



Deposited via The University of Leeds.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/id/eprint/179491/>

Version: Accepted Version

---

**Article:**

Chen, W, Kemp, DB, He, T et al. (2021) First record of the early Toarcian Oceanic Anoxic Event in the Hebrides Basin (UK) and implications for redox and weathering changes. *Global and Planetary Change*, 207. 103685. ISSN: 0921-8181

<https://doi.org/10.1016/j.gloplacha.2021.103685>

---

© 2021, Elsevier. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

**Reuse**

This article is distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) licence. This licence only allows you to download this work and share it with others as long as you credit the authors, but you can't change the article in any way or use it commercially. More information and the full terms of the licence here: <https://creativecommons.org/licenses/>

**Takedown**

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing [eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk) including the URL of the record and the reason for the withdrawal request.

1 **First record of the early Toarcian oceanic anoxic event in the Hebrides**  
2 **Basin (UK) and implications for redox and weathering changes**

3  
4 Wenhan Chen <sup>a</sup>, David B. Kemp <sup>a\*</sup>, Tianchen He <sup>b</sup>, Chunju Huang <sup>a</sup>, Simin Jin <sup>a</sup>, Yijun  
5 Xiong <sup>b</sup>, Robert J. Newton <sup>b</sup>

6  
7 <sup>a</sup> State Key Laboratory of Biogeology and Environmental Geology, School of Earth  
8 Sciences, China University of Geosciences, Wuhan 430074, P.R. China

9 <sup>b</sup> School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK

10  
11 \*Corresponding author: David B. Kemp ([davidkemp@cug.edu.cn](mailto:davidkemp@cug.edu.cn))

12  
13 **Abstract**

14 The early Toarcian (~183 Ma) was characterized by a prominent volcanism-  
15 induced warming event associated with a massive addition of <sup>12</sup>C-enriched carbon to  
16 the ocean-atmosphere system. This warming likely contributed to marked ocean  
17 deoxygenation during this time, giving the event its name: the early Toarcian oceanic  
18 anoxic event (T-OAE). Although the T-OAE has been recognized globally, clear  
19 geographic differences in the character of the event and its environmental effects have  
20 been noted. Here we present new carbon isotope, element abundance and organic  
21 geochemical data from a lower Toarcian succession on the Isle of Raasay, Scotland  
22 (Hebrides Basin, Northwest European Shelf). These data provide the first evidence of  
23 the T-OAE in Scotland. The succession is generally enriched in organic matter through  
24 the T-OAE interval, though redox-sensitive trace element data indicate that oxic-  
25 suboxic bottom water conditions prevailed, potentially interspersed with ephemeral  
26 anoxic episodes. Our elemental data contrast with evidence for persistent  
27 anoxia/euxinia in nearby basins, and emphasizes how deoxygenation was spatially  
28 variable and dependent on water depth and basin hydrography. Similarly, the data  
29 emphasize how anoxia was not a prerequisite for the deposition of organic-rich  
30 lithologies during the T-OAE. Sedimentological evidence, coupled with inorganic  
31 geochemical data, indicates increased coarse-grained detrital flux and enhanced  
32 chemical weathering during the T-OAE. Our findings support emerging evidence for a

33 marked strengthening of hydrological cycling and increased storminess at tropical and  
34 subtropical latitudes globally in response to global warming during the T-OAE.

35

## 36 **1. Introduction**

37 The early Toarcian oceanic anoxic event (T-OAE, ~183 Ma) (Jenkyns, 1988) was  
38 one of the most significant paleoenvironmental change events of the Phanerozoic. The  
39 interval was characterized by extinction of marine organisms (Harries and Little, 1999),  
40 floral turnover on land (Slater et al., 2019), and elevated seawater temperatures (Bailey  
41 et al., 2003; Ruebsam et al., 2020). A crisis in carbonate production also occurred (e.g.  
42 Han et al., 2018), putatively associated with ocean acidification (Suan et al., 2008;  
43 Ettinger et al., 2021). The event was also associated with a prominent sea-level rise  
44 (Hesselbo, 2008; Thibaut et al., 2018), widespread deposition of organic-rich sediments  
45 (Jenkyns, 1988), enhanced continental weathering (Cohen, et al., 2004; Them, et al.,  
46 2017; Kemp et al., 2020), and increased storm activity (Krencker et al., 2015; Han et  
47 al., 2018; Izumi et al., 2018a). Of particular significance is a pronounced negative  
48 carbon isotope excursion (CIE) recorded in marine organic carbon (Hesselbo et al.,  
49 2000), terrestrial organic carbon and fossil wood (Hesselbo et al., 2000; Xu et al., 2017),  
50 hemipelagic and shallow-water carbonates (Hesselbo et al., 2007; Han et al., 2018), and  
51 individual organic biomarkers (e.g. Schouten et al., 2000).

52 The CIE is interpreted to reflect a substantial injection of  $^{12}\text{C}$ -enriched carbon into  
53 the ocean-atmosphere system, potentially caused by volcanism from the Karoo-Ferrar  
54 Large Igneous Province, the thermogenic emission of  $^{12}\text{C}$  via intrusion of Karoo-Ferrar  
55 sills in Gondwanan coal deposits (McElwain et al., 2005; Svensen et al., 2007), and/or  
56 the dissociation of methane gas hydrates (Hesselbo et al., 2000, 2007; Kemp et al.,  
57 2005). The CIE is commonly broadly coeval with the deposition of organic-rich rocks,  
58 and the deposition of these facies worldwide has been linked to a significant episode of  
59 seawater deoxygenation (Jenkyns, 1988; Pearce et al., 2008). Nevertheless, the extent  
60 of seawater deoxygenation during the T-OAE is debated, and redox conditions appear  
61 to have been highly variable between different basins, water depths and oceans  
62 worldwide (e.g. Ramirez and Algeo, 2020a). Given the fact that the oceanic

63 environment has profound influences on extinction and radiation, it is important to  
64 dissect the reasons for this spatial variability in redox. Moreover, research on  
65 paleoclimate conditions during the T-OAE is of key importance for understanding the  
66 Earth system responses to large-scale carbon release, and necessitates global analysis  
67 from a range of geographic settings and environments.

68 In this paper, we present the first carbon isotope record of the T-OAE from the  
69 Hebrides Basin, deposited in the sub-Boreal realm (Figs. 1 and 2). Our dataset  
70 comprises bulk organic carbon isotope ( $\delta^{13}\text{C}_{\text{org}}$ ), palynological carbon isotope ( $\delta^{13}\text{C}_{\text{paly}}$ ),  
71 total organic carbon (TOC), Rock Eval pyrolysis, and element abundance data from a  
72 lower Toarcian succession on the Isle of Raasay, Scotland. Our results reveal the  
73 negative CIE in the sub-Boreal realm during the early Toarcian, which is coeval with  
74 deposition of organic-rich dark grey-black shales. Our new geochemical data permit a  
75 detailed investigation of seawater redox conditions through the T-OAE in the Hebrides  
76 Basin, and also provide insights into continental weathering and hydrological cycling  
77 in the sub-Boreal realm in response to T-OAE warming.

78

## 79 **2. Geological setting**

80 The Jurassic rocks of the Hebrides Basin are exposed in westerly-tilted fault blocks  
81 in a major half-graben (Fig. 2). The Hebrides Basin is one of a series of basins on the  
82 margins of the North Atlantic formed during early extensional phases in the evolution  
83 of the Central and North Atlantic Oceans (Tankard and Balkwill, 1989). The western  
84 margin of the Hebrides Basin is constrained by the Minch Fault Zone, east of the Outer  
85 Hebrides (Stein, 1988). The unfaulted eastern margin is adjacent to the present coastline  
86 of mainland Scotland (Morton and Hudson, 1995). Three phases of subsidence related  
87 to extension (Late Triassic to Early Toarcian, Latest Toarcian to Late Bathonian, and  
88 Early Oxfordian to Early Kimmeridgian) were separated by episodes of tectonic  
89 quiescence (Toarcian and Callovian) (Morton, 1989).

90 Successions spanning the upper Pliensbachian to lower Toarcian are exposed on  
91 the Isles of Skye and Raasay (Fig. 2; see, for example, Morton and Hudson, 1995). For  
92 this study, Toarcian samples were collected from Raasay, and are augmented by two

93 samples collected from just below the Pliensbachian-Toarcian boundary on Skye (Figs.  
94 2 and 3). Both localities were situated at a paleolatitude of ~40°N, close to the Viking  
95 corridor, which connected the Boreal Sea to northwestern Europe (Fig. 1).

96

## 97 2.1 Lithostratigraphy and depositional environment

98 The Toarcian succession on Raasay is exposed in and around disused ironstone  
99 mine workings at Inverarish Burn in the south of the island (UK Grid Reference NG  
100 573365; Figs. 2 and 3). Here, the section (in ascending stratigraphic order) consists of  
101 a ~6 m succession of fine-grained sandstones of the uppermost Scalpa Sandstone  
102 Formation, dark grey-black micaceous shales of the Portree Shale Formation, and  
103 oolitic ironstones of the Raasay Ironstone Formation (Figs. 3 and 4; Lee, 1920; Howarth,  
104 1956, 1992). The top of the Scalpa Sandstone Formation and fairly sharp transition to  
105 the darker and finer-grained Portree Shale Formation are exposed in a tributary to the  
106 northeast of the main ironstone workings (NG 5719 3688; Figs. 3B and 3C). The  
107 transition from the Portree Shale Formation to the Raasay Ironstone Formation is  
108 marked by dark grey-black shales with scattered chamosite ooids (Morton and Hudson,  
109 1995), and can be observed on the floor of the opencast workings (NG 5690 3645).  
110 Nearby, numerous randomly oriented belemnites occur on a bedding surface (the  
111 “belemnite battlefield”), representing the top of the Portree Shale Formation (Fig. 3D;  
112 Doyle and Macdonald, 1993; Price, 2010). An abundant ammonite fauna in the Portree  
113 Shale Formation (Howarth, 1992) indicates deposition in a marine environment. A lack  
114 of observed sedimentary structures observed within this formation potentially indicates  
115 deposition in a quiescent environment. The transition from the Scalpa Sandstone  
116 Formation to the finer-grained Portree Shale Formation likely resulted from a relative  
117 sea-level rise (e.g. Morton, 1989).

118 The Raasay Ironstone Formation is characterized by thin, unevenly bedded  
119 chamosite oolitic ironstones, intercalated with thin argillaceous beds (Morton and  
120 Hudson, 1995; Figs. 3E and 3F). Previous work has indicated that some levels display  
121 cross-bedding, ostensibly suggesting that the ironstones formed in a shallow water  
122 environment with current action (Fig. 3F; Morton and Hudson, 1995). Hesselbo (2008)

123 suggested that the ironstone represents an interval of sediment starvation during a sea  
124 level highstand. The samples collected from just below the Pliensbachian-Toarcian  
125 boundary on the Isle of Skye are from near the top of the Scalpa Sandstone Formation  
126 from a section exposed on the east coast of the island (NG 5156 4710; Figs. 2 and 3A).

127

## 128 2.2 Biostratigraphy

129 The *Dactylioceras tenuicostatum* Zone, marked by the first occurrence of the  
130 ammonite genus *Dactylioceras*, indicates the base of the Toarcian stage (Lee, 1920;  
131 Howarth, 1956, 1992). Poorly preserved *Dactylioceras tenuicostatum* fossils occur  
132 within the top 2 m of the Scalpa Sandstone Formation on Skye and Raasay, indicating  
133 that the base of the Toarcian is within this formation, and the *tenuicostatum* Zone  
134 extends into the lowest part of the overlying Portree Shale Formation (Howarth, 1992;  
135 Fig. 4). Above this, the *Harpoceras falciferum* Zone (equivalent to the *Harpoceras*  
136 *serpentinum* Zone) occurs within the rest of the Portree Shale Formation and overlying  
137 Raasay Ironstone Formation. The *falciferum* Zone can be subdivided into the  
138 *Cleviceras exaratum* and *Harpoceras falciferum* subzones. The *exaratum* Subzone in  
139 the Portree Shale Formation has been defined on the basis of the recognition of  
140 *Cleviceras exaratum*, coincident with the occurrence of dark grey-black shales (Lee,  
141 1920; Howarth, 1992). The Raasay Ironstone Formation was assigned by Howarth  
142 (1992) to the *falciferum* Subzone and includes part of the *exaratum* Subzone based on  
143 the occurrence of *Cleviceras elegans* in the ironstone (Fig. 4). Importantly, previous  
144 studies (e.g. Lee, 1920; Price, 2010) erroneously assigned the Raasay Ironstone  
145 Formation to the *Hildoceras bifrons* Zone based on the purported presence of  
146 *Dactylioceras commune*. However, work by Howarth (1992) did not identify this  
147 species, and the presence of *Cleviceras elegans* confirms instead an (upper) *exaratum*  
148 Subzone age. All other species found in the Raasay Ironstone Formation indicate a  
149 *falciferum* Subzone age (Howarth, 1992), and thus the Raasay Ironstone Formation  
150 must span at least the upper part of the *exaratum* Subzone and an unknown proportion  
151 of the *falciferum* Subzone (Howarth, 1992; Fig. 4).

