43 **terrestrial ecosystem stress.**

44

## 45 1. INTRODUCTION

46

47 Global warming due to increased atmospheric concentrations of greenhouse  
48 gases, initiated by the breakup of the supercontinent Pangaea and eruption of the Central  
49 Atlantic Magmatic Province (CAMP; Marzoli et al., 1999; Schaller et al., 2011), led to  
50 mass extinctions in the marine and terrestrial realms ~200 million years ago at the end of  
51 the Triassic period (Raup and Sepkoski, 1982; McElwain et al., 1999; Schoene et al.,  
52 2010; Blackburn et al., 2013). Stomatal indices from fossil *Gingkoales* leaves recovered  
53 from terrestrial Triassic–Jurassic boundary (TJB) sections in East Greenland and Scania,  
54 Sweden point to a fourfold increase in  $p\text{CO}_2$  (Fig. 1a) coinciding with an 80% extinction  
55 of plant species and negative excursions in the stable carbon isotopic composition ( $\delta^{13}\text{C}$ )  
56 of fossil leaves (McElwain et al., 1999; Bacon et al., 2011) and wood (Hesselbo et al.,  
57 2002; Fig. 1b). Subsequent  $p\text{CO}_2$  reconstructions based on stomatal indices  
58 (Steinthorsdottir et al., 2011; Fig. 1a) and pedogenic carbonates (Schaller et al., 2011)  
59 have strengthened this interpretation. Decreasing leaf width and increasing leaf dissection  
60 across the TJB section at Astartekløft, East Greenland suggest selection for an ability to  
61 mitigate heat stress (McElwain et al., 1999). The resulting, relatively narrow-leaved  
62 floras would have been more susceptible to fire, which increased significantly at the  
63 boundary as evidenced by fossil charcoal concentrations (Belcher et al., 2010).

64 Global carbon cycle perturbation across the TJB was initially recognized from  
65  $\delta^{13}\text{C}$  records of bulk organic matter and carbonate (Palfy et al., 2001; Ward et al., 2001;  
66 Hesselbo et al., 2002; Guex et al., 2004; Galli et al., 2005; Kuerschner et al., 2007; Ward  
67 et al., 2007; Williford et al., 2007; van de Schootbrugge et al., 2008; Ruhl et al., 2009;

68 Bachan et al., 2012). Stratigraphic records of bulk organic  $\delta^{13}\text{C}$  are affected by changes  
69 in the relative contribution of source components with different isotopic compositions,  
70 but some of this uncertainty is removed with compound specific isotope analysis (CSIA;  
71 Hayes et al., 1990). For instance, long chain *n*-alkanes with odd carbon numbers, largely  
72 derived from terrestrial plant leaf waxes (Eglinton and Hamilton, 1967) in  
73 communication with the atmosphere, offer a more specific proxy for the  $\delta^{13}\text{C}$  of  
74 atmospheric  $\text{CO}_2$  than bulk organic matter. CSIA of long chain *n*-alkanes has recently  
75 been employed to resolve TJB carbon cycle perturbation in marine (Ruhl et al., 2011) and  
76 lacustrine (Whiteside et al., 2010) settings.

77 Plant lipids record the hydrogen isotopic composition ( $\delta^2\text{H}$ ) of source water  
78 available during growth, thus enabling the use of these compounds as tracers of  
79 paleohydrologic change (Sachse et al., 2012). Fidelity of compound specific  $\delta^2\text{H}$  records  
80 declines with thermal maturity, as carbon-bound hydrogen exchanges with formation  
81 water over geologic timescales (Sessions et al., 2004). However, the preservation of  
82 hydrogen isotopic offsets consistent with biosynthetic processes on  $10^8$  yr timescales  
83 suggests that such exchange is negligible in some ancient sedimentary organic matter of  
84 low maturity (Dawson et al., 2004; Dawson et al., 2005; Dawson et al., 2007).

85 Beyond *n*-alkanes, the distribution and abundance of other lipid biomarkers  
86 records paleoecological change in the environment of deposition. For example, increases  
87 in isorenieratane and aryl-isoprenoids (biomarkers indicative of photic zone euxinia) in  
88 marine rocks suggest that hydrogen sulfide toxicity may have played a role in both the  
89 end-Permian (Grice et al., 2005) and end-Triassic (Richoz et al., 2012; Jaraula et al.,  
90 2013) mass extinctions.

91           Here we report the distribution and isotopic composition of individual organic  
92 molecules (biomarkers, molecular fossils) in an investigation of the response of a  
93 terrestrial ecosystem to increasing atmospheric CO<sub>2</sub> and global warming across the TJB.  
94 The reader should carefully consider the context of the data presented here: nine discreet  
95 “time slices” from an evolving, but generally fluvial environment over perhaps more than  
96 a million years. The four samples analyzed within the “boundary interval” (46.48–46.98  
97 m) are likely to be separated in time to some extent, but it is difficult to constrain the  
98 degree to which they were reworked during or after deposition. Nevertheless, the organic  
99 record from Astartekløft offers a valuable complement to similar records from marine  
100 and lacustrine environments.

101

## 102 **2. SAMPLES AND METHODS**

103

104           Detailed lithology and paleontology for the Astartekløft locality, including  
105 identification and numbering of individual plant beds, are discussed in a previous  
106 publication (McElwain et al., 2007). Briefly, the locality exposes river channel  
107 sandstones interbedded with shaley, organic rich, immature, and fossiliferous overbank  
108 deposits, or “plant beds,” of the Rhaetian–Hettangian Primulaev Formation, one of three  
109 formations that comprise the Kap Stewart Group (Surlyk, 2003). One mudstone sample  
110 from each of plant Beds 1, 2, 3, 4, 6, 7, 8 and 9, and three samples from the TJB Bed 5  
111 were analyzed in this study. Sample heights and organic geochemical data are given in  
112 Table 1.

113

## 114 **2.1. Sample processing**

115

116 Fresh, unweathered subsamples were prepared from larger hand samples collected  
117 by J. McElwain in 2002. Exterior surfaces of all subsamples were washed by sonicating  
118 for 10 min each in deionized water, dichloromethane (DCM) and hexane. Washed  
119 samples were ground to a fine powder using a vibratory ring mill, cleaned between each  
120 sample by grinding combusted quartz sand three times for 60 seconds and rinsing with  
121 methanol, DCM and hexane.

