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1 **The Pliensbachian-Toarcian paleoclimate transition: New insights**
2 **from organic geochemistry and C, H, N isotopes in a continental**
3 **section from Central Asia**

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25 **Highlights**

- 26 ⇒ Well-preserved Jurassic $\delta^2\text{H}$ signal of *n*-alkanes enables paleoclimatic interpretations.
- 27 ⇒ Oldest ever glycerol dialkyl glycerol tetraethers temperatures are reconstructed.
- 28 ⇒ Humid/cool temperate Late Pliensbachian, associated with high seasonality.
- 29 ⇒ Slightly less humid/warmer conditions in the Early Toarcian.
- 30 ⇒ No drastic changes recorded by the $\delta^{15}\text{N}_{\text{org}}$ values.

31

32 **Abstract**

33 The Taskomirsay section (South Kazakhstan) is a unique Pliensbachian-Toarcian
34 sequence of lignites, clayey layers and silty-sandstones deposited in a fluvial/lacustrine
35 environment with nearby swampy areas. This period, characterized by a drastic climate
36 change, has been particularly studied in Western Tethyan marine environments, whereas very
37 few studies focused on continental settings. Paleoflora analyses, associated with a multi-
38 isotope approach, based on well-preserved Type-III bulk organic nitrogen isotopes ($\delta^{15}\text{N}_{\text{org}}$)
39 and hydrogen isotopic composition ($\delta^2\text{H}$) of *n*-alkanes, were developed to document
40 paleoclimatic changes in the area. Sporomorph associations and fossil woods revealed a
41 globally warm- to cool-temperate climate – characterized by *Xenoxylon*, a conifer
42 morphogenus biogeographically related to cool/humid settings – apart from slightly less
43 humid and warmer conditions in the early Toarcian. Warmer conditions are supported by
44 reconstructed Mean Annual Air Temperatures (MAATs), based on the first branched glycerol
45 dialkyl glycerol tetraethers (brGDGTs) ever recorded in the Early Jurassic. Nevertheless, no
46 drastic changes were recorded in the $\delta^{15}\text{N}_{\text{org}}$ values; its signal being attributed to tenuous
47 equilibrium between water- and nutrient-availability via intense N-recycling. Based on *n*-
48 alkane distributions, sources of organic matter were separated in two pools: (i) a purely

49 terrestrial ($n\text{-C}_{27}$) and (ii) an “aquatic” pool ($n\text{-C}_{23}$) constituted of vegetation that thrived
50 under almost permanent water supply. The n -alkane $\delta^2\text{H}$ values (-248 to -151 ‰) as well as
51 their amounts and average chain lengths (ACL) are in agreement with cool-temperate
52 conditions in the Pliensbachian and less humid/warmer conditions in the early Toarcian. The
53 isotopic difference between $\delta^2\text{H}$ values of $n\text{-C}_{27}$ and $n\text{-C}_{23}$ ($\Delta^2\text{H}_{\text{ter-aq}}$) suggests enhanced
54 seasonality during the Pliensbachian-Toarcian transition and low seasonality in the early
55 Toarcian, in agreement with temperate climate-regime. Finally, contrasted response to
56 paleoclimate changes between markers suggests different spatial integration of those proxies.
57 The role of sea-level variations for $\delta^2\text{H}$ values might also resolve this contrasted response.

58

59 **Keywords**

60 n -Alkanes, $\delta^2\text{H}$, $\delta^{15}\text{N}_{\text{org}}$, *Xenoxylon*, brGDGT

61 **1. Introduction**

62 Major paleoenvironmental changes have been documented during the Early Jurassic and
63 particularly in Western Tethyan marine sections during the Pliensbachian-Toarcian transition
64 (Jenkyns, 1988; Bassoulet and Baudin, 1994; Bailey et al., 2003; Morard et al., 2003;
65 Rosales et al., 2004; Hesselbo et al., 2007; Suan et al., 2010; Hermoso et al., 2012; Korte et
66 al., 2015). During the late Pliensbachian, a $5^\circ\text{--}6^\circ\text{C}$ decrease in sea surface temperatures has
67 been evidenced by $\delta^{18}\text{O}$ and Mg/Ca of carbonates, possibly related to ice sheet development
68 at high latitudes (Bailey et al., 2003; Rosales et al., 2004; van de Schootbrugge et al., 2005;
69 Suan et al., 2010), and a sea level drop (Hallam, 1967; Hesselbo and Jenkyns, 1998). Then, a
70 period of drastic warming ($\sim 8^\circ\text{C}$) has been recorded in sea-surface temperatures during the
71 early Toarcian (Bailey et al., 2003; Rosales et al., 2004; Suan et al., 2010), associated with a
72 sea level rise (Hallam, 1967; Hesselbo and Jenkyns, 1998). The global scale of

73 paleoenvironmental disturbances during the Pliensbachian-Toarcian transition was confirmed
74 by studies on sites located outside Europe in (i) the Neuquén Basin in Argentina (Al-Suwaidi
75 et al., 2010), (ii) the High Atlas, Morocco (Bodin et al., 2010), (iii) the Qaidam Basin,
76 Northwest China (Wang et al., 2005), (iv) the Clarence-Moreton Basin, Eastern Australia
77 (Jansson et al., 2008) and (v) the Arctic (Suan et al., 2011). However, only few studies have
78 focused on non-marine records (Wang et al., 2005; Jansson et al., 2008), mainly because
79 well-dated terrestrial records for the Early Jurassic are much less common than marine ones
80 (Sobel, 1999).

81 The Taskomirsay section (South Kazakhstan, Central Asia) is made of non-marine, coal-
82 rich sediments that encompass the Pliensbachian-Toarcian transition (Schnyder et al.,
83 accepted). This section is a unique target for paleoclimatic reconstructions prior to and during
84 the Pliensbachian-Toarcian transition in a continental setting. A multi-proxy approach was
85 developed to document paleoclimatic changes in the area based on (i) palynological and
86 paleobotanical records, (ii) bulk geochemistry (Rock-Eval and $\delta^{15}\text{N}_{\text{org}}$), (iii) *n*-alkane
87 distribution and their hydrogen isotopic composition ($\delta^2\text{H}$), and (iv) branched glycerol dialkyl
88 glycerol tetraethers (brGDGTs).

89 Palynological records (Schnyder et al., accepted), combined with paleobotanical
90 evidences can help to decipher paleoclimatic background as some wood taxa are
91 paleoecologically well constrained (Philippe and Thévenard, 1996; Philippe and
92 Tchoumatchenco, 2008; Philippe et al., 2013; Oh et al., 2015). Recently, $\delta^{15}\text{N}_{\text{org}}$ measured in
93 lignites and clayey layers was used to indicate wet/dry cycles during the Paleocene-Eocene
94 transition (Storme et al., 2012) and the Eocene-Oligocene transition (Tramoy et al., 2016).
95 Early studies indeed showed that $\delta^{15}\text{N}_{\text{org}}$ values were positively correlated to temperature and
96 negatively to precipitation in Quaternary and modern plants (Austin and Vitousek, 1998;
97 Handley et al., 1999; Amundson et al., 2003; Swap et al., 2004; Liu and Wang, 2008).

98 Considering the potential of $\delta^{15}\text{N}_{\text{org}}$ as a paleoclimatic marker for pre-Quaternary sediments
99 (Storme et al., 2012; Tramoy et al., 2016), it will be tested in the Early Jurassic of the
100 Taskomirsay sequence. Similarly, compound-specific $\delta^2\text{H}$ values are often used as a
101 paleohydrological proxy (Sachse et al., 2012; Sessions, 2016). Major calibration efforts
102 during the last decade allowed improving their use for paleoclimatic reconstructions in the
103 Quaternary (e.g., Hou et al., 2006; Jacob et al., 2007; Mügler et al., 2008; Aichner et al.,
104 2010), but also in the Cenozoic (Andersen et al., 2001; Pagani et al., 2006; Garel et al., 2013),
105 and even in the Paleozoic (Dawson et al., 2004; Izart et al., 2012). However, to the best of our
106 knowledge, compound-specific $\delta^2\text{H}$ values have only been scarcely used in Mesozoic
107 sediments and not for paleoclimatic purpose (Radke et al., 2005). Yet, the $\delta^2\text{H}$ of *n*-alkanes
108 preserved in ancient sediments has great potential because *n*-alkanes are much less prone to
109 diagenetic effect than other compounds, because H is strongly bound to C and thus alkanes
110 retain their original hydrogen isotopic composition (Yang and Huang, 2003; Izart et al., 2012;
111 Sessions, 2016). During the last decade, proxies based on branched bacterial membrane lipids
112 (brGDGTs; Schouten et al., 2013), have been developed to reconstruct Mean Annual Air
113 Temperatures in terrestrial settings (MAAT; Weijers et al., 2007; Peterse et al., 2012;
114 Coffinet et al., 2014) and their use for ancient sediments deserves evaluation.

115 The aim of the present study was to assess the paleoclimatic conditions during the
116 Pliensbachian-Toarcian transition in the sedimentary succession of Taskomirsay using multi-
117 proxy analyses: paleobotany, $\delta^{15}\text{N}_{\text{org}}$, *n*-alkane distributions and $\delta^2\text{H}$ values, and, although
118 restricted to a selected set of samples, brGDGTs.

119

120 **2. Material and methods**

121 *2.1. Taskomirsay section*

122 The Taskomirsay section is located in the Karatau (Leontiev Graben), South Kazakhstan,
123 which is one of the numerous continental basins, in central Asia, aligned along the North
124 Tethyan-paleomargin (Fig. 1). These basins were formed by collisions between Eurasia and
125 several blocks (Tarim, Tian Shan and Pamir Kunlun) in a transtensional/transpressional
126 context between the Late Triassic and the Early Jurassic (Sobel, 1999). During the Early
127 Jurassic, the paleolatitudinal position of the Karatau basin was estimated to $36^{\circ} \pm 8^{\circ}$ N,
128 based on paleomagnetic reconstructions (B. Vrielynck, pers. com. 2014), in agreement with
129 paleofloral assemblages (40° N; Kirichkova and Doludenko, 1996), which is very close to
130 present latitudes (Fig. 1). Thick piles of terrestrial sediments were deposited thanks to the
131 coexisting high tectonic subsidence.

132 The study section is 53.5 m thick (0 m represents the base of the section) and shows 6
133 organic-rich sedimentary cycles (Fig. 2; Schnyder et al., accepted). Each cycle exhibits lignite
134 beds (noted LB1 to LB6) overlaid by non-laminated clayey layers and silty-sandstone
135 showing root and trunk surfaces at their top. The succession of lignites, clayey layers and
136 silty-sandstones suggests a meandering river system, in which developed oxbow lakes and
137 peat deposits thanks to the lateral migration of the river system. At the top of the section, a
138 more open and less marginal lacustrine environment under storm influence is deduced from
139 *Botryococcus*, clay/silt alternations and hummocky cross-beddings (HCS) (Schnyder et al.,
140 accepted). Wood fragments are frequent along the section and are particularly concentrated in
141 three surfaces labeled TP1, TP2 and TP3 (Fig. 2). Macroscopically, they exhibit an excellent
142 morphological preservation and are found in the tops and insides of silty-sandstones, and
143 always in vertical position, suggesting *in situ* trunks or roots (Schnyder et al., accepted).
144 These sedimentological features are in agreement with peaty/swampy forests in lowland

145 terrains and trees in sandy river banks and/or in upland forests, as might be expected from the
146 paleoclimatic latitudinal patterns during the Early Jurassic, with warm to cool-temperate
147 conditions prevailing from mid to high boreal latitudes (Miao et al., 1989; Rees et al., 2000;
148 Wang et al., 2005).

149 Despite the common difficulty to date such continental settings, the Pliensbachian-
150 Toarcian transition was identified between ~26 m and ~35 m, based on sporomorph
151 associations and organic carbon isotopes ($\delta^{13}\text{C}_{\text{org}}$; Schnyder et al., accepted). The section was
152 thus dated no younger than the early Toarcian and no older than the mid-Pliensbachian.

153 *2.2. Analytical methods*

154 *2.2.1. Fossil wood analyses*

155 Fossil wood samples were studied with collodion micro-casting, following a method
156 described in Marynowski et al. (2013). Despite their good macroscopic morphological
157 preservation, woody axes were revealed to be microscopically degraded by both bacterial and
158 fungal rots. This condition is consistent with a relatively slow burial history, before
159 diagenesis stopped biological decay. As a consequence, only one specimen was preserved
160 enough for specific identification, although the others did not display significantly different
161 features that could suggest a different systematic position. The wood specimen was identified
162 at a generic level from the Philippe and Bamford (2008) key and at a species level with the
163 Philippe et al. (2013) key.

164

165 *2.2.2. Bulk organic analyses*

166 Total organic carbon (TOC) values were obtained for 100 samples, sampled regularly
167 along the study section, using a Leco automatic carbon analyzer (IR-212) that gives more
168 reliable TOC values for samples containing large amounts of terrestrial OM than Rock-Eval

169 pyrolysis (Espitalié et al., 1985). A total of 88 samples, including 3 replicates, were analyzed
170 by Rock-Eval pyrolysis using a Rock-Eval 6. For this study, the following Rock-Eval
171 parameters were used: (i) Hydrogen Index (HI, mg HC/g TOC), which is the amount of
172 products released during pyrolysis normalized to TOC values; (ii) Oxygen Index (OI, mg
173 CO₂/g TOC), calculated from the amounts of CO and CO₂ released during pyrolysis, which
174 represents the oxygen content of the OM; and (iii) T_{max}, which is the temperature of the
175 pyrolysis oven recorded at the maximum of HC production (Espitalié et al., 1985). After
176 Rock-Eval pyrolysis, a few samples were suspected to contain siderite that compromised
177 measurements of the Rock-Eval parameters, especially for OI values. This suspicion was
178 supported by very low dissolution rate of carbonates in 6N HCl. Concerned samples were
179 removed from the dataset. In addition, samples with low S2 peak values (S2 <0.3) – leading
180 to misestimation of HI values, were also removed. In total, 29 samples were removed from
181 the dataset and will not be discussed further.

182

183 2.2.3. Bulk organic nitrogen isotopes ($\delta^{15}N_{org}$)

184 A total of 52 samples were analyzed for $\delta^{15}N_{org}$. Only samples with TOC values >1 wt. %
185 were selected, because nitrogen content in Taskomirsay sediments is usually very low.
186 Because inorganic nitrogen (N_{bnd}) is strongly bound to clay minerals as ammonium (Müller,
187 1977), it is easier to remove organic nitrogen (N_{org}) and recalculate the $\delta^{15}N_{org}$ by mass-
188 balance, knowing total nitrogen (N_{tot}), N_{bnd} and their respective isotopic signatures $\delta^{15}N_{tot}$ and
189 $\delta^{15}N_{bnd}$ (Storme et al., 2012). N_{tot} and $\delta^{15}N_{tot}$ were measured on powdered/decalcified
190 samples, whereas N_{bnd} and $\delta^{15}N_{bnd}$ were measured on subsamples that were treated with
191 KOB_r-KOH solution (2 mol/l) to eliminate the N_{org} (Silva and Bremner, 1966; Schubert and
192 Calvert, 2001). The solution consisted of 6 ml pure bromine added at 0.5 mL/min to 200 ml
193 of 2M KOH cooled with ice. Between 500 to 1000 mg of subsamples were immersed in 20

194 ml of the K₂OBr-KOH solution with magnetic stirring. After 2 hours, 60 ml of distilled water
195 was added to each subsample before being boiled in an oil-bath at ~200 °C for at least 5 min.
196 With this treatment, organic nitrogen is liberated in ammonium form and stays in solution.
197 The mixture was washed the next day by repetitive centrifugation (2x; 4000 rpm; 1.5 min)
198 with 0.5 M of KCl to remove the released ammonium. Potassium added to the solution
199 process prevents the adsorption by clay minerals of the ammonium released during the
200 previous oxidation. Then, subsamples were washed again with distilled water to remove
201 nitrogen complex salts from the solution. Samples were finally dried and powdered again for
202 isotope analyses.