152

### 153 3. Materials and methods

#### 154 3.1 Sample collection

155 At Inverarish Burn, 20 rock samples were collected from the upper part of the  
156 Portree Shale Formation and Raasay Ironstone Formation from the main opencast  
157 workings (NG 5690 3645) at approximately 15 cm intervals. Thirty-eight samples were  
158 also obtained from the uppermost Scalpa Sandstone Formation and Portree Shale  
159 Formation from the tributary northeast of the main opencast workings (NG 5719 3688)  
160 at intervals of 10 cm or less. Based on the orientation of the bedding in this area, an  
161 exposure gap of ~13 cm separates the two sample sets (Fig. 4). On Skye, 2 samples  
162 were collected from the uppermost Scalpa Sandstone Formation from the highest  
163 exposed and accessible outcrop (NG 5156 4710; Figs. 2 and 3A). According to the  
164 litho- and biostratigraphy of Morton (2009), these samples are from the *P. hawskerense*  
165 Subzone of the *Pleuroceras spinatum* Zone (Pliensbachian stage) (Fig. 4).

166

#### 167 3.2 Carbon isotopes, TOC, and nitrogen abundance

168 All 60 samples were analyzed for bulk organic carbon isotope ratios ( $\delta^{13}\text{C}_{\text{org}}$ ), total  
169 organic carbon (TOC), and nitrogen abundance at the State Key Laboratory of  
170 Geological Processes and Mineral Resources, China University of Geosciences  
171 (Wuhan). For each sample, approximately 1g of powdered rock was reacted with 20%  
172 HCl for at least 24 hours to remove carbonate phases. Samples were then repeatedly  
173 washed with distilled water to remove residual acid. After drying, around 50 mg of each  
174 sample powder was sealed in Sn foil for isotope analyses through a Thermo Finnigan  
175 MAT 253 mass spectrometer, which yielded an instrumental precision (standard  
176 deviation) of 0.1‰. Standard samples GBW04407 ( $-22.43\text{‰} \pm 0.07$ ) and GBW04408  
177 ( $-36.91\text{‰} \pm 0.10$ ) were used for the calibration, and the results are reported relative to  
178 the Vienna Pee Dee Belemnite (VPDB) standard. TOC and N abundance analyses were  
179 conducted on samples using a Vario MACRO cube elemental analyzer. Phenylalanine  
180 was used as the calibration standard and the analytical precision for C and N was better  
181 than 0.2 wt.%. Additionally, 22 samples spread evenly through the succession were  
182 analyzed for palynological carbon isotope composition ( $\delta^{13}\text{C}_{\text{paly}}$ ). This analysis was

183 carried out to specifically test the veracity of the bulk organic matter  $\delta^{13}\text{C}$  analyses,  
184 since the likely presence of siderite in the Raasay Ironstone (Morton, 2009) could lead  
185 to recalcitrant carbonate carbon resistant to decalcification using dilute HCl. For this  
186 process, ~1g of powdered sample was reacted with concentrated HCl and HF, before  
187 the addition of zinc bromide to remove residual mineral grains. The organic matter  
188 residue was then measured using a MAT 253 mass spectrometer, with a precision  
189 (standard deviation) obtained from standards (USGS 40, USGS 41A, QUB) of  $\leq 0.13\%$ .

190

### 191 3.3 Rock Eval pyrolysis

192 Rock Eval pyrolysis generates hydrogen index (HI, mg hydrocarbons/g TOC),  
193 oxygen index (OI, mg  $\text{CO}_2$ /g TOC) and  $T_{\text{max}}$  ( $^{\circ}\text{C}$ ) data, which can be useful for  
194 understanding the type and maturity of organic matter (Espitalié et al., 1985). Organic  
195 matter pyrolysis of 11 whole-rock powdered samples spread through the Raasay section  
196 was conducted at the Guangzhou Institute of Geochemistry, Chinese Academy of  
197 Sciences using a Rock Eval 6 instrument, following the method described in Espitalié  
198 et al. (1985). The IFP 160000 standard was used to calibrate results.

199

### 200 3.4 Elemental analysis

201 Thirty-five powdered samples were analyzed for element abundances. Twenty-two  
202 of them were analyzed at the University of Leeds. For these samples, 80mg of powdered  
203 sample was dissolved in a  $\text{HNO}_3$ -HF- $\text{HClO}_4$  mixture, followed by evaporation to  
204 dryness. Boric acid was then added to the residue, before achieving total dissolution  
205 with hot  $\text{HNO}_3$ . Major and trace elements were measured by ICP-OES and ICP-MS  
206 with multiple replicate analyses of one sample yielding relative standard deviations  
207 (RSDs) of  $<2\%$ . The other 13 samples were sent to Nanjing FocuMS Technology Co.  
208 Ltd, because they were difficult to fully digest with the above method. For these  
209 samples, about 40 mg of powdered sample was mixed with  $\text{HNO}_3$  and HF in high-  
210 pressure PTFE bombs. These bombs were then placed in an oven at  $195^{\circ}\text{C}$  for at least  
211 48 hours to ensure digestion, after which the digested diluent was nebulized into an  
212 Agilent Technologies 7700x quadrupole ICP-MS to determine the major and trace

213 elements. Multiple replicate analyses of one sample and standards yielded RSDs of  
214 <5%.

215

## 216 **4. Results**

### 217 4.1 Carbon isotopes, TOC and TOC/N

218 Bulk organic carbon isotope ( $\delta^{13}\text{C}_{\text{org}}$ ), palynological carbon isotope ( $\delta^{13}\text{C}_{\text{paly}}$ ), and  
219 TOC data are plotted against the stratigraphy in Fig. 4 (data available in Table S1). The  
220  $\delta^{13}\text{C}_{\text{org}}$  values in the Raasay section range from  $-27.17\text{‰}$  to  $-24.49\text{‰}$ , and show a  
221 decrease of  $\sim 2.7\text{‰}$  upwards through the studied section. This overall decrease in  $\delta^{13}\text{C}_{\text{org}}$   
222 comprises three abrupt negative shifts (each <30 cm thick) between the uppermost  
223 Scalpa Sandstone Formation (*tenuicostatum* Zone), and the base of the Raasay  
224 Ironstone Formation (*exaratum* Subzone). This is followed by a plateau and a slight  
225 recovery (i.e. positive trend in  $\delta^{13}\text{C}_{\text{org}}$ ) to the top of the Raasay Ironstone Formation.  
226 The variations of paired  $\delta^{13}\text{C}_{\text{paly}}$  values show a similar trend and match well with  $\delta^{13}\text{C}_{\text{org}}$   
227 measured on the same samples. The two samples collected from Skye in the Scalpa  
228 Sandstone Formation below the Pliensbachian-Toarcian boundary (*spinatum* Zone)  
229 show relatively high  $\delta^{13}\text{C}_{\text{org}}$  values ( $-24.80\text{‰}$  and  $-24.58\text{‰}$ ) that are similar to those of  
230 the uppermost Scalpa Sandstone Formation at the base of the Raasay section.

231 In detail, the onset of the first negative shift (shift 1) is at -40 cm section height in  
232 the Raasay section, and spans  $\sim 20$  cm of the *tenuicostatum* Zone in the Scalpa  
233 Sandstone Formation with a magnitude of  $\sim 1.0\text{‰}$ . Subsequently, values are broadly  
234 stable before the second abrupt shift (shift 2) of  $\sim 1.0\text{‰}$  at 140 cm in the Portree Shale  
235 Formation, which spans  $\sim 30$  cm. The third abrupt negative shift (shift 3,  $\sim 1.1\text{‰}$ ) occurs  
236  $\sim 120$  cm above the top of shift 2 ( $\sim 290$  cm section height), and is characterized by a  
237 sharp decrease to minimum  $\delta^{13}\text{C}_{\text{org}}$  ( $-27.07\text{‰}$ ) over  $\sim 20$  cm in the lower part of the  
238 Raasay Ironstone Formation (*exaratum* Subzone). Through the rest of the Raasay  
239 Ironstone Formation,  $\delta^{13}\text{C}_{\text{org}}$  is broadly stable but with a slight increasing trend of  
240  $\sim 1.3\text{‰}$ .

241 TOC values in the Raasay section range from 0.24% to 8.01% (mean 2.05%), and  
242 TOC in the two Skye samples is 0.04% and 0.05% (Fig. 4). TOC gradually increases

243 from 0.55% at the base of the Raasay section to 3.27% at 155 cm in the Portree Shale  
244 Formation. Following a decline to 1.03% in the lowermost Raasay Ironstone Formation  
245 (260 cm), TOC rises abruptly to the highest value (8.01%) at 355 cm in the Raasay  
246 Ironstone Formation. This is close to the level where minimum  $\delta^{13}\text{C}_{\text{org}}$  occurs. Above  
247 this, TOC values show an overall decrease towards the top of the succession. TOC/N  
248 ratios in the Raasay section range from ~8 to ~29, with a mean of ~20 (Fig. 5). A  
249 pronounced increase to ~29 occurs from the lower part of the Portree Shale Formation  
250 through to the Raasay Ironstone Formation, followed by a drop to ~11 towards the top  
251 of the section (Fig. 5; Table S1).

252

## 253 4.2 Rock Eval pyrolysis

254 Hydrogen index (HI) values range between 16 and 168 (mean 48 mg HC/g TOC),  
255 and are relatively steady throughout the succession, with the highest value recorded  
256 within the Raasay Ironstone Formation (Figs. 5 and 6). Oxygen index (OI) values range  
257 between 5 and 67 (mean 22 mg  $\text{CO}_2$ /g TOC, Figs. 5 and 6).  $T_{\text{max}}$  is also broadly stable,  
258 ranging from 337°C to 426°C with no abrupt fluctuations, except an outlying value  
259 (583°C) within the Portree Shale Formation (Fig. 5; Table S1).

260

## 261 4.3 Elemental abundances

### 262 4.31 Redox-sensitive elements

263 Mo, U, V, and Re have long been used to assess paleoredox conditions, and the  
264 relative enrichment of Ni can be a useful indicator of primary productivity (e.g.  
265 Tribovillard et al., 2006, 2012; Algeo and Tribovillard, 2009; Liu et al., 2021). In this  
266 study, enrichment factors (EFs) have been used to describe and assess the abundance  
267 of these elements relative to average shale values (Fig. 7). Enrichment factors are  
268 calculated as  $X_{\text{EF}} = (X/\text{Al})_{\text{sample}} / (X/\text{Al})_{\text{PAAS}}$ , where PAAS refers to post-Archean  
269 average Australian shale (from Taylor and McLennan, 1985). If  $X_{\text{EF}}$  is greater than 1,  
270 then element X is enriched relative to the average shale, otherwise it is depleted. In  
271 practical terms, an  $X_{\text{EF}} > 3$  can be regarded as detectably enriched, and an  $X_{\text{EF}} > 10$  is  
272 substantially enriched (Algeo and Tribovillard, 2009).

273 In general,  $Mo_{EF}$  is  $<1$  from the base of the Raasay section up to  $\sim 310$  cm in the  
274 Raasay Ironstone Formation. Above this level,  $Mo_{EF}$  increases to  $>1$ , reaching a  
275 maximum ( $\sim 8$ ) at 494 cm in the Raasay Ironstone Formation (Fig. 7). Mean  $Mo_{EF}$  in  
276 the succession is  $\sim 1.13$ . From the base of the succession to  $\sim 100$  cm,  $U_{EF}$  values are  
277 generally  $<3$ . Above this level, there are some fluctuations and a marked increase (up  
278 to  $\sim 113$ ) at 193 cm in the Portree Shale Formation. Values then decrease to  $\sim 12$  at 213  
279 cm and remain steady ( $\sim 7$ ) until 370 cm section height, followed by a marked rise (up  
280 to  $\sim 27$ ) to the top of the succession through the Raasay Ironstone Formation (Fig. 7).  
281 Mean  $U_{EF}$  in the succession is  $\sim 12.41$ .  $V_{EF}$  ranges between  $\sim 1$  and  $\sim 11$  (mean  $\sim 3.61$ )  
282 throughout the succession. Overall,  $V_{EF}$  rises progressively from the base of the  
283 succession to  $\sim 3$  at 370 cm in the Raasay Ironstone Formation, before increasing more  
284 abruptly to  $\sim 10$  at 406 cm and remaining high above this (Fig. 7).  $Ni_{EF}$  values are low  
285 and generally stable ( $\sim 1$ ) from the base of the succession to  $\sim 100$  cm. Subsequently,  
286  $Ni_{EF}$  increases to  $\sim 3$  at  $\sim 180$  cm in the upper Portree Shale Formation, followed by a  
287 marked decrease to  $\sim 1$  at  $\sim 300$  cm. Higher in the section,  $Ni_{EF}$  rises again (up to  $\sim 8$ )  
288 within the Raasay Ironstone Formation and remains high at the top of the succession  
289 (Fig. 7).