122 Approximately 20 g of each sample were extracted using a Dionex Accelerated  
123 Solvent Extractor and a 9:1 mixture of DCM:methanol at 1500 psi and 100°C. Elemental  
124 sulfur was removed by passing the extracts over solvent-rinsed, HCl-activated Cu  
125 powder. Extracts were brought to incipient dryness by evaporating solvent under a stream  
126 of high purity nitrogen. Recovered extracts ranged in mass from 6 to 104 mg. Total lipid  
127 extracts were separated into aliphatic, aromatic and polar fractions by adding to the top of  
128 a column (20 cm x 0.9 cm internal diameter) of activated silica gel (120°C, 8 hrs) and  
129 eluting with hexane, 3:7 (v/v) DCM in hexane and 1:1 (v/v) DCM:methanol,  
130 respectively.

131

## 132 **2.2. Gas chromatography-mass spectrometry (GC-MS)**

133

134 Aliphatic and aromatic fractions were analyzed by GC-MS using a Hewlett  
135 Packard (HP) 5973 mass selective detector interfaced to a 6890 GC. Fractions were  
136 dissolved in *n*-hexane and injected by the HP6890 autosampler into a split-splitless

137 injector using pulsed-splitless mode. A DB-5MS (J&W Scientific, 5%  
138 phenylmethylsiloxane stationary phase) GC column was used with He as the carrier gas.  
139 The GC oven was programmed from 40°C to 310°C at a rate of 3°C/minute and held  
140 isothermally for 30 minutes. Data were acquired in full-scan ( $m/z$  50–500) mode with an  
141 ionization energy of 70 eV.

142 Individual compound abundances were quantified using relative GC-MS peak  
143 areas on the total ion chromatogram. After fraction collection and transfer to 2 ml  
144 autosampler vials, appropriate masses of squalane and deuterated terphenyl standards  
145 were injected into saturate and aromatic fractions, respectively, such that the  
146 concentration of the standard compound in the fraction would approximate that of the  
147 most abundant sample compound (n.b. aromatic fractions containing the deuterated  
148 terphenyl standard were not processed on the instrument used for  $\delta^2\text{H}$  measurements). A  
149 single response factor was calculated for each sample analysis by dividing the peak area  
150 of the standard compound in the total ion chromatogram by its known concentration in  
151 the analysis. Semi-quantitative individual compound abundances were calculated as  $\mu\text{g}$   
152 per g total organic carbon (TOC; calculated using starting sample mass and weight  
153 percent organic carbon as previously measured by elemental analyzer).

154

### 155 **2.3. Compound specific carbon and hydrogen isotope analysis**

156

157 Compound specific  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  were measured on aliphatic fractions using gas  
158 chromatography-isotope ratio mass spectrometry (GCirMS) following a protocol  
159 described previously by Dawson et al. (2004). Isotope ratio analyses were performed



160 using a HP 6890 GC equipped with a HP 6890 autosampler and coupled to a Micromass  
161 isotope ratio monitoring mass spectrometer. The GC oven was held at 50°C for 1 min,  
162 increased to 310°C at 3°C/min, and held isothermally for 20 min, using a J&W Scientific  
163 DB-5MS GC column (60 m x 0.25 mm i.d. x 0.25 mm film thickness) and He as the  
164 carrier gas with a flow rate of 1ml/min.

165 For  $\delta^{13}\text{C}$ ,  $\text{CO}_2$  was produced during the oxidation of each chromatographically  
166 separated component after being passed through a quartz furnace containing copper oxide  
167 pellets (heated to 850°C). Values of  $\delta^{13}\text{C}$  were determined by integrating mass 44, 45 and  
168 46 ion currents of the  $\text{CO}_2$  peaks. For hydrogen isotope measurements,  $\text{H}_2$  was produced  
169 during pyrolysis of each chromatographically separated component, after passing through  
170 a quartz furnace containing chromium powder and heated to 1050°C.  $\text{H}_3^+$  correction was  
171 performed by measuring mass 3 at different  $\text{H}_2$  reference gas pressures. Values of  $\delta\text{D}$   
172 were determined by integrating the mass 2 and 3 ion currents of the  $\text{H}_2$  peaks. Samples  
173 were analysed 1–3 times (depending upon the quantity of aliphatic fraction recovered),  
174 and the average  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  values and standard deviations are reported relative to  $\text{CO}_2$   
175 reference gas calibrated to Vienna Peedee Belemnite (VPDB) and  $\text{H}_2$  reference gas  
176 calibrated to Vienna Standard Mean Ocean Water (VSMOW).

177

### 178 2.3.1. Precision and accuracy

179

180 In order to monitor the precision and accuracy of compound specific isotope  
181 analyses, a mixture of six reference compounds ( $n\text{-C}_{11}$ ,  $n\text{-C}_{13}$ ,  $n\text{-C}_{14}$ ,  $n\text{-C}_{17}$ ,  $n\text{-C}_{18}$ ,  $n\text{-C}_{19}$ ,  
182  $n\text{-C}_{25}$ ) whose isotopic compositions had been previously measured by elemental analyzer

183 isotope ratio mass spectrometry (EA-irMS) was analyzed using the same  $\delta^{13}\text{C}$  or  $\delta^2\text{H}$   
184 methods as sample analysis before, after, and sometimes during analytical sessions. Data  
185 from these analyses are available in the supplemental material (Figs. S1–S3). For all  
186 analyses of the standard mixture, the difference between returned and known values for  
187 each compound (accuracy) and the standard deviation (precision) for each compound  
188 were calculated. For 17  $\delta^{13}\text{C}$  analyses of the reference mixture, the differences between  
189 returned and known values ranged between 0 and 0.6‰, and the average difference was  
190  $-0.03\text{‰}$ . Standard deviations for the  $\delta^{13}\text{C}$  analyses of individual reference compounds  
191 ranged from 0.25‰ to 0.45‰ with an average of 0.35‰. For 38  $\delta^2\text{H}$  analyses of the  
192 reference mixture, the difference between returned and known values ranged from 0 to  
193 11‰, with an average of 0‰. Standard deviations for repeat analyses of individual  
194 compounds ranged from 2‰ to 8‰ with an average of 5‰.

