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# Carbonate clumped isotope evidence for latitudinal seawater temperature gradients and the oxygen isotope composition of Early Cretaceous seas

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1	Carbonate clumped isotope evidence for latitudinal seawater temperature gradients and the
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#### 15 Abstract

In this study, we investigated Early Cretaceous (Valanginian, ca. 135 million years ago) 16 climate from subtropical to boreal palaeolatitudes. Combined carbonate clumped isotope and 17 18 oxygen isotope data derived from sub-arctic, boreal, and sub-tropical fossil belemnite rostra 19 (Mollusca: Cephalopoda) provide new palaeotemperature estimates as well as a constraint on the oxygen isotope composition of seawater. Our belemnite data reveal balmy high-latitude 20 21 marine temperatures (ca. 22 °C) and warm sub-tropical temperatures (ca. 31 °C). 22 Supplementing our clumped isotope-based temperature estimates with published TEX<sub>86</sub> data results in a conservative reconstruction of a latitudinal temperature gradient that is reduced 23 24 compared to modern conditions. We find that modelling efforts are close to reproducing 25 tropical temperatures when high pCO<sub>2</sub> levels are considered. Warm polar temperatures imply, 26 however, that data-model discrepancies remain. Early Cretaceous seawater oxygen isotope 27 values show a modern profile and are much more positive (up to 1.5‰ SMOW) than typically assumed. Based on our findings, if the positive Cretaceous seawater  $\delta^{18}$ O values are not 28 considered, carbonate  $\delta^{18}$ O thermometry would underestimate temperatures, most acute at 29 middle and tropical latitudes. 30

31 **1** Introduction

Existing proxy data suggest that the Cretaceous latitudinal sea-surface temperature 32 (SST) gradient was reduced (Barron, 1983; Naafs and Pancost, 2016; Littler et al., 2011; Voigt et 33 34 al., 2003; Pucéat et al., 2003). The presence of extensive polar ice at this time, as suggested by Miller (2009) for example, is at odds with contemporaneous warm polar ocean temperatures, 35 36 variable but high atmospheric CO<sub>2</sub> level (Berner and Kothavala, 2001; Wang et al., 2014; 37 Witkowski et al., 2018) and the occurrence of tropical flora at mid- to high latitudes (Grasby et al., 2017). During much of the Cretaceous, stable oxygen isotope and TEX<sub>86</sub> evidence suggests 38 39 that equatorial surface waters were warmer (ca. 30–40 °C) and greater than the maximum SSTs recorded in the modern ocean (e.g. O'Brien et al., 2017; Huber et al., 2018). Mid to higher 40 latitude surface waters were also 10-20 °C warmer than today (Naafs and Pancost, 2016; Littler 41 42 et al., 2011; O'Brien et al., 2017; Huber et al., 1995; Jenkyns et al., 2012; Vickers et al., 2019; 43 O'Connor et al., 2019).

The stable oxygen isotope composition ( $\delta^{18}$ O) of skeletal marine carbonates is perhaps 44 45 the most widely used palaeotemperature proxy (Barron, 1983; Voigt et al., 2003; Pucéat et al., 2003; Huber et al., 2018; Mutterlose et al., 2012; Price et al., 2018). The challenge is, however, 46 47 that the oxygen isotope composition of skeletal carbonates in marine systems vary as a 48 function of both ambient temperatures and the oxygen isotope composition of seawater ( $\delta^{18}O_{sw}$ ). Obtaining a value for  $\delta^{18}O_{sw}$  is complicated because of variables that cannot be easily 49 50 independently quantified, such as freshwater input, evaporation, and the extent of polar ice 51 (Frakes and Francis, 1988; Price, 1999; Miller, 2009; Wierzbowski et al., 2018). Additionally, a 52 proposed change in the mode of mid-ocean ridge hydrothermal alteration over tens of million 53 year timescales suggests that the  $\delta^{18}O_{sw}$  value has increased gradually through Earth's history, 54 from ca. -6‰ SMOW in the Cambrian to its present value of ca. 0‰ SMOW (Standard Mean 55 Ocean Water) (Veizer and Prokoph, 2015; Jaffrés et al., 2007). Nevertheless, the implied

climatic warmth, derived from the  $\delta^{18}$ O values of skeletal marine carbonates, is consistent with 56 more qualitative data derived from thermophilic floras and faunas from the high latitudes 57 (Frakes and Francis, 1988; Tarduno, et al., 1998; Hurum et al., 2006; Spicer et al., 2008; Spicer 58 59 and Herman 2010). However, Cretaceous General Circulation Model (GCM) simulations indicate that the latitudinal temperature gradient was much steeper than what the geological record 60 suggests (Donnadieu et al., 2016; Lunt et al., 2016; Zhou et al., 2008; Poulsen et al., 2007). 61 62 The clumped isotope palaeothermometry technique measures the abundance of heavy  $(^{13}C-^{18}O)$  bond bearing, mass 47) carbonate isotopologues within the single carbonate phase 63 64 relative to its stochastic distribution, which is expressed as the  $\Delta_{47}$  value. Clumped isotope-65 derived seawater temperatures are independent of the oxygen isotope composition of the waters (Ghosh et al., 2006). In this study, we analyse belemnite rostra (fossil remains of extinct 66 67 marine cephalopods) using clumped isotope thermometry to provide new  $\Delta_{47}$  data from the 68 Early Cretaceous (Valanginian). Further, we examine equator-to-pole seawater temperature gradients and the  $\delta^{18}O_{sw}$  values to aid temperature reconstructions and palaeoclimate 69 70 modelling efforts. 71 72 2 Materials and methods 73 2.1 Stratigraphic and environmental setting 74 Belemnite rostra for this study were collected from four locations: the Khatanga Basin 75 (Boyarka River, Russia, 70.592611° N, 97.369083° E), the Pechora Basin (Izhma River, Russia, 76 64.835150° N, 53.782200° E), the Cleveland Basin (Speeton, UK, 54.160555° N, 0.236111° W), 77 and Caravaca (Southern Spain, 38.086944° N, 1.853889° W). These sites are spread across

78 Tethyan, sub-Boreal, and Boreal locations, with palaeolatitudes ranging from 24° N to 74° N

79 (Fig. 1).

80 The Lower Cretaceous part of the Boyarka River section is ca. 300 m thick and consists of marine sandstones, siltstones, and clays deposited in water depths of less than 100 m (Nunn 81 et al., 2010). The fully marine macrofauna includes belemnites and ammonites, allowing a 82 83 detailed Valanginian biostratigraphic zonation consistent with the Boreal biostratigraphic 84 schemes (Fig. 2) and correlatable to Tethyan ammonite biostratigraphy (Nunn et al., 2010; 85 Shulgina et al., 1994; Zakharov et al., 1997). Burial-history analysis of the Boyarka River region 86 of the Khatanga Basin, suggests that a maximum burial depth is likely to be ca. 500 m and 87 geothermal gradients to be moderate ca. 40 °C/km (Klett et al., 2011; Dobretsov et al., 2013). 88 The ca. 62-m-thick Izhma River section comprises shallow marine clastics with 89 belemnites and ammonites present throughout. A detailed Berriasian (Ryazanian) to 90 Valanginian biostratigraphic zonation is consistent with the Boreal biostratigraphic schemes 91 and correlatable to Tethyan ammonite biostratigraphy (Nunn et al., 2010; Baraboshkin, 2004; 92 Zakharov et al., 1997). Burial history curves suggest that the burial depth is likely to be no more 93 than 1000 m, and the present thermal gradients in the Pechora Basin are moderate ca. 19-94 35 °C/km (Lindquist, 1999). 95 The Lower Cretaceous successions located near Caravaca, Southern Spain (Mai Valera,

96 Sierra de Quipar, Canada Luenga) consist of nodular limestones with abundant marine fossils, 97 including crinoid fragments, overlain by hemipelagic marl-limestone alternations (Aguado et al., 98 2000). The successions are thought to have been deposited in a low-energy marine basinal 99 setting, with an estimated water depth of a few hundreds of meters (Company and Tavera, 100 2015). Here, the macrofauna consists mainly of belemnites and well-preserved ammonites, 101 allowing detailed biostratigraphic zonation and correlation of the sections (Aguado et al., 2000; 102 Janssen, 2003; Company and Tavera, 2015; Price, et al., 2018). The maturity of the organic 103 matter in these Subbetic sections and other diagenetic observations imply that the burial depth

104 was no more than 1000 m and that the sediments never reached more than 80 °C (Reicherter105 et al., 1996).