290 Ratios of  $Mo_{EF}/U_{EF}$  and  $V_{EF}/Mo_{EF}$  show obvious negative correlation throughout  
291 the succession (Fig. 7). Two intervals, characterized by generally increasing  $Mo_{EF}/U_{EF}$   
292 and decreasing  $V_{EF}/Mo_{EF}$ , can be observed in the shaded intervals of Fig. 7 (labelled  
293 intervals A and B) and contrast with the overall decreasing trends in  $Mo_{EF}/U_{EF}$  in the  
294 rest of the section. Re/Mo values show a prominent rise from  $\sim 35$  at the base of the  
295 succession to  $\sim 193$  at  $\sim 110$  cm, followed by a sharp decrease to  $\sim 21$  at  $\sim 180$  cm in the  
296 Portree Shale Formation. Above this, values increase to  $\sim 116$  and are relatively high  
297 ( $\sim 105$ ) from  $\sim 190$  to  $\sim 250$  cm, after which values fall sharply up-section, and are close  
298 to 0 at the top of the succession (Fig. 7).

299

#### 300 4.32 Detrital and chemical weathering proxies

301 Variations in the flux and nature of detrital components can be tracked using  
302 elements that are typically enriched in terrigenous sediments. Proxies for variations in

303 detrital flux and grain size (Ti/Al, Ti/K and Zr/Rb) show similar trends with differing  
304 magnitudes through the section (Fig. 8). These proxies are generally relatively low and  
305 stable from the base of the section to ~80 cm. Subsequently, there is a prominent rise  
306 in Ti/K and Zr/Rb to the top of the Portree Shale Formation (Fig. 8, note logarithmic  
307 scales), and a smaller magnitude rise in Ti/Al. Ti/Al, Ti/K and Zr/Rb values increase  
308 abruptly near the base of the Raasay Ironstone Formation (Fig. 8). Chemical weathering  
309 proxies (K/Al and Rb/Al) show some fluctuations from the base of the section to ~20  
310 cm. Above this, K/Al and Rb/Al drop sharply to ~100 cm, followed by a plateau to  
311 ~250 cm near the base of the Raasay Ironstone Formation. Further up-section, values  
312 decrease again to ~360 cm, and remain low to the top of the section (Fig. 8).

313

## 314 **5. Discussion**

### 315 5.1 The Toarcian OAE and CIE in the Hebrides Basin

316 The available ammonite age constraints for the Raasay succession (Section 2.2)  
317 indicate an early Toarcian age that is contemporaneous with the Toarcian OAE  
318 recognized globally. As such, the ~2.7‰ decrease in  $\delta^{13}\text{C}_{\text{org}}$  through the uppermost  
319 Scalpa Sandstone Formation (*tenuicostatum* Zone), Portree Shale Formation (*exaratum*  
320 Subzone), and the lowermost Raasay Ironstone Formation (*exaratum* Subzone) can be  
321 unambiguously correlated with the fall in  $\delta^{13}\text{C}_{\text{org}}$  recognized from the same ammonite  
322 zones in other basins. Specifically, our new  $\delta^{13}\text{C}_{\text{org}}$  data can be correlated with the well-  
323 studied and nearby Yorkshire section from the Cleveland Basin (Figs. 1B and 9). Within  
324 the constraints of the available ammonite biostratigraphy from both sites, the 3 abrupt  
325 negative  $\delta^{13}\text{C}_{\text{org}}$  shifts observed on Raasay may correlate with 3 similar abrupt shifts  
326 recognized in Yorkshire (Fig. 9; Kemp et al., 2005). In the Yorkshire section, the shifts  
327 are more abrupt (<10 cm each) and more closely spaced than on Raasay (Fig. 9). A  
328 similar pattern of 2 or 3 shifts within the decreasing part of the T-OAE CIE has been  
329 recognized elsewhere (see for example Xu et al., 2018 and Izumi et al., 2018a). This  
330 correlation implies that the Raasay section (which does not capture the CIE in its  
331 entirety) may be stratigraphically expanded relative to Yorkshire. Nevertheless, the  
332 veracity of the correlation is difficult to confirm owing to the lack of additional

333 independent time constraints in the Raasay section (Fig. 9).

334 One important difference between the Raasay  $\delta^{13}\text{C}_{\text{org}}$  data and those of the nearest  
335 high-resolution  $\delta^{13}\text{C}_{\text{org}}$  record in Yorkshire is that the magnitudes of the negative shifts  
336 are smaller on Raasay (Fig. 9). In the Yorkshire succession, the overall decrease in bulk  
337  $\delta^{13}\text{C}_{\text{org}}$  from the *tenuicostatum* Zone to *exaratum* Subzone is  $\sim 7\%$ , and each negative  
338 shift is  $\sim 2\%$  or larger (Fig. 9). In other nearby basins in Europe, the magnitude of the  
339 T-OAE CIE also tends to be greater than we observe on Raasay, with more negative  
340 background (i.e. pre-excursion) values (see Remirez and Algeo, 2020a for a review).  
341 Globally, the magnitude of the CIE is variable (e.g. Remirez and Algeo, 2020a), and  
342 the CIE magnitude we observe on Raasay is consistent with  $\delta^{13}\text{C}_{\text{org}}$  data from a number  
343 of sections globally, including Switzerland (Fantasia et al., 2018), Canada (Them et al.,  
344 2017), Japan (Ikeda et al., 2018) and Tibet (Han et al., 2018).

345 Thermal maturity and variations in organic matter (OM) sources can have a  
346 potentially large impact on bulk organic carbon isotopes (e.g. Suan et al., 2015; Kemp  
347 et al., 2019). Rock Eval pyrolysis metrics, specifically HI, OI and  $T_{\text{max}}$ , can be used to  
348 track OM sources and assess thermal maturity (van Krevelen, 1981; Espitalié et al.,  
349 1985). Kerogens can be classified into four types (I–IV) based on different OM sources.  
350 In detail, algal and marine-derived OM (kerogen Type I and II) is hydrogen-rich with  
351 correspondingly high HI values. Type III primarily derives from terrestrial higher plants  
352 with relatively depleted hydrogen content, while type IV commonly consists of  
353 inertinite of terrestrial origin that is oxidized/reworked with extremely low HI values.  
354  $T_{\text{max}}$  is an indicator of thermal maturity. As shown in Figs. 5 and 6, low HI values (16  
355 to 168 mg, mean 48 HC/g TOC) and OI values (5 to 67 mg, mean 22 mg  $\text{CO}_2/\text{g TOC}$ )  
356 characterize the Raasay section, likely indicating a mix of terrestrially derived Type III  
357 and Type IV OM. In spite of an outlier ( $583^\circ\text{C}$ ) at 170 cm,  $T_{\text{max}}$  values are generally  
358 low (below  $430^\circ\text{C}$ ). This observation suggests little post-depositional diagenetic  
359 alteration of the organic matter or elemental data presented. Overall, the data suggest  
360 the predominance of relatively immature organic matter with negligible thermal  
361 alteration that could otherwise affect the  $\delta^{13}\text{C}_{\text{org}}$  signal or our other data.

362 In addition to Rock Eval, TOC/N can be used as a supplementary proxy to assess

363 organic matter source. Vascular land plants typically have TOC/N >20, whereas algal  
364 organic matter of marine origin generally has TOC/N <10 (e.g. Meyers, 1997). Mean  
365 TOC/N in the Raasay section is ~20, and the values increase during the T-OAE (Fig.  
366 5), likely reflective of a predominance of terrestrial organic matter in this interval. The  
367 reliability of using TOC/N in this way has been questioned (e.g. Wang et al., 2021), but  
368 the results obtained are consistent with the Rock Eval data in that they indicate a  
369 predominantly terrestrial source of organic matter. In detail, there is a weak trend in  
370 TOC/N that broadly mirrors the shape of the CIE on Raasay (Fig. 5; Fig S1A). However,  
371 the correlation between  $\delta^{13}\text{C}_{\text{org}}$  and TOC/N is relatively weak ( $R^2 \sim 0.17$ ). As such, any  
372 changes in organic matter source through the section likely had only a minor impact on  
373 the magnitude and morphology of the CIE. Similarly, the good match between the  
374 measured  $\delta^{13}\text{C}_{\text{paly}}$  values and the bulk  $\delta^{13}\text{C}_{\text{org}}$  data ( $R^2 \sim 0.82$ ; Fig. S1B) suggests that  
375 incomplete decalcification of refractory carbonate carbon is also unlikely to explain the  
376 lower magnitude change in  $\delta^{13}\text{C}_{\text{org}}$  and higher overall values in the Raasay section  
377 relative to nearby basins.

378 Suan et al. (2015) showed that the magnitude of the Toarcian CIE in a number of  
379 sections, including Yorkshire, is amplified by changing organic matter source through  
380 the excursion. They suggested a more realistic global magnitude of ~3-4‰ for the CIE  
381 (3.2‰ in Yorkshire). This is close to the magnitude observed in the Raasay section  
382 (Suan et al., 2015).

383

## 384 5.2 Redox conditions in the Hebrides Basin during the T-OAE

385 Mean TOC in the Raasay section is ~2.0%, and the progressive increase in TOC  
386 (up to ~8.01%) in the lower part of the Raasay Ironstone Formation may suggest the  
387 development of oxygen-deficient bottom water conditions. Our RSTE (redox-sensitive  
388 trace element) data can help discriminate between different seawater redox conditions,  
389 generally classified as oxic (>2.0 ml O<sub>2</sub> L<sup>-1</sup>), suboxic (~0.2-2.0 ml O<sub>2</sub> L<sup>-1</sup>), anoxic–  
390 nonsulfidic (<0.2 ml O<sub>2</sub> L<sup>-1</sup>, 0 ml H<sub>2</sub>S L<sup>-1</sup>), and euxinic (0 ml O<sub>2</sub> L<sup>-1</sup>, >0ml H<sub>2</sub>S L<sup>-1</sup>)  
391 (Wignall, 1994).

392 Mo, U and V accumulate strongly under reducing conditions. In some modern

393 marine systems characterized by intense Mn-Fe redox cycling within the water column  
394 (e.g. Cariaco Basin), the accumulation of authigenic Mo in sediments will be  
395 strengthened via a “particulate shuttle” (Algeo and Tribovillard, 2009). In highly  
396 restricted settings, the resupply of dissolved Mo available for enrichment in sediments  
397 may be limited, resulting in a low Mo abundance and low Mo/TOC even under euxinic  
398 conditions (Algeo and Lyons, 2006; McArthur et al., 2008). The possible spread of  
399 anoxic/euxinic conditions worldwide during the OAE (e.g. Dickson, 2017) could have  
400 caused a global seawater Mo drawdown, leading to a universal decrease in Mo  
401 concentration even in organic-rich sediments (e.g. Algeo, 2004; Goldberg et al., 2016).  
402 The reduction of U starts at the Fe (II)–Fe (III) redox boundary and links directly with  
403 Fe redox reactions rather than the presence of free H<sub>2</sub>S in the water column (euxinia)  
404 (Algeo and Maynard, 2004). Consequently, enrichment of U takes place under less  
405 intensely reducing conditions compared to Mo. V is much more sensitive to redox  
406 variation and tends to be well preserved after burial with little reworking or  
407 remobilization (Algeo, 2004). Therefore, the enrichment of V in sediments can be a  
408 useful tracer for weakly reducing (suboxic) or oscillating redox conditions (Calvert and  
409 Pedersen, 1993). Variations in  $Mo_{EF}/U_{EF}$  and  $V_{EF}/Mo_{EF}$  ratios are useful for monitoring  
410 relative enrichment among these redox-sensitive elements, providing additional  
411 indications for the degree of deoxygenation in bottom waters (e.g. Scholz, 2018).  
412 Similarly, Re is conservative in seawater under oxic settings, and accumulates strongly  
413 under suboxic conditions in particular (Crusius et al., 1996). Because Mo accumulation  
414 tends to be strengthened under euxinic conditions, Re/Mo can thus be employed to  
415 discriminate between suboxic and euxinic conditions.

416 In the Raasay section, Mo is typically depleted relative to PAAS values (Fig. 7).  
417 Mo/TOC ratios are extremely low during the negative trend in  $\delta^{13}C_{org}$ , and similar to  
418 values recorded across the T-OAE in the Yorkshire and Sakuraguchi-dani sections  
419 (Cleveland and Tabe Basins, respectively; Fig. 10). Low Mo and Mo/TOC ratios in the  
420 Cleveland Basin reflect extreme hydrographic restriction and persistent euxinia during  
421 the T-OAE (McArthur et al., 2008; Ramirez and Algeo, 2020b). By contrast, low Mo  
422 and Mo/TOC in the Tabe Basin and lack of strong enrichment in other redox elements

423 indicate the predominance of oxic to suboxic bottom water conditions (Kemp and Izumi,  
424 2014), perhaps with intermittent anoxia/euxinia based on limited pyrite framboid  
425 evidence (Izumi et al., 2018b). Therefore, two scenarios could be proposed to explain  
426 the low  $Mo_{EF}$  and  $Mo/TOC$  ratios observed in the Raasay section. In the first scenario,  
427 the Hebrides Basin became restricted like the Cleveland Basin with an anoxic  
428 environment from the onset of the negative trend in  $\delta^{13}C_{org}$ , during which inadequate  
429 replenishment of Mo led to both low  $Mo_{EF}$  and  $Mo/TOC$  values. The increase in  $Mo_{EF}$   
430 within the Raasay Ironstone Formation could indicate a more open environment in the  
431 Hebrides Basin at this time, and consequent resupply of Mo, possibly supported by a  
432 global sea level rise during the interval (Hesselbo, 2008). The alternative scenario is  
433 that low Mo and  $Mo/TOC$  ratios simply reflect a predominantly oxic to suboxic  
434 environment within an unrestricted setting. In this case, the high TOC (which is  
435 predominantly terrestrial in origin based on the Rock Eval and TOC/N data) could have  
436 resulted primarily from high input of terrestrial material, with preservation potentially  
437 aided by relatively high sedimentation rates and/or suboxic conditions at the sea floor.