195         Average peak height for all  $\delta^2\text{H}$  measurements of  $n\text{-C}_{25}\text{-}n\text{-C}_{29}$  alkanes in this  
196 study was 1.8 nA (major area  $\approx 1 \times 10^{-8}$ ), and the maximum peak height was 4.3 nA  
197 (major area  $\approx 2.5 \times 10^{-8}$ ). In samples 3363, 3771, and 4137, no  $n$ -alkane  $\delta^2\text{H}$   
198 measurement had a peak height above 0.2 nA (major area  $\approx 1 \times 10^{-9}$ ), outside the  
199 linearity range of the instrument. Because we estimate that the reduction in accuracy of  
200 measurements with peak heights lower than 0.2 nA is sufficient to affect our  
201 interpretations,  $\delta^2\text{H}$  data from these samples are excluded from figures and discussion.  
202 Similarly, the relatively low concentration of hopanoids and of the resin derivative (in  
203 samples other than those in and slightly above the boundary interval) relative to  $n$ -alkanes  
204 led to  $\delta^{13}\text{C}$  analyses of these compounds with peak heights as low as 0.4 nA. In contrast  
205 to analyses of  $\delta^2\text{H}$ , however, the estimated reduction of accuracy in the  $\delta^{13}\text{C}$

206 measurements is insufficient (<2‰, or ~3x the typical 2S uncertainty of 0.7‰) to affect  
207 our interpretations of the data.

208

#### 209 **2.4. Isolation of unknown resin (molecular weight 270)**

210

211 A total of 280 g of ground rock from bed 5 was extracted in a large Soxhlet  
212 apparatus using a 9:1 mixture of DCM: methanol for ca. 48 hours. Activated copper was  
213 used in the round bottom flask of the Soxhlet apparatus in order to remove elemental  
214 sulfur. The extract was brought to incipient dryness by evaporating solvent under a  
215 stream of high purity nitrogen. The total lipid extract was separated into saturate,  
216 aromatic and polar fractions by adding to the top of a column (20 cm x 0.9 cm i.d.) of  
217 activated silica gel (120°C, 8 hrs) and eluting with hexane, 3:7 (v/v) DCM:hexane and 1:1  
218 (v/v) DCM:methanol, respectively. The saturate fraction (18 mg) was subjected to 5A  
219 molecular sieving to separate straight chain and branched/cyclic fractions (Grice et al.,  
220 2008). Preparative GC was performed on the branched/cyclic fraction using a HP 5890  
221 GC fitted with a flame ionization detector (FID). An aliquot of the branched/cyclic  
222 fraction was analyzed by GC-FID in order to establish the retention time of the resin  
223 derivative of interest. One third of the fraction was separated by preparative GC 125  
224 times over a three-month period. The sample (ca. 2 µL of an original aliquot of 5 mg of  
225 the branched/cyclic fraction dissolved in 1.5 ml of cyclohexane) was subjected to  
226 preparative GC column (60 m x 0.32 mm i.d.) using a DB-5MS GC column with helium  
227 as the carrier gas. The FID was removed from the GC just prior to the retention time at  
228 which the resin eluted. The GC oven was programmed from 40°C to 300°C at a rate of

229 3°C/min and the sample was collected manually by using a Pasteur pipette inserted into  
230 the FID port. The sample was vaporized into the Pasteur pipette, and the compound was  
231 collected with a hexane rinse.

232

## 233 **2.5. <sup>1</sup>H NMR and heteronuclear single quantum correlation spectroscopy (HSQC)**

234

235         Approximately 0.5 mg of the resin derivative was obtained for <sup>1</sup>H NMR analyses.  
236 The minimum volume (~0.4 ml) of CDCl<sub>3</sub> was first placed in an NMR tube and the <sup>1</sup>H  
237 spectrum was recorded on a Bruker Avance 600 MHz NMR Spectrometer. The CDCl<sub>3</sub>  
238 was transferred into the sample container to dissolve the sample and then pipetted back  
239 into the same NMR tube using the same Pasteur pipette. The <sup>1</sup>H signals due to the  
240 *isopropyl* protons (16-Me, 17-Me and H15) match those reported in the literature (Hanari  
241 et al., 2002) similar to the *isopropyl* identified in dehydroabietane (Fig. 6) showing a  
242 doublet at 1.23 ppm relative to CDCl<sub>3</sub> at 7.62 ppm and a septet at 2.84 ppm relative to  
243 CDCl<sub>3</sub> at 7.62 ppm. The sample was too small to obtain a normal <sup>13</sup>C spectrum.  
244 However, it is sometimes possible to determine <sup>13</sup>C chemical shifts of carbons with  
245 attached protons using an HSQC experiment, a proton-detected 2D method that correlates  
246 <sup>1</sup>H signals with those of their directly attached carbon. The HSQC experiment, recorded  
247 over a 72 h period, showed extremely weak signals, and only the signals due to the  
248 *isopropyl* methyl groups were identified. These <sup>13</sup>C signals due to the *isopropyl* methyls  
249 (C16, C17) are consistent with values reported in the literature (Nishida et al., 1977;  
250 Delcorral et al., 1994).  
251

## 252 2.6. Geochemical indices and statistics

253

254 Two maturity indices were used in this study. The methylphenanthrene index  
255 (MPI-1) estimates the degree to which less stable methylphenanthrene isomers (1-MP  
256 and 9-MP) and phenanthrene transformed into methylphenanthrene isomers of higher  
257 stability (2-MP and 3-MP) as a result of thermal alteration, and the index is calculated as  
258 follows

259

$$260 \text{ MPI-1} = 1.5 * ((2\text{-MP} + 3\text{-MP}) / (\text{P} + 1\text{-MP} + 9\text{-MP})) \quad (1)$$

261

262 with lower values indicating lower maturity (Radke et al., 1982; Radke and Welte, 1983).

263 The odd-to-even predominance (OEP-2) estimates thermal maturity based on the relative  
264 abundance of odd versus even carbon-numbered *n*-alkanes, and is calculated as follows

265

$$266 \text{ OEP-2} = (\text{C}_{25} + 6\text{C}_{27} + \text{C}_{29}) / (4\text{C}_{26} + 4\text{C}_{28}) \quad (2)$$

267

268 with values significantly above 1 indicating low maturity (Peters et al., 2005).