203 N_{tot} , N_{bnd} of samples and their respective isotopic signature $\delta^{15}N_{\text{tot}}$ and $\delta^{15}N_{\text{bnd}}$ were
204 determined by mass spectrometry using a Thermo Scientific Delta V plus mass spectrometer
205 connected to a ConFlo IV dilution system, coupled with a Flash 2000 analyzer for elemental
206 analyses. The analytical accuracy and precision of the system were monitored using tyrosine
207 ($\delta^{15}N = 10.01 \text{ ‰}$) as an internal laboratory standard, that was calibrated on international
208 standards IAEA-N-1 ($\delta^{15}N = 0.4 \text{ ‰}$), IAEA-N-2 ($\delta^{15}N = 20.3 \text{ ‰}$) and IAEA-NO-3 ($\delta^{15}N =$
209 4.7 ‰). Isotopic values were then expressed relative to the international N₂ air reference. The
210 overall precision was better than 0.2 ‰ above 40 µg of nitrogen and 0.3 ‰ below this
211 amount. Replicate analyses led to a mean standard deviation better than 0.1 ‰ for $\delta^{15}N$
212 values and better than 0.001 % for the nitrogen content. For isotopic values measured with
213 nitrogen amount above 40 µg, the replicate standard deviation was applied. For those
214 measured below this amount, the standard deviation based on tyrosine (0.3 ‰) was applied,
215 even if the standard deviation based on replicates was lower.

216

217 2.2.4. Lipid extraction

218 Lipid extractions were performed on 11 lignites, 2 trunk/root-like samples, and 12 clayey
219 layers. Samples were extracted with an accelerated solvent extractor (ASE 100, DionexTM),
220 using a dichloromethane (DCM):methanol (MeOH) (2:1, v:v) mixture. A 34 mL cell was
221 used with the following extraction protocol: temperature at 60 °C, pressure at 10⁶ Pa, one
222 static time during 20 min, 100 % flush and 100 s purge, all repeated 3 times. The lipid extract
223 was then concentrated under vacuum and further evaporated under a smooth nitrogen flow to
224 avoid loss of volatile molecules. The total lipid extracts (TLE) were then weighed, dissolved
225 in heptane and separated on alumina solid phase extraction columns into an apolar and a
226 polar fraction. The apolar fraction was eluted with heptane:DCM (99:1, v:v) and the polar
227 fraction was eluted with DCM:MeOH (2:1, v:v). C₁₂-alkane was added as an internal
228 standard before analysis by gas chromatography-mass spectrometry (GC-MS) for
229 identification and quantification purposes. *n*-Alkane content, their Carbon Preference Index
230 (CPI) and average chain length (ACL) were calculated as follows, over the range C₂₁-C₃₅:

231

232 $n\text{-alkane content} = \Sigma[C_i]$ (1)

233

234
$$CPI = \frac{1}{2} \times \left(\frac{\Sigma[C_{odd(21-35)}]}{\Sigma[C_{even(20-34)}]} \right) + \frac{1}{2} \times \left(\frac{\Sigma[C_{odd(21-35)}]}{\Sigma[C_{even(22-36)}]} \right)$$
 (2)

235

236 $ACL = \Sigma(C_i \times [C_i]) / [C_i]$ (3)

237

238 where $[C_i]$ is the concentration of the odd *n*-alkanes (µg/g TOC) with carbon number C_i.

239 Apolar fractions were further eluted with heptane on silica gel-type silica columns in
240 order to purify the *n*-alkane fraction before δ²H analysis by gas chromatography-isotope ratio

241 mass spectrometry (GC-irMS). Silica was previously extracted with DCM, then activated at
242 120 °C for 24 h and finally deactivated with 5 wt. % H₂O.

243

244 2.2.5. LC-MS analysis

245 Polar fractions obtained after separation of the TLEs over alumina columns were rotary
246 evaporated, re-dissolved in 1 ml heptane and centrifuged using an Eppendorf Mini Spin
247 centrifuge (1 min, 7000 rpm). The supernatant was collected and analyzed by high
248 performance liquid chromatography-atmospheric pressure chemical ionization mass
249 spectrometry (HPLC/APCI-MS). HPLC/APCI-MS analyses were performed with a
250 Shimadzu LCMS-2020. GDGTs were analyzed using a procedure described in Huguet et al.
251 (2013). MAAT were calculated using Weijers et al. (2007) and Peterse et al. (2012)
252 calibrations, based on MBT and CBT indices as described in Coffinet et al. (2014).

253

254 2.2.6. GC-MS analysis

255 GC-MS analyses were performed on an Agilent 6890N gas chromatograph coupled with
256 an Agilent 5973 Mass Selective Detector mass-spectrometer. The GC was fitted with a
257 Restek RTX-5Sil-MS column (30 m × 0.25 mm i.d., 0.5 µm film thickness) under constant
258 helium flow of 1 ml/min. Samples were dissolved in heptane and 1 µl injected in splitless
259 mode with the injector temperature set at 320 °C. GC operating conditions were as follow:
260 initial temperature hold at 80 °C for 30 s, then increased from 80 to 100 °C at 10 °C/min and
261 from 100 to 320 °C at 4 °C/min with a final isothermal hold at 320 °C for 20 min. The mass
262 spectrometer was operated in the electron ionization (EI) mode at 70 eV ionization energy
263 and scanned from 35 to 800 Da. Biomarkers were identified based on mass spectra and
264 retention times. Quantification was performed thanks to the peak area in Total Ion Current

265 (TIC) of each identified molecule. The peak areas were then normalized to the peak area of
266 the internal standard C₁₂-alkane, measured on the TIC and then normalized to the total
267 organic carbon (TOC) of the sample.

268

269 2.2.7. GC-irMS analysis ($\delta^2\text{H}$)

270 The hydrogen isotopic composition of *n*-alkanes ($\delta^2\text{H}$) was determined by GC-irMS using
271 a Trace GC chromatograph equipped with a Triplus autosampler, connected to a GC-Isolink
272 pyrolysis interface, a ConFlo IV dilution system coupled to a DeltaV Advantage isotope ratio
273 mass spectrometer, all from ThermoElectron (Bremen, Germany). A mixture of *n*-alkanes (*n*-
274 C₁₆ to *n*-C₃₀, Arndt Schimmelmann, Indiana University, Bloomington, IN, USA) was
275 analyzed before and after each set of 5 injections, allowing monitoring the precision and
276 accuracy of the system. The overall precision for the *n*-alkane standard $\delta^2\text{H}$ values was better
277 than 6 ‰ and were in good agreement with those measured off line. H₂ gas with known
278 isotopic composition was used as an internal reference and $\delta^2\text{H}$ values of samples were
279 normalized to the VSMOW international isotopic scale by using the standard *n*-alkane
280 mixture. The mean precision (standard deviation) for triplicate analyses was better than 6 ‰
281 for $\delta^2\text{H}$ values of the C₁₇ to C₃₅ *n*-alkanes and of pristane, and better than 7 ‰ for phytane.
282 The H₃⁺ factor was calculated prior to analyses and was consistently below 3 ppm V⁻¹.
283 Because of the low amount of biomarkers in some samples, only 18 samples could be
284 analyzed for $\delta^2\text{H}$ out of 25 lipid extracts. Among the 18 samples, it was not possible to
285 measure accurately the whole range of *n*-alkanes for all samples, depending on their
286 respective concentration.

287

288 3. Results

289 3.1. Fossil woods

290 Many pieces of fossil woods are present along the section, although only one sample was
291 positively identified as *Xenoxylon fuxinense* Ding in the TP3 trunk surface. The other samples
292 (trunk surfaces 1, 2 and 3) did not seem to differ. However, their preservation state was too
293 poor for safe identification. *X. fuxinense* is a secondary xylem documented from the Later
294 Liassic (Negoya Fm.) of the Kuruma Group, Japan, to the Early Cretaceous (Aptian-Albian,
295 Fuxin Fm.) of Liaoning, China. It is an Asian endemic taxon usually restricted to relatively
296 high paleolatitudes (Philippe and Thévenard, 1996; Philippe et al., 2013).

297

298 3.2. Bulk geochemistry

299 Exhaustive TOC values and Rock-Eval data are available in supplementary data. TOC
300 values range from 38.7 to 75.8 wt. % in lignites, from 0 to 24.4 wt. % in clayey layers and
301 from 0 to 0.9 wt. % in silty-sandstones. Except for one coalified root/trunk, T_{\max} values are
302 always below 440 °C (424 °C in average). In lignites, HI values range from 38 to 217
303 mg HC/g TOC (128 mg HC/g on average) and OI values range from 19 to 80 mg CO₂/g TOC
304 (35 mg CO₂/g TOC on average). In clayey layers, HI values range from 29 to 136
305 mg HC/g TOC (74 mg HC/g on average) and OI values range from 19 to 165 mg CO₂/g TOC
306 (52 mg CO₂/g TOC on average). In an HI-OI diagram, the Taskomirsay samples plot in the
307 Type-III zone (Fig. 3), suggesting an OM dominated by terrestrial plants (Espitalié et al.,
308 1985).

309 Total nitrogen contents range between 0.05 and 1.48 wt. % (Table 1). Considering high
310 TOC values (>40 %) in lignites and the very low amount of clay in this lithology, we assume
311 that N_{tot} is almost equal to N_{org} . In a plot of % N_{tot} vs %TOC (Fig. 4), there is an intercept of

312 0.04 % N at 0 % TOC showing a significant fraction of inorganic N bound in clay minerals
313 (Schubert and Calvert, 2001) for samples below 20 % of TOC (clayey layers), whereas there
314 is a negligible intercept of 0.002 % N when considering %N_{org} vs %TOC. Thus, to calculate
315 accurate atomic C/N ratios, we used N_{tot} for lignites and N_{org} for clayey layers. In
316 Taskomirsay, C/N ratios range from 38 to 132 (Table 1).

317

318 3.3. Nitrogen isotopes

319 Together with the absence of clay – prone to adsorb inorganic nitrogen (Müller,
320 1977) – in lignites or coalified trunks, we argue for the use of the $\delta^{15}\text{N}_{\text{tot}}$ values as
321 representatives of the $\delta^{15}\text{N}_{\text{org}}$ values. Indeed, Tramoy et al. (2016) have shown that $\delta^{15}\text{N}_{\text{tot}}$
322 values were driven by $\delta^{15}\text{N}_{\text{org}}$ values in Eocene-Oligocene terrestrial sediments. In
323 Taskomirsay, the $\delta^{15}\text{N}_{\text{tot}}$ values range between 2.5 and 3.8 wt. ‰ (3.2 ‰ on average; Table 1
324 and Fig. 2). Except for one sample (TP3-224), $\delta^{15}\text{N}_{\text{org}}$ values of clay samples were almost
325 equal to their $\delta^{15}\text{N}_{\text{tot}}$ values

326

327 3.4. Alkanes

328 *n*-Alkane amount range between 11 and 621 $\mu\text{g/g}$ TOC (192 $\mu\text{g/g}$ TOC on average;
329 Table 2), except TP1-65 (clay) that yielded ~ 3300 $\mu\text{g/g}$ TOC. It is noteworthy that the
330 amount of *n*-alkanes decreases from the base of the section to the base of LB5 at 32.3 m,
331 before it increases to the top. These trends are even more marked within lignite beds, with
332 values gradually decreasing from LB1 to LB5 (315 $\mu\text{g/g}$ TOC to 18 $\mu\text{g/g}$ TOC on average),
333 while TOC values remain similar (Table 2; Fig. 5).

334 The distribution of *n*-alkanes is highly variable along the section, with patterns
335 generally not being related to lithology or depth (Fig. 5). The distribution of *n*-alkanes in
336 lignite beds from the bottom part (LB1 and LB2) is similar, with a bimodal distribution: a

337 strong maximum at C₃₅ and a sub-maximum at C₂₉. In LB3, distribution is also bimodal with
338 a maximum at C₂₁ or C₂₃ and strong sub-maximum at C₃₅. The lignites from the middle part
339 of the section in LB4 and LB5 have a unimodal distribution maximizing at C₂₁ or C₂₃. In
340 LB6, three different patterns are recorded: a unimodal distribution maximizing at C₂₅ in TP3-
341 195, at C₂₁ in TP3-203 and pattern similar to those reported in LB1 and LB2 in TP3-216.
342 Clayey samples TP1-22, TP3-157 and TP3-176 show a unimodal distribution maximizing at
343 C₂₅ or C₂₇, whereas the distribution is affected by an unusual amount of C₁₈ in most of the
344 others, leading to a bimodal and even trimodal distribution in TP3-224 that results from a
345 strong contribution of C₃₅ (Fig. 5). In particular, the two trunk/root samples (TP1-65 and
346 TP1-114) show similar patterns clearly maximizing at C₂₃.

347 Most of the samples have a marked odd/even predominance in the range C₂₁ to C₃₅.
348 They often exhibit Carbon Preference Indices (CPI) higher than 2 and sometimes reaching
349 5.5 (Table 2). This odd predominance is mainly driven by the longest homologues (> C₂₅),
350 which are usually attributed to higher plant leaf-wax input (Eglinton et al., 1962; Eglinton
351 and Hamilton, 1967; Meyers, 1997). Shorter-chain *n*-alkanes (<C₂₁) – generally attributed to
352 algal/bacterial sources (Blumer et al., 1971; Cranwell et al., 1987; Giger et al., 1980; Meyers,
353 1997; Ladygina et al., 2006) – are in relatively low amounts (24 wt. % ± 15%) when
354 compared to *n*-alkanes above C₂₁.

355 The ACL values of the *n*-alkanes were calculated over the range C₂₁-C₃₅ to cover the
356 range of *n*-alkanes found in aquatic and terrestrial plants (e.g., Eglinton and Hamilton, 1967;
357 Ficken et al., 2000; Diefendorf et al., 2011). ACL values range between 22.4 and 31.8 (Table
358 2; Fig. 5). A similar trend is observed for the evolution of the ACL values and that of the
359 amount of *n*-alkanes, *i.e.* the ACL and *n*-alkane amounts show maximal values in LB1 to
360 decrease toward LB4 and LB5. Another minimal value is observed for LB6, before it
361 increases again to the top of the section.

362 Pristane (Pr) and phytane (Ph) were detected in all samples in small amounts at level
363 of ~9 and ~8 $\mu\text{g/g}$ TOC on average, respectively (not shown). Pr/Ph ratios show large
364 variations, ranging from 0.3 in clayey samples with poor organic matter content up to 7.6 in a
365 lignite. The highest values are observed in lignites or clayey OM-rich samples (Table 2).