438 Persistent anoxic or euxinic conditions through the T-OAE on Raasay are unlikely  
439 owing to the lack of strong evidence in the other redox data and the paleoecology of the  
440 section (Fig. 7). U and V are only moderately enriched through the succession,  
441 suggesting suboxic conditions.  $Ni_{EF}$  is a useful proxy to assess organic carbon flux  
442 related to primary productivity, as well as redox conditions (Tribovillard et al., 2006),  
443 and on Raasay  $Ni_{EF}$  values are generally  $<3$ . Paleontological data from NW Europe  
444 indicate that four bivalve species commonly dominate the lower Toarcian: *Bositra*  
445 *radiata*, *Pseudomytiloides dubius*, *Meleagrinnella substriata*, and *Bositra buchi* (Little,  
446 1995). Facies containing primarily *Meleagrinnella* and *Bositra* may indicate oxic-  
447 suboxic bottom water conditions, whereas *P. dubius* has been considered a low-oxygen  
448 specialist, i.e. the most tolerant or well adapted species (Little, 1995; Caswell et al.,  
449 2009). *Meleagrinnella substriata*, *Liostrea hisingeri*, and *Propeamussium pumilum*  
450 occur in the Portree Shale Formation and Raasay Ironstone Formation, and *P. dubius* is  
451 not recorded. Thus, combined with the presence of low-oxygen intolerant taxa like  
452 *Chariocrinus wuerttembergicus* and *Orthotoma sp. A* in the Raasay Ironstone

453 Formation (Little, 1995), the Hebrides Basin can be interpreted as suboxic-oxic during  
454 the T-OAE, consistent with our redox-sensitive element data. Anoxia was not a  
455 prerequisite for the deposition of organic-rich lithologies during the T-OAE, as also  
456 found at other sites (e.g. Kemp and Izumi, 2014).

457 Interestingly, there is a prominent decline in  $Re/Mo$  and  $V_{EF}/M_{OEF}$ , concurrent with  
458 an increase in  $U_{EF}$ ,  $V_{EF}$ ,  $Ni_{EF}$  and  $M_{OEF}/U_{EF}$ , from ~110 to ~180 cm in the Portree Shale  
459 Formation (the shaded interval A on Fig. 7), indicating the probable occurrence of  
460 anoxia during this interval. However, similar variations in  $M_{OEF}/U_{EF}$  and  $V_{EF}/M_{OEF}$   
461 ratios from ~240 to ~370 cm (the shaded interval B on Fig. 7) in the Raasay Ironstone  
462 Formation instead may be interpreted as the preferred trapping of Mo by Fe oxides  
463 minerals via a particulate shuttle in an oxic-suboxic setting (e.g. Algeo and Tribovillard,  
464 2009; Percival et al., 2016).

465 The interpretation of oxic-suboxic bottom-water conditions in the Hebrides Basin  
466 during the T-OAE contrasts with data from the nearby Cleveland Basin, as well as a  
467 number of other basins in northern Europe, where anoxia/euxinia was pervasive (e.g.  
468 McArthur et al., 2008). This finding helps to emphasize that the T-OAE was not  
469 characterized by a single and continuous anoxic interval on the Northwest European  
470 Shelf (NWES). A shallower water depth and/or unrestricted setting at the Raasay site  
471 could be key reasons for this. Equally, ocean-atmosphere models of the Toarcian (Dera  
472 and Donnadieu, 2012; Ruvalcaba Baroni et al., 2018) indicate that southward flow from  
473 the Arctic through the Viking Corridor might have been strengthened during the T-OAE.  
474 This current would have potentially delivered colder oxygenated waters into the NWES  
475 area and significantly influence the local redox conditions. Given its proximity to the  
476 Viking corridor (Fig. 1), the bottom water of the Hebrides Basin might have been kept  
477 oxygenated by this flow.

478

### 479 5.3 Detrital and chemical weathering signals in the Hebrides Basin during the T-OAE

480 Ti and Zr are typically enriched in coarse grained rocks like siltstones and  
481 sandstones owing to their presence in heavy minerals like rutile and zirconium, which  
482 are typically transported with coarse fraction sediments. By contrast, Al, Rb and K are

483 typically relatively abundant in K-feldspar, mica and clay minerals (Calvert and  
484 Pedersen, 2007). Therefore, proxies such as Ti/Al, Zr/Rb and Ti/K (in combination with  
485 sedimentological observations) are useful for revealing variations in detrital fluxes in  
486 marine sediments (Calvert and Pedersen, 2007). At the same time, Rb and K in  
487 terrestrial sediments are also useful for inferring changes in weathering. Due to ionic  
488 size similarities between Rb and K, Rb can substitute for K in potassium feldspars  
489 (Calvert and Pedersen, 2007). K and Rb are sensitive to strong chemical weathering,  
490 resulting in K and Rb loss from sediments via leaching, leaving Al relatively enriched  
491 in clay mineral products. Consequently, K/Al and Rb/Al ratios can be utilized to reveal  
492 variations in continental chemical weathering.

493 On Raasay, Ti/K and Zr/Rb ratios show large-scale increases through the section,  
494 suggesting sediment coarsening (Fig. 8). At ~310 cm near the base of the Raasay  
495 Ironstone Formation, for instance, an increase of over two orders of magnitude is  
496 coincident with the change from shale to ironstone (Fig. 8). Nevertheless, we also  
497 observe that K/Al and Rb/Al ratios decrease synchronously up-section (Fig. 8) and  
498 broadly mirror the Ti/K and Zr/Rb data. The steady loss of K and Rb through this part  
499 of the succession, despite being clay-rich, suggests increasing chemical weathering in  
500 the sediment source area. Similarly, the near-total absence of K and Rb in the Raasay  
501 Ironstone above ~360 cm suggests intensified weathering. Given the likely influence of  
502 weathering on the relative abundance of K and Rb, a more robust proxy for grain-size  
503 changes in the section is Ti/Al. These data show a much subtler but steady rise through  
504 the Portree Shale Formation and lower part of the Raasay Ironstone Formation,  
505 indicative of coarsening (Fig. 8). A more marked increase in Ti/Al occurs at ~370 cm,  
506 indicating abrupt sediment coarsening coeval with minimum values in  $\delta^{13}\text{C}_{\text{org}}$  (Fig. 8).  
507 Taken together, the data suggest an enhancement of continental chemical weathering  
508 through the T-OAE that is broadly coincident with a rise in coarse-grained terrigenous  
509 sediment input.

510 The occurrence of wavy-bedded and cross-bedded oolitic ironstones in the Raasay  
511 Ironstone Formation (see Section 2.1) ostensibly suggests a shallow marine  
512 depositional environment (Morton and Hudson, 1995). Because global sea level was

513 rising through this interval (Hesselbo, 2008; Thibault et al., 2018), previous work has  
514 argued that the ironstones did not form *in situ*, and that instead the ooids were derived  
515 from shoals on nearby fault-bounded topographic highs, with the muddy layers  
516 representing the background sedimentation (Little, 1995). Hesselbo (2008) suggested  
517 that sea-level highstand during deposition of the Raasay Ironstone Formation may have  
518 led to sediment starvation that promoted ironstone formation. Importantly, however, it  
519 is now widely recognized that hydrological cycling intensified during the Toarcian  
520 OAE (e.g. Krencker et al., 2015; Izumi et al., 2018a; Han et al., 2018). If an increase in  
521 hydrological cycling occurred in the Hebrides Basin, this could have increased the  
522 frequency and/or magnitude of storm events and wave action, resulting in high energy  
523 conditions that winnowed fine-grained clastic material leaving behind denser, iron-rich  
524 coarse sediments (i.e. ooids, see for example Akande and Mücke, 1993). At the same  
525 time, intense chemical weathering on land could have leached reactive Fe, providing  
526 the source for ironstone formation. Strong current action can also explain the cross-  
527 bedding in the ironstone previously reported (Morton and Hudson, 1995).

528       The Raasay section was situated at a higher paleolatitude (~40°N) than the tropical  
529 locations where previous evidence of increased storminess has generally been found  
530 (Krencker et al., 2015; Han et al., 2018). Winter storms, normally generated at mid to  
531 high latitudes by air mass disturbances (i.e. mixing of warm air currents from the low  
532 latitudes and cold air currents from the polar areas; Masselink and van Heteren, 2014),  
533 may have been a cause of storms during deposition of the Raasay Ironstone Formation.  
534 On the other hand, intensified and more frequent tropical cyclones, associated with the  
535 known increase in atmospheric CO<sub>2</sub> and seawater temperature during the Toarcian OAE  
536 (McElwain et al., 2005; Bailey et al., 2003; Ruebsam et al., 2020), could have affected  
537 higher latitudes. Coupled ocean-atmosphere climate models have predicted significant  
538 enhancement of hydrological cycling as well as a poleward expansion of tropical  
539 summer storms as a consequence of rapid rises in *p*CO<sub>2</sub> and seawater temperature, both  
540 in the Toarcian and at the present day (Dera and Donnadieu, 2012; Emanuel, 2016;  
541 Korty et al., 2017). Storm activity in the Hebrides Basin may have prevented the  
542 development of a stable chemocline, further helping to maintain more oxygenated

543 conditions relative to the nearby (and likely deeper) Cleveland Basin.

544

## 545 **6. Conclusions**

546 Sedimentological and geochemical analyses of a Toarcian section on the Isle of  
547 Raasay reveal the expression of the Toarcian Oceanic Anoxic Event in the Hebrides  
548 Basin for the first time. Organic carbon isotope data reveal a significant negative trend  
549 ( $\sim -2.7\text{‰}$ ) during the early Toarcian, which is similar to the trend and pattern observed  
550 in contemporaneous carbon isotope data globally. Redox-sensitive trace element data,  
551 coupled with paleontological information, indicate oxygenated to suboxic conditions in  
552 the Hebrides Basin through the T-OAE. This contrasts with the strong anoxia and  
553 euxinia recorded in nearby basins, and can likely be attributed at least in part to water  
554 depth differences, the unrestricted nature of the basin, and proximity to the possible  
555 southward flow of cold oxygenated water through the Viking corridor. A significant  
556 strengthening of continental weathering through the T-OAE on Raasay is inferred from  
557 sediment coarsening and decreasing K/Al and Rb/Al ratios. In the context of the global  
558 warming known to have occurred during the event, we suggest that intensified  
559 hydrological cycling accelerated continental weathering and increased riverine  
560 transport capacity and coarse grain sediment delivery to the basin. High-energy  
561 conditions linked to storm activity may have further limited seawater deoxygenation in  
562 the basin.

563

## 564 **Acknowledgements**

565 This work was supported by the National Natural Science Foundation of China  
566 (Grant No. 41888101) to DBK and TH, and the National Recruitment Program for  
567 Young Professionals (P.R. China) to DBK. RN was funded by the Natural Environment  
568 Research Council (grant NE/N018559/1). This manuscript is a contribution to the  
569 Integrated Understanding of the Early Jurassic Earth System and Timescale (JET)  
570 project and IGCP 739. We thank Jinyoung Gil for help in the field and Sen Li, Yinggang  
571 Zhang for assistance in the lab. We are grateful to Zhixiang Wang and Dongyang Liu  
572 for the helpful discussion.

573

574 **Appendix A. Supplementary material**

575 Supplementary material related to this article can be found on-line at <https://>

576

577 **References**

578 Akande, S.O., Mücke, A., 1993. Depositional environment and diagenesis of carbonates  
579 at the Mamu/Nkporo Formation, Anambra basin, Southern Nigeria. *Journal of*  
580 *African Earth Sciences* 17 (4), 445–456.

581 Algeo, T.J., 2004. Can marine anoxic events draw down the trace element inventory of  
582 seawater? *Geology* 32, 1057–1060.

583 Algeo, T.J., Maynard, J.B., 2004. Trace-element behavior and redox facies in core  
584 shales of Upper Pennsylvanian Kansas-type cyclothems. *Chem. Geol.* 206, 289–  
585 318.

586 Algeo, T.J., Lyons, T.W., 2006. Mo-total organic carbon covariation in modern anoxic  
587 marine environments: implication for analysis of paleoredox and -hydrographic  
588 conditions. *Paleoceanography* 21, PA1016 23 pp.

589 Algeo, T.J., Tribovillard, N., 2009. Environmental analysis of paleoceanographic  
590 systems based on molybdenum–uranium covariation. *Chem. Geol.* 268 (3–4),  
591 211–225.