269 Average Chain Length (ACL) and Carbon Preference Index (CPI) were also  
270 calculated, using the following formulae

271

$$272 \text{ ACL} = (25\text{C}_{25} + 27\text{C}_{27} + 29\text{C}_{29} + 31\text{C}_{31} + 33\text{C}_{33}) / (\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31} + \text{C}_{33}) \quad (3)$$

273

274 and

275

$$\text{CPI} = 0.5 * [(C_{25} + C_{27} + C_{29} + C_{31} + C_{33}) / (C_{24} + C_{26} + C_{28} + C_{30} + C_{32})] + 0.5 * [(C_{25} + C_{27} + C_{29} + C_{31} + C_{33}) / (C_{26} + C_{28} + C_{30} + C_{32} + C_{34})]$$

278 (4)

279

280 (Peters et al., 2005), using peak areas in GC-MS total ion chromatograms for individual  
281 *n*-alkane abundances.

282 Least squares linear regressions were used to assess relations between variables,  
283 with the coefficient of determination ( $r^2$ ) calculated using the difference between the total  
284 sum of squares (sum of squared differences between individual values and the average  
285 value of the dependent variable) and the residual sum of squares (sum of squared  
286 differences between the actual and predicted values of the dependent variable) divided by  
287 the total sum of squares. Estimated linear regression slopes were tested for significance at  
288 the 95% confidence level ( $\alpha = 0.05$ ) by calculating the probability ( $p$ ) of exceeding a  
289 critical F value by chance using the FDIST function in the StatPlus software package  
290 (AnalystSoft Inc.).

291

### 292 3. RESULTS

293

294 Total organic carbon (TOC) decreases from 1.9% at the bottom of the section to a  
295 minimum of 0.7% at 41.37 m, increases to 1.6% within the boundary interval, and  
296 increases again to maximum values between 2 and 4% near the top of the sampled  
297 interval. Fig. 2 shows GC-MS chromatograms of aliphatic and aromatic fractions

298 separated from 13.58, 46.88, and 94.03 m, adjusted for concentration and varying TOC in  
299 order to show relative abundance of individual compounds. Aliphatic fractions of the  
300 twelve samples analyzed include a series of *n*-alkanes with odd-over-even predominance  
301 from 1.2 to 1.6, hopanes and steranes.

302 A monoaromatic diterpenoid compound (similar to dehydroabietane) elutes in  
303 both the aliphatic and aromatic fractions of most samples. Our quantitation method  
304 suggests that the compound elutes predominantly in the aliphatic fraction: only three  
305 samples had more than 1  $\mu\text{g/g}$  TOC in their aromatic fractions, and the maximum  
306 concentration observed in an aromatic fraction was 5  $\mu\text{g/g}$  TOC (as compared to between  
307 100 and 200  $\mu\text{g/g}$  TOC in the aliphatic fractions of the boundary crossing samples).  
308 Unidentified compounds with similar mass spectra have been reported with abundant  
309 triterpenoids of higher plant origin in Miocene sediments from Baffin Bay off the west  
310 coast of Greenland (ten Haven et al., 1992) and in a sub-bituminous coal from the East  
311 Elbian coal basin (Hazai et al., 1986). Relative ion peak values for the most abundant  
312 monoaromatic diterpenoid observed in this study are 270 (100), 255 (70), 185 (20), 160  
313 (10), 146 (45), 131 (35), whereas the values reported by Hazai et al. (1986) are 270 (100),  
314 255 (70), 185 (30), 160 (45), 146 (70), 131 (40). By contrast, relative peak values for  
315 dehydroabietane are as follows: 270 (40), 255 (100), 185 (60), 173 (80), 159 (80), 143  
316 (40), 129 (50): particularly notable are the abundance of the *m/z* 255 ion relative to the  
317 base peak and presence of large *m/z* 173 and 159 peaks in dehydroabietane (Righi et al.,  
318 2013). The mass spectrum of the unidentified monoaromatic diterpenoid is shown in Fig.  
319 6, and  $^1\text{H-NMR}$  data support an *isopropyl* moiety as in dehydroabietane (Fig. 7).

320 Concentration of long chain *n*-alkanes varies considerably throughout the section,  
321 with the lowest values (<50 µg/g TOC) occurring in beds 2–4, intermediate values (100–  
322 200 µg/g TOC) in the boundary interval (with the exception of a low value in bed 5B),  
323 and highest values (>200 µg/g TOC) above bed 6. The resin derivatives are present in all  
324 samples, but in the boundary crossing interval (46.48 to 46.98 m) the concentration of  
325 these compounds increases by a factor of ~40. Pristane to phytane ratios (Pr/Ph) are >1  
326 (avg. = 3) in all samples except 60.86 m, which has a ratio of 0.8. ACL decreases from  
327 ~28 at the bottom of the section to a minimum of ~27 at 41.37 m, increases to ~28 again  
328 within the TJB interval, and remains relatively constant throughout the rest of the  
329 sampled interval.

330 Aromatic fractions also show significant changes across the TJB at Astartekløft.  
331 Polycyclic aromatic hydrocarbons (PAHs) including retene, benzo(*g,h,i*)perylene, and  
332 coronene are present only at low (1–5 µg/g TOC) concentrations in beds 1–3. Coronene  
333 and benzo(*g,h,i*)perylene increase to 8 and 17 µg/g TOC, respectively, in bed 4, and  
334 retene increases to 33 µg/g TOC in bed 5. Retene decreases somewhat in the uppermost  
335 sample from bed 5, but remains relatively elevated (4–17 µg/g TOC) through the rest of  
336 the section. Benzo(*g,h,i*)perylene and coronene return to lower concentrations above bed  
337 5.

338 Carbon isotopic compositions of *n*-alkanes from *n*-C<sub>25</sub> to *n*-C<sub>29</sub> track the  
339 composition of fossil wood and leaves (that have slightly higher δ<sup>13</sup>C) in the lower part of  
340 the section (Fig. 1b). A 1.5‰ increase in δ<sup>13</sup>C between 37.71 and 41.37 m is followed by  
341 a ~4.5‰ negative excursion, with a TJB minimum value of –29.8‰ at 46.88 m. A slight  
342 increase in δ<sup>13</sup>C is followed by a further decrease to a low for the section of –30.5‰ at



343 60.86 m, nearly 4‰ lower than previously reported values for fossil wood and leaves  
344 from this bed. Values for *n*-alkanes increase to -27‰ at 72.69 m, approaching values for  
345 fossil wood and leaves, and then decrease again at the top of the sampled interval, ~3‰  
346 lower than fossil wood and leaves. The most abundant hopanoid (C<sub>30</sub> 17 $\alpha$ ,21 $\beta$ ) in the  
347 TJB sample at 46.48 m has an anomalously low  $\delta^{13}\text{C}$  of  $-55 \pm 1\text{‰}$ , in contrast to other  
348 samples in the section within which  $\delta^{13}\text{C}$  of this compound varies between -30 and -  
349 45‰ (Fig. 1c).