366 3.5. Compound-specific hydrogen isotopes ($\delta^2\text{H}$)

367 $\delta^2\text{H}$ values were determined for C_{17} to C_{35} *n*-alkanes and for the isoprenoid pristane
368 and phytane (Table 3; Fig. 6). Results for *n*-alkanes as well as pristane and phytane are
369 reported along the section in Fig. 7.

370

371 3.5.1. Alkanes

372 $\delta^2\text{H}$ values range between -248 and -151 ‰. Maximal variability is observed for *n*- C_{27}
373 with 90 ‰ between minimum (-242 ‰) and maximum (-152 ‰) values. The variability of
374 $\delta^2\text{H}$ values is also high for *n*- C_{19} to *n*- C_{25} (Fig. 6). In addition, the longer the chain, the more
375 ^2H -enriched are the *n*-alkanes, except for the *n*- C_{35} . The latter is ^2H -depleted when compared
376 to common vascular plant *n*-alkanes (C_{27} to C_{31} , Eglinton and Hamilton, 1967), but is still ^2H -
377 enriched when compared to $<\text{C}_{27}$ *n*-alkanes.

378 Along the section, $\delta^2\text{H}$ values exhibit generally parallel trends (Fig. 7). In detail, three
379 main features are recorded. First, the offset between $\delta^2\text{H}$ values of two groups of *n*-alkanes
380 increases from the base of LB1 to the base of LB5: the most negative values are recorded for
381 *n*-alkanes $<\text{C}_{25}$, whereas longer chain *n*-alkanes show more positive values. Second, $\delta^2\text{H}$
382 values of all the *n*-alkanes increase drastically in the intercalated organic-rich clayey layer in
383 LB5 (TP3-157) and then remain at almost constant high values (-174 ± 11 ‰) until LB6. At
384 this point, $\delta^2\text{H}$ decreases to lower values (-191 ± 17 ‰) before increasing again in the
385 overlaying clayey layer (-169 ± 10 ‰). This general increase in $\delta^2\text{H}$ values occurs for all the

386 *n*-alkanes. Third, lower $\delta^2\text{H}$ values were measured in lignites, alternating with higher values
387 measured in clayey layers and trunk/root samples (Fig. 6). However, this feature is less
388 obvious for *n*-alkanes $>\text{C}_{27}$.

389

390 3.5.2. Isoprenoids

391 The $\delta^2\text{H}$ values of pristane and phytane range between -303 and -260 ‰ (-283 ‰ on
392 average) and between -311 and -233 ‰ (-274 ‰ on average), respectively. Pristane and
393 phytane are systematically ^2H -depleted when compared to *n*-alkanes with $\Delta^2\text{H} = -80$ ‰ on
394 average, where $\Delta^2\text{H}$ is the difference between the average $\delta^2\text{H}$ value of the isoprenoids and
395 the average $\delta^2\text{H}$ value of the *n*-alkanes (Fig. 6).

396 3.6. brGDGT

397 The brGDGTs required for MAAT calculation were detected and could be quantified
398 in only 7 samples (see supplementary data for details). They represent the oldest GDGTs ever
399 recorded to date (Schouten et al., 2013). The use of this proxy is therefore attempted for the
400 first time in the Early Jurassic and must be taken with caution. According to the calibration of
401 Weijers et al. (2007), MAATs range between -1.1 °C and 18.0 °C, while they range between
402 4.0 °C and 15.9 °C based on the Peterse et al. (2012) calibration (Table 2). Although they
403 show the same trends, negative MAATs values during the Early Jurassic are very unlikely.
404 Thus, the first set of MAATs values will not be further considered, and only trends will be
405 considered for the second one. Here, an increasing trend was observed during the early
406 Toarcian (cf. Fig. 9).

407 **4. Discussion**

408 *4.1. Preservation of organic matter*

409 The organic matter is mainly immature ($T_{\max} < 440$ °C) and experienced a limited burial,
410 allowing paleoenvironmental interpretations (Espitalié et al., 1985, see supplementary data
411 1). Higher HI values in lignites as compared to clayey layers suggest a relatively better
412 organic matter preservation in lignites, although a matrix mineral effect in clayey layers
413 leading to lower HI values cannot be excluded (Espitalié et al., 1985). However, higher OI
414 values in clayey layers relative to lignites are in agreement with a slightly less preserved
415 organic matter in clayey layers, probably resulting from oxidative conditions at the water-
416 sediment interface or during transport processes for silty-sediments (Espitalié et al., 1985). In
417 addition, no significant correlation was recorded between $\delta^{15}\text{N}$ values and either TOC or TN
418 values ($n=52$; $p \gg 0.05$), suggesting a relative independence between the isotopic composition
419 and the organic content.

420 The $\delta^2\text{H}$ values of individual lipid biomarkers are much less prone to diagenetic alteration
421 when compared to bulk organic matter, because (i) specific compounds are not influenced by
422 preferential degradation of less stable compounds (Andersen et al., 2001) and (ii) hydrogen in
423 lipids is strongly bound to carbon and considered non exchangeable, which allows the
424 conservation of the primary $\delta^2\text{H}$ values of lipids at temperatures above 150 °C
425 (Schimmelmann et al., 1999). To this respect, Dawson et al. (2004) reported *n*-alkanes and
426 isoprenoids that retained their original $\delta^2\text{H}$ values in relatively immature torbanites as old as
427 the Late Carboniferous.

428 It has been suggested that the transfer of hydrogen from water to organic matter is the
429 most important mechanism leading to hydrogen-isotope exchange (Schimmelmann et al.,
430 2006), whereas hydrogen is thought to be totally exchanged on very long geological
431 timescale (hundreds of million years, Koepp, 1978; Sessions, 2016). This mechanism leads to

432 the homogenization of $\delta^2\text{H}$ values of specific compounds, thus overprinting their primary $\delta^2\text{H}$
433 values (Yang and Huang, 2003; Sessions et al., 2004; Pedentchouk et al., 2006). In
434 Taskomirsay, such a homogenization of $\delta^2\text{H}$ values was not observed as indicated by both the
435 large variability in $\delta^2\text{H}$ values of homologous *n*-alkanes (up to 90 ‰) and between adjacent
436 sedimentary layers (i.e. samples TP2-140 vs. TP3-151; Fig. 6 and 7). The high CPI (>1) also
437 argues against post-depositional alteration of the $\delta^2\text{H}$ values (Pedentchouk et al., 2006). Most
438 importantly, an offset ($\Delta^2\text{H} = 80$ ‰ on average, Fig. 6) between the $\delta^2\text{H}$ values of *n*-alkanes
439 and isoprenoids was recorded. In Taskomirsay, this offset is similar to the offset recorded in
440 modern biological samples (Sessions et al., 1999; Chikaraishi et al., 2004) and rules out any
441 extensive homogenization of $\delta^2\text{H}$ values (Andersen et al., 2001; Dawson et al., 2004;
442 Sessions et al., 2004).

443 On the basis of these lines of evidence, we can conclude that the organic proxies mainly
444 reflect primary environmental signals, thus allowing paleoenvironmental interpretations.

445

446 4.2. Sources of organic matter

447 The sporomorph associations as well as fossil woods argue for a well-developed
448 terrestrial macro-paleoflora. The presence of *Xenoxylon* from LB2 to the transition zone,
449 inferred from fossil woods, is also confirmed by infra-millimeter wood fragments, belonging
450 to *Xenoxylon*, observed in palynological slides (Schnyder et al., accepted). After the transition
451 zone, lacustrine areas are suggested by sedimentology and the presence of *Botryococcus* sp.
452 and *Ovoidites* from ~45 m (Schnyder et al., accepted). However, the Type-III organic matter
453 points to a major contribution of vascular plants to the organic matter through the entire
454 section (Fig. 3; Espitalié et al., 1985), confirmed by (i) woods *in situ*, (ii) wood fragments

455 associated with sporomorphs (Schnyder et al., accepted) and (iii) the combination of atomic
456 C/N ratios and $\delta^{13}\text{C}_{\text{org}}$ values (Tyson, 1995; Meyers, 1997; Fig. 8).

457 The terrestrial origin of the organic matter is confirmed at the molecular level by the
458 distribution of *n*-alkanes dominated by $>\text{C}_{21}$ *n*-alkanes associated with CPI >1 (Eglinton and
459 Hamilton, 1967; Ficken et al., 2000; Diefendorf et al., 2011), whereas a minor algal/bacterial
460 contribution is deduced from the relatively low amount of shorter chain *n*-alkanes, except in
461 clayey and OM poor samples where *n*- C_{18} usually dominates (Fig. 5; Blumer et al., 1971;
462 Cranwell et al., 1987; Giger et al., 1980; Meyers, 1997; Ladygina et al., 2006). Despite
463 various possible sources of pristane and phytane, Pr/Ph ratios <1 observed in those samples
464 are consistent with the development of bacteria in anoxic/suboxic hypersaline environments,
465 whereas Pr/Ph ratios $\gg 1$ in OM-rich sediments agree with a terrestrial organic matter
466 deposited in oxic environments (Table 2; Didyk et al., 1978; Peters et al., 2005; Riboulleau et
467 al., 2007).

468 Long-chain *n*-alkanes (C_{27} , C_{29} , C_{31}) are usually attributed to land-plant waxes (Eglinton
469 et al., 1962; Eglinton and Hamilton, 1967). In Taskomirsay, they are likely produced by
470 gymnosperms since the major diversification of angiosperms occurred much later, during the
471 Early Cretaceous (Gee, 2000), about 50 My after the study period. However, long-chain *n*-
472 alkanes (C_{27} - C_{31}) with strong odd/even carbon predominance could also result from an algal
473 input (e.g., *Botryococcus* spp., Lichtfouse et al., 1994; Riboulleau et al., 2007). Thus, an algal
474 influence on the long-chain *n*-alkanes in TP3-224 cannot be ruled out, in agreement with the
475 lowest C/N ratio recorded (C/N = 38) in the section.

476 *n*-Alkanes C_{21} to C_{25} are generally predominant in lignites and trunk/root samples from
477 LB3 to the base of LB6 (Fig. 5). They have been reported to originate from modern
478 *Sphagnum* (Baas et al., 2000; Nott et al., 2000) and aquatic macrophytes (Ficken et al., 2000;
479 Bechtel et al., 2007), thus representing an aquatic environment. But, sphagnums are unlikely

480 important sources for those *n*-alkanes, because they radiated during the Miocene and only
481 rare fossils and spores related to proto-sphagnums have been reported in the Mesozoic (Shaw
482 et al., 2010). Alternatively, mosses might be a valuable source of these *n*-alkanes since they
483 have been recognized at least from the lower Carboniferous (Thomas, 1972). However, no
484 sporomorph of mosses or sphagnums could be recognized (Schnyder et al., accepted).

485 The major contribution of the C₂₃ in most of the samples (Fig. 5) is more likely attributed
486 to conifers as this distribution is close to the general trend observed in the latter, with maxima
487 at C₂₃ and C₂₅ (Oros et al., 1999; Nakamura et al., 2010). This is supported by the unimodal
488 distribution maximizing at C₂₃ observed in the two trunk/root samples TP1-65 and TP1-114.
489 Further evidence come from the high concentration of fossil trunks/roots in life positions
490 through the section in agreement with peaty/swampy forests – inferred from the numerous
491 coal-rich formations in the North Hemisphere – characterizing the Early Jurassic (Miao et al.,
492 1989; Rees et al., 2000; Wang et al., 2005). In addition, C₂₀-C₂₃ alkanes have been reported in
493 Carboniferous coalified paleoflora (Disnar and Harouna, 1994), in Carboniferous-Permian
494 terrigenous/coaly sediments (Scheffler et al., 2003), and in the Late Oligocene *Taxodium*
495 *dubium* (*Cupressaceae s.l.*) fossil plant maximizing at C₂₁ (Stefanova et al., 2013). The first
496 authors attributed the Carboniferous coals to Paleozoic Gondwana swamp flora made of
497 conifer precursors, whereas Stefanova et al. (2013) emphasized that *Taxodium dubium* was
498 known in marshy environments and flooded lowland terrains. Finally, the distribution of *n*-
499 alkanes in *Xenoxylon* fossil woods collected in the Bajocian/Callovian of Poland and
500 Germany – paleoecologically related to environments with no water restriction, usually
501 riparian forests and swamps (Oh et al., 2015) – also maximizes at C₂₃ (Marynowski et al.,
502 2008), although these authors attributed the presence of *n*-alkanes to contaminations by host
503 clays. This is not the case here when compared the root/trunk TP1-65 to its host clays (TP1-
504 65bis) as they show large differences in their *n*-alkane distribution (Fig. 5). To our opinion,

505 all these lines of evidence support the hypothesis that C₂₁–C₂₃ *n*-alkanes in our samples could
506 result from conifers like *Xenoxylon* that thrived in flooded environments.

507 In summary, those evidences support the use of *n*-C₂₁–*n*-C₂₃ as representing an
508 environment under an almost permanent shallow water layer, and the use of *n*-C₂₇–*n*-C₃₁ as
509 strictly terrestrial vascular plant biomarkers (eg. Ficken et al., 2000; Sachse et al., 2004;
510 Mügler et al., 2008). Accordingly, C₂₁–C₂₃ *n*-alkanes will be considered as deriving from an
511 “aquatic pool” and C₂₇–C₃₁ *n*-alkanes from a “terrestrial pool”, respectively, for this study. As
512 δ²H values of C₂₃ and C₂₇ *n*-alkanes were accurately measured for all samples, they will be
513 considered as representative of the aquatic and terrestrial pool, respectively.

514 The existence of these two different pools could explain the offset between the δ²H values
515 of the ²H-depleted aquatic pool and the ²H-enriched terrestrial pool (Fig. 6 and 7). ²H-
516 enriched C₂₇–C₃₁ *n*-alkanes suggest hydrogen loss by evaporation and/or vascular plant
517 transpiration (Sachse et al., 2004, 2006), whereas the ²H-depleted C₂₁–C₂₃ *n*-alkanes suggest
518 that they originate from organisms that do not evapotranspire (e.g., aquatic macrophytes;
519 Ficken et al., 2000; Nott et al., 2000; Bechtel et al., 2007) or from organisms living in high
520 relative humidity sub-environments (e.g., ombrotrophic peatlands; Nichols et al., 2009).

521 The origin of the C₃₃ and C₃₅ *n*-alkanes that are dominant at the base and at the top of the
522 section (Fig. 5) is uncertain as such a predominance has never been reported in sediments to
523 date. However, these homologues were found to be major *n*-alkanes in some modern
524 *Cupressaceae* (Dodd et al., 1998; Diefendorf et al., 2011; Street et al., 2013), suggesting a
525 terrestrial higher plant origin for these compounds. The relatively high δ²H signal of those
526 compounds is in agreement with a vascular plant origin that would be subject to
527 evapotranspiration.

528

529 4.3. Paleoclimate evolution

530 The Taskomirsay section is separated into three parts for discussion purposes. The
531 first part includes the base of the section to the base of the transition zone at ~26 m and is
532 named “Phase 1”. It corresponds to the mid- to late Pliensbachian (Fig. 9; Schnyder et al.,
533 accepted). The second part is the transition zone, corresponding to the transition between
534 Pliensbachian and Toarcian, based on sporomorph associations and $\delta^{13}\text{C}_{\text{org}}$ (Fig. 9; Schnyder
535 et al., accepted). The $\delta^{13}\text{C}_{\text{org}}$ curve is described in Schnyder et al., accepted. The transition
536 zone ends at ~35 m. The rest of the section, corresponding to the early Toarcian is named
537 “Phase 2” (Fig. 9).