592 Bailey, T.R., Rosenthal, Y., McArthur, J.M., van de Schootbrugge, B., Thirlwall, M.F.,  
593 2003. Paleoceanographic changes of the Late Pliensbachian–Early Toarcian  
594 interval: a possible link to the genesis of an Oceanic Anoxic Event. *Earth Planet.*  
595 *Sci. Lett.* 212 (3–4), 307–320.

596 Calvert, S.E., Pedersen, T.F., 1993. Geochemistry of Recent oxic and anoxic marine  
597 sediments: Implications for the geological record. *Mar. Geol.* 113, 67–88.

598 Calvert, S.E., Pedersen, T.F., 2007. Chapter Fourteen Elemental Proxies for  
599 Palaeoclimatic and Palaeoceanographic Variability in Marine Sediments:  
600 Interpretation and Application. *Developments in Marine Geology* 1 (4), 567–644.

601 Caswell, B.A., Coe, A.L., Cohen, A.S., 2009. New range data for marine invertebrate  
602 species across the early Toarcian (Early Jurassic) mass extinction. *Journal of the*  
603 *Geological Society* 166 (5), 859–872.

604 Cohen, A.S., Coe, A.L., Harding, S.M., Schwark, L., 2004. Osmium isotope evidence  
605 for the regulation of atmospheric CO<sub>2</sub> by continental weathering. *Geology* 32 (2),  
606 157–160.

607 Crusius, J., Calvert, S., Pedersen, T., Sage, D., 1996. Rhenium and molybdenum  
608 enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of  
609 deposition. *Earth Planet. Sci. Lett.* 145, 65–78.

610 Dera, G., Pellenard, P., Neige, P., Deconinck, J.F., Pucéat, E., Dommergues, J.-L., 2009.  
611 Distribution of clay minerals in Early Jurassic Peritethyan seas: palaeoclimatic  
612 significance inferred from multiproxy comparisons. *Palaeogeogr. Palaeoclimatol.*  
613 *Palaeoecol.* 271, 39–51.

614 Dera, G., Donnadieu, Y., 2012. Modeling evidences for global warming, Arctic

615 seawater freshening, and sluggish oceanic circulation during the Early Toarcian  
616 anoxic event. *Paleoceanography* 27, 1–15.

617 Dickson, A.J., 2017. A molybdenum-isotope perspective on Phanerozoic  
618 deoxygenation events. *Nat. Geosci.* 10, 721–726.

619 Espitalié, J., Deroo, G., Marquis, F., 1985. La pyrolyse Rock-Eval et ses applications. Deuxieme partie. *Revue de*  
620 *l'Institut francais du Petrole* 40 (6), 755–784.

621 Doyle, P., Macdonald, D.I.M., 1993. Belemnite battlefields. *Lethaia* 26, 65–80.

622 Emanuel, K.A., 2016. Will global warming make hurricane forecasting more difficult?  
623 *Bull. Am. Meteorol. Soc.* 98 (3), 495–501.

624 Ettinger, N.P., Larson, T.E., Kerans, C., Thibodeau, A.M., Hattori, K.E., Kacur, S.M.,  
625 Martindale, R.C., 2021. Ocean acidification and photic-zone anoxia at the  
626 Toarcian Oceanic Anoxic Event: Insights from the Adriatic Carbonate Platform.  
627 *Sedimentology* 68 (1), 63–107.

628 Fantasia, A., Follmi, K.B., Adatte, T., Spangenberg, J.E., Montero-Serrano, J.C., 2018.  
629 The Early Toarcian oceanic anoxic event: Paleoenvironmental and paleoclimatic  
630 change across the Alpine Tethys (Switzerland). *Glob. Planet. Chang.* 162, 53–68.

631 Goldberg, T., Poulton, S.W., Wagner, T., Kolonic, S.F., Rehkämper, M., 2016.  
632 Molybdenum drawdown during Cretaceous Oceanic Anoxic Event 2. *Earth Planet.*  
633 *Sci. Lett.* 440, 81–91.

634 Han, Z., Hu, X., Kemp, D.B., Li, J., 2018. Carbonate-platform response to the Toarcian  
635 Oceanic Anoxic Event in the southern hemisphere: Implications for climatic  
636 change and biotic platform demise. *Earth Planet. Sci. Lett.* 489, 59–71.

637 Harries, P.J., Little, C.T.S., 1999. The early Toarcian (Early Jurassic) and the  
638 Cenomanian-Turonian (Late Cretaceous) mass extinctions: similarities and  
639 contrasts. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 154, 39–66.

640 Hesselbo, S.P., Grocke, D.R., Jenkyns, H.C., Bjerrum, C.J., Farrimond, P., Bell, H.S.M.,  
641 Green, O.R., 2000. Massive dissociation of gas hydrate during a Jurassic oceanic  
642 anoxic event. *Nature* 406 (6794), 392–395.

643 Hesselbo, S.P., Jenkyns, H.C., Duarte, L.V., Oliveira, L.C., 2007. Carbon-isotope  
644 record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood  
645 and marine carbonate (Lusitanian Basin, Portugal). *Earth Planet. Sci. Lett.* 253 (3–  
646 4), 455–470.

647 Hesselbo, S.P., 2008. Sequence stratigraphy and inferred relative sea-level change from  
648 the onshore British Jurassic. *Proceedings of the Geologists' Association* 119, 19–  
649 34.

650 Howarth, M.K., 1956. The Scalpa Sandstone of the Isle of Raasay. *Proceedings of the*  
651 *Yorkshire Geological Society* 30, 353–370.

652 Howarth, M.K., 1992. The ammonite family Hildoceratidae in the Lower Jurassic of  
653 Britain. *Monograph of the Palaeontographical Society* 145, 1–106.

654 Ikeda, M., Hori, R.S., Ikehara, M., Miyashita, R., Chino, M., Yamada, K., 2018. Carbon  
655 cycle dynamics linked with Karoo-Ferrar volcanism and astronomical cycles  
656 during Pliensbachian-Toarcian (Early Jurassic). *Glob. Planet. Chang.* 170, 163–  
657 171.

658 Izumi, K., Kemp, D.B., Itamiya, S., Inui, M., 2018a. Sedimentary evidence for

659 enhanced hydrological cycling in response to rapid carbon release during the early  
660 Toarcian oceanic anoxic event. *Earth Planet. Sci. Lett.* 481, 162–170.

661 Izumi, K., Endo, K., Kemp, D.B., Inui, M., 2018b. Oceanic redox conditions through  
662 the late Pliensbachian to early Toarcian on the northwestern Panthalassa margin:  
663 Insights from pyrite and geochemical data. *Palaeogeogr. Palaeoclimatol.*  
664 *Palaeoecol.* 493, 1–10.

665 Jenkyns, H.C., 1988. The early Toarcian (Jurassic) anoxic event-stratigraphic,  
666 sedimentary, and geochemical evidence. *Am. J. Sci.* 288 (2), 101–151.

667 Kemp, D.B., Coe, A.L., Cohen, A.S., Schwark, L., 2005. Astronomical pacing of  
668 methane release in the Early Jurassic period. *Nature* 437 (7057), 396–399.

669 Kemp, D.B., Izumi, K., 2014. Multiproxy geochemical analysis of a Panthalassic  
670 margin record of the early Toarcian oceanic anoxic event (Toyora area, Japan).  
671 *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 414, 332–341.

672 Kemp, D.B., Baranyi, V., Izumi, K., Burgess, R.D., 2019. Organic matter variations and  
673 links to climate change across the early Toarcian oceanic anoxic event (T-OAE) in  
674 Toyora area, southwest Japan. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 530, 90–  
675 102.

676 Kemp, D.B., Selby, D., Izumi, K., 2020. Direct coupling between carbon release and  
677 weathering during the Toarcian oceanic anoxic event. *Geology* 48, 976–980.

678 Korty, R.L., Emanuel, K.A., Huber, M., Zamora, R.A., 2017. Tropical cyclones down-  
679 scaled from simulations with very high carbon dioxide levels. *J. Climate* 30 (2),  
680 649–667.

681 Krencker, F.N., Bodin, S., Suan, G., Heimhofer, U., Kabiri, L., Immenhauser, A., 2015.  
682 Toarcian extreme warmth led to tropical cyclone intensification. *Earth Planet. Sci.*  
683 *Lett.* 425, 120–130.

684 Lee, G.W., 1920. The Mesozoic Rocks of Applecross, Raasay and North-East Skye  
685 (with Contributions and Appendix by S.S. Buckman), Memoir of the Geological  
686 Survey of Great Britain, sheets 81 and 71 (Scotland), HMSO, Edinburgh, 93 pp.

687 Little, C.T.S. 1995. The Pliensbachian–Toarcian (Lower Jurassic) extinction event.  
688 PhD thesis, Bristol University.

689 Liu, D., Huang, C., Ogg, J.G., Kemp, D.B., Li, M., Yu, M., Foster, W.J., 2021.  
690 Astronomically forced changes in chemical weathering and redox during the  
691 Anisian (Middle Triassic): Implications for marine ecosystem recovery following  
692 the end-Permian mass extinction. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 569,  
693 110355.

694 Masselink, G., van Heteren, S., 2014. Response of wave-dominated and mixed-energy  
695 barriers to storms. *Mar. Geol.* 352, 321–347.

696 McArthur, J.M., Algeo, T.J., van de Schootbrugge, B., Li, Q., Howarth, R.J., 2008.  
697 Basinal restriction, black shales, Re-Os dating, and the Early Toarcian (Jurassic)  
698 oceanic anoxic event. *Paleoceanography* 23 (4), PA4217.

699 McElwain, J.C., Wade-Murphy, J., Hesselbo, S.P., 2005. Changes in carbon dioxide  
700 during an oceanic anoxic event linked to intrusion into Gondwana coals. *Nature*  
701 435 (7041), 479–482.

702 Meyers, P.A., 1997. Organic geochemical proxies of paleoceanographic,

703 palaeolimnologic, and paleoclimatologic processes. *Org. Geochem.* 27, 213–250.  
704 Morton, N., 1989. Jurassic sequence stratigraphy in the Hebrides Basin, NW Scotland.  
705 *Marine and Petroleum Geology* 6, 243–260.  
706 Morton, N., Hudson, J.D., 1995. Field guide to the Jurassic of the Isles of Raasay and  
707 Skye, Inner Hebrides, NW Scotland. In *Field Geology of the British Jurassic* (ed.  
708 P.D. Taylor), Geological Society, London 209–280.  
709 Morton, N., 2009. Cadha Carnach, Isle of Raasay, Highlands. *Geological Conservation*  
710 *Review Series British Lower Jurassic Stratigraphy*.  
711 Pearce, C.R., Cohen, A.S., Coe, A.L., Burton, K.W., 2008. Molybdenum isotope  
712 evidence for global ocean anoxia coupled with perturbations to the carbon cycle  
713 during the early jurassic. *Geology* 36 (3), 231–234.  
714 Percival, L.M.E., Cohen, A.S., Davies, M.K., Dickson, A.J., Hesselbo, S.P., Jenkyns,  
715 H.C., Leng, M.J., Mather, T.A., Storm, M.S., Xu, W., 2016. Osmium isotope  
716 evidence for two pulses of increased continental weathering linked to Early  
717 Jurassic volcanism and climate change. *Geology* 44 (9), 759–762.  
718 Price, G.D., 2010. Carbon-isotope stratigraphy and temperature change during the  
719 Early–Middle Jurassic (Toarcian–Aalenian), Raasay, Scotland, UK. *Palaeogeogr.*  
720 *Palaeoclimatol. Palaeoecol.* 285 (3–4), 255–263.  
721 Ramirez, M., Algeo, T.J., 2020a. Carbon-cycle changes during the Toarcian (Early  
722 Jurassic) and implications for regional versus global drivers of the Toarcian  
723 oceanic anoxic event. *Earth Sci. Rev.* 209, 103283.  
724 Ramirez, M., Algeo, T.J., 2020b. Paleosalinity proxy evidence for watermass restriction  
725 in the Cleveland Basin (UK) during the Toarcian OAE. *Earth Sci. Rev.* 201,  
726 103072.  
727 Roberts, A.M., Holdsworth, R.E., 1999. Linking onshore and offshore structures:  
728 Mesozoic extension in the Scottish Highlands. *Journal of the Geological Society,*  
729 *London* 156, 1061–1064.  
730 Ruebsam, W., Reolid, M., Sabatino, N., Masetti, D., Schwark, L., 2020. Molecular  
731 paleothermometry of the early Toarcian climate perturbation. *Glob. Planet. Chang.*  
732 195, 103351.  
733 Ruvalcaba Baroni, I., Pohl, A., van Helmond, N.A.G. M., Papadomanolaki, N.M., Coe,  
734 A.L., Cohen, A.S., van de Schootbrugge, B., Donnadieu, Y., Slomp, C.P., 2018.  
735 Ocean circulation in the Toarcian (Early Jurassic), a key control on deoxygenation  
736 and carbon burial on the European Shelf. *Paleoceanography and Paleoclimatology*  
737 33 (9), 994–1012.  
738 Scholz, F., 2018. Identifying oxygen minimum zone-type biogeochemical cycling in  
739 Earth history using inorganic geochemical proxies. *Earth Sci. Rev.* 184, 29–45.  
740 Schouten, S., Kaam-Peters, H. M.E.V., Schoell, M., Sinninghe-Damste, J.S., 2000.  
741 Effects of an oceanic anoxic event on the stable carbon isotopic composition of  
742 early Toarcian carbon. *American Journal of Science* 300 (1), 1–22.  
743 Slater, S.M., Twitchett, R.J., Danise, S., Vajda, V., 2019. Substantial vegetation  
744 response to Early Jurassic global warming with impacts on oceanic anoxia. *Nat.*  
745 *Geosci.* 12, 462–467.  
746 Stein, A., 1988. Basement controls upon basin development in the Caledonian foreland,

747 NW Scotland. Basin Research 1, 107–119.

748 Suan, G., Pittet, B., Bour, I., Mattioli, E., Duarte, L.V., Mailliot, S., 2008. Duration of  
749 the Early Toarcian carbon isotope excursion deduced from spectral analysis:  
750 consequence for its possible causes. *Earth Planet. Sci. Lett.* 267 (3–4), 666–679.