350 An increase of ~30‰ in the weighted average  $\delta^2\text{H}$  of odd numbered *n*-C<sub>25-29</sub>  
351 alkanes ( $\delta^2\text{H}_{n\text{-C}25\text{-}29\text{avg}}$ ) from the base of the section to the boundary interval coincides  
352 with the increase in CO<sub>2</sub> and abrupt ecosystem collapse, and is followed by a decrease in  
353  $\delta^2\text{H}$  of ~30‰ from the TJB to the top of the sampled interval (Fig. 1d). In samples for  
354 which it was possible to measure the quantity, the offset in  $\delta^2\text{H}$  between the *n*-C<sub>29</sub> alkane  
355 and phytane varies between 75 and 130‰, and this offset is not correlated with  $\delta^2\text{H}_{n\text{-C}29}$   
356 ( $r^2 = 0.03$ ). It is therefore unlikely that post-depositional hydrogen exchange was a  
357 significant driver of stratigraphic trends in  $\delta^2\text{H}$  (see Discussion).

358

## 359 4. DISCUSSION

360

### 361 4.1. Trends in $\delta^{13}\text{C}$ of *n*-alkanes

362

363 Plant lipids are typically <sup>13</sup>C-depleted by up to 10‰ on average relative to bulk  
364 wood and leaves due to the kinetic effect of the decarboxylation of pyruvic acid (DeNiro  
365 and Epstein, 1977). This relative depletion is lower at Astartekløft, more similar in

366 magnitude to that observed in lacustrine sediments from the Newark and Hartford basins,  
367 USA (Whiteside et al., 2010) than marine sediments from Kuhjoch and Hochalpgraben,  
368 Austria (Ruhl et al., 2011), perhaps reflecting the relatively pristine nature of organic  
369 matter in the Austrian sections. Only odd-numbered *n*-alkanes (*n*-C<sub>25</sub>, *n*-C<sub>27</sub>, *n*-C<sub>29</sub>) are  
370 plotted in Fig. 1 for clarity, and because these compounds derive from plant waxes,  
371 whereas even-numbered *n*-alkanes in this range likely represent remnants of partially  
372 cleaved molecules with higher original carbon numbers. It is possible that some  
373 component of odd-numbered *n*-alkanes also derives from cleavage. For this and other  
374 reasons, including variable production of different chain lengths by different plant groups  
375 and varying biosynthetic fractionation in alkanes of different chain lengths (Diefendorf et  
376 al., 2011), we hesitate to draw conclusions about trends in individual *n*-alkanes. In the  
377 Electronic Annex (EA), we report data from all *n*-alkanes present in sufficient  
378 concentrations to obtain isotope measurements in all samples analyzed (*n*-C<sub>25</sub> to *n*-C<sub>29</sub>),  
379 but we argue that these data are best considered in aggregate (e.g., using the  
380 concentration-weighted average *n*-C<sub>25-29avg</sub>).

381 Values of  $\delta^{13}\text{C}_{n\text{-C}_{25-29}}$  are not correlated with CPI ( $r^2 = 0.0004$ ), and an apparent  
382 negative relation with ACL is not significant at the 95% confidence level ( $r^2 = 0.29$ ;  $p =$   
383  $0.07$ ; Fig. 3; EA). Changes in the distribution of long chain *n*-alkanes have been used as a  
384 proxy for paleoecological change, based on the reasoning that different plant groups  
385 synthesize different characteristic distributions (Cranwell, 1973). However, a recent and  
386 comprehensive compilation of published *n*-alkane distribution data showed large  
387 heterogeneities among individual plant groups and concluded that biosynthetic responses  
388 to local environmental change may be as important as ecological change in determining

389 the distribution of *n*-alkanes within a given ecosystem (Bush and McInerney, 2013).  
390 Given the uncertainty about relations between *n*-alkane distributions and ecology in  
391 studies of modern ecosystems, we are unable to determine the extent to which changing  
392 *n*-alkane distributions at Astartekløft were driven by ecological or environmental effects.

393         The high relative abundance of herbaceous taxa (e.g., 78% relative abundance of  
394 ferns; McElwain et al., 2007; Mander et al., 2010) may contribute indirectly to the low  
395  $\delta^{13}\text{C}$  value in bed 6. Leaves of herbaceous taxa close to the forest floor typically have low  
396  $\delta^{13}\text{C}$  values relative to those of woody canopy taxa due to photosynthetic recycling of  
397 soil-respired  $\text{CO}_2$  (the “canopy effect”; Vandermerwe and Medina, 1991). Notably, this is  
398 the only sample that has a Pr/Ph < 1 (0.8), which may suggest relatively reducing  
399 conditions during deposition, consistent with the interpretation of bed 6 as a “coal  
400 swamp”.

401         Although significant divergence in  $\delta^{13}\text{C}$  is observed between *n*-alkanes and fossil  
402 wood and leaves from the TJB to the top of the sampled interval, a negative relation  
403 between the weighted average  $\delta^{13}\text{C}_{n\text{-C}25\text{-}29}$  and estimated atmospheric  $\text{CO}_2$  concentration  
404 with  $-0.0009 \leq \text{slope} \leq -0.005$  (95% CI;  $r^2 = 0.74$ ,  $p = 0.01$ ) is observed (Fig. 1a,b). Peak  
405  $\text{CO}_2$  (Steinthorsdottir et al., 2011) corresponds to the  $\delta^{13}\text{C}$  minimum in bed 6, a  
406 coincidence that could record stable photosynthetic fractionation under a relatively  $^{13}\text{C}$ -  
407 depleted atmosphere after peak extinction or increased photosynthetic fractionation under  
408 high  $p\text{CO}_2$ . Notably, the prominent gymnosperm resin derivative exhibits a minimum  
409  $\delta^{13}\text{C}$  value for the section ( $-28.1\text{‰}$ ) in bed 6, 2.5‰ lower than the average value for this  
410 compound in other samples in this study.