538

539 4.3.1. Paleoflora

540 The morphogenus conifer *Xenoxylon* Gothan is biogeographically related to cool/humid
541 settings and thus, usually to high latitudes (Philippe and Thévenard, 1996; Philippe and
542 Tchoumatchenco, 2008; Philippe et al., 2009). Recent isotopic studies confirmed these
543 paleoclimatic requirements for *Xenoxylon* (Amiot et al., 2015). In addition, *Xenoxylon*
544 occurred at lower latitudes during the Jurassic and even thrived in Western Europe during
545 cold episodes, such as in the late Pliensbachian or in the early Oxfordian (Philippe and
546 Thévenard, 1996). Therefore, the occurrence of *Xenoxylon* at mid-latitudes in Taskomirsay in
547 Phase 1 and in the transition zone suggests a cool/humid period, followed by less humid
548 and/or warmer conditions in the early Toarcian (Phase 2), deduced from the demise of
549 *Xenoxylon* (Fig. 9).

550 During the Jurassic, the Euro-Sinian (West-Kazakhstan) and the West-Siberian (East-
551 Kazakhstan) floral provinces were separated by a NW/SE axis through Kazakhstan
552 (Vakhrameev, 1991) that may have fluctuated in the Jurassic (Kirichkova and Doludenko,
553 1996). Sporomorph associations (Schnyder et al., accepted) prior to the transition zone

554 suggest an influence of the West-Siberian province with a monotonous flora dominated by
555 ferns, few Cycadales, Ginkgoales, Czekanowskiales, Bennettitales and Coniferales,
556 characteristic of a moderate-warm climate (Vakhrameev, 1991), in agreement with the
557 occurrence of *Xenoxylon* in the same part of the section (Fig. 9). The influence of the Euro-
558 Sinian province (warm-temperate) progressively increased through the section with the
559 emergence of *Manumia delcourtii* (Pocock) (Dybkaer, 1991) and later of *Ischyosporites*
560 *variegatus* (Couper) (Schulz, 1967) in Phase 2, which is one of the taxon used to identify the
561 early Toarcian (Schnyder et al., accepted). Then, the early Toarcian (Phase 2) is marked by
562 the occurrence of more thermophilic taxa such as *Callialasporites* spp. or *Ischyosporites*
563 *variegatus*, while a slight decrease in humidity is recorded by rare *Corollina* spp., associated
564 with the demise of *Xenoxylon* (Fig. 9; Schnyder et al., accepted). Accordingly, a similar
565 climatic trend has been evidenced regionally by other palynological studies during the Early
566 Jurassic in Central Asia (Iljina, 1985; Vakhrameev, 1991; Mogutcheva, 2014). Thus, globally
567 humid conditions along the section probably favored high production of biomass that enabled
568 the formation of the numerous lignite beds (Flores, 2002; Kalaitzidis et al., 2004).
569 Alternatively, changes in depositional environments or taphonomic conditions could have
570 driven the occurrence of the wood *Xenoxylon* and the mentioned sporomorphs. But, there is
571 no evidences to such hypothesis as no drastic changes in depositional environments occurred
572 until the top of the section, where lacustrine conditions took place. Most importantly, the
573 other organic markers do support a climatic interpretation of the data (see below) together
574 with other regional paleobiogeographical studies mentioned above.

575

576 4.3.2. What do $\delta^{15}N$ values record?

577 Many studies have concluded that the $\delta^{15}N_{org}$ values in terrestrial environments are
578 mainly driven by climate via water-availability and nutrient cycling, the $\delta^{15}N$ of plants and

579 soils being correlated negatively with precipitation and positively with temperatures (Austin
580 and Vitousek, 1998; Handley et al., 1999; Amundson et al., 2003; Swap et al., 2004; Liu and
581 Wang, 2008). In brief, $\delta^{15}\text{N}_{\text{org}}$ values in humid environments are driven by intense N-
582 recycling between dead and alive biomass through a rapid turnover of a small N-mineral
583 pool, whereas this cycle is interrupted in arid environments (low biomass activity) leading to
584 N-excess in a large mineral pool (Austin and Vitousek, 1998; Handley et al., 1999; Swap et
585 al., 2004). The latter is then subjected to N-loss by leaching and gas emission leading to high
586 $\delta^{15}\text{N}$ values in the remaining N-pool (Handley et al., 1999; Aranibar et al., 2004). In turn,
587 $\delta^{15}\text{N}_{\text{org}}$ values are controlled by the relative openness of the N-cycle by changes in water- or
588 N-availability as illustrated by Martinelli et al., 1999, who reported significant higher $\delta^{15}\text{N}_{\text{org}}$
589 (+6.5 ‰) values in humid tropical forests (N-excess) than in temperate forests (N-limited).
590 Considerable variations exist in $\delta^{15}\text{N}$ values from one site to another, ranging from around
591 -8 to $+22$ ‰ in actual soil organic matter (Craine et al. 2015).

592 In Taskomirsay, $\delta^{15}\text{N}_{\text{org}}$ values were calculated for samples in which TOC is <20 % and
593 do not strongly differ from the $\delta^{15}\text{N}_{\text{tot}}$ values, justifying the use of $\delta^{15}\text{N}_{\text{tot}}$ values as
594 representative of the $\delta^{15}\text{N}_{\text{org}}$ values (Fig. 2), except for TP3-224 that might be influenced by
595 an algal contribution and hence will not be considered for paleoclimate reconstructions. In the
596 light of the previous interpretations, the relatively low and stable $\delta^{15}\text{N}_{\text{org}}$ values ($\sim+3$ ‰) –
597 when compared to those compiled by Handley et al. (1999) in arid to semi-arid sites ($>+5$ ‰)
598 – are in agreement with a globally closed N-cycle, suggesting humid conditions and/or
599 limited nutrients in the system.

600 Although $\delta^{15}\text{N}_{\text{org}}$ values remain in a rather narrow range (~ 2.5 to ~ 3.5 ‰), the small
601 excursions recorded in $\delta^{15}\text{N}_{\text{org}}$ values, either negative (LB1, LB2 and LB6) or positive (LB5),
602 together with the scattered feature in LB4 and LB3 might reflect the tenuous equilibrium
603 between water-availability and nutrient cycling. This pattern would imply that (i) despite

604 paleoflora indices in Phase 2, no drastic changes occurred along the section whether in the
605 nutrient dynamics or regarding water-availability (Fig. 9), (ii) the vegetation has adapted to
606 environmental changes ensuring an efficient N-recycling and thus almost constant $\delta^{15}\text{N}_{\text{org}}$
607 values. The latter hypothesis suggests a strong influence of the local environment on $\delta^{15}\text{N}_{\text{org}}$
608 values as suspected by Amundson et al. (2003), who compiled $\delta^{15}\text{N}$ values of modern plants
609 and soils. The influence of local environments is supported by the high variability of $\delta^{13}\text{C}_{\text{org}}$
610 values, especially in LB4 and fossil woods (Fig. 9), which could result from changes of
611 vegetation assemblages or changes of ^{13}C -fractionation rate tuned by temperature, altitude
612 and/or relative humidity (Warren et al., 2001; Bowen and Revenaugh, 2003; Bowling et al.,
613 2008). A better sampling resolution for biomarkers studies would help to decipher the real
614 causes of variability of the $\delta^{13}\text{C}_{\text{org}}$ values, while a global and long-term influence is suggested
615 by Schnyder et al. (accepted) to highlight the recognition of the Pliensbachian-Toarcian
616 transition.

617 To sum up, no drastic changes in the $\delta^{15}\text{N}_{\text{org}}$ are recorded as compared to those reported
618 in the Paleocene-Eocene (Storme et al., 2012) or in the Eocene-Oligocene (Tramoy et al.,
619 2016) that exhibit much higher variations in amplitude of up to 6 ‰.

620

621 4.3.3. *Molecular response of plants*

622 Leaf waxes are produced by plants as a protection against external environment,
623 especially to prevent water loss. Accordingly, lower production of *n*-alkanes along with
624 shorter chain lengths is believed to reflect a decreasing need for protection against water loss
625 and/or a deficiency of energy for biosynthesizing long chain *n*-alkanes (Weete et al., 1978;
626 Gagosian and Peltzer, 1986; Gauvrit and Gaillardon, 1991; Shepherd and Wynne Griffiths,
627 2006), indicative of humid conditions. Conversely, higher amounts of *n*-alkanes and higher
628 ACL values suggest water stress for plants, drier conditions and higher temperatures. In this

629 respect, decreasing ACL values and *n*-alkane amounts from Phase 1 to the transition zone
630 suggest increasing humidity and decreasing temperatures (Fig. 9). Then, increasing ACL
631 values and *n*-alkane amounts point to drier conditions and higher temperatures in the early
632 Toarcian (Phase 2). MAATs, reconstructed based on brGDGTs distributions, depict the same
633 trends with decreasing temperatures in Phase 1 and increasing temperatures in Phase 2,
634 although the number of samples is limited. It is noteworthy that relations between ACL
635 values and *n*-alkane amounts are particularly robust in lignites, whereas no correlation exists
636 for clayey layers (Fig. 10). In order to explain this discrepancy, we hypothesize that the
637 organic matter in swampy forest is dominated by autochthonous vascular plant inputs,
638 responding promptly to relative changes in humidity, whereas organic matter in clayey layers
639 could contain significant part of allochthonous plant products or algal/bacterial organic
640 matter (*n*-C₁₈; Fig. 5) that is less influenced by water loss (Hoffmann et al., 2013). Notice that
641 the highest amount of *n*-alkanes was recorded in the clayey layer TP1-65, which is very poor
642 in organic matter (<0.05 %). As the amount of *n*-alkanes is expressed relative to %TOC, the
643 very low %TOC results in a very high concentration of *n*-alkanes in this specific sample.

644

645 4.3.4. Interpretation of *n*-alkane δ^2H values

646 According to Sachse et al. (2012), the δ^2H values of higher plant *n*-alkanes are mainly
647 influenced by (i) the δ^2H values of precipitation (Huang et al., 2004; Sachse et al., 2004,
648 2012), (ii) the extent of evapotranspiration from soils and leaves (Smith and Freeman, 2006;
649 Feakins and Sessions, 2010) and (iii) to a minor extent, by the interspecies variability (Smith
650 and Freeman, 2006; Chikaraishi and Naraoka, 2007). δ^2H values of precipitations are
651 positively correlated with temperature at the precipitation site and negatively correlated with
652 the amount of precipitation and with the distance from the shore line (Dansgaard, 1964;
653 Epstein and Yapp, 1976; Gat, 1996; Sachse et al., 2004). Also, the amount of precipitation is

654 the most important factor in low latitudes, whereas the temperature effect predominates in
655 higher latitudes (Sachse et al., 2012). At the global scale, a latitudinal/climatic distribution
656 pattern of $\delta^2\text{H}$ values has been reported in modern precipitation patterns and also for
657 geological times with $\delta^2\text{H}$ values being negatively correlated with latitudes (Bowen and
658 Revenaugh, 2003; Dawson et al., 2004).

659 The terrestrial signal in our samples is expressed by the absolute $\delta^2\text{H}$ values of the *n*-
660 alkane C_{27} (-242 to -151 ‰; -192 ± 21 ‰), which are closer to those reported from the
661 Paleocene-Eocene at mid-latitudes in the intracontinental Bighorn Basin (-195 to -185 ‰;
662 Smith et al., 2007) and at high latitudes in the Arctic (-210 to -160 ‰, Pagani et al., 2006),
663 than those reported for the same period in coastal regions from mid- to low-latitudes (-165 to
664 -140 ‰; Handley et al., 2012; -174 to -112 ‰; Garel et al., 2013). They are also closer to
665 early Permian $\delta^2\text{H}$ values recorded in high latitudes with glacial to cool-temperate
666 environments (*ca.* -200 ‰), than those recorded for the same period in tropical regions (Fig.
667 6; *ca.* -150 ‰; Dawson et al., 2004; *ca.* -100 ‰; Izart et al., 2012). These results are in
668 agreement with the estimated mid-paleolatitudes of the Taskomirsay section ($36^\circ \text{N} \pm 8^\circ$,
669 Bruno Vrielynck, pers. comm., 2014), associated with a warm to cool-temperate global
670 climate during the Early Jurassic at those paleolatitudes (Rees et al., 2000). It may also point
671 to the intra-continental character of the Karatau Basin during the Pliensbachian-Toarcian.

672 Considering these paleolatitudinal/paleoclimatic settings, the location of the Karatau
673 Basin during the Jurassic ($\sim 40^\circ \text{N}$) and the large excursions of the $\delta^2\text{H}$ values, air
674 temperatures and precipitation amount were probably both important factors driving
675 precipitation $\delta^2\text{H}$ values. Then, $\delta^2\text{H}$ values of *n*-alkanes were more or less affected by
676 evapotranspiration with respect to their environment whether aquatic or terrestrial (Sachse et
677 al., 2006; Smith and Freeman, 2006; Feakins and Sessions, 2010). To constrain the

678 evapotranspiration effect of terrestrial plants, the aquatic $n\text{-C}_{23}$ will be considered for
679 paleohydrological reconstructions.

680 $\delta^2\text{H}$ values of n -alkanes are usually well correlated with that of the source water used by
681 organisms and thus constitute good markers for paleohydrological reconstructions (Sachse et
682 al., 2004; Mügler et al., 2008; Aichner et al., 2010; Nichols et al., 2010; Sachse et al., 2012).
683 Because the $n\text{-C}_{23}$ is associated with the aquatic pool in the study section, its low $\delta^2\text{H}$ values
684 (-248 to -168 ‰; -201 ± 25 ‰, similar to $n\text{-C}_{21}$ $\delta^2\text{H}$ values) argue for very humid
685 conditions either in a cool-temperate or glacial climate regime (Fig. 6). However, no
686 sedimentological evidence has been found for a glacial environment, and this kind of
687 environment is highly inconsistent with plant assemblages in Taskomirsay (Schnyder et al.,
688 accepted). Thus, cool-temperate conditions are most likely, whereas the very negative $\delta^2\text{H}$
689 values could reflect a long distance from the source water (Gat, 1996). Although the exact
690 distance from the shore line is currently unknown (either to the South or West), it is most
691 probably on the order of tens to hundreds of kilometers (B. Vrielynck, pers. Comm., 2014).

692 Along the section, the decrease in $n\text{-C}_{23}$ $\delta^2\text{H}$ values from the base of the section to the
693 transition zone could result from a decrease in source-water $\delta^2\text{H}$ values, indicating an
694 increase in humidity and decrease in temperature, the coolest/most humid interval being
695 recorded from LB4 to the base of LB5 within the transition zone (-236 ± 11 ‰; Fig. 9).
696 Then, a strong increase in $n\text{-C}_{23}$ $\delta^2\text{H}$ values (-188 ± 18 ‰) suggests relatively drier
697 conditions in the early Toarcian, associated with higher temperatures. ACL values are in
698 agreement with those two general trends. Nevertheless, slightly lower $n\text{-C}_{23}$ $\delta^2\text{H}$ values in
699 LB6 (-209 ± 6 ‰) suggest a more humid period that favored swampy environments. But,
700 those $\delta^2\text{H}$ values are ~ 27 ‰ higher than in LB4/LB5, probably resulting from the deposition
701 of LB6 in warmer conditions instead of drier conditions. This interpretation is supported by

702 concomitant thermophilic paleoflora and increasing temperatures recorded by GDGTs in the
703 early Toarcian (Fig. 9).