751 Suan, G., Van De Schootbrugge, B., Adatte, T., Fiebig, J., Oschmann, W., 2015.  
752 Calibrating the magnitude of the Toarcian carbon cycle perturbation.  
753 *Paleoceanography* 30 (5), 495–509.

754 Svensen, H., Planke, S., Chevallier, L., Malthe-Sorensen, A., Corfu, F., Jamtveit, B.,  
755 2007. Hydrothermal venting of greenhouse gases triggering Early Jurassic global  
756 warming. *Earth Planet. Sci. Lett.* 256 (3–4), 554–566.

757 Tankard, A.J., Balkwill, H.R., 1989. Extensional tectonics and Stratigraphy of the  
758 North Atlantic Margins. *American Association of Petroleum Geologists, Memoirs*  
759 46.

760 Taylor, S.R., McLennan, S.M., 1985. *The Continental Crust: Its Composition and*  
761 *Evolution*. Blackwell, Malden, Mass.

762 Them, T.R., Gill, B.C., Caruthers, A.H., Grocke, D.R., Tulsy, E.T., Martindale, R.C.,  
763 Poulton, T.P., Smith, P.L., 2017. High-resolution carbon isotope records of the  
764 Toarcian Oceanic Anoxic Event (Early Jurassic) from North America and  
765 implications for the global drivers of the Toarcian carbon cycle. *Earth Planet. Sci.*  
766 *Lett.* 459, 118–126.

767 Thibault, N., Ruhl, M., Ullmann, C.V., Korte, C., Kemp, D.B., Grocke, D.R., Hesselbo,  
768 S.P., 2018. The wider context of the Lower Jurassic Toarcian oceanic anoxic event  
769 in Yorkshire coastal outcrops, UK. *Proc. Geol. Assoc.* 129 (3), 372–391.

770 Thierry, J., 2000. Middle Toarcian, map. 8. In: Dercourt, J., Gaetani, M., Vrielynck, B.,  
771 Barrier, E., Biju-Duval, B., Brunet, M.F. ... Sandulescu, M. (Eds.), *Atlas Peri-*  
772 *Tethys Palaeogeographical Maps*. CCGM/CGMW, Paris, pp. 61–70.

773 Tribovillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as  
774 paleoredox and paleoproductivity proxies: an update. *Chem. Geol.* 232 (1–2), 12–  
775 32.

776 Tribovillard, N., Algeo, T.J., Baudin, F., Riboulleau, A., 2012. Analysis of marine  
777 environmental conditions based on molybdenum–uranium covariation—  
778 Applications to Mesozoic paleoceanography. *Chem. Geol.* 324–325, 45–58.

779 van Krevelen, D.W., 1981. In: Van Krevelen, D.W. (Ed.), *Coal Science and Technology*.  
780 *Coal*, Elsevier, Amsterdam, pp. 129–314.

781 Wang, Y., Ossa, F.O., Spangenberg, J.E.,  
782 Wille, M., et al., 2021. Restricted oxygen-deficient basins on the Northern  
783 European epicontinental shelf across the Toarcian carbon isotope excursion  
784 interval. *Paleoceanography and Paleoclimatology* 36, e2020PA004207.

785 Wignall, P.B., 1994. *Black Shales*, 127 pp., Clarendon, Oxford, UK.

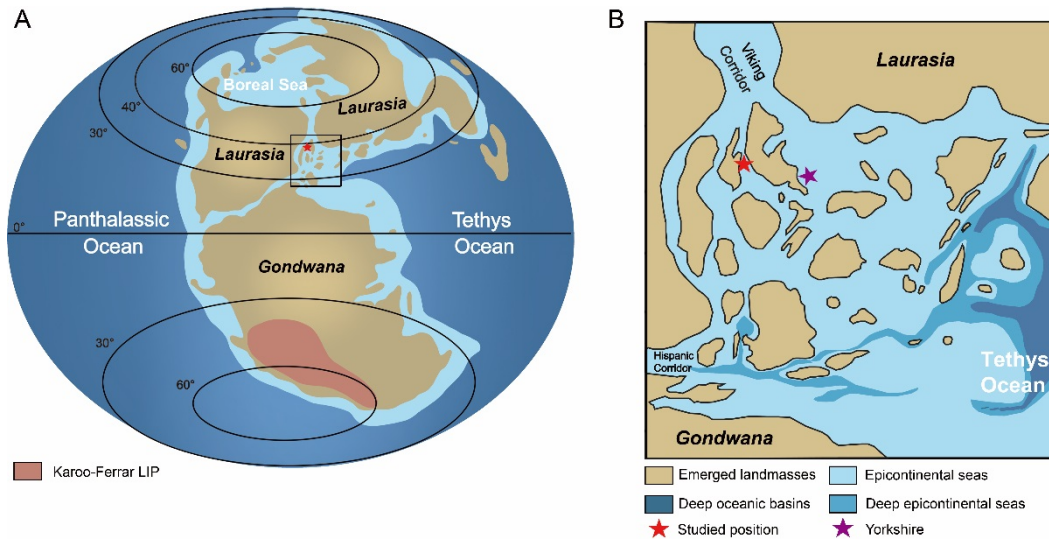
786 Xu, W., Ruhl, M., Jenkyns, H.C., Hesselbo, S.P., Riding, J.B., Selby, D., Naafs, B.D.A.,  
787 Weijers, J.W.H., Pancost, R.D., Tegelaar, E.W., Idiz, E.F., 2017. Carbon  
788 sequestration in an expanded lake system during the Toarcian oceanic anoxic event.  
789 *Nat. Geosci.* 10 (2), 129–134.

790 Xu, W., Ruhl, M., Jenkyns, H.C., et al., 2018. Evolution of the Toarcian (Early Jurassic)  
791 carbon-cycle and global climatic controls on local sedimentary processes

791 (Cardigan Bay Basin, UK). *Earth Planet. Sci. Lett.* 484, 396–411.  
792

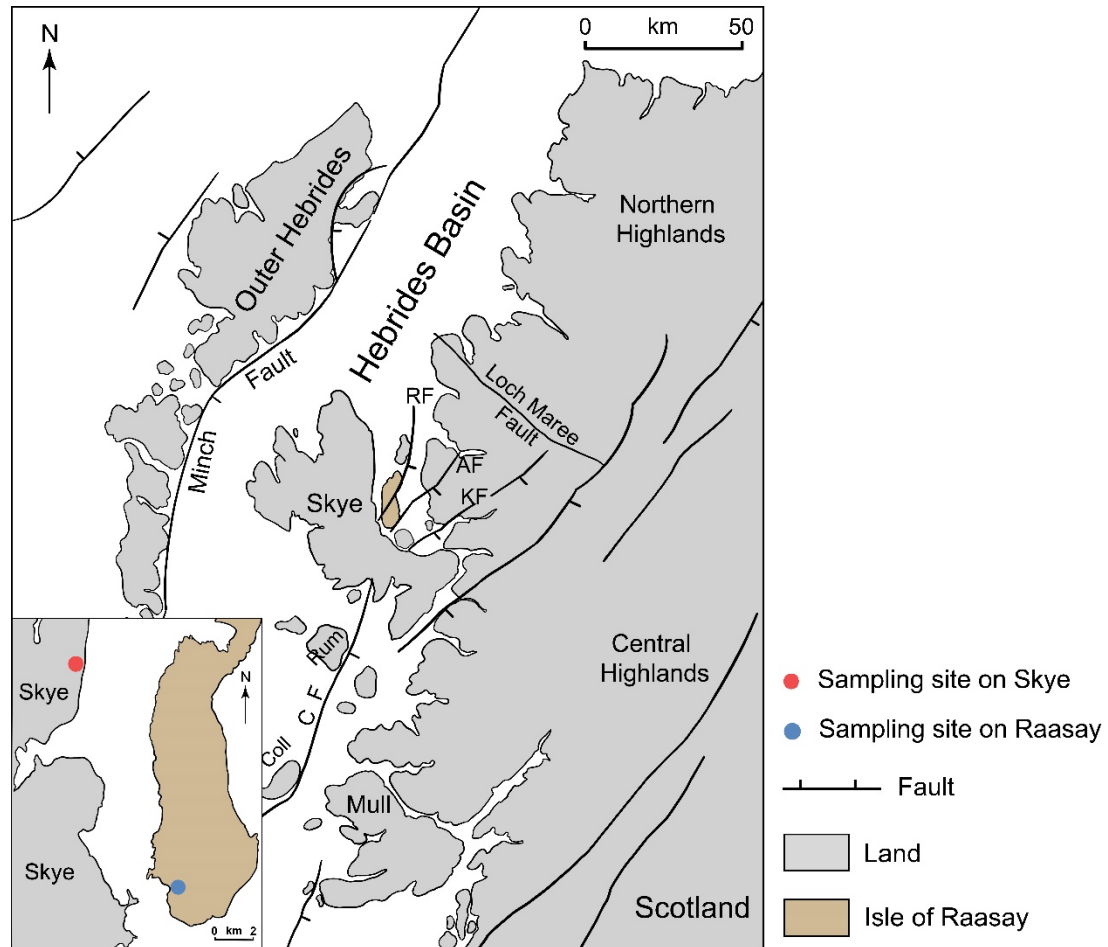
793 **Figures**

794



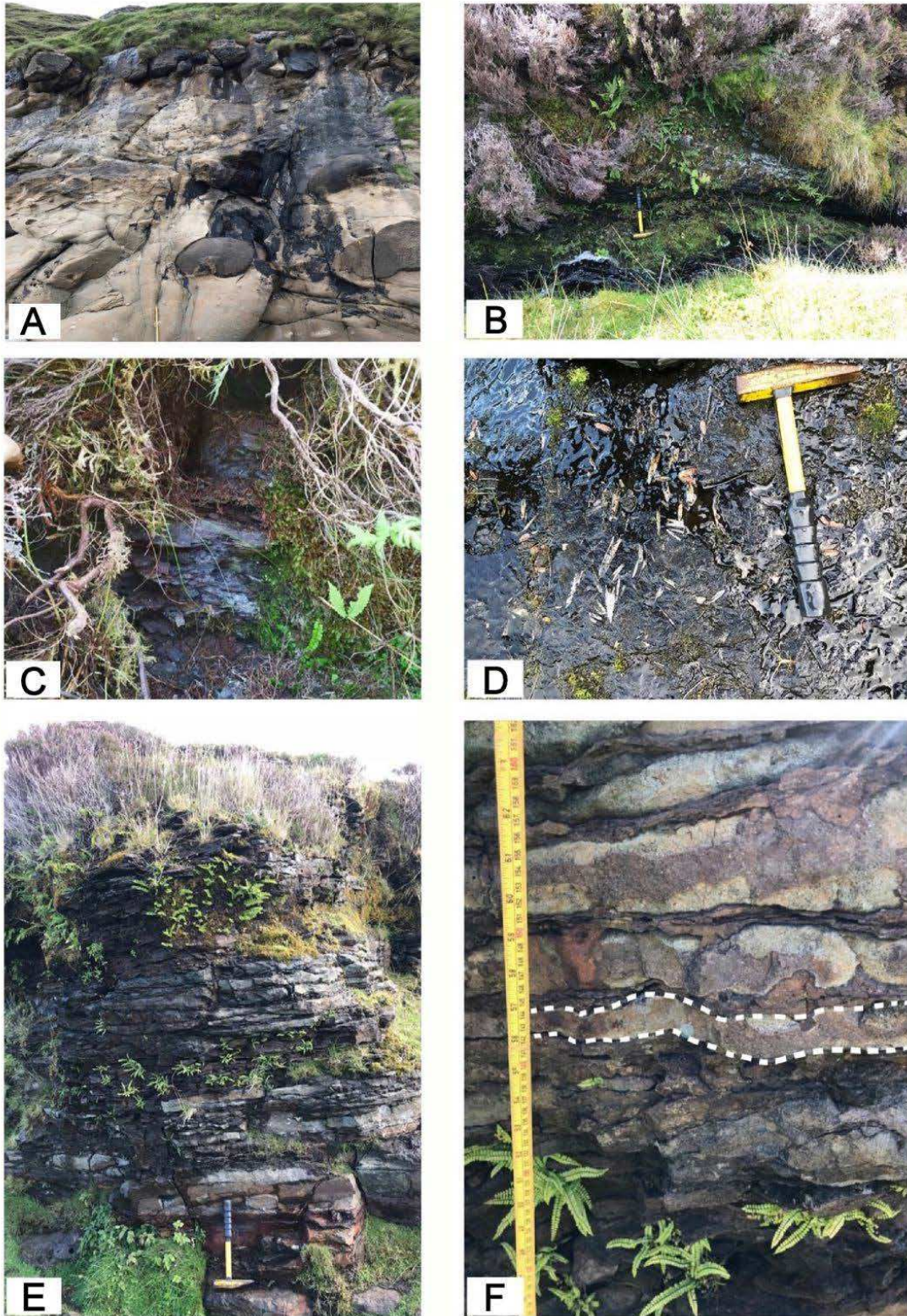
795

796 Fig. 1. (A) Global Toarcian paleogeographic reconstruction with the location of the  
797 Karoo-Ferrar Large Igneous Province (shaded red) in southern Gondwana (after Dera  
798 et al., 2009), and the location of the Raasay section (red star). (B) Detailed  
799 paleogeographic map of the Northwest European Shelf (NWES) and western Tethys  
800 (after Thierry, 2000), with the locations of the Raasay section (Hebrides Basin, red star)  
801 and nearby Yorkshire section (Cleveland Basin, purple star) also shown.