411 Most marine Triassic–Jurassic boundary sections around the world record a  
412 relatively short decrease in  $\delta^{13}\text{C}$  coinciding with extinction, and some record an increase  
413 of longer duration sometime during the Hettangian (Williford et al., 2007; Bartolini et al.,  
414 2012). Paired  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  records show an increase in  $\Delta^{13}\text{C}$  ( $\delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$ ) in  
415 the recovery interval (Bachan et al., 2012). This is consistent with the view that the  $^{13}\text{C}$ -  
416 depleted values of individual compounds above the extinction interval at Astartekløft  
417 resulted from preferential preservation (in lipids relative to fossil wood or leaves) of  
418 increased photosynthetic fractionation under increased atmospheric  $p\text{CO}_2$ .

419

#### 420 **4.2. Trends in $\delta^2\text{H}$ of *n*-alkanes**

421

422 During the interval with rising  $\text{CO}_2$  levels prior to the TJB,  $\delta^2\text{H}_{n\text{C}25-29\text{avg}}$  shifts  
423 positively from  $-133\text{‰}$  to  $-104\text{‰}$  (Fig. 1d). After peak plant extinctions,  $\delta^2\text{H}$  of *n*-  
424 alkanes (1) decreases, but remains relatively elevated through bed 6, which records the  
425 highest  $\text{CO}_2$  and lowest  $\delta^{13}\text{C}$  values, (2) decreases during the  $\text{CO}_2$  decrease and  $\delta^{13}\text{C}$   
426 increase between bed 6 and 7, and (3) decreases slightly to the lowest recorded values  
427 between beds 7 and 9 (Fig 1c). The various environmental and biological factors that  
428 control the  $\delta^2\text{H}$  of lipids in phototrophic organisms were recently reviewed by Sachse et  
429 al. (2012). In the discussion below, we consider the relative contribution of the following  
430 factors towards the observed positive shift in  $\delta^2\text{H}$  of *n*-alkanes that co-occurs with end-  
431 Triassic ecosystem collapse at Astartekløft: 1) equilibrium hydrogen exchange during  
432 thermal maturation of organic matter, 2) vegetation change, and 3) temperature. As is the  
433 case for all such sedimentary successions, isotopic trends observed at Astartekløft are

434 driven by a combination of local and global effects. This is, to our knowledge, the first  
435 TJB record of *n*-alkane  $\delta^2\text{H}$  – a small dataset from a single locality; similar evaluation of  
436 well-preserved organic matter from other TJB localities can constrain the degree to which  
437 the changes observed at Astartekløft are representative of global biogeochemical change.

438

#### 439 *4.2.1. Hydrogen exchange*

440

441 Equilibrium isotopic exchange of carbon bound hydrogen with formation water  
442 over geologic timescales can obscure original isotopic compositions (Sessions et al.,  
443 2004), especially at high maturity levels (Dawson et al., 2005). Two parameters were  
444 used to evaluate the relative thermal maturity of the organic matter in the Astartekløft  
445 sediments: the methylphenanthrene index (MPI-1; Radke et al., 1982; Radke and Welte,  
446 1983) and odd-to-even predominance (OEP-2; Peters et al., 2005). Previous studies  
447 comparing MPI-1 to  $\delta\text{D}$  of *n*-alkanes and isoprenoids show evidence for some exchange  
448 in isoprenoids, but little to no apparent exchange in alkanes extracted from rocks having  
449 MPI-1 < 0.6 (Dawson et al., 2005; Radke et al., 2005). The samples in this study are of  
450 uniformly low maturity (MPI-1=0.38–0.60; OEP-2=1.24–1.64), with a range of  
451 calculated vitrinite reflectance values ( $R_c$ ; Radke et al., 1982) between 0.60 and 0.73. We  
452 conclude that that Astartekløft organic matter was not subject to significant exchange due  
453 to maturity (Fig. 4a), an interpretation further supported by the preservation of offsets  
454 between the *n*-C<sub>29</sub> alkane and phytane (Wang et al., 2009) ranging between 76 and  
455 129‰. This offset is not correlated with  $\delta^2\text{H}$ , and it is therefore unlikely that post-

456 depositional hydrogen exchange was a significant driver of stratigraphic trends discussed  
457 here.

458

#### 459 4.2.2. *Vegetation change*

460

461 The TJB at Astartekløft is defined by the large vegetation changes that occur  
462 across the boundary interval (Harris, 1926, 1937; McElwain et al., 1999; McElwain et al.,  
463 2007; Mander et al., 2010, 2013). Studies of modern ecosystems have demonstrated that  
464  $\delta^2\text{H}$  of *n*-alkanes can vary considerably within and among different plant groups and  
465 emphasized the importance of accounting for vegetation change when using  $\delta^2\text{H}$  as a  
466 paleoproxy (Chikaraishi and Naraoka, 2003; Sachse et al., 2004, 2006; Hou et al., 2007;  
467 Sachse et al., 2012). To what degree did these vegetation changes affect the  $\delta^2\text{H}$  of  
468 sedimentary *n*-alkanes at Astartekløft?

469 A negative relation is observed between  $\delta^2\text{H}_{n\text{-C}25\text{-}29}$  and ACL with a slope  
470 between  $-40$  and  $-14$  (95% CI;  $r^2 = 0.71$ ;  $p = 0.001$ ). As previously mentioned, relations  
471 between *n*-alkane distributions and plant species distributions are unclear, as ACL varies  
472 widely within individual plant groups (Bush and McInerney, 2013). An increase in ACL  
473 from  $<29$  to  $>30$  coincides with the PETM negative carbon isotope excursion in the  
474 Bighorn basin and is interpreted to record an increase in long chain *n*-alkane production  
475 in order to mitigate water loss in plants subjected to rising temperatures (Smith et al.,  
476 2007). Whereas we do observe an overall increase in ACL from the base to the top of the  
477 Astartekløft section, a *decrease* in ACL coincides with the onset of ecosystem collapse  
478 and isotopic change (Fig. 3). This likely reflects a combination of vegetation change as

479 well as changes in *n*-alkane production by plants in response to changing environmental  
480 conditions.