106 The Speeton Clay Formation of the Cleveland Basin comprises about 100 m of 107 interbedded shallow marine claystones deposited in water depths of less than 100 m. The 108 stratigraphical succession contains abundant belemnite rostra and well-preserved ammonites, 109 allowing detailed biostratigraphy (Rawson, 1973; McArthur et al., 2004) and correlation to Boreal and Tethyan zonation schemes (Fig. 2). Measured <sup>87</sup>Sr/<sup>86</sup>Sr values (McArthur et al., 2004) 110 111 show a good agreement between the biostratigraphic data. Vitrinite reflectance data collected 112 and analysed by Hemingway and Riddler (1982) for the Middle Jurassic, which lies beneath the 113 Speeton Clay Formation provides a temperature value of 95 °C for these Jurassic rocks. Holliday 114 (1999) took this information and assuming an average thermal conductivity provided a 115 geothermal gradient of approximately 30 °C/km and estimated maximum burial depths of ca. 116 2000 m. For the Cretaceous, the estimated sediment surface temperature used was 20 °C 117 (Holliday, 1999). These temperature estimates are consistent with the thermal history model 118 presented by Słowakiewicz et al. (2015) that suggests that the maximum temperatures for the 119 Lower Cretaceous succession reached ca. 40–50 °C during the early Cenozoic. 120 Theoretical calculations based on laboratory experiments evidence that solid-state 121 diffusion, even in wet and high-pressure conditions, is insignificant below 100 °C burial 122 temperatures on a timescale of 135 million years (Passey and Henkes 2012; Brenner et al., 123 2018). Thus, the belemnite rostra analysed from these four sections should not have been 124 affected by solid-state reordering.

125

126 2.2 Sample selection

Belemnite rostra consist of diagenetically stable low-Mg calcite (Saelen, 1989). The
rostra selected for analysis in this study were those deemed to be the best-preserved samples

129 in the previous studies of McArthur et al. (2004), Nunn et al. (2010), Price et al. (2000), and 130 Price et al. (2018). The excellent preservation of the analysed material is indicated by trace element concentrations and petrographic analyses, including cathodoluminescence. Diagenetic 131 132 alteration of marine calcites often leads to significant enrichments in Mn and Fe (Veizer, 1974). 133 Diagenetic Mn<sup>2+</sup> ions are also an activator of orange cathodoluminescence in calcites, which is 134 indicative of the alteration under reducing conditions (Marshall, 1992). All the belemnites 135 analysed for clumped isotopes, in this study, had low concentrations of Fe (< 120 ppm) and Mn 136 (< 25 ppm) indicative of good sample preservation (e.g. McArthur et al., 2007; Mutterlose et al., 137 2012). These 20 Valanginian belemnite rostra were: Acroteuthis sp. from Speeton from the 138 Polyptychites Ammonite zone; Berriasibelus, Hibolithes and Duvalia from Caravaca from the 139 Pertransiens–Verrucosum Ammonite zones; Acroteuthis and Pachyteuthis from Pechora Basin 140 from the Klimovskiensis to Michalskii Ammonite zones, and Acroteuthis, Lagonibelus and 141 Pachyteuthis from Khatanga Basin from the Klimovskiensis to Michalskii Ammonite zones 142 schemes (Fig. 2). Calcite subsamples (ca. 50 mg carbonate powder) were taken from previously 143 investigated rostra (see above), re-sampled across multiple growth bands, in order to get a 144 representative amount for clumped isotope analysis. During sampling the belemnite rostra 145 margins and calcite around the apical zones were avoided, as diagenetic alteration is typically 146 observed in these parts. Visual inspection also showed belemnite rostra preservation to be 147 excellent with all specimen displaying honey coloured translucent calcite. This is consistent with petrographic and cathodoluminescence observations (e.g. non-luminescent rostra) made in 148 149 previous research (McArthur et al., 2004; Nunn et al., 2010; Price et al., 2000, 2018).

150

#### 151 2.3 Clumped and stable isotope analyses

152 Clumped isotope analyses were performed using a ThermoFisher MAT 253 gas-source 153 isotope-ratio mass spectrometer connected to an automated gas extraction and purification

154 line at the Institute of Geosciences, Goethe University Frankfurt. Carbonates were digested at 155 90 °C in a common acid bath. Background correction for the clumped isotope analyses was performed as described in Fiebig et al. (2016). Raw isotope values were calculated using the 156 157 [Brand]/IUPAC set of isotopic parameters as suggested by Daëron et al. (2016). The raw  $\Delta_{47}$ 158 data were projected to the carbon dioxide equilibrium scale using empirical transfer functions that were determined using equilibrated gases (25 °C and 1000 °C, respectively) of various bulk 159 160 isotope composition (Petersen et al., 2019). A 90–25 °C acid fractionation factor of 0.088‰ was 161 applied to all  $\Delta_{47 (RFAC)}$  values (Petersen et al., 2019). To verify the consistency and precision of the clumped isotope measurements six carbonate standards were independently analysed 162 163 along with the samples. The  $\Delta_{47 (RFAC)}$  (1 standard deviation, N = number of replicates) values of 164 the reference material are: Carrara 0.407‰ (0.019‰, N = 335), MuStd 0.749‰ (0.018‰, N = 181), ETH 1 0.301‰ (0.016‰, N = 78), ETH 2 0.301‰ (0.019‰, N = 37), ETH 3 0.711‰ 165 166 (0.018%, N = 92), ETH 4 0.556‰ (0.020%, N = 10) (Data S1). To convert  $\Delta_{47 (RFAC)}$  values to temperatures, we used a synthetic calcite calibration:  $\Delta_{47 (RFAC)} = 0.0383(\pm 1.7E-06) \times 10^6/T^2 +$ 167 0.258((±1.7E-05) (Petersen et al., 2019), where T is in K and  $\Delta_{47 (RFAC)}$  is in ‰.  $\delta^{18}O_{sw}$  estimates 168 169 (Table 1, Data S1) were calculated using the  $\Delta_{47}$ -derived temperature, the measured  $\delta^{18}$ O value 170 of each belemnite, and the  $1000 ln \alpha_{calcite-water}$ -temperature relationships of Kim and O'Neil 171 (1997) (corrected for a CO<sub>2</sub>-calcite acid fractionation factor of 10.25, Kim et al. (2007)) and of 172 Coplen (2007). Coplen (2007) provided an equation based on water and vein calcite 173 precipitated at extreme slow rates subaqueously at Devils Hole, Nevada, USA. The widely 174 accepted Kim and O'Neil (1997) equation is based on inorganic precipitation experiments. 175

176 **3 Results** 

- 177
- 3.1 Bele
  - Belemnite  $\Delta_{47}$ -based temperatures

178 The average  $\Delta_{47}$ -derived temperatures of this study range from 19 °C to 27 °C (Fig. 3, 179 Table 2, Supplementary Figure 1, Data S1). Some studies have postulated that belemnites 180 calcified their rostra, possibly seasonally, in the upper part of the water column (Klug et al., 181 2016; Price et al., 2015; Stevens et al., 2014), whereas others consider belemnites as 182 nektobenthic organisms (Wierzbowski et al., 2013). For shallow marine settings (i.e. typically 183 less than 100 m), comparable to the locations investigated in this study (see above), one could 184 assume a low temperature gradient in the water column. Thus, here we presume that 185 belemnites indicate mean seawater temperatures at these sites at the time of rostra growth. 186 The range of  $\Delta_{47}$ -derived temperatures encountered at each of the individual sample site was 187 from 4 °C to 15 °C. This relatively large temperature range is similar to that seen in other 188 clumped isotope studies (e.g. Petersen et al., 2016; Evans et al., 2018; Meyer et al., 2018). Such 189 a range in the  $\Delta_{47}$ -derived temperature data is of a similar magnitude as the modern 190 temperature range (e.g. 4–12 °C) in similar latitudes (Locarnini et al., 2013) and is attributed to 191 a combination of the influence of seasonal temperature variability, different belemnite 192 ecologies combined with the impact of local geography and a reflection of the range of 193 temperature variability over the timescales represented by the belemnite sample set (see Fig. 194 2).