802

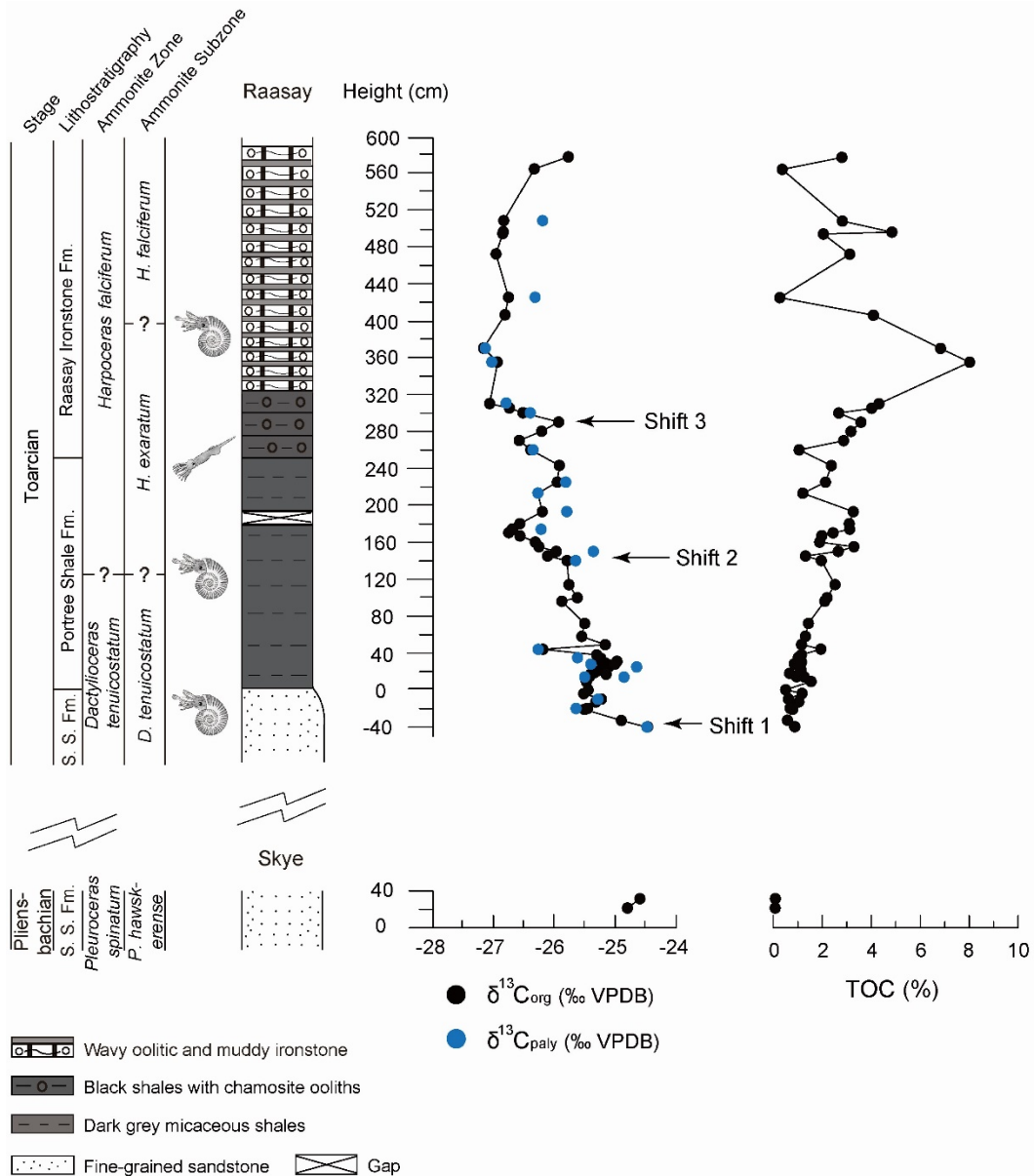
803 Fig. 2. Simplified map of Hebrides Basin (after Roberts and Holdsworth, 1999).  
 804 Abbreviations: AF, Applecross Fault; CF, Camasunary Fault; RF, Raasay Fault; KF,  
 805 Kishorn fault. The red dot shows the location of the sampling site on Skye and the blue  
 806 dot shows the location of the sampling site on Raasay.



807

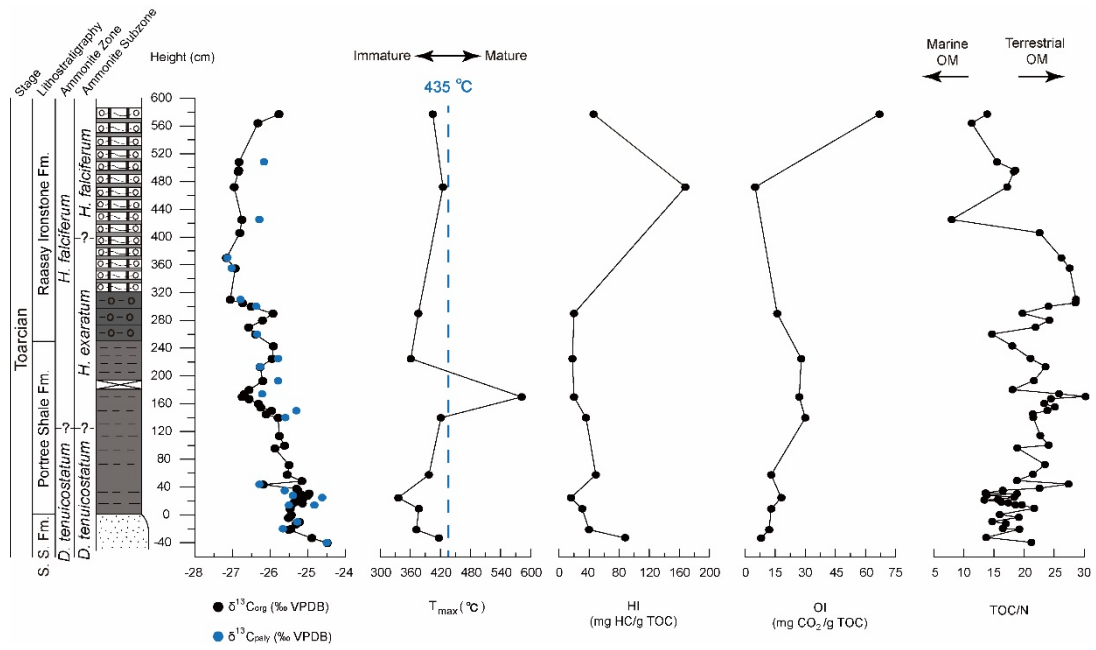
808 Fig. 3. Field photographs of the Skye and Raasay sections. (A) top of the Scalpa  
 809 Sandstone Formation exposed on the east coast of Skye (NG 5156 4710) (top 50 cm of  
 810 ruler is visible at base of the image). (B) Portree Shale Formation outcrop in Inverarish  
 811 Burn (NG 5719 3688) (exposed section thickness is ~60 cm in this image). The top of  
 812 the Scalpa Sandstone Formation is hidden in the stream ~40 cm below the hammer. (C)

813 Portree Shale Formation at Inverarish Burn, characterized by fissile dark shales. (D)  
814 “Belemnite battlefield” marking the top of the Portree Shale Formation, exposed nearby  
815 Inverarish Burn. (E) Raasay Ironstone Formation exposed in the area of the main  
816 opencast ironstone workings (NG 5690 3645). (F) Unevenly bedded ironstones  
817 intercalated with mudstones (white dashed lines highlight bed boundaries).



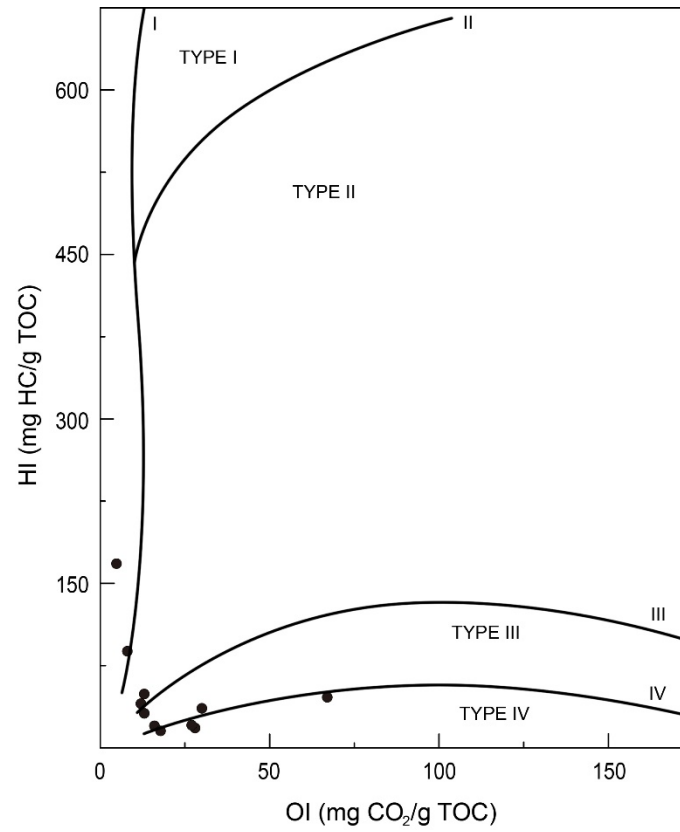
818

819 Fig. 4. Litho- and bio-stratigraphy, bulk organic carbon isotope ( $\delta^{13}C_{org}$ ), palynological  
 820 carbon isotope ( $\delta^{13}C_{paly}$ ) and total organic carbon (TOC) data from the uppermost  
 821 Pliensbachian to Toarcian from the Skye and Raasay sections. Bedding in the ironstone  
 822 is shown schematically, but at the correct general scale. Fossil images indicate horizons  
 823 with observed enrichment. Biostratigraphy of the sections is derived from Lee (1920),  
 824 Howarth (1956, 1992) and Morton and Hudson (1995) (see Section 2.2 for details). Fm.  
 825 = Formation. S. S. = Scalpa Sandstone



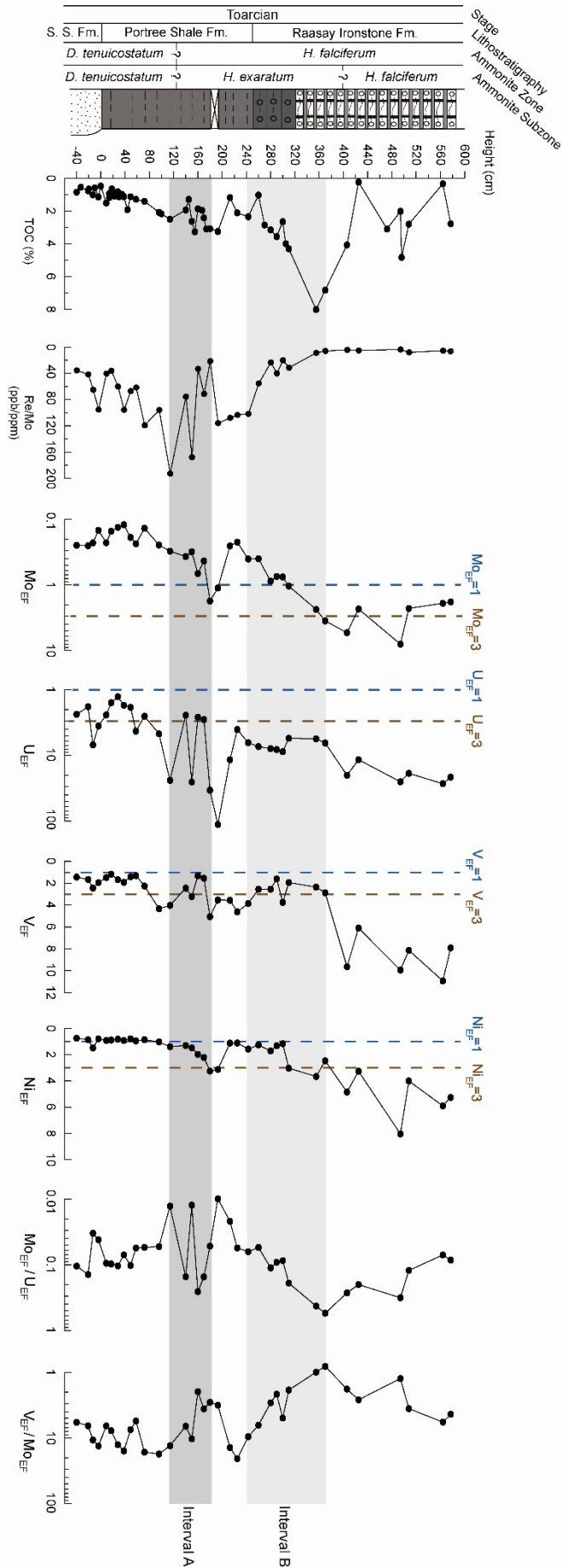
826

827 Fig. 5. Carbon isotope, Rock Eval, and TOC/N data through the Raasay section. The  
 828 blue vertical dashed line denotes the threshold of the oil window for Type III kerogen.  
 829 See main text for details. OM = organic matter.