481 To test the dependence of  $\delta^2\text{H}$  on vegetation assemblages, regression analysis was  
482 performed using the most recent, high-resolution sporomorph record from Astartekløft  
483 (Mander et al., 2010). Four distinct vegetation zones were recognized on the basis of  
484 sporomorph distribution in samples from plant Beds 1–7: Zone A1 (Beds 1, 1.5, and 2),  
485 in which the liverwort *Riccisporites tuberculatus* constitutes 40–50% of the assemblages,  
486 Zone A2 (Beds 3 and 4), the base of which is marked by the local acme (up to 51%  
487 relative abundance) of the lycopod *Limbosporites lundbladii*, Zone A3 (Bed 5), in which  
488 the lycopod *Uvaesporites reisseringerii* and the fern *Baculatisporites comaumensis* co-  
489 dominate, and the conifer *Perinopollenites elatoides* reaches a local acme, and Zone A4  
490 (Beds 6 and 7), the base of which is marked by local acmes of the ferns *Deltoidospora*  
491 *toralis* (55%) and *Punctatisporites globosus* (25%) (Mander et al., 2013). Fig. 5 shows  
492 relations (including least squares lines and  $r^2$  values) between  $\delta^2\text{H}_{nC_{25-29\text{avg}}}$  and relative  
493 abundance of eight sporomorph groups in Beds 1–7. None of the sporomorph groups  
494 shows a correlation with  $\delta^2\text{H}$  that is significant at the 95% level. Mosses show a  
495 moderate, negative relation with  $\delta^2\text{H}_{nC_{25-29\text{avg}}}$  ( $r^2 = 0.62$ ;  $p = 0.06$ ). However, the few data  
496 that exist comparing mosses to other plant groups in the same environments suggest that  
497 mosses have higher  $\delta^2\text{H}$  than trees, attributed in part to increased evaporative leaf water  
498 enrichment due to the lack of stomata in mosses (Sachse et al., 2006). We find no  
499 compelling evidence that vegetation change exerted a significant control on the  $\delta^2\text{H}$  of  
500 sedimentary *n*-alkanes at Astartekløft.

501

502 4.2.3. *Temperature*

503

504 The traditional interpretation of changes in  $\delta^2\text{H}$  values of sedimentary long chain  
505 alkanes with odd carbon numbers is that they reflect changes in  $\delta^2\text{H}$  of meteoric water,  
506 dominantly driven at low latitudes by the amount of precipitation and at high latitudes by  
507 temperature (Dansgaard, 1964; Sachse et al., 2012). Assuming a net fractionation for *n*-  
508  $\text{C}_{29}$  ( $\Delta_{n\text{C}29} = \delta^2\text{H}_{\text{H}_2\text{O}} - \delta^2\text{H}_{n\text{C}29}$ ) of 100 to 130‰ (Sachse et al., 2004),  $\delta^2\text{H}$  of Astartekløft  
509 *n*-alkanes indicates a meteoric  $\delta^2\text{H}$  shift from values measured in modern temperate  
510 environments ( $-50$  to  $-20$ ‰) to values measured in low latitude regions with high rates  
511 of evaporation such as the Red Sea (0 to 20‰; Bowen and Revenaugh, 2003). However,  
512 paleobotanical (McElwain et al., 2007) and paleolimnological (Clemmensen et al., 1998)  
513 records from East Greenland suggest increasing humidity during the Triassic–Jurassic  
514 transition, indicating that a mechanism other than local aridity was responsible for any  
515 change in  $\delta^2\text{H}$  of meteoric water recorded by *n*-alkanes.

516 During the Late Triassic, Astartekløft was likely at temperate latitudes, drifting  
517 north (Kent and Tauxe, 2005). All else being equal, greenhouse warming at the TJB  
518 would have led to an increase in  $\delta^2\text{H}$  of meteoric source water at Astartekløft in two  
519 ways: 1) warmer air has a higher capacity to hold moisture, so less  $^2\text{H}$ -enriched  
520 condensate would have been lost during transport from evaporative source regions, and  
521 2) equilibrium fractionation between vapor and condensate decreases with increasing  
522 temperature (Dansgaard, 1964; Sachse et al., 2012). A similar scenario, evidenced by a  
523 large negative excursion in  $\delta^{13}\text{C}$  and a large positive excursion in  $\delta^2\text{H}$ , is recorded in  
524 Arctic sediments crossing the PETM (Pagani et al., 2006), although records of  $\delta^{18}\text{O}$  from



525 soil carbonates suggest that <sup>2</sup>H-enrichments would have been slightly lower at mid-  
526 latitudes (Fricke et al., 1998).

527

### 528 **4.3. Fire activity**

529

530 High concentrations of combustion-ascribed polycyclic aromatic hydrocarbons  
531 (PAHs) in the Early Jurassic of Poland have been interpreted as evidence for increased  
532 wildfire activity (Marynowski and Simoneit, 2009), and a fivefold increase in charcoal  
533 across the TJB at Astartekløft (Fig. 4c), indicates that fire activity increased with  
534 atmospheric CO<sub>2</sub> (Belcher et al., 2010) at this locality. We find increased concentrations  
535 of combustion-ascribed PAHs coronene and retene (Ramdahl, 1983; Freeman and Cattell,  
536 1990) in the same stratigraphic interval (Fig 3d). Retene is also known to be a  
537 degradation product of dehydroabietic acid in sediments (Tavendale et al., 1997), and the  
538 similarity observed in the relative abundance of retene and resin byproducts related to  
539 dehydroabietane (Fig. 4d–e and discussion below) could be related to early diagenetic  
540 transformations. High PAH concentrations in TJB sediments from the Danish-German  
541 basin have been attributed directly to CAMP volcanism on the basis of high coronene to  
542 benzo(*a*)pyrene ratios (up to 3.46 with an average of 1.11; (van de Schootbrugge et al.,  
543 2009). By contrast, the average coronene to benzo(*a*)pyrene ratio for this study is 0.33.