195 Our  $\Delta_{47}$ -derived temperature estimate for the Valanginian low latitudes (27 °C) is lower 196 than the average temperature values of ca. 35 °C obtained from Valanginian TEX<sub>86</sub><sup>H</sup> data (Littler 197 et al., 2011) but is comparable with modern mean annual surface temperature observations. 198 Our  $\Delta_{47}$ -based temperatures suggest, therefore, that belemnites were calcifying their rostra in 199 waters slightly cooler than those surface waters indicated by the TEX<sub>86</sub> data. Notably, the 200 belemnites from Caravaca occur in hemipelagic marly-limestone beds formed at a depth of a 201 few hundred meters (see above) and may have lived at times below a thermocline layer, so 202 their clumped isotope record may be subject to lower temperatures. Vickers et al. (2019) also

203 showed that  $\Delta_{47}$ -derived palaeotemperatures were slightly cooler than TEX<sub>86</sub>-based estimates. 204 Multiple studies have now found that clumped temperatures of molluscs are always colder than TEX<sub>86</sub>, temperature estimates, whether using the TEX<sub>86</sub><sup>H</sup> or BAYSPAR TEX<sub>86</sub> calibration. The 205 206 temperature difference is commonly too great to be explained by surface vs. benthic modes of 207 life alone (see Meyers et al., 2018). Despite the relatively large uncertainty in our temperatures estimates, our average Valanginian temperatures (19-24 °C) for the middle latitudes are 208 warmer by up to 13 °C than other Valanginian temperature estimates derived from  $\delta^{18}$ O 209 210 thermometry of belemnites (Schootbrugge et al., 2000; Price et al., 2000; McArthur et al., 2004), although similar to Pucéat et al. (2003), who inferred temperatures from the oxygen 211 212 isotope composition of fish tooth enamels. Our average Valanginian temperatures are also 213 comparable to TEX<sub>86</sub><sup>H</sup> data from other Cretaceous intervals (Mutterlose et al., 2010, 2012; 214 Naafs and Pancost, 2016; O'Brien et al., 2017). For example, Mutterlose et al. (2012) suggest TEX<sub>86</sub><sup>H</sup> seawater temperature estimates ranging from 22 °C to 24 °C for the Hauterivian of 215 216 Speeton, UK. The temperature estimate for higher paleolatitudes (74° N) from this study is 217 19 °C and is warmer than previous Valanginian carbonate  $\delta^{18}$ O-based estimates (Price and Nunn, 2010; Ditchfield, 1997) but similar to Late Cretaceous TEX<sub>86</sub><sup>H</sup> seawater temperature 218 219 estimates (Super et al., 2018). Different calibrations have been proposed to translate TEX<sub>86</sub> into 220 SST. Of these calibrations, the global nonlinear logarithmic TEX<sub>86</sub><sup>H</sup> calibration of Kim et al. 221 (2010) and the BAYSPAR TEX<sub>86</sub> calibration of Tierney and Tingley (2014) are the most commonly 222 chosen for higher-temperature settings, such as in the Cretaceous. It is the more conservative 223 TEX<sub>86</sub><sup>H</sup> estimates that provide a better match to our clumped isotope temperature estimates 224 (see also Vickers et al., 2019). The BAYSPAR TEX<sub>86</sub> calibration of Tierney and Tingley (2014) 225 provides higher temperatures (ca. 8 °C higher) at the upper limit of the proxy (e.g. O'Brien et al. 2017; O'Connor et al., 2019). Our Valanginian seawater temperatures across all latitudes are 226

also 1–14 °C warmer than modern SST observations, although at middle latitudes, they

approach the warmest recent observations (Locarnini et al., 2013).

229 The interpretation of relatively warm past ocean temperatures at middle-high latitudes 230 is consistent with palaeobotanical temperature constraints derived from Cretaceous fossil 231 floras (Spicer and Herman, 2010). In contrast, data from the Lower Cretaceous of Canada 232 (Grasby et al., 2017), Svalbard (Vickers et al., 2016), and Siberia (Rogov et al., 2017) suggest that 233 numerous boreal cool events interrupted otherwise warm conditions. These authors describe 234 abundant glendonites (pseudomorphs after marine sedimentary ikaite) in Valanginian and 235 Aptian strata that are thought to be critical markers of cold conditions. These observations are 236 not incompatible with our data from the Valanginian, as Grasby et al. (2017) conclude that cold 237 periods were brief, punctuating an overall warm Early Cretaceous climate.

238

#### 239 4 Discussion

#### 240 4.1 Early Cretaceous latitudinal temperature gradient

241 Using the average palaeotemperatures and the palaeolatitude (Young et al., 2019) at 242 each of the sites examined here, together with Valanginian  $\Delta_{47}$  data from Price and Passey 243 (2013) and TEX<sub>86</sub> data from Littler et al. (2011), we can conservatively reconstruct an Early 244 Cretaceous latitudinal temperature profile with an estimated gradient of ca. 0.32 °C per degree 245 of latitude, between 15° N and 74° N (Fig. 3). TEX<sub>86</sub> data from other Early Cretaceous intervals 246 (Naafs and Pancost, 2016) and Late Cretaceous  $\delta^{18}$ O-derived palaeotemperatures (Voigt et al., 247 2003; Pucéat et al., 2003) also reveal a similar gradient. Available TEX<sub>86</sub> data evidence (O'Brien 248 et al. 2017; O'Connor et al., 2019) suggests that latitudinal temperature gradients were lower in 249 the Coniacian to Campanian compared with the present day. The implied shallow meridional 250 temperature gradient for the Early Cretaceous contrasts with a modern average gradient of ca. 251 0.45 °C per degree of latitude in the Northern Hemisphere (Young et al., 2019).

252 Most evidence suggests that the Cretaceous was characterised by high atmospheric CO<sub>2</sub> 253 levels (e.g. Berner and Kothavala, 2001; Wang et al., 2014; Witkowski et al., 2018) and 254 consequently, its climate was warmer and more equable (Frakes 1979; Huber et al., 1995; Bice 255 et al., 2003). Although, as noted above, transient cool events have been suggested (Grasby et 256 al., 2017; Mutterlose et al., 2010; McArthur et al., 2007), data typically point to warm polar 257 regions (Spicer and Herman, 2010; Ditchfield 1997; Frakes, 1979; McArthur et al., 2007) 258 consistent with our temperature estimates. The presence of such a reduced temperature 259 gradient requires a climate mechanism in a high  $pCO_2$ -world that yields temperate polar regions 260 while not overheating the tropics. Proposed mechanisms to increase the transfer of heat 261 toward the poles include increased oceanic (Schmidt and Mysak, 1996) and atmospheric 262 poleward heat transport (Bice et al., 2003), together with amplification of polar warmth by 263 cloud feedbacks (Kump and Pollard 2008; Sagoo et al., 2013; Upchurch et al., 2015).