704 At high frequency, higher $\delta^2\text{H}$ values intercalated in clayey layers may represent local
705 changes in sub-environments between lignites and clayey layers with more humid conditions
706 for lignites than for clays (Fig. 7 and 9). Whereas paleoclimatic variations may have
707 overprinted local changes at a broader scale when taking into account differences in $\delta^2\text{H}$
708 values between the different sedimentary cycles.

709

710 4.3.5. Paleoclimate reconstructions based on $\Delta^2\text{H}_{\text{ter-aq}}$

711 The influence of relative humidity and temperature on $\delta^2\text{H}$ values is also recorded by the
712 evapotranspiration of the ecosystem (Sachse et al., 2006; Mügler et al., 2008). The ecosystem
713 evapotranspiration can be evaluated by the hydrogen isotopic difference between terrestrial *n*-
714 alkanes and aquatic *n*-alkanes, based on two assumptions: (i) in a given ecosystem, water
715 source is the same for terrestrial and aquatic organisms and (ii) aquatic and terrestrial
716 organisms synthesize their *n*-alkanes with the same biosynthetic fractionation ($\varepsilon = -157$ ‰;
717 Sachse et al., 2006). However, terrestrial flora synthesize their *n*-alkanes from ^2H -enriched
718 leaf-water after soil evaporation and leaf-transpiration, leading to ^2H -enrichment of long-
719 chain *n*-alkanes (eg. Sachse et al., 2006). Indeed, *n*-alkanes from surface sediments of
720 European lakes showed an isotopic difference as large as +30 ‰ between the terrestrial and
721 the aquatic pool (Sachse et al., 2004, 2006).

722 In the Taskomirsay samples, evapotranspiration was estimated from the isotopic
723 difference between $\delta^2\text{H}$ values of the C_{27} and the C_{23} *n*-alkanes and was noted as $\Delta^2\text{H}_{\text{ter-aq}}$
724 (Fig. 9). Notice that the aquatic pool defined for this study differs from that of the other
725 studies by the origin of the aquatic *n*-alkanes, which are attributed here to swampy or riparian

726 vegetation with no water restriction (*e.g.*, *Xenoxylon* vegetation type; Oh et al., 2015).
727 Contributions from mosses and aquatic plants are also possible. The $\Delta^2\text{H}_{\text{ter-aq}}$ was always
728 positive in lignites, up to +76 ‰ in LB4, whereas it remained close to 0 ‰ or slightly
729 negative in clayey layers. According to Mügler et al. (2008), who calculated $\Delta^2\text{H}_{\text{ter-aq}}$ values
730 in a Tibetan lake, positive $\Delta^2\text{H}_{\text{ter-aq}}$ values are typical for humid environments. They result
731 from evapotranspiration of terrestrial vegetation leading to ^2H -enrichment in the terrestrial
732 pool, whereas ^2H -enrichment of the aquatic pool is limited by low evaporation rates. $\Delta^2\text{H}_{\text{ter-aq}}$
733 values in the section are thus in agreement with humid conditions. In contrast, under arid to
734 semi-arid conditions, significant ^2H -enrichment occurs in the aquatic pool relatively to the
735 terrestrial pool, resulting from long term lake water evaporation, which counterbalances plant
736 evapotranspiration: a negative $\Delta^2\text{H}_{\text{ter-aq}}$ is thus recorded (~ -60 ‰; Mügler et al., 2008; Rao et
737 al., 2014). Because the most negative $\Delta^2\text{H}_{\text{ter-aq}}$ recorded did not exceed -6 ‰, arid to semi-
738 arid conditions during deposition of clayey layers are unlikely and generally humid
739 conditions are suggested, in agreement with paleoflora, $\delta^{15}\text{N}_{\text{org}}$ and absolute $\delta^2\text{H}$ values.

740 In addition, maximal $\Delta^2\text{H}_{\text{ter-aq}}$ positive values (+41 and +76 ‰ in LB4), suggest a
741 considerable evapotranspiration rate (Fig. 9). This interpretation is in apparent contradiction
742 with the coolest/most humid interval deduced from low $\delta^2\text{H}$ values of *n*-alkanes from the
743 aquatic pool and low $\delta^{15}\text{N}_{\text{org}}$ values. A possible explanation for this discrepancy is that higher
744 input of allochthonous terrestrial *n*-alkanes from distant areas with a heavier isotopic
745 composition of meteoric water might have led to higher $\Delta^2\text{H}_{\text{ter-aq}}$ (~ 70 ‰; Sachse et al.,
746 2004). Alternatively, high $\Delta^2\text{H}_{\text{ter-aq}}$ could be explained by seasonal differences in water
747 uptake and *n*-alkane production between the aquatic and terrestrial pools (Jacob et al. 2007),
748 which is typical under temperate climate-regime. Indeed, higher plant *n*-alkanes are mostly
749 produced during the growing season in spring and summer (Sachse et al., 2004, 2009), *i.e.*
750 under relatively drier/warmer conditions, which could account for the production of ^2H -

751 enriched long-chain *n*-alkanes. Conversely, the aquatic pool of *n*-alkanes might have been
752 produced under more humid/cool conditions during a wet season, which could explain their
753 low $\delta^2\text{H}$ values (Fig. 9).

754 The hypothesis of alternating wet/dry season responsible for high $\Delta^2\text{H}_{\text{ter-aq}}$ could also
755 explain the scatter in $\delta^{15}\text{N}_{\text{org}}$ values in LB4 by the dual influences of wet and dry seasons
756 (Swap et al., 2004): (i) low N-recycling rate during dry season, leading to N mineralization
757 and ^{15}N -enrichment, and (ii) intense N-recycling by microbial biomass during the growing
758 season that re-processes the accumulated N, leading to ^{15}N -depletion. In other words, if the
759 dry season effects of ^{15}N -enrichment exceed the wet season effects of ^{15}N -depletion, $\delta^{15}\text{N}$
760 values of the remaining organic matter would increase and *vice versa*. Following the
761 interpretation of $\Delta^2\text{H}_{\text{ter-aq}}$ values as a seasonal indicator, $\Delta^2\text{H}_{\text{ter-aq}}$ values close to 0 ‰ in Phase
762 2 might suggest low seasonality (Fig. 9). Precisely, recent spectral analysis of $\delta^{13}\text{C}$ values
763 measured in carbonates, used in cyclostratigraphy, revealed that astronomical configuration
764 of the Earth would have enhanced seasonality at the Pliensbachian-Toarcian transition and
765 favored low seasonality in the early Toarcian (Martinez and Dera, 2015).

766

767 **5. Reconciling proxies**

768 Proxies used in this study yield contrasting responses to the inferred climate changes.
769 An absence of drastic changes were recorded by $\delta^{15}\text{N}_{\text{org}}$ values and paleoflora revealed
770 globally humid conditions apart from slightly less humid and warmer conditions in the early
771 Toarcian. This warming was confirmed by MAATs reconstructed from brGDGTs. In
772 contrast, molecular proxies (*n*-alkane amount, ACL, $\delta^2\text{H}$ values, $\Delta^2\text{H}_{\text{ter-aq}}$ values and
773 brGDGTs) were highly variable along the section, especially $\delta^2\text{H}$ values. These proxies argue
774 for maximal humidity and minimal temperatures in the Pliensbachian-Toarcian transition.

775 This period could thus correspond to the cool late Pliensbachian (Bailey et al., 2003; Morard
776 et al., 2003; Suan et al., 2010). Molecular proxies also supported drier/warmer conditions at
777 the base of the section (middle Pliensbachian?) and in the early Toarcian as well as
778 humid/dry cycles between lignites (humid) and clayey layers (drier).

779 The absence of a correlation between $\delta^{15}\text{N}_{\text{org}}$ and $\delta^2\text{H}$ values, which are both
780 influenced by water availability, might point to different spatial integration of those proxies,
781 $\delta^{15}\text{N}_{\text{org}}$ and $\delta^2\text{H}$ reflecting local (Szpak, 2014) and regional (precipitation regimes, air-mass
782 temperatures; Sachse et al., 2012) influences, respectively. Sea level variations may influence
783 $\delta^2\text{H}$ values of precipitation by modifying the distance between shore lines and the study area
784 (Gat, 1996). Consequently, low sea level may increase the distance from the shore line
785 leading to lower $\delta^2\text{H}$ values of the precipitation and *vice versa*, and concomitant
786 temperature/humidity variations could lead to over- or underestimation of paleohydrological
787 changes (e.g., Garel et al., 2013). It is therefore likely that the low sea level and the low
788 temperatures (higher ^2H -fractionation) recorded in the late Pliensbachian led to an
789 overestimation of humidity and reversely for the early Toarcian, which is marked by global
790 warming and sea-level rising (Hallam, 1967; Hesselbo and Jenkyns, 1998; Bailey et al., 2003;
791 Rosales et al., 2004; Suan et al., 2010). The recognition of *Botryococcus* in the uppermost
792 part of the section and the alternation between silts and clay suggest a lacustrine/deltaic
793 environment (Schnyder et al., accepted). This kind of environment would have been favored
794 by the early Toarcian global transgression (Hallam, 1967; Hesselbo and Jenkyns, 1998) that
795 increased the regional water level base and consequently buried the older sediments. Thus,
796 variations of sea level may reconcile the drastic paleohydrological changes recorded by the
797 $\delta^2\text{H}$ values and the rather stable climatic conditions implied by the $\delta^{15}\text{N}_{\text{org}}$ values. This
798 hypothesis is strongly supported by Korte et al. (2015) who demonstrated the influence of the
799 ocean dynamic on the global climate in the Early and Middle Jurassic.

800

801 **6. Conclusions**

802 The Taskomirsay section is a unique continental record that encompasses the
803 Pliensbachian-Toarcian transition and contains well-preserved Type-III organic matter.
804 Sources of organic matter were separated into two pools: (i) a purely terrestrial and (ii) an
805 “aquatic” pool constituted of vegetation that thrived under almost permanent water supply,
806 with possible contributions from mosses and aquatic plants.

807 Our multi-proxy analysis argues for globally humid condition through the section,
808 probably under a warm- to cool-temperate regime, as constrained by *Xenoxylon* wood.
809 However, paleoflora and $\delta^2\text{H}$ values suggest slightly less humid and warmer conditions
810 starting from the early Toarcian, as also usually recorded in the marine realm. This interval
811 was preceded by the probably coolest/most humid period that may correspond to the late
812 Pliensbachian. In addition, enhanced seasonality has been hypothesized, starting from the
813 mid-late Pliensbachian and maximizing at the Pliensbachian-Toarcian transition, in
814 agreement with a temperate climate regime. The combination of sedimentological and
815 organic analyses provide the most probable picture of landscapes in Taskomirsay: fluvial
816 systems cutting through swampy forests from the base of the section (mid- to late
817 Pliensbachian) to the transition zone (Pliensbachian-Toarcian transition) followed by
818 relatively open lacustrine conditions in the upper part (early Toarcian).

819 Finally, this study sheds new light on the use of compound-specific $\delta^2\text{H}$ values in ancient
820 sediments and stresses the complexity of the $\delta^{15}\text{N}_{\text{org}}$ as a paleoclimatic proxy. Those proxies
821 still need to be combined with other parameters like clay mineralogy, palynofacies or other
822 biomarker molecules (e.g., terpenoids). Paleoclimate changes should also be constrained at
823 the regional scale with other continental sections in Central Asia to link paleoclimate changes

824 recorded in the marine realm to those in continental settings, even though inter-linkages could
825 be challenging.

826

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1260

Figure 1-revised

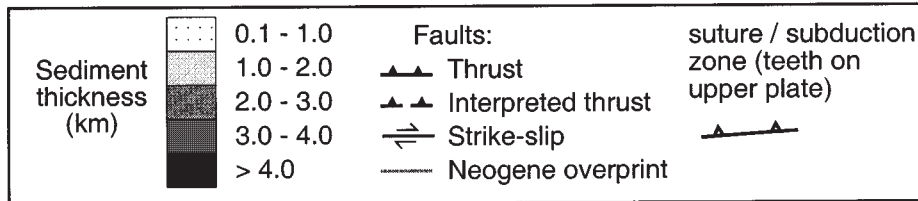
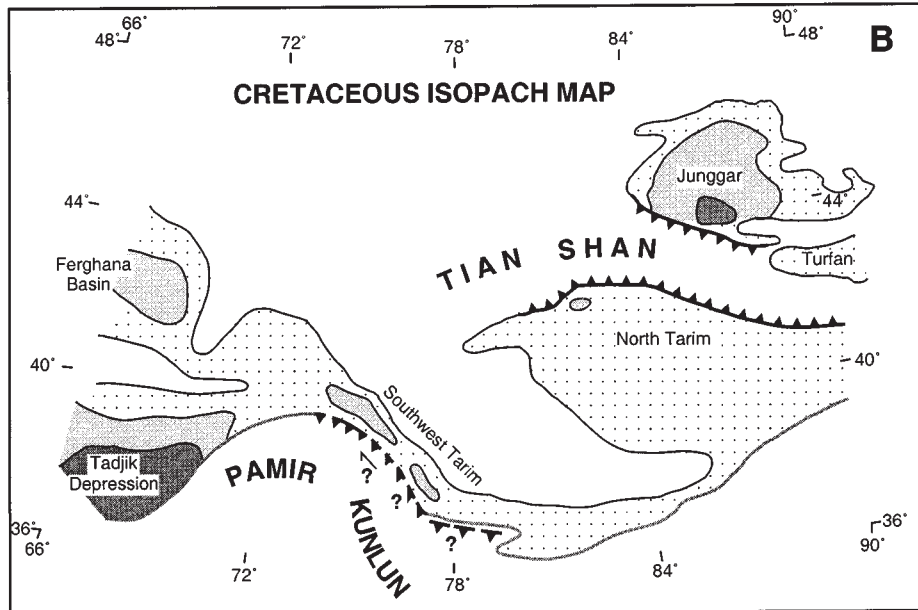
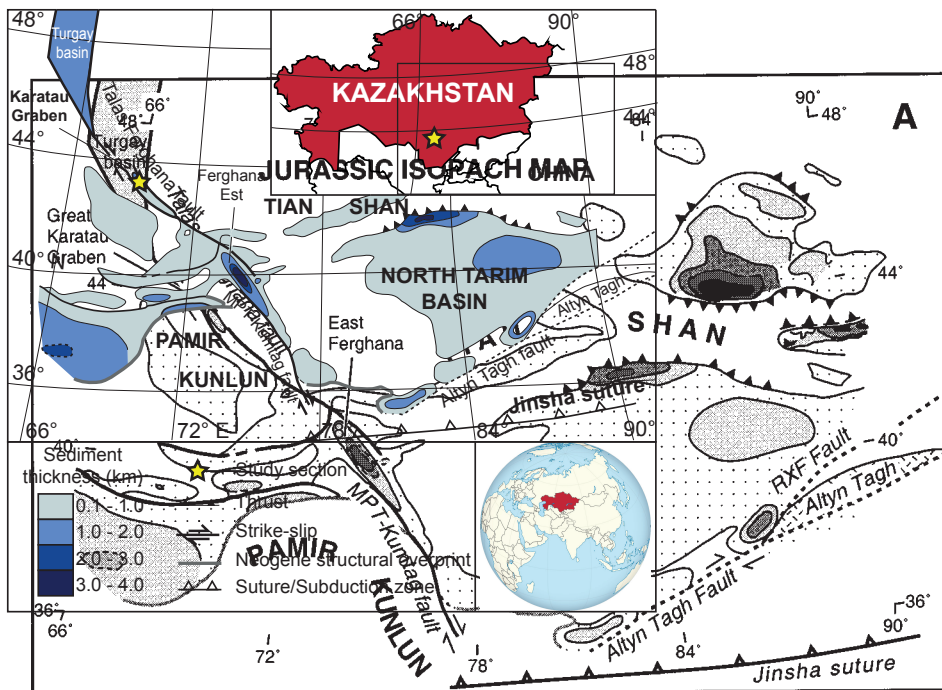