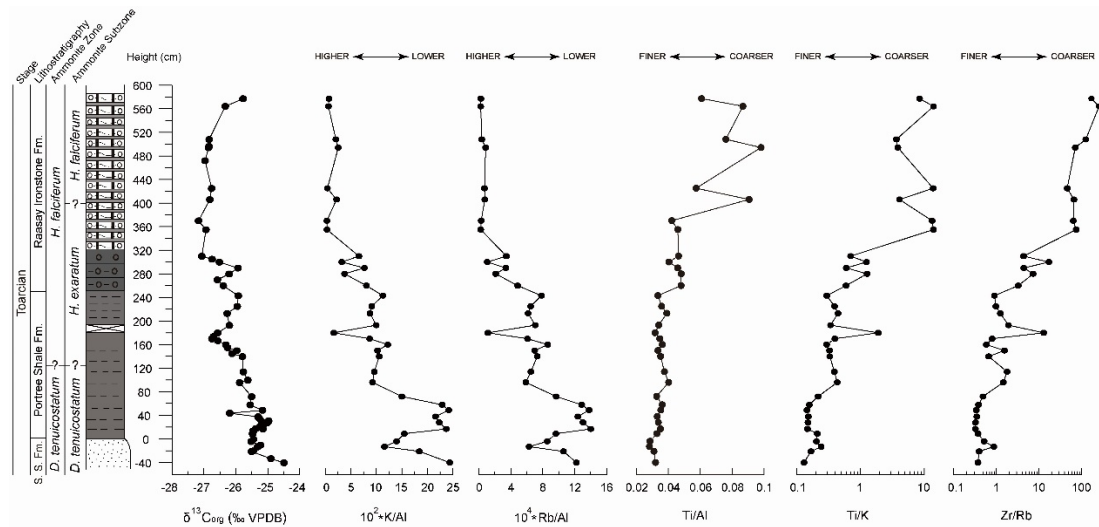


830

831 Fig. 6. Cross plot (van Krevelen diagram) of HI versus OI from Rock Eval  
 832 measurements of the Raasay samples. The plot indicates that the Raasay samples are  
 833 mainly composed of type III to type IV organic matter, of likely terrestrial origin.

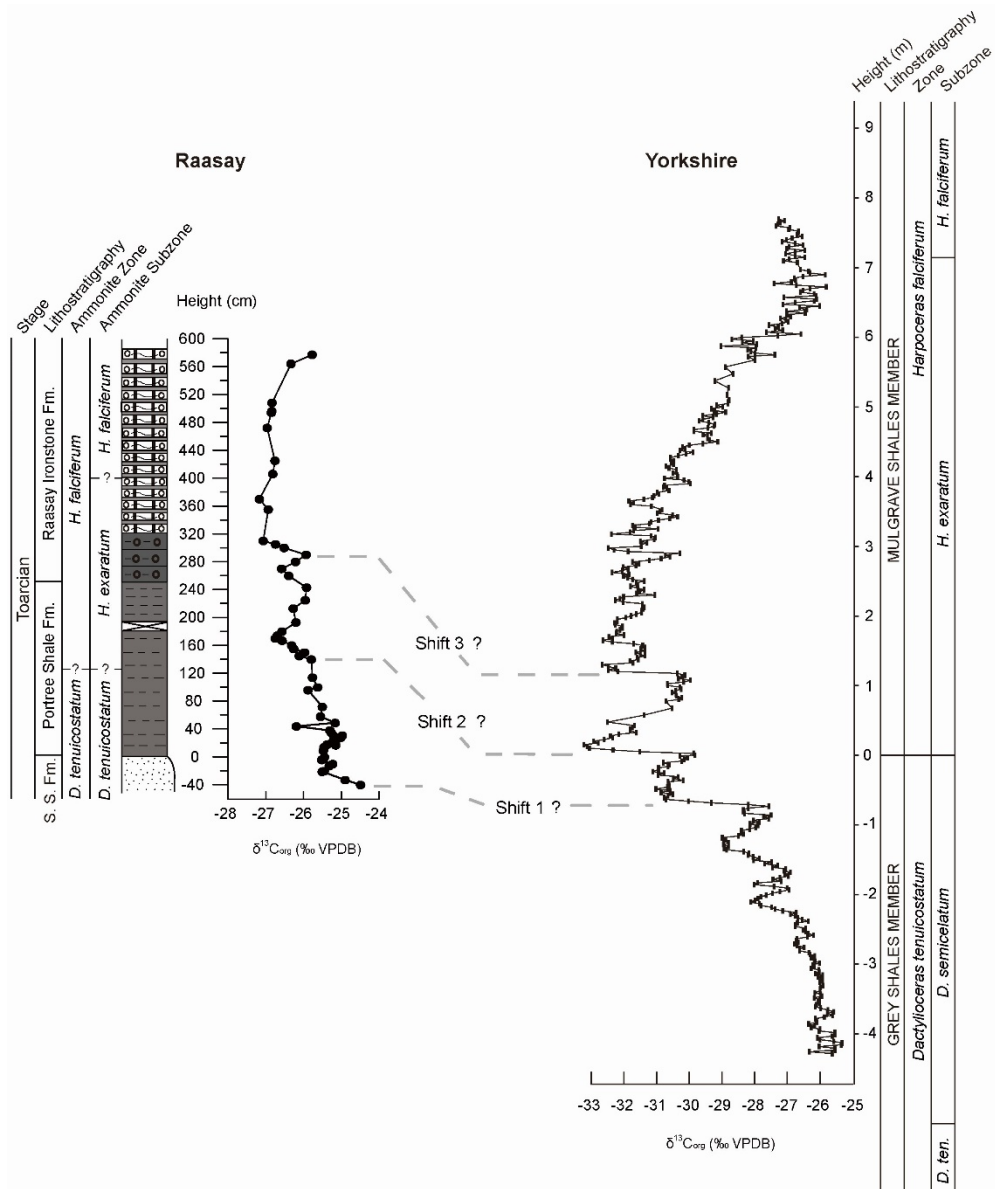


835 Fig. 7. Total organic carbon (TOC) and redox-sensitive proxies ( $\text{Mo}_{\text{EF}}$ ,  $\text{U}_{\text{EF}}$ ,  $\text{V}_{\text{EF}}$ ,  $\text{Ni}_{\text{EF}}$ ,  
836  $\text{Re}/\text{Mo}$ ,  $\text{Mo}_{\text{EF}}/\text{U}_{\text{EF}}$ , and  $\text{V}_{\text{EF}}/\text{Mo}_{\text{EF}}$ ) through the Raasay section. Note that  $\text{Mo}_{\text{EF}}$ ,  $\text{U}_{\text{EF}}$ ,  
837  $\text{Mo}_{\text{EF}}/\text{U}_{\text{EF}}$  and  $\text{V}_{\text{EF}}/\text{Mo}_{\text{EF}}$  are shown on logarithmic scales. The blue dashed line ( $X_{\text{EF}}=1$ )  
838 represents the boundary of enrichment versus depletion, and the brown dashed line  
839 ( $X_{\text{EF}}=3$ ) represents 'detectable' enrichment (see main text for details). The shaded  
840 intervals indicate the relative enrichment of Mo compared to U and V based on changes  
841 in  $\text{Mo}_{\text{EF}}/\text{U}_{\text{EF}}$  and  $\text{V}_{\text{EF}}/\text{Mo}_{\text{EF}}$  ratios (see main text for details).



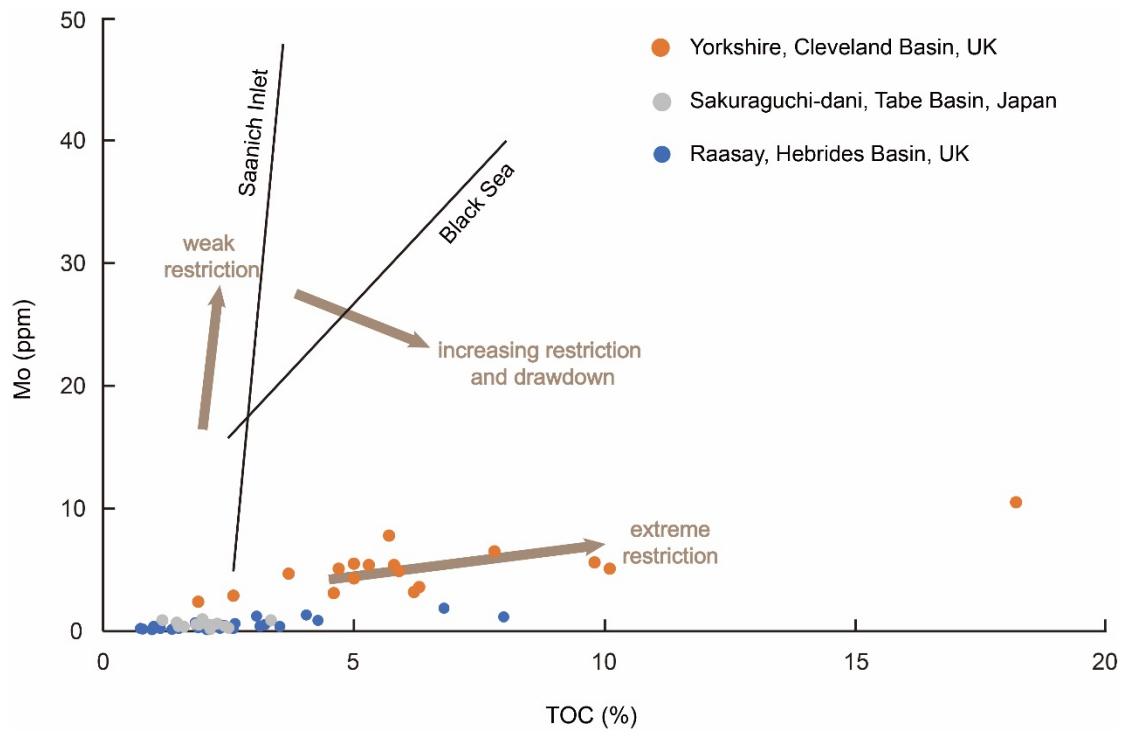
842

843 Fig. 8. Carbon isotope ( $\delta^{13}C_{org}$ ) data, chemical weathering proxies (K/Al and Rb/Al),  
 844 and detrital proxies (Ti/Al, Ti/K and Zr/Rb) through the Raasay section. The horizontal  
 845 arrows above the figures denote the inferred variations in chemical weathering rate  
 846 (higher versus lower) and grain sizes (finer versus coarser). Note the logarithmic scales  
 847 for Ti/K and Zr/Rb.



848

849 Fig. 9. Suggested carbon isotope correlation between the Raasay section (this study)  
 850 and the Yorkshire section, Cleveland Basin (Yorkshire data from Kemp et al., 2005).  
 851 The  $\delta^{13}\text{C}_{\text{org}}$  profiles in these two sections exhibit generally similar trends, characterized  
 852 by a pronounced negative trend and subsequent positive recovery. The profiles have  
 853 been tentatively correlated (grey dashed lines) based on the presence of three abrupt  
 854 shifts in each section, which is also consistent with the available biostratigraphy. ten. =  
 855 tenuicostatum.



856

857 Fig. 10. Cross plot of Mo and TOC from Raasay (this study), Yorkshire (Cleveland  
 858 Basin, UK; McArthur et al., 2008), and Sakuraguchi-dani (Tabo Basin, Japan; Kemp  
 859 and Izumi, 2014) within the T-OAE interval of each section. This plot can be used to  
 860 interpret either the degree of water mass restriction in oxygen-limited marine basins (in  
 861 the case of the Cleveland Basin), or a lack of appreciable Mo enrichment in oxygenated  
 862 settings (in the case of the Tabo and Hebrides Basin). The black solid lines show the  
 863 trends in two modern basins characterized by watermass restriction (see also Algeo and  
 864 Lyons, 2006). See main text for discussion.