264

#### 265 *4.2 Cretaceous model-data comparisons*

266 Climate modelling of past warm periods has received much attention as it has long been 267 suggested that simulations may not capture the extent to which the latitudinal temperature 268 gradient is reduced (Spicer, et al., 2008). The  $\Delta_{47}$  reconstructions and temperature compilation 269 demonstrate that Early Cretaceous tropical warming was of a magnitude consistent with some 270 models (e.g. using the fast ocean atmosphere model (FOAM), for the Late Cretaceous, 271 Donnadieu et al., 2016) at 12-times pre-industrial pCO<sub>2</sub> (Fig. 3). Other simulations indicate 272 cooler tropical temperatures. For example, modelled Valanginian sea surface temperatures 273 (using the UK Met Office HadCM3L model) with 4x pre-industrial  $pCO_2$  (Lunt et al., 2016) shows 274 less of a fit particularly with the Littler et al. (2011) TEX<sub>86</sub> temperature data, which represents 275 the sea surface, as does the model. For higher latitudes, our temperature proxy data are 276 warmer than some simulations (Donnadieu et al., 2016; Lunt et al., 2016; Poulsen et al., 2007;

277 Upchurch et al., 2015) for the Early and Late Cretaceous even at 12-times pre-industrial pCO<sub>2</sub>. In contrast to these Cretaceous simulations, climate models of other "greenhouse" intervals 278 (e.g. for the Eocene, Sagoo et al., 2013; Zhu et al., 2019), show warmer higher latitudes. 279 280 Although many aspects contributed to the warmth seen at higher latitudes in the model of 281 Sagoo et al., (2013), a strong sensitivity to albedo changes associated with cloud cover was 282 apparent. However, for the highest latitude proxy data, the magnitude of warming simulated 283 by most climate models is still less than indicated by the  $\Delta_{47}$  data and published TEX<sub>86</sub> (Jenkyns 284 et al., 2012) temperature estimates. This could suggest that some climate models for the 285 Cretaceous are still missing key processes. Notably, Upchurch et al. (2015) using a fully coupled 286 GCM come close to reproduce warm Cretaceous polar temperatures and the latitudinal 287 temperature gradient without overheating the tropics. For a cool greenhouse interval of the 288 latest Cretaceous (Maastrichtian) the best fits of Upchurch et al. (2015) for mean annual 289 temperature are simulations that use 6-times pre-industrial levels of atmospheric CO<sub>2</sub>, or 2-290 times pre-industrial levels of atmospheric CO<sub>2</sub> and liquid cloud properties that may reflect pre-291 anthropogenic levels of cloud condensation nuclei. It is important to note that Cretaceous TEX<sub>86</sub> 292 data and  $\Delta_{47}$ -derived temperatures are limited by the distribution of suitably preserved 293 sediments at high latitudes. Indeed, Cretaceous TEX<sub>86</sub> data is available from just a few Arctic 294 sites (Jenkyns et al., 2004; Super et al., 2018). As such, the high temperatures so far identified 295 may not be fully representative of regional averages.

296

### 297 4.3 The oxygen isotope composition of Early Cretaceous seas

Estimations of ancient oceans  $\delta^{18}O_{sw}$  values are controversial. Complexity arises from variables such as the input of freshwater and evaporation, the presence or absence of polar ice, whether the oxygen isotope composition of the seawater is buffered by submarine hydrothermal processes, or whether lower  $\delta^{18}O$  values of ancient marine carbonates reflect the

302	fact that the $\delta^{18} O_{sw}$ value has varied significantly over time (see Jaffrés et al., 2007). The
303	average of our $\delta^{ m ^{18}O_{sw}}$ estimates is calculated as -0.1‰ SMOW using the Coplen (2007) equation
304	or 1.4‰ SMOW using the Kim and O'Neil (1997) equation (Table 2, Data S1). Both values are
305	more positive than the estimated global average $\delta^{18}O_{sw}$ value for the modern ocean (-0.28‰
306	SMOW) or an ice-free world (-1.0‰ SMOW) (Shackleton and Kennett, 1975) (Fig. 4). The $\delta^{18} { m O}_{ m sw}$
307	value of -1.0‰ SMOW is widely cited as the mean seawater oxygen isotope composition for the
308	Cretaceous. Nevertheless, our data from four new sites, in conjunction with data from Price
309	and Passey (2013), suggests a gentle decrease in average values poleward (Fig. 4,
310	Supplementary Figure 2) (see also Zhou et al., 2008). The difference between our calculated
311	$\delta^{18}O_{sw}$ values and modern $\delta^{18}O_{sw}$ values, or the assumed $\delta^{18}O_{sw}$ values for ancient seas in ice-
312	free hothouse worlds, may be due to (1) differences in the absolute $\Delta_{47}$ -temperature calibration
313	producing temperatures that are too warm, (2) vital effects in the belemnites resulting in
314	carbonate $\delta^{18}$ O values enriched relative to equilibrium with seawater, (3) diagenesis causing
315	lower $\Delta_{47}$ and higher $\delta^{18}$ O values in carbonates, or (4) changes in $\delta^{18}$ O <sub>sw</sub> values of ancient seas.
316	Differences in the $\Delta_{47}$ -temperature calibration would influence absolute temperature
317	and calculated $\delta^{ m 18}  m O_{ m sw}$ values. As noted above, we used the synthetic ${\it \Delta}_{ m 47}$ –temperature
318	calibration of Petersen et al. (2019) to convert the measured clumped isotope values to
319	precipitation temperatures of calcium carbonate. This calibration is fairly robust as it considers
320	451 carbonate datapoints. In comparison, the in-house Wacker et al. (2014) or the steeper
321	sloped Kelson et al. (2017) calibrations give temperatures that are ca. 3 $^\circ$ C warmer (Data S1).
322	Hence our choice of calibration eliminates potential biasing towards too warm temperatures.
323	Alternatively, the high $\delta^{ m 18} O_{ m sw}$ values could be caused by diagenetic effects that
324	increased temperatures. Modelling of burial at all sites suggests that the belemnite rostra
325	analysed should not have been affected by solid-state reordering. Alternatively, the high $\delta^{18} { m O}_{ m sw}$
326	values may be due to vital effects. Should Kim and O'Neil (1997) represent equilibrium, then

327 our mean  $\delta^{18}O_{sw}$  value would be on average 2.4‰ higher than the value assumed for an icefree ocean (see below). Kinetic isotope effects generally, however, discriminate against the 328 heavier isotope (e.g. McConnaughey 1989), although Price et al. (2015) do suggest a possible 329 330 offset between belemnite calcite  $\delta^{18}$ O and equilibrium of ca. 1‰. Data from a number of other 331 Cretaceous studies applying the clumped isotope palaeothermometer to molluscs (Dennis et 332 al., 2013; Meyer et al., 2018; Vickers et al., 2019), also indicates that the isotopic composition 333 of seawater predicted was markedly positive, using the equation of Kim and O'Neil (1997) and 334 exceeding modern seawater values. Further work comparing the clumped isotope 335 temperatures to different molluscs (see Meyer et al. 2018) could resolve whether these high  $\delta^{18}O_{sw}$  values could be caused by vital effects. 336

337 In addition to those studies noted above, data from a number of other studies applying 338 the clumped isotope palaeothermometer (Petersen and Schrag 2015; Wierzbowski et al 2018), 339 also note that the isotopic composition of seawater predicted was, at times, markedly positive. This poses a challenge, as the average value of modern  $\delta^{18}O_{sw}$  is a consequence of ice 340 341 accumulation largely on Greenland and Antarctica. Although modest-sized Cretaceous ice 342 sheets have been postulated (DeConto and Pollard, 2003; Frakes and Francis, 1988; Price, 343 1999), the volume of this ice is likely to be insufficient to see  $\delta^{18}O_{sw}$  values around 1‰ SMOW.  $\delta^{18}O_{sw}$  values of 1‰ SMOW require ice volumes in excess of the Last Glacial Maximum, when 344 345 ice sheets covered large parts of North America and Europe as well as Antarctica. Unlike at the 346 Last Glacial Maximum, it is thought that in the Cretaceous, ice was considerably more limited 347 and is, therefore, not sufficient to explain such high  $\delta^{18}O_{sw}$  values. Any ice would also have to 348 be isotopically very light. Studies have also postulated that water could be stored as 349 (isotopically light) freshwater on land (e.g. Jacobs and Sahagian, 1993). As this study, however, 350 suggests that the latitudinal temperature gradient during the Early Cretaceous was less steep than today, it is conceivable that the  $\delta^{18}$ O<sub>ice</sub> and any stored freshwater was also less extreme. If 351

the  $\delta^{18}O_{ice}$  value was less negative, this would make it even harder to get  $\delta^{18}O_{sw}$  values to 1‰ SMOW or more, as even greater ice volumes would be required. This is consistent with studies of the Antarctic ice sheet during the early Miocene when the latitudinal temperature gradient was less extreme and Antarctic temperatures were warmer than today resulting in significantly higher  $\delta^{18}O_{ice}$  values in the Miocene ice sheet (e.g. ca. -35‰ SMOW) than values today (i.e. -45‰ to -55‰ SMOW) (Pekar and DeConto, 2006).