Figure 2-revised

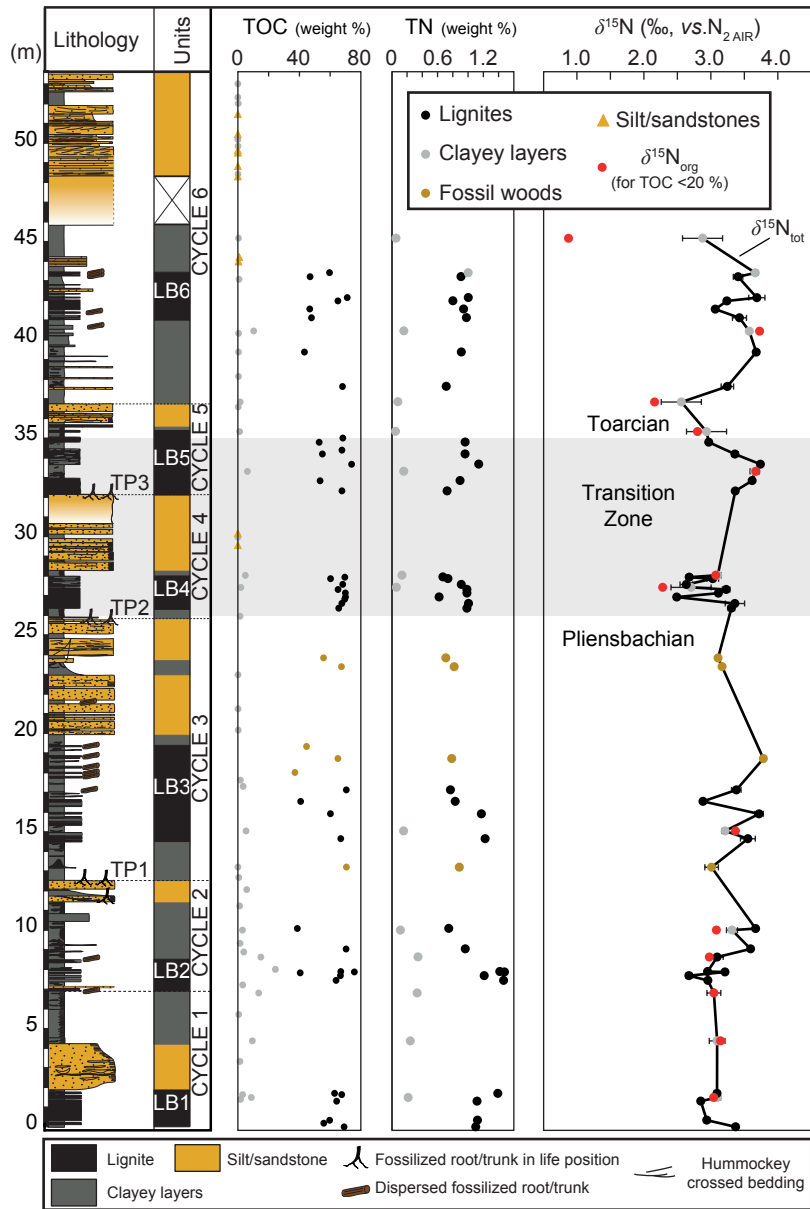


Figure 3

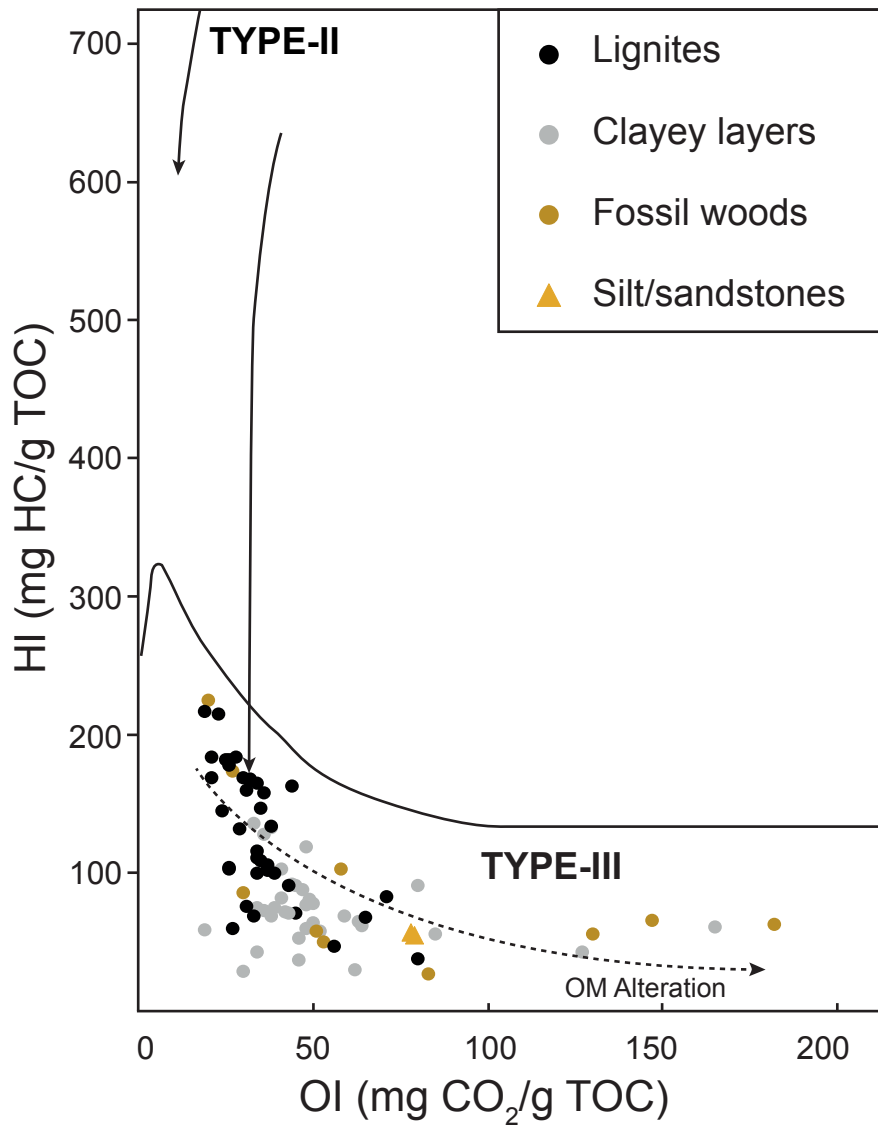


Figure 4-revised

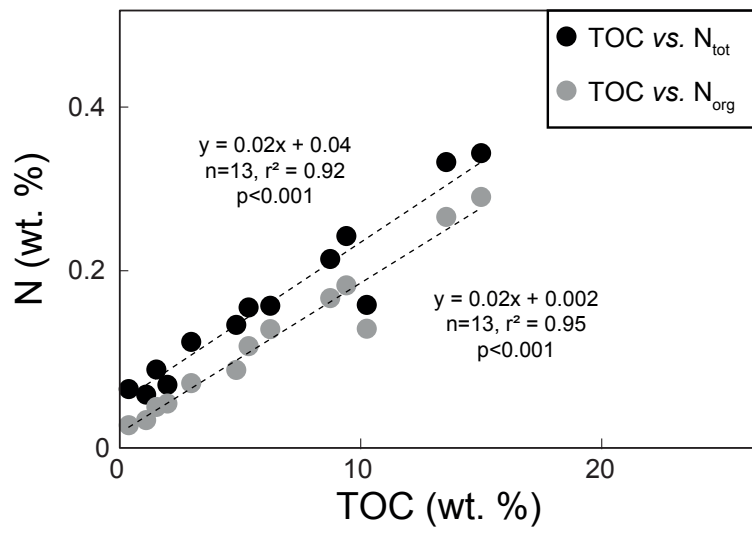


Figure 5-revised

Taskomirsay section

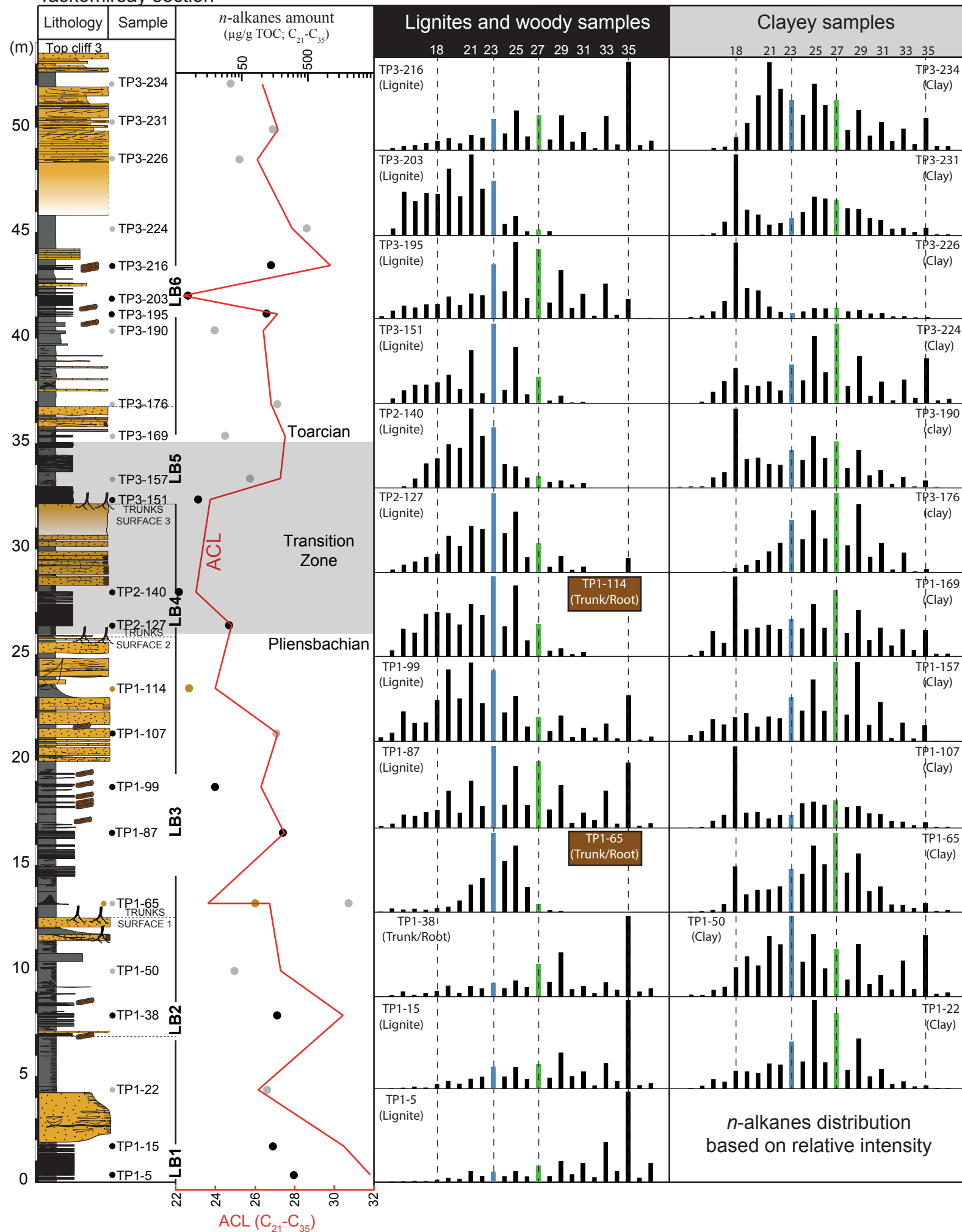


Figure 6-revised

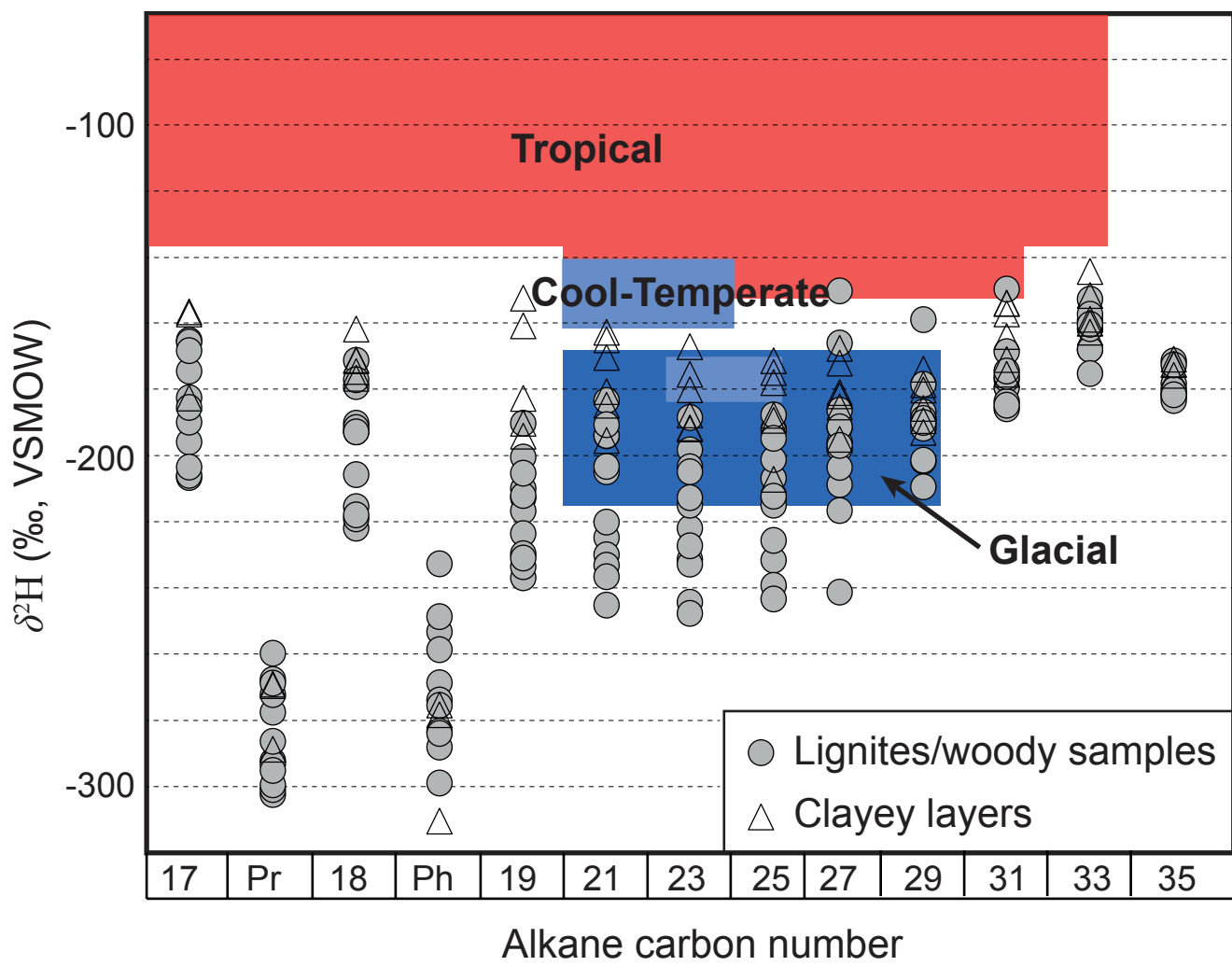


Figure 7-revised

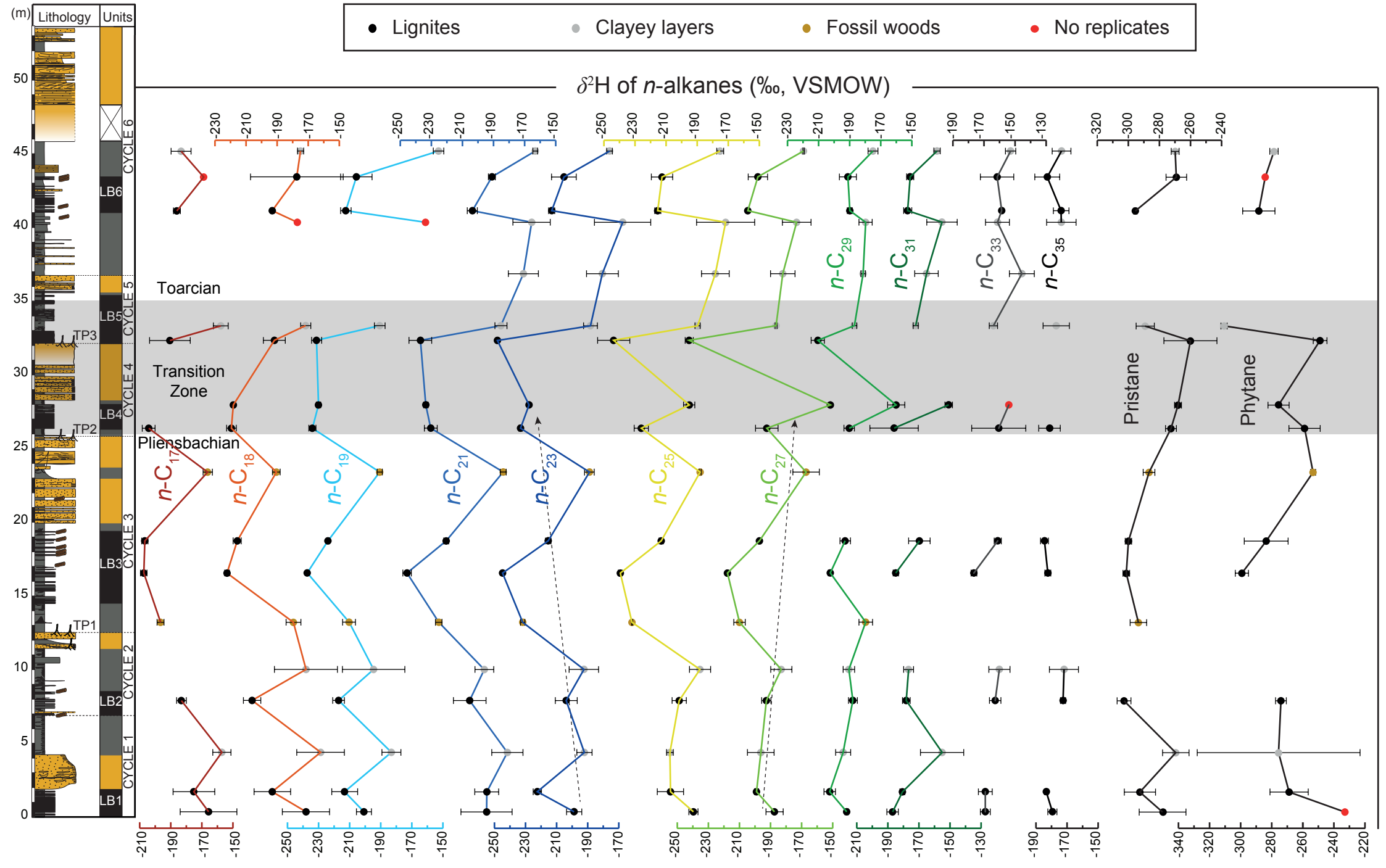


Figure 8

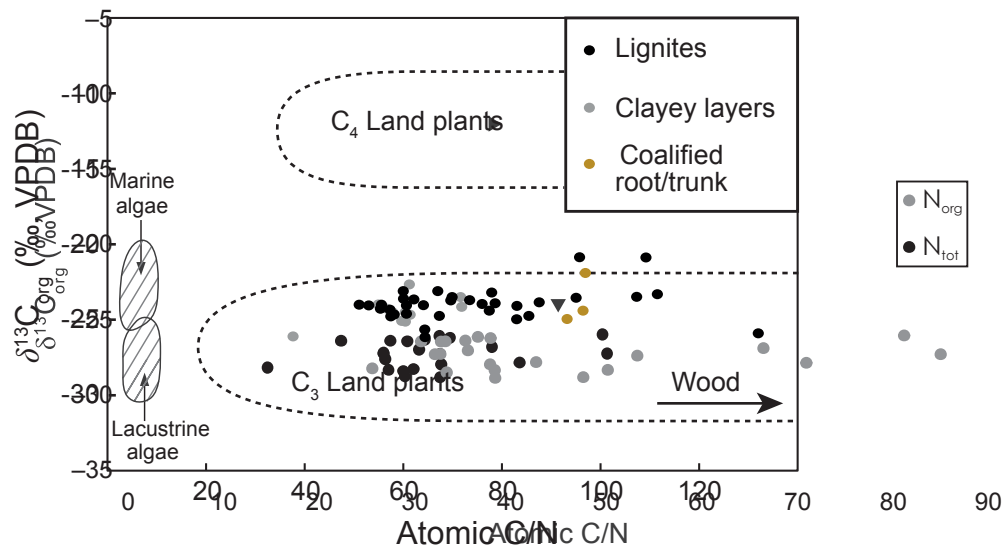


Figure 9-revised

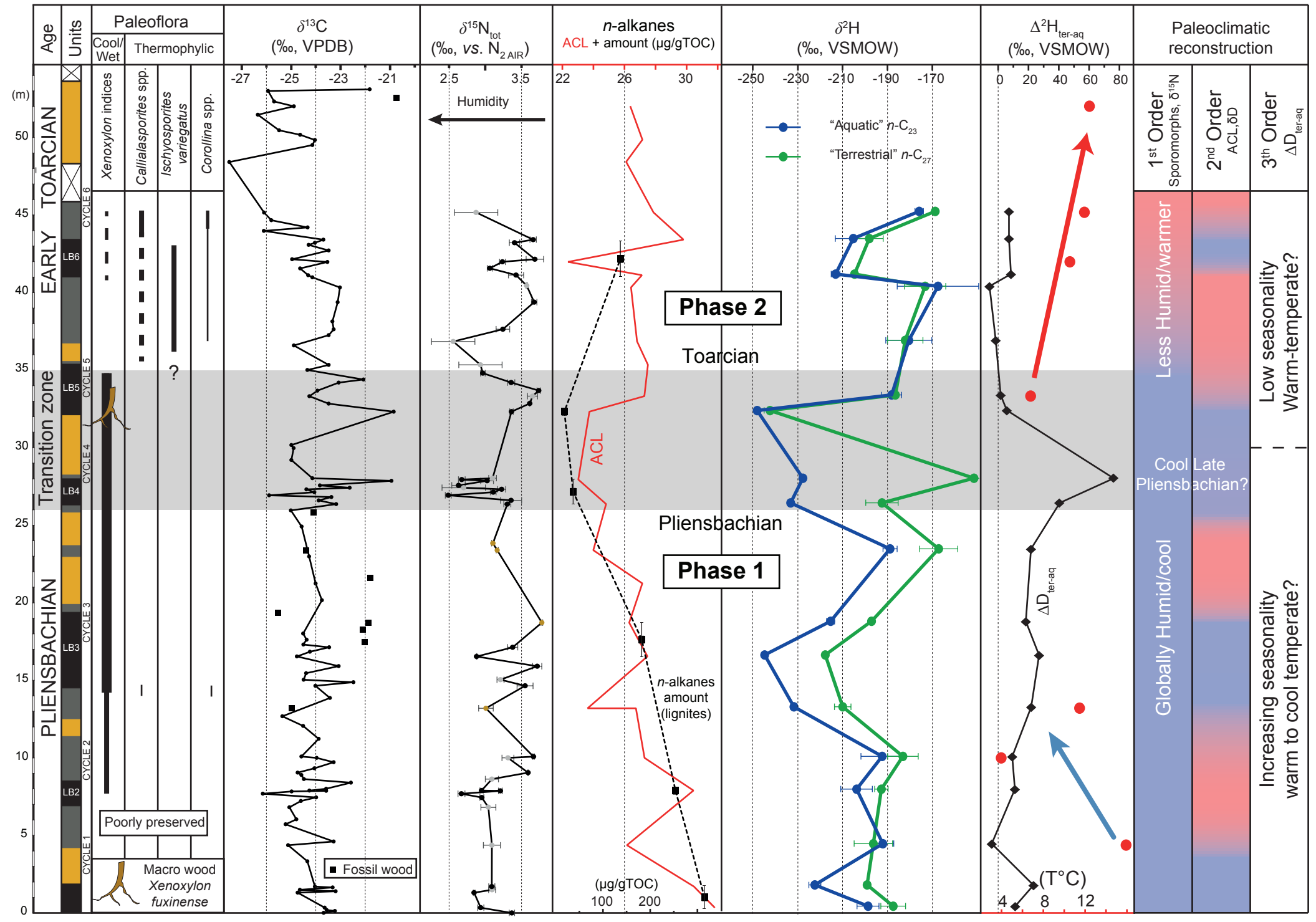


Figure 10

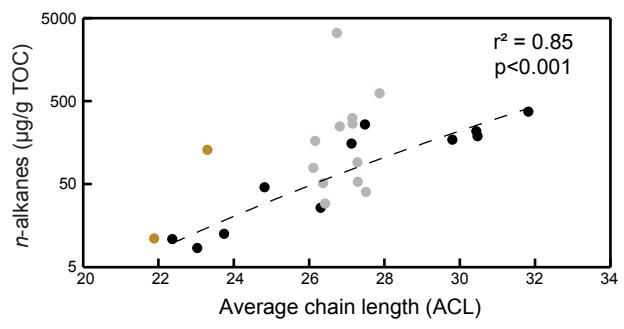


Table 1

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Table 1

Sample	Position (m)	Lithology	^a TOC (%)	^b TN (%)	^c C/N	^d N _{bnd} (%)	^e N _{org} (%)	^δ ¹⁵ N (‰)		^δ ¹⁵ N _{org} (‰)
								mean	SD	
TP3-234	52.02	Clay	0.2	-	-	-	-	-	-	
TP3-231	49.85	Clay	0.1	-	-	-	-	-	-	
TP3-226	48.43	Clay	0.1	-	-	-	-	-	-	
TP3-224	45.17	Clay	0.4	0.06	*38	0.04	0.01	2.9	0.30	0.9
TP3-216	43.41	Lignite	59.6	1.00	70	-	0.24	3.7	0.04	
TP3-212	43.21	Lignite	47.0	0.91	61	-	0.53	3.4	0.07	
TP3-205	42.15	Lignite	71.2	1.00	83	-	0.16	3.7	0.12	
TP3-203	41.98	Lignite	65.1	0.80	95	-	0.13	3.2	0.04	
TP3-201	41.57	Lignite	46.8	0.94	58	-	0.38	3.1	0.04	
TP3-195	41.12	Lignite	47.9	0.98	57	-	0.42	3.4	0.11	
TP3-191	40.45	OM-rich Clay	10.3	0.16	*93	0.03	0.13	3.6	0.01	3.7
TP3-190	40.34	Clay	0.4	-	-	-	-	-	-	
TP3-185bis	39.38	Lignite	43.3	0.91	56	-	0.28	3.7	0.04	
TP3-179	37.63	Lignite	68.1	0.71	112	-	0.14	3.2	0.09	
TP3-176	36.85	Clay	1.5	0.08	*53	0.05	0.03	2.6	0.30	
TP3-169	35.34	Clay	1.1	0.05	*72	0.03	0.02	2.9	0.30	2.8
TP3-165	34.80	Lignite	52.9	0.96	64	-	0.38	3.0	0.03	3.7
TP3-162	34.20	Lignite	55.0	0.96	67	-	0.46	3.4	0.05	
TP3-159	33.68	Lignite	74.0	1.14	76	-	0.22	3.7	0.02	
TP3-157	33.32	OM-rich Clay	6.2	0.16	*57	0.03	0.13	3.7	0.07	3.7
TP3-153	32.84	Lignite	53.5	0.90	70	-	0.26	3.6	0.00	
TP3-151	32.32	Lignite	67.7	0.73	109	-	0.37	3.4	0.02	
TP2-141	28.03	Clay	4.8	0.13	*72	0.06	0.08	3.1	0.05	3.1