544

### 545 **4.4 Resin derivatives as biomarkers of terrestrial ecosystem stress**

546

547 The rise in CO<sub>2</sub>, δ<sup>2</sup>H, charcoal, and PAHs at the TJB is accompanied by  
548 increasing concentration of a monoaromatic diterpenoid likely derived from gymnosperm  
549 resins (Fig. 4e, 6). Oleoresins are an important part of the defense system of conifers  
550 exposed to herbivory, infection, and wounding stress (Phillips and Croteau, 1999), and  
551 significant increases in oleoresin production result from burning (Cannac et al., 2009;  
552 Perrakis et al., 2011). We attribute the dramatic increase in gymnosperm-resin derivatives  
553 at the TJB to environmental stress including fire, and more generally, we suggest that  
554 these compounds are potential biomarkers for terrestrial ecosystem stress. For example,  
555 correlations between resin compounds and fungal biomarkers or abundance of  
556 herbivorous insects could also record responses to disease and predation stress.

557

## 558 **5. CONCLUSIONS**

559

560 The results presented here are consistent with the view that greenhouse warming  
561 due to CAMP eruptions led to severe terrestrial ecosystem stress. Carbon isotopic  
562 compositions of individual *n*-alkanes record a >4‰ negative excursion coinciding with  
563 the interval of greatest plant turnover. A further decrease in δ<sup>13</sup>C above the TJB coincides  
564 with peak atmospheric CO<sub>2</sub> concentration as calculated from stomatal indices, but may  
565 have been amplified by a shift in depositional environment from overbank to coal swamp  
566 deposits. A ~30‰ positive shift in δ<sup>2</sup>H of long chain *n*-alkanes coinciding with CO<sub>2</sub> rise,  
567 global warming, and plant diversity loss is consistent with increased δ<sup>2</sup>H of local  
568 meteoric source water (due to a temperature-driven decrease in rainout of <sup>2</sup>H-enriched  
569 condensate during vapor transport from evaporative source regions). Increases in the

570 relative abundance of combustion-derived PAHs and gymnosperm resin derivatives in the  
571 TJB interval record a terrestrial ecosystem under extreme stress by heat and fire.

572

573

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892

893 **Table and Figure Captions**

894

895

896 **Table 1.** Molecular and average isotopic data for Triassic–Jurassic boundary samples  
897 from Astartekløft, East Greenland.

898

899 **Fig. 1.** Lithostratigraphy, plant beds, (a) estimated CO<sub>2</sub> concentration (Steinthorsdottir et  
900 al., 2011), (b) δ<sup>13</sup>C of C<sub>25</sub>–C<sub>29</sub> *n*-alkanes, fossil leaf cuticle \*(McElwain et al., 1999;  
901 Bacon et al., 2011) and fossil wood \*\*(Hesselbo et al., 2002), (c) δ<sup>13</sup>C of C<sub>25</sub> hopane, and  
902 (d) δ<sup>2</sup>H of C<sub>25</sub>–C<sub>29</sub> *n*-alkanes with height at Astartekløft. Gray field in (a) represents full  
903 range of stomatal index data in Steinthorsdottir et al. (2011), black line represents  
904 average. Gray field in (b) represents the range of leaf cuticle data reported by Bacon et al.  
905 (2011). Dotted black line in (b) and (d) represent weighted averages of odd numbered *n*-  
906 C<sub>25–29</sub> alkanes, and insets show expanded boundary interval (Bed 5). Average analytical  
907 uncertainty for individual *n*-alkane values, (calculated as the average variability at one  
908 standard deviation of replicate analyses of individual compounds) is 0.3‰ for δ<sup>13</sup>C and  
909 7‰ for δ<sup>2</sup>H (see Tables S1 and S2 for individual values). Horizontal, solid gray line  
910 indicates the level of 80% plant species turnover, and dotted gray line indicates onset of  
911 plant diversity loss (McElwain et al., 1999; McElwain et al., 2007; McElwain et al.,  
912 2009).

913

914 **Fig. 2.** GC-MS Total ion chromatograms from aliphatic and aromatic fractions from  
915 13.58, 46.88, and 94.03 m. Chromatogram heights are adjusted for concentration using  
916 internal standards (squalane and terphenyl-d14 for aliphatic and aromatic fractions,  
917 respectively) and then for variable TOC to show differences in relative abundance of  
918 individual compounds (e.g., note anomalously high concentration of resin derivative in  
919 the aliphatic fraction from 46.88 m). Compounds discussed in the text are indicated as  
920 follows: pristane (Pr), resin derivative (*m/z* 270), *n*-alkanes (C<sub>25</sub>, C<sub>27</sub>, C<sub>29</sub>, C<sub>31</sub>), squalane  
921 (Sq), C<sub>30</sub> 17α, 21β hopane (C<sub>30</sub>Hop), naphthalene (N), methylnaphthalenes (MN),  
922 dimethylnaphthalenes (DMN), phenanthrene (P), methylphenanthrenes (MP),  
923 dimethylphenanthrenes (DMP), terphenyl-d14 (t-d14), retene (Ret), benzo(*g,h,i*)perylene  
924 (BePery), coronene (Cor).

925

926 **Fig. 3.** Average chain length (ACL) and carbon preference index (CPI) values with  
927 height at Astartekløft.

928

929 **Fig. 4.** Plant beds, (a) the maturity indicators methylphenanthrene index (MPI-1) and  
930 odd-over-even preference (OEP-2), (b) sum of long chain (C<sub>25</sub>–C<sub>33</sub>) *n*-alkanes, (c)  
931 charcoal content (Belcher et al., 2010), (d) PAH concentration and (e) semi-quantitative  
932 concentration (in saturate fraction) of resin derivative with *m/z* 270 base peak with height  
933 at Astartekløft. Horizontal, solid gray line indicates the level of 80% plant species  
934 turnover, and dotted gray line indicates onset of plant diversity loss (McElwain et al.,  
935 1999; McElwain et al., 2007; McElwain et al., 2009).

936

937 **Fig. 5.** Linear regressions, including least squares fit lines and r<sup>2</sup> values, between relative  
938 abundances of eight sporomorph groups counted in a high resolution record from Beds 1–

939 7 (Mander et al., 2010) and  $\delta^2\text{H}_{n\text{-C}25\text{-}29\text{avg}}$  at Astartekløft. None of the apparent  
940 correlations is significant at the 95% level.

941

942 **Fig. 6.** Mass spectrum of an unidentified monoaromatic tricyclic terpenoid compound  
943 (containing *isopropyl* group cf. dehydroabietane type structure), likely derived from  
944 gymnosperm resins.

945

946 **Fig. 7.** Structure of dehydroabietane, with carbon atoms numbered as discussed in text.