Alternatively, the high  $\delta^{18}O_{sw}$  values could be caused by relatively high rates of 358 359 evaporation leading to higher salinities. Although, salinity can be estimated from salinity  $-\delta^{18}$ O models for marine basins (e.g. Railsback et al., 1989), to reconcile our belemnite  $\delta^{18}$ O data with 360 361 the  $\Delta_{47}$ -derived temperatures, salinities in excess of 41 PSU are required (see also Wierzbowski 362 et al., 2018). As such, each of the sites examined here would need to be dominated by 363 evaporation. As the belemnite samples were derived from open marine systems (based upon 364 the presence of a fully marine fauna, including ammonites), high salinities contributing to high  $\delta^{18}O_{sw}$  values seems unlikely. 365

The marine carbonate  $\delta^{18}$ O record also depends on seawater pH (Wallmann, 2004). 366 Seawater pH is strongly influenced by changes in *p*CO<sub>2</sub> (Zeebe, 1999, 2001; Wallmann, 2004). 367 368 An increase of seawater pH of 0.2–0.3 units, for example, is considered to result in a decrease 369 of about 0.22–0.33‰ in the  $\delta^{18}$ O values of foraminiferal calcite, which would normally be 370 interpreted as a temperature increase of seawater, although the magnitude of the effect may 371 be species-dependent (Zeebe, 2001). During periods of high atmospheric CO<sub>2</sub> levels such as the 372 Cretaceous (Berner and Kothavala, 2001; Wang et al., 2014; Witkowski et al., 2018), this pH effect (Zeebe, 2001) if applicable to belemnites, would lead to an increase in the  $\delta^{18}$ O value of 373 374 calcite. However, the magnitude of pH change in seawater needed to explain the observed offset in  $\delta^{18}O_{sw}$  value between an ice-free -1‰ SMOW and the average of our estimate of 375 376 +1.5‰ SMOW (using the Kim and O'Neil, 1997 equation) and scaling of ca. 0.1 pH unit for every

377 0.1‰  $\delta^{18}$ O, means that oceans would need to be ca. 2.5 pH units more acidic. Such a

378 magnitude of change is not realistic (see Caldeira and Wickett, 2003).

Changes in the oxygen isotope composition of ancient oceans is a debated issue. Veizer 379 380 and Prokoph (2015) and Jaffrés et al. (2007) for example suggest that the  $\delta^{18}O_{sw}$  value has 381 increased gradually through Earth's history, from -6% SMOW in the Cambrian to its present 382 value of ca. 0‰ SMOW. Other studies, applying the clumped isotope palaeothermometer, indicate more or less constant  $\delta^{18}O_{sw}$  values through geologic time (e.g. Ryb and Eiler, 2018; 383 Henkes, et al., 2018). Most models of the geological <sup>18</sup>O-cycle conclude that seawater/rock 384 385 interaction with silicates of oceanic crust at high and low temperatures balance each other and, 386 thus buffer the  $\delta^{18}O_{sw}$  value at about  $0(\pm 2)$ % SMOW (Muehlenbachs and Clayton, 1976; 387 Holland, 1984). Hence, it has been considered that the  $\delta^{18}O_{sw}$  value of the global ocean has not changed significantly over time, but has been buffered by hydrothermal and weathering 388 389 processes (low-temperature interactions with silicates) at mid-ocean ridges and on ridge flanks, 390 based on results of ophiolite studies (e.g. Coogan et al., 2019). High-temperature alteration (mainly via hydrothermal fluids) leads to an increase in  $\delta^{18}O_{sw}$  values, while low-temperature 391 alteration (e.g. weathering processes) leave the ocean <sup>18</sup>O-depleted (Muehlenbachs and 392 393 Clayton, 1976; Holland, 1984; Muehlenbachs, 1998). These mass balance calculations, however, 394 do not rule out minor variations in the average  $\delta^{18}O_{sw}$  value that could conceivably produce a minor change towards more positive values reconciling our belemnite  $\delta^{18}$ O data and 395 corresponding  $\Delta_{47}$ -derived temperatures. 396 397 Conclusions 5

The Early Cretaceous  $\Delta_{47}$ -derived temperatures of this study point to Arctic regions above freezing. Our data argue against an extended ice sheet in the Northern Hemisphere and shows congruence with TEX<sub>86</sub> temperatures. Our clumped isotope-based temperature reconstruction suggests the existence of a strongly reduced equator-to-pole temperature

gradient in the Northern Hemisphere. We find that modelling efforts are close to reproducing
the tropical temperatures when high atmospheric CO<sub>2</sub> levels are invoked, however, our data
suggests warmer temperatures at higher latitudes that are not shown in the models.

405 The results of this study indicate that it is unlikely that the oxygen isotope composition of the seawater was homogenous. Our Early Cretaceous  $\delta^{18}O_{sw}$  results are a conservative 406 407 reconstruction of a latitudinal gradient that shows a gentle decrease in values poleward and 408 also, using the Kim and O'Neil (1997) and Coplen (2007) equations plot in the upper portion or wholly within the field of modern seawater. Early Cretaceous  $\delta^{18}O_{sw}$  values with modern 409 characteristics implies some storage of light isotopes away from the ocean, e.g. as ice 410 411 accumulation on Antarctica. The constraints we provide on the oxygen isotope composition of 412 Early Cretaceous seawater, underpins our understanding of the evolution of the Earth's temperature. Disregarding positive Early Cretaceous  $\delta^{18}O_{sw}$  values results in an 413 414 underestimation of temperatures, most acute at middle and tropical latitudes.

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#### 427 References

- 428 Aguado, R., Company, M., Tavera, J.M., 2000. The Berriasian/Valanginian boundary in the
- 429 Mediterranean region: New data from the Caravaca and Cehegín sections, SE Spain.
- 430 Cretac. Res. 21, 1-21. https://doi.org/10.1006/cres.2000.0198
- 431 Baraboshkin, E.Y., 2004. Boreal-Tethyan correlation of Lower Cretaceous ammonite scales.
- 432 Moscow Univ. Geol. Bull. 59, 9-20.
- 433 Barron, E.J., 1983. A warm, equable Cretaceous: The nature of the problem. Earth-Sci. Rev. 19,
- 434 305-338. https://doi.org/10.1016/0012-8252(83)90001-6
- 435 Berner, R.A., Kothavala, Z., 2001. GEOCARB III: A revised model of atmospheric CO<sub>2</sub> over
- 436 phanerozoic time. Am. J. Sci. 301, 182-204. https://doi.org/10.2475/ajs.301.2.182
- 437 Bice, K.L., Huber, B.T., Norris, R.D., 2003. Extreme polar warmth during the Cretaceous
- 438 greenhouse? Paradox of the late Turonian  $\delta^{18}$ O record at Deep Sea Drilling Project Site
- 439 511. Paleoceanography 18, 1031. https://doi.org/10.1029/2002pa000848
- 440 Brenner, D.C., Passey, B.H., Stolper, D.A., 2018. Influence of water on clumped-isotope bond
- 441 reordering kinetics in calcite. Geochim. Cosmochim. Acta 224, 42-63.
- 442 https://doi.org/10.1016/j.gca.2017.12.026
- 443 Caldeira, K., Wickett, M.E., 2003. Oceanography: Anthropogenic carbon and ocean pH. Nature
- 444 425, 365. https://doi.org/10.1038/425365a
- 445 Company, M., Tavera, J.M., 2015. Lower Valanginian ammonite biostratigraphy in the Subbetic
- 446 Domain (Betic Cordillera, southeastern Spain). Carnets Geol. 15, 71-88.
- 447 Coogan, L.A., Daëron, M., Gillis, K.M., 2019. Seafloor weathering and the oxygen isotope ratio in
- 448 seawater: Insight from whole-rock  $\delta^{18}$ O and carbonate  $\delta^{18}$ O and  $\Delta_{47}$  from the Troodos
- 449 ophiolite. Earth Planet. Sci. Lett. 508, 41-50. https://doi.org/10.1016/j.epsl.2018.12.014