TP2-140	27.94	Lignite	69.6	0.67	121	-	0.09	2.7	0.05	
TP2-139	27.86	Lignite	60.3	0.74	96	-	0.15	3.0	0.09	
TP2-135	27.57	Lignite	68.2	0.91	88	-	0.18	2.6	0.09	
TP2-133	27.42	Clay	2.0	0.06	*61	0.02	0.04	2.7	0.30	2.3
TP2-132	27.31	Lignite	65.2	0.99	77	-	0.19	3.2	0.06	
TP2-131	27.13	Lignite	69.9	0.99	83	-	0.23	3.1	0.04	
TP2-130	26.93	Lignite	70.0	0.62	132	-	0.09	2.5	0.04	
TP2-128	26.60	Lignite	67.6	1.01	79	-	0.25	3.4	0.15	
TP1-127	26.36	Lignite	65.6	0.99	78	-	0.29	3.3	0.05	
TP1-117	23.84	Coalified root/trunk	55.7	0.71	92	-	0.16	3.1	0.02	
TP1-114	23.39	Coalified root/trunk	67.4	0.82	96	-	0.18	3.2	0.01	
TP3-107	21.24	Clay	0.1	-	-	-	-	-	-	
TP1-99	18.72	Coalified root/trunk	65.1	0.79	97	-	0.13	3.8	0.01	
TP1-89	17.13	Lignite	70.6	0.77	107	-	0.08	3.4	0.07	
TP1-87	16.54	Lignite	40.8	0.83	57	-	0.48	2.9	0.00	
TP1-84	15.91	Lignite	60.2	1.17	60	-	0.34	3.7	0.06	
TP1-76	15.04	Clay	5.3	0.16	*58	0.05	0.11	3.2	0.05	3.4
TP1-71	14.65	Lignite	67.0	1.22	64	-	0.26	3.6	0.11	
TP1-65	13.20	Coalified root/trunk	70.6	0.89	93	-	0.15	3.0	0.10	
TP3-65	13.20	Clay	0.02	-	-	-	-	-	-	
TP1-51	10.08	Lignite	38.7	0.75	61	-	0.42	3.7	0.01	
TP1-50	9.99	Clay	3.0	0.11	*55	0.05	0.06	3.3	0.08	3.1
TP1-46	9.04	Lignite	70.4	0.96	85	-	0.13	3.6	0.00	
TP1-43	8.63	OM-rich Clay	15.0	0.34	*60	0.05	0.29	3.1	0.09	3.0

TP1-38	7.89	Lignite	67.0	1.42	55	-	0.24	2.9	0.02	
TP1-38base	7.87	Lignite	75.8	1.48	60	-	0.31	3.2	0.03	
TP1-35	7.68	Lignite	66.7	1.21	64	-	0.19	2.7	0.05	
TP1-33	7.44	Lignite	63.9	1.47	51	-	0.37	3.0	0.03	
TP1-29	6.80	OM-rich Clay	13.6	0.33	*60	0.07	0.27	3.0	0.10	3.0
TP1-22	4.36	OM-rich Clay	9.4	0.24	*60	0.06	0.18	3.1	0.12	3.1
TP1-15	1.70	Lignite	62.9	1.39	53	-	0.32	3.1	0.04	
TP1-11	1.48	OM-rich Clay	8.7	0.21	*61	0.05	0.17	3.1	0.05	3.0
TP1-8	1.30	Lignite	64.3	1.12	67	-	0.38	2.8	0.01	
TP1-5	0.33	Lignite	59.7	1.12	62	-	0.29	2.9	0.04	
TP1-1	0.00	Lignite	69.1	1.10	73	-	0.56	3.4	0.04	
Average				0.77			0.23	3.2		

Table 2

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Table 2.