- 450 Coplen, T.B., 2007. Calibration of the calcite–water oxygen-isotope geothermometer at Devils
- 451 Hole, Nevada, a natural laboratory. Geochim. Cosmochim. Acta 71, 3948-3957.
- 452 https://doi.org/10.1016/j.gca.2007.05.028
- 453 Daëron, M., Blamart, D., Peral, M., Affek, H.P., 2016. Absolute isotopic abundance ratios and
- 454 the accuracy of  $\Delta_{47}$  measurements. Chem. Geol. 442, 83-96.
- 455 https://doi.org/10.1016/j.chemgeo.2016.08.014
- 456 DeConto, R.M., Pollard, D., 2003. Rapid Cenozoic glaciation of Antarctica induced by declining
- 457 atmospheric CO<sub>2</sub>. Nature 421, 245-249. https://doi.org/10.1038/nature01290
- 458 Dennis, K.J., Cochran, J.K., Landman, N.H., Schrag, D.P., 2013. The climate of the Late
- 459 Cretaceous: New insights from the application of the carbonate clumped isotope
- 460 thermometer to Western Interior Seaway macrofossil. Earth Planet. Sci. Lett. 362, 51-65.
- 461 https://doi.org/10.1016/j.epsl.2012.11.036
- 462 Ditchfield, P.W., 1997. High northern palaeolatitude Jurassic-Cretaceous palaeotemperature
- 463 variation: new data from Kong Karls Land, Svalbard. Palaeogeogr. Palaeoclimatol.
- 464 Palaeoecol. 130, 163-175. https://doi.org/10.1016/S0031-0182(96)00054-5
- 465 Dobretsov, N.L., Polyansky, O.P., Reverdatto, V.V., Babichev, A.V., 2013. Dynamics of the Arctic
- 466 and adjacent petroleum basins: a record of plume and rifting activity. Russ. Geol.

467 Geophys. 54, 888-902. https://doi.org/10.1016/j.rgg.2013.07.009

- 468 Donnadieu, Y., Puceat, E., Moiroud, M., Guillocheau, F., Deconinck, J.F., 2016. A better-
- 469 ventilated ocean triggered by Late Cretaceous changes in continental configuration. Nat.
- 470 Commun. 7, 10316. https://doi.org/10.1038/ncomms10316
- 471 Evans, D., Sagoo, N., Renema, W., Cotton, L.J., Müller, W., Todd, J.A., Saraswati, P.K., Stassen,
- 472 P., Ziegler, M., Pearson, P.N., Valdes, P.J., Affek, H.P., 2018. Eocene greenhouse climate
- 473 revealed by coupled clumped isotope-Mg/Ca thermometry. Proc. Natl. Acad. Sci. U.S.A.
- 474 115, 1174-1179. https://doi.org/10.1073/pnas.1714744115

- 475 Fiebig, J., Hofmann, S., Niklas, L., Lüdecke, T., Methner, K., Wacker, U., 2016. Slight pressure
- 476 imbalances can affect accuracy and precision of dual inlet-based clumped isotope
- 477 analysis. Isotopes Environ. Health Stud. 52, 12-28.
- 478 https://doi.org/10.1080/10256016.2015.1010531
- 479 Frakes, L.A., 1979. Climates throughout geologic time. Elsevier, Amsterdam.
- 480 Frakes, L.A., Francis, J.E., 1988. A guide to Phanerozoic cold polar climates from high-latitude
- 481 ice-rafting in the Cretaceous. Nature 333, 547-549. https://doi.org/10.1038/333547a0
- 482 Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W., Schauble, E.A., Schrag, D., Eiler, J.M., 2006.
- 483 <sup>13</sup>C<sup>-18</sup>O bonds in carbonate minerals: A new kind of paleothermometer. Geochim.
- 484 Cosmochim. Acta 70, 1439-1456. https://doi.org/10.1016/j.gca.2005.11.014
- 485 Gradstein, F.M., Ogg, J.G., Schmitz, M.D., Ogg, G.M., 2012. The Geologic Time Scale 2012.
- 486 Elsevier, p. 1176.
- 487 Grasby, S.E., McCune, G.E., Beauchamp, B., Galloway, J.M., 2017. Lower Cretaceous cold snaps
- 488 led to widespread glendonite occurrences in the Sverdrup Basin, Canadian High Arctic.
- 489 Geol. Soc. Am. Bull. 129, 771-787. https://doi.org/10.1130/B31600.1
- Hemingway, J.E., Riddler, G.P., 1982. Basin inversion in North Yorkshire. T. I. Min. Metall. B 91,
  B175-B186.
- 492 Henkes, G.A., Passey, B.H., Wanamaker, A.D., Grossman, E.L., Ambrose, W.G., Carroll, M.L.,
- 493 2013. Carbonate clumped isotope compositions of modern marine mollusk and
- 494 brachiopod shells. Geochim. Cosmochim. Acta 106, 307-325.
- 495 https://doi.org/10.1016/j.gca.2012.12.020
- 496 Henkes, G.A., Passey, B.H., Grossman, E.L., Shenton, B.J., Yancey, T.E., Pérez-Huerta, A., 2018.
- 497 Temperature evolution and the oxygen isotope composition of Phanerozoic oceans from
- 498 carbonate clumped isotope thermometry. Earth Planet. Sci. Lett. 490, 40-50.
- 499 https://doi.org/10.1016/j.epsl.2018.02.001

- 500 Holland, H.D., 2004. The geologic history of seawater, in: Elderfield, H., Holland, H.D., Turekian,
- 501 K.K. (Eds.), Treatise on Geochemistry, Vol. 6. The Oceans and Marine Geochemistry.
- 502 Elsevier Pergamon, Kidlington, Oxford, pp. 583–625.
- 503 Holliday, D.W., 1999. Palaeotemperatures, thermal modelling and depth of burial studies in
- 504 northern and eastern England. Proc. Yorkshire Geol. Soc. 52, 337-352.
- 505 https://doi.org/10.1144/pygs.52.4.337
- 506 Huber, B.T., Hodell, D.A., Hamilton, C.P., 1995. Middle-Late Cretaceous climate of the southern
- 507 high latitudes: Stable isotopic evidence for minimal equator-to-pole thermal gradients.
- 508 Geol. Soc. Am. Bull. 107, 1164-1191. https://doi.org/10.1130/0016-
- 509 7606(1995)107<1164:MLCCOT>2.3.CO;2
- 510 Huber, B.T., MacLeod, K.G., Watkins, D.K., Coffin, M.F., 2018. The rise and fall of the Cretaceous
- 511 hot greenhouse climate. Glob. Planet. Change 167, 1-23.
- 512 https://doi.org/10.1016/j.gloplacha.2018.04.004
- 513 Hurum, J.H., Milan, J., Hammer, O., Midtkandal, I., Amundsen, H., Saether, B., 2006. Tracking
- polar dinosaurs new finds from the Lower Cretaceous of Svalbard. Norw. J. Geol. 86,397-402.
- 516 Jacobs, D.K., Sahagian, D.L., 1993. Climate-induced fluctuations in sea level during non-glacial
- 517 times. Nature 361, 710-712. https://doi.org/10.1038/361710a0
- 518 Jaffrés, J.B.D., Shields, G.A., Wallmann, K., 2007. The oxygen isotope evolution of seawater: A
- 519 critical review of a long-standing controversy and an improved geological water cycle
- 520 model for the past 3.4 billion years. Earth-Sci. Rev. 83, 83-122.
- 521 https://doi.org/10.1016/j.earscirev.2007.04.002
- 522 Janssen, N.M.M., 2003. Mediterranean Neocomian belemnites, part 2: The Berriasian-
- 523 Valanginian boundary in southeast Spain (Río Argos, Cañada Lengua and Tornajo). Scr.
- 524 Geol. 126, 121-183.

- 525 Jenkyns, H.C., Forster, A., Schouten, S., Sinninghe Damsté, J.S., 2004. High temperatures in the
- 526 late Cretaceous Arctic Ocean. Nature 432, 888-892. https://doi.org/10.1038/nature03143
- 527 Jenkyns, H.C., Schouten-Huibers, L., Schouten, S., Sinninghe Damsté, J.S., 2012. Warm Middle
- 528 Jurassic–Early Cretaceous high-latitude sea-surface temperatures from the Southern
- 529 Ocean. Clim. Past 8, 215-226. https://doi.org/10.5194/cp-8-215-2012
- 530 Kelson, J.R., Huntington, K.W., Schauer, A.J., Saenger, C., Lechler, A.R., 2017. Toward a universal
- 531 carbonate clumped isotope calibration: Diverse synthesis and preparatory methods
- 532 suggest a single temperature relationship. Geochim. Cosmochim. Acta 197, 104-131.
- 533 https://doi.org/10.1016/j.gca.2016.10.010
- 534 Kim, S.-T., O'Neil, J.R., 1997. Equilibrium and nonequilibrium oxygen isotope effects in synthetic
- 535 carbonates. Geochim. Cosmochim. Acta 61, 3461-3475. https://doi.org/10.1016/S0016-
- 536 7037(97)00169-5
- 537 Kim, S.-T., Mucci, A., Taylor, B.E., 2007. Phosphoric acid fractionation factors for calcite and
- 538 aragonite between 25 and 75 °C: Revisited. Chem. Geol. 246, 135-146.
- 539 https://doi.org/10.1016/j.chemgeo.2007.08.005
- 540 Kim, J.-H., van der Meer, J., Schouten, S., Helmke, P., Willmott, V., Sangiorgi, F., Koç, N.,
- 541 Hopmans, E.C., Damsté, J.S.S., 2010. New indices and calibrations derived from the
- 542 distribution of crenarchaeal isoprenoid tetraether lipids: Implications for past sea surface
- 543 temperature reconstructions. Geochim. Cosmochim. Acta 74, 4639-4654.
- 544 https://doi.org/10.1016/j.gca.2010.05.027
- 545 Klett, T.R., Wandrey, C.J., Pitman, J.K., 2011. Geology and petroleum potential of the north and
- 546 east margins of the Siberian Craton, north of the Arctic Circle. Arct. Pet. Geol. 35, 413-
- 547 431. https://doi.org/10.1144/M35.27

- 548 Klug, C., Schweigert, G., Fuchs, D., Kruta, I., Tischlinger, H., 2016. Adaptations to squid-style
- 549 high-speed swimming in Jurassic belemnitids. Biol. Lett. 12, 1-5.
- 550 https://doi.org/10.1098/rsbl.2015.0877
- 551 Kump, L.R., Pollard, D., 2008. Amplification of Cretaceous warmth by biological cloud
- 552 feedbacks. Science 320, 195. https://doi.org/10.1126/science.1153883
- 553 LeGrande, A.N., Schmidt, G.A., 2006. Global gridded data set of the oxygen isotopic
- 554 composition in seawater. Geophys. Res. Lett. 33, 1-5.
- 555 https://doi.org/10.1029/2006gl026011
- 556 Lindquist, S.J., 1999. The Timan-Pechora Basin province of northwest Arctic Russia; Domanik,
- 557 Paleozoic total petroleum system. USGS Open-File Report 99-50, 1-24.
- 558 https://doi.org/10.3133/ofr9950G
- Littler, K., Robinson, S.A., Bown, P.R., Nederbragt, A.J., Pancost, R.D., 2011. High sea-surface
- temperatures during the Early Cretaceous Epoch. Nat. Geosci. 4, 169-172.
- 561 https://doi.org/10.1038/ngeo1081
- 562 Locarnini, R.A., Mishonov, A.V., Antonov, J.I., Boyer, T.P., Garcia, H.E., Baranova, O.K., Zweng,
- 563 M.M., Paver, C.R., Reagan, J.R., Johnson, D.R., Hamilton, M., Seidov, D., 2013. World
- 564 Ocean Atlas 2013, Volume 1: Temperature.
- 565 Lunt, D.J., Farnsworth, A., Loptson, C., Foster, G.L., Markwick, P., apos, Brien, C.L., Pancost, R.D.,
- 566 Robinson, S.A., Wrobel, N., 2016. Palaeogeographic controls on climate and proxy
- 567 interpretation. Clim. Past 12, 1181-1198. https://doi.org/10.5194/cp-12-1181-2016
- 568 Marshall, J.D., 1992. Climatic and oceanographic isotopic signals from the carbonate rock
- record and their preservation. Geol. Mag. 129, 143-160.
- 570 https://doi.org/10.1017/s0016756800008244
- 571 McArthur, J.M., Mutterlose, J., Price, G.D., Rawson, P.F., Ruffell, A., Thirlwall, M.F., 2004.
- 572 Belemnites of Valanginian, Hauterivian and Barremian age: Sr-isotope stratigraphy,

- 573 composition ( ${}^{87}$ Sr/ ${}^{86}$ Sr,  $\delta^{13}$ C,  $\delta^{18}$ O, Na, Sr, Mg), and palaeo-oceanography. Palaeogeogr.
- 574 Palaeoclimatol. Palaeoecol. 202, 253-272. https://doi.org/10.1016/s0031-0182(03)00638-
- 575

- 576 McArthur, J.M., Janssen, N.M.M., Reboulet, S., Leng, M.J., Thirlwall, M.F., van de Schootbrugge,
- 577 B., 2007. Palaeotemperatures, polar ice-volume, and isotope stratigraphy (Mg/Ca,  $\delta^{18}$ O,
- 578  $\delta^{13}$ C, <sup>87</sup>Sr/<sup>86</sup>Sr): The Early Cretaceous (Berriasian, Valanginian, Hauterivian). Palaeogeogr.
- 579 Palaeoclimatol. Palaeoecol. 248, 391-430. https://doi.org/10.1016/j.palaeo.2006.12.015
- 580 McConnaughey, T., 1989. <sup>13</sup>C and <sup>18</sup>O isotopic disequilibrium in biological carbonates: II. *In vitro*
- 581 simulation of kinetic isotope effects. Geochim. Cosmochim. Acta 53, 163-171.
- 582 https://doi.org/10.1016/0016-7037(89)90283-4
- 583 Meyer, K.W., Petersen, S.V., Lohmann, K.C., Winkelstern, I.Z., 2018. Climate of the Late
- 584 Cretaceous North American Gulf and Atlantic Coasts. Cretac. Res. 89, 160-173.
- 585 https://doi.org/10.1016/j.cretres.2018.03.017
- 586 Miller, K.G., 2009. Broken greenhouse windows. Nat. Geosci. 2, 465-466.
- 587 https://doi.org/10.1038/ngeo563
- 588 Muehlenbachs, K., Clayton, R.N., 1976. Oxygen isotope composition of the oceanic crust and its
- bearing on seawater. J. Geophys. Res. 81, 4365-4369.
- 590 https://doi.org/10.1029/JB081i023p04365
- 591 Muehlenbachs, K., 1998. The oxygen isotopic composition of the oceans, sediments and the
- 592 seafloor. Chem. Geol. 145, 263-273. https://doi.org/10.1016/S0009-2541(97)00147-2
- 593 Mutterlose, J., Malkoc, M., Schouten, S., Sinninghe Damsté, J.S., Forster, A., 2010. TEX<sub>86</sub> and
- 594 stable  $\delta^{18}$ O paleothermometry of early Cretaceous sediments: Implications for belemnite
- 595 ecology and paleotemperature proxy application. Earth Planet. Sci. Lett. 298, 286–298.
- 596 https://doi.org/10.1016/j.epsl.2010.07.043