Sample	Lithology	Position (m)	TOC (%)	^a Lipid content (%)	<i>n</i> -alkane range (max; sub-maxs)	<i>n</i> -alkane content (µg/gTOC)	CPI (C ₂₁ -C ₃₅)	ACL (C ₂₁ -C ₃₅)	Pr/Ph ratio	^b MAAT (°C)
TP3-234	Clay	52.02	0.2	0.01	C ₁₆ -C ₃₇ (C ₂₁ ; C ₂₅ ; C ₃₅)	51	1.7	26.4	0.3	12.4
TP3-231	Clay	49.85	0.1	<0.01	C ₁₄ -C ₃₇ (C ₂₃)	268	1.1	27.2	0.3	-
TP3-226	Clay	48.43	0.1	<0.01	C ₁₄ -C ₃₅ (C ₁₈ ; C ₂₇)	78	1.1	26.1	0.3	-
TP3-224	Clay	45.17	0.6	0.13	C ₁₄ -C ₃₇ (C ₂₇ ; C ₃₅ ; C ₁₈)	621	3.2	27.9	0.7	11.9
TP3-216	Lignite	43.41	59.6	1.85	C ₁₃ -C ₃₇ (C ₃₅ ; C ₂₅ ; C ₂₉)	172	4.0	29.8	3.9	-
TP3-203	Lignite	41.98	65.1	0.86	C ₁₄ -C ₂₈ (C ₂₁)	11	2.0	22.4	2.0	10.5
TP3-195	Lignite	41.12	47.9	2.08	C ₁₃ -C ₃₇ (C ₂₃ ; C ₃₃)	154	3.2	27.1	5.7	-
TP3-190	Clay	40.34	0.4	0.01	C ₁₃ -C ₃₆ (C ₁₈ ; C ₂₅)	29	1.8	26.4	1.0	-
TP3-176	Clay	36.85	1.5	0.03	C ₁₇ -C ₃₅ (C ₂₇)	247	2.3	26.8	2.1	-
TP3-169	Clay	35.34	1.1	<0.01	C ₁₄ -C ₃₇ (C ₁₈ ; C ₂₇)	40	2.1	27.5	0.8	-
TP3-157	OM-rich Clay	33.32	6.2	0.21	C ₁₄ -C ₃₆ (C ₂₉ ; C ₂₇)	92	2.6	27.3	7.6	6.8
TP3-151	Lignite	32.32	73.1	2.49	C ₁₄ -C ₃₅ (C ₂₃)	13	5.5	23.7	2.7	-
TP2-140	Lignite	27.94	69.6	1.27	C ₁₅ -C ₃₁ (C ₂₁)	8	1.6	23.0	2.6	-
TP2-127	Lignite	26.36	65.6	2.06	C ₁₄ -C ₃₅ (C ₂₃)	46	2.1	24.8	6.7	-
TP1-114	Coalified root/trunk	23.39	67.4	3.64	C ₁₄ -C ₃₅ (C ₂₃ ; C ₁₈)	11	2.3	24.0	6.0	-
TP1-107	Clay	21.24	0.1	<0.01	C ₁₄ -C ₃₇ (C ₁₈ ; C ₂₇)	311	1.1	27.2	0.6	-
TP1-99	Coalified root/trunk	18.72	75.4	2.35	C ₁₃ -C ₃₇ (C ₂₁ ; C ₃₅ ; C ₂₉)	26	2.7	26.3	6.1	-
TP1-87	Lignite	16.54	38.6	1.90	C ₁₃ -C ₃₇ (C ₂₃ ; C ₂₇ ; C ₃₅)	262	3.8	27.5	3.3	-
TP1-65	Coalified root/trunk	13.20	70.6	2.23	C ₁₃ -C ₂₉ (C ₂₃)	129	1.6	23.6	1.7	11.5
TP1-65bis	Clay	13.20	0.02	<0.01	C ₁₄ -C ₃₇ (C ₂₇ ; C ₁₈)	3313	1.6	26.7	0.9	-
TP1-50	Clay	10.00	3.0	0.1	C ₁₄ -C ₃₇ (C ₂₃ ; C ₃₅ ; C ₂₉)	53	2.4	27.3	3.2	4.0
TP1-38	Lignite	7.89	67.0	3.90	C ₁₁ -C ₃₇ (C ₃₅ ; C ₂₉ ; C ₁₉)	218	3.5	30.4	4.5	-
TP1-22	Clay	4.36	9.4	0.58	C ₁₄ -C ₃₇ (C ₂₅)	166	2.6	26.2	2.9	15.9
TP1-15	Lignite	1.70	62.9	2.65	C ₁₄ -C ₃₇ (C ₃₅ ; C ₂₉ ; C ₂₃)	189	3.4	30.5	6.6	-
TP1-5	Lignite	0.34	59.7	2.43	C ₁₄ -C ₃₇ (C ₃₅ ; C ₂₉ ; C ₂₃)	374	4.4	31.8	5.4	-
Average							2.5	26.7	3.1	

Table 3

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Table 3.

Sample	Lithology	C ₁₇	SD (1σ)	C ₁₈	SD (1σ)	C ₁₉	SD (1σ)	C ₂₁	SD (1σ)	C ₂₃	SD (1σ)	C ₂₅	SD (1σ)
TP3-224	Clay	-183	6	-175	2	-153	3	-163	2	-176	2	-175	2
TP3-216	Lignite	-169	-	-177	30	-206	10	-191	2	-205	8	-213	7
TP3-195	Lignite	-186	2	-193	1	-212	3	-204	3	-213	2	-215	2
TP3-190	Clay	-	-	-177	-	-161	-	-166	12	-168	18	-172	19
TP3-176	Clay	-	-	-	-	-	-	-171	10	-181	10	-178	9
TP3-157	OM-rich clay	-158	5	-172	3	-191	3	-185	4	-188	4	-190	2
TP3-151	Lignite	-190	13	-192	7	-231	3	-237	7	-248	1	-244	10
TP2-140	Lignite	-	-	-218	1	-230	1	-234	2	-228	<1	-195	4
TP2-127	Lignite	-204	4	-220	3	-234	2	-230	4	-233	1	-226	5
TP1-114	Coalified root/trunk	-166	3	-191	2	-191	2	-184	2	-189	3	-188	1
TP1-99	Coalified root/trunk	-206	2	-216	3	-224	1	-220	2	-215	2	-213	1
TP1-87	Lignite	-207	2	-222	2	-237	1	-246	3	-245	<1	-240	1
TP1-65	Coalified root/trunk	-196	2	-180	5	-210	4	-225	2	-232	1	-232	<1
TP1-50	Clay	-	-	-172	20	-195	20	-196	6	-192	9	-188	7
TP1-38	Lignite	-183	3	-206	6	-217	4	-205	11	-204	7	-202	5
TP1-22	Clay	-157	6	-162	15	-183	6	-181	10	-192	5	-208	2
TP1-15	Lignite	-175	13	-193	12	-213	8	-194	8	-222	3	-207	9
TP1-5	Lignite	-166	18	-172	15	-201	5	-194	16	-199	5	-193	3
Average		-182	6	-190	8	-205	5	-201	6	-207	5	-204	5

Table 3. continued

Sample	C ₂₇	SD (1σ)	C ₂₉	SD (1σ)	C ₃₁	SD (1σ)	C ₃₃	SD (1σ)	C ₃₅	SD (1σ)	Pr	SD (1σ)	Ph	SD (1σ)
TP3-224	-169	1	-175	3	-158	2	-153	3	-174	6	-270	3	-279	3
TP3-216	-198	6	-191	6	-176	2	-162	11	-183	8	-269	7	-284	-
TP3-195	-205	<1	-190	2	-177	3	-159	1	-174	5	-295	1	-288	10
TP3-190	-173	9	-180	4	-155	10	-161	8	-174	10	-	-	-	-
TP3-176	-182	8	-181	2	-165	8	-146	8	-	-	-	-	-	-
TP3-157	-187	1	-187	1	-172	2	-164	3	-177	9	-289	6	-311	2
TP3-151	-242	3	-211	4	-	-	-	-	-	-	-260	17	-249	4
TP2-140	-152	<1	-160	6	-151	3	-154	-	-	-	-268	2	-276	7
TP2-127	-192	7	-190	3	-186	16	-160	17	-181	7	-273	4	-259	10
TP1-114	-167	9	-	-	-	-	-	-	-	-	-287	4	-254	2
TP1-99	-197	1	-193	3	-170	7	-161	2	-185	3	-300	2	-284	14
TP1-87	-218	1	-203	1	-185	2	-176	2	-182	2	-301	2	-299	4
TP1-65	-210	4	-180	4	-	-	-	-	-	-	-294	5	-	-
TP1-50	-183	7	-191	4	-177	3	-160	7	-172	9	-	-	-	-
TP1-38	-193	3	-188	3	-178	3	-163	4	-173	2	-303	4	-274	3
TP1-22	-196	9	-194	5	-155	14	-	-	-	-	-269	9	-276	-
TP1-15	-199	1	-203	4	-181	2	-169	4	-183	1	-293	10	-269	12
TP1-5	-187	6	-192	1	-187	4	-169	3	-180	3	-278	15	-233	-
Average	-192	4	-189	3	-172	5	-161	6	-178	5	-283	6	-274	7

- 1 **Fig. 1.** Geological and geographical situation of the Taskomirsay section (modified from Schnyder et al.
2 accepted).
- 3
- 4 **Fig. 2.** Total organic carbon (TOC), Total Nitrogen (TN), $\delta^{15}\text{N}_{\text{tot}}$ and $\delta^{15}\text{N}_{\text{org}}$ values along the Taskomirsay
5 section with respect to lithology. Lignites are in black, clayey layers in gray, silts-sandstones in orange triangles
6 and coalified wood trunks or roots in brown. Transition zone, Pliensbachian-Toarcian transition.
- 7
- 8 **Fig. 3.** Taskomirsay samples plotted in a HI (Hydrogen Index)/OI (Oxygen Index) diagram. Arrows indicate
9 pathways of OM alteration.
- 10
- 11 **Fig. 4.** TOC values of clayey layers plotted against corresponding N_{tot} and N_{org} values.
- 12
- 13 **Fig. 5.** ACL values, *n*-alkane amount and *n*-alkane distribution in lipid extracts of the Taskomirsay section. Blue
14 bars refer to the “aquatic pool” (C_{23}) and green bars to the “terrestrial pool” (C_{27}) (see text, section 4.2).
- 15
- 16 **Fig. 6.** Variability of $\delta^2\text{H}$ values of *n*-alkanes and isoprenoid pristane (Pr) and phytane (Ph). Also represented
17 are compiled typical values under tropical, cool temperate and glacial regime from Dawson et al. (2004) and
18 Izart et al. (2012).
- 19
- 20 **Fig. 7.** $\delta^2\text{H}$ values of *n*-alkanes and isoprenoid pristane and phytane along the Taskomirsay section. Error bars
21 (based on triplicates) are smaller than the symbol if not visible, except for red points, which correspond to single
22 analyses.
- 23
- 24 **Fig. 8.** Elemental atomic C/N ratio and organic isotopic values ($\delta^{13}\text{C}_{\text{org}}$) of bulk organic matter from
25 Taskomirsay. Also represented are typical zones for different organic sources (modified from Meyers et al.,
26 1997 with typical C/N values from Tyson, 1995). The $\delta^{13}\text{C}_{\text{org}}$ values are from Schnyder et al., accepted.
- 27
- 28 **Fig. 9.** Synthesized paleoclimatic parameters in Taskomirsay. Sporomorphs data and the $\delta^{13}\text{C}_{\text{org}}$ curve are from
29 Schnyder et al., accepted. Temperatures (large red points) are based on brGDGTs and arrows show a cooling

30 trend (blue) and a warming trend (red). $\Delta^2\text{H}_{\text{ter-aq}}$ values were calculated as follows: mean $\delta^2\text{H-C}_{27}$ value minus
31 mean $\delta^2\text{H-C}_{23}$ value.

32

33 **Fig. 10.** ACL values vs. *n*-alkane amounts. Significant logarithmic correlation occurs in lignites (black points).

34 See Fig. 2 for color caption.

35

Table 1. Bulk organic results. Isotopic values are reported with their standard deviation (1σ) calculated on replicates analyses (2 at least). Standard deviation calculated on tyrosines ($\pm 0.3\%$) was applied for samples below $40 \mu\text{g N}$ (highlighted in grey).

^a total organic carbon

^b total nitrogen

^c atomic C/N ratio

^d inorganic bound nitrogen

^e organic nitrogen calculated by $\text{TN} - \text{N}_{\text{bnd}}$.

* $\text{TOC}/\text{N}_{\text{org}}$ for clayey samples.

Table 2. Molecular geochemistry of the lipid extracts. Relative abundances of brGDGTs used for MAAT calculations are in supplementary data.

^a Percentage of lipids in dry sediments

^b brGDGT-derived temperatures calculated from Peterse et al. (2012)

Table 3. Hydrogen isotopes ($\delta^2\text{H}$) of n-alkanes. $\delta^2\text{H}$ values and their standard deviation (SD) are expressed in per mille (‰) from C_{17} to C_{35} and of pristane and phytane.

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[Click here to download Supplementary Interactive Plot Data \(CSV\): Schnyder-Cent-As-Bas-Revision 2.docx](#)