- 597 Mutterlose, J., Malkoc, M., Schouten, S., Sinninghe Damsté, J.S., 2012. Reconstruction of
- 598 vertical temperature gradients in past oceans Proxy data from the Hauterivian–early
- 599 Barremian (Early Cretaceous) of the Boreal Realm. Palaeogeogr. Palaeoclimatol.
- 600 Palaeoecol. 363-364, 135-143. https://doi.org/10.1016/j.palaeo.2012.09.006
- Naafs, B.D.A., Pancost, R.D., 2016. Sea-surface temperature evolution across Aptian Oceanic
- 602 Anoxic Event 1a. Geology 44, 959-962. https://doi.org/10.1130/g38575.1
- 603 Nunn, E.V., Price, G.D., Gröcke, D.R., Baraboshkin, E.Y., Leng, M.J., Hart, M.B., 2010. The
- 604 Valanginian positive carbon isotope event in Arctic Russia: Evidence from terrestrial and
- 605 marine isotope records and implications for global carbon cycling. Cretac. Res. 31, 577-
- 606 592. https://doi.org/10.1016/j.cretres.2010.07.007
- 607 O'Brien, C.L., Robinson, S.A., Pancost, R.D., Sinninghe Damsté, J.S., Schouten, S., Lunt, D.J.,
- Alsenz, H., Bornemann, A., Bottini, C., Brassell, S.C., Farnsworth, A., Forster, A., Huber,
- 609 B.T., Inglis, G.N., Jenkyns, H.C., Linnert, C., Littler, K., Markwick, P., McAnena, A.,
- 610 Mutterlose, J., Naafs, B.D.A., Püttmann, W., Sluijs, A., van Helmond, N.A.G.M., Vellekoop,
- 511 J., Wagner, T., Wrobel, N.E., 2017. Cretaceous sea-surface temperature evolution:
- 612 Constraints from TEX<sub>86</sub> and planktonic foraminiferal oxygen isotopes. Earth-Sci. Rev. 172,
- 613 224-247. https://doi.org/10.1016/j.earscirev.2017.07.012
- 614 O'Connor, L.K., Robinson, S.A., Naafs, B.D.A., Jenkyns, H.C., Henson, S., Clarke, M., Pancost,
- 615 R.D., 2019. Late Cretaceous temperature evolution of the southern high latitudes: a TEX<sub>86</sub>
- 616 perspective. Paleoceanography and Paleoclimatology 34, 436-454.
- 617 https://doi.org/10.1029/2018pa003546
- 618 Passey, B.H., Henkes, G.A., 2012. Carbonate clumped isotope bond reordering and
- 619 geospeedometry. Earth Planet. Sci. Lett. 351-352, 223-236.
- 620 https://doi.org/10.1016/j.epsl.2012.07.021

- 621 Pekar, S.F., DeConto, R.M., 2006. High-resolution ice-volume estimates for the early Miocene:
- 622 Evidence for a dynamic ice sheet in Antarctica. Palaeogeogr. Palaeoclimatol. Palaeoecol.
- 623 231, 101-109. https://doi.org/10.1016/j.palaeo.2005.07.027
- 624 Petersen, S.V., Schrag, D.P., 2015. Antarctic ice growth before and after the Eocene-Oligocene
- 625 transition: New estimates from clumped isotope paleothermometry. Paleoceanography
- 626 30, 1305-1317. https://doi.org/10.1002/2014PA002769
- 627 Petersen, S.V., Tabor, C.R., Lohmann, K.C., Poulsen, C.J., Meyer, K.W., Carpenter, S.J., Erickson,
- 528 J.M., Matsunaga, K.K.S., Smith, S.Y., Sheldon, N.D., 2016. Temperature and salinity of the
- 629 Late Cretaceous Western Interior Seaway. Geology 44, 903-906.
- 630 https://doi.org/10.1130/g38311.1
- 631 Petersen, S.V., Defliese, W.F., Saenger, C., Daëron, M., Huntington, K.W., John, C.M., Kelson,
- J.R., Coleman, A.S., Kluge, T., Olack, G.A., Schauer, A.J., Bajnai, D., Bonifacie, M.,
- Breitenbach, S.F., Fiebig, J., Fernandez, A.B., Henkes, G.A., Hodell, D., Katz, A., Kele, S.,
- 634 Lohmann, K.C., Passey, B.H., Peral, M.Y., Petrizzo, D.A., Rosenheim, B.E., Tripati, A.,
- 635 Venturelli, R., Young, E.D., Winkelstern, I.Z., 2019. Effects of improved <sup>17</sup>O correction on
- 636 interlaboratory agreement in clumped isotope calibrations, estimates of mineral-specific
- 637 offsets, and temperature dependence of acid digestion fractionation. Geochem. Geophys.

638 Geosyst. 20, 3495-3519. https://doi.org/10.1029/2018GC008127

- Poulsen, C.J., Pollard, D., White, T.S., 2007. General circulation model simulation of the  $\delta^{18}$ O
- 640 content of continental precipitation in the middle Cretaceous: A model-proxy
- 641 comparison. Geology 35, 199-202. https://doi.org/10.1130/G23343A.1
- 642 Price, G.D., 1999. The evidence and implications of polar ice during the Mesozoic. Earth-Sci.
- 643 Rev. 48, 183-210. https://doi.org/10.1016/s0012-8252(99)00048-3

- 644 Price, G.D., Ruffell, A.H., Jones, C.E., Kalin, R.M., Mutterlose, J., 2000. Isotopic evidence for
- 645 temperature variation during the early Cretaceous (late Ryazanian-mid-Hauterivian). J.
- 646 Geol. Soc. 157, 335-343. https://doi.org/10.1144/jgs.157.2.335
- 647 Price, G.D., Nunn, E.V., 2010. Valanginian isotope variation in glendonites and belemnites from
- 648 Arctic Svalbard: Transient glacial temperatures during the Cretaceous greenhouse.
- 649 Geology 38, 251-254. https://doi.org/10.1130/g30593.1
- 650 Price, G.D., Passey, B.H., 2013. Dynamic polar climates in a greenhouse world: Evidence from
- 651 clumped isotope thermometry of Early Cretaceous belemnites. Geology 41, 923-926.
- 652 https://doi.org/10.1130/g34484.1
- 653 Price, G.D., Hart, M.B., Wilby, P.R., Page, K.N., 2015. Isotopic analysis of Jurassic (Callovian)
- 654 mollusks from the Christian Malford lagerstätte (UK): Implications for ocean water
- temperature estimates based on belemnoids. Palaios 30, 645-654.
- 656 https://doi.org/10.2110/palo.2014.106
- 657 Price, G.D., Janssen, N.M.M., Martinez, M., Company, M., Vandevelde, J.H., Grimes, S.T., 2018.
- 658 A high-resolution belemnite geochemical analysis of Early Cretaceous (Valanginian-
- Hauterivian) environmental and climatic perturbations. Geochem. Geophys. Geosyst. 19,
- 660 3832-3843. https://doi.org/10.1029/2018gc007676
- 661 Pucéat, E., Lecuyer, C., Sheppard, S.M.F., Dromart, G., Reboulet, S., Grandjean, P., 2003.
- 662 Thermal evolution of Cretaceous Tethyan marine waters inferred from oxygen isotope
- 663 composition of fish tooth enamels. Paleoceanography 18, 1029.
- 664 https://doi.org/10.1029/2002pa000823
- Railsback, L.B., Anderson, T.F., Ackerly, S.C., Cisne, J.L., 1989. Paleoceanographic modeling of
- temperature-salinity profiles from stable isotopic data. Paleoceanography 4, 585-591.
- 667 https://doi.org/10.1029/PA004i005p00585

- 668 Rawson, P.F., 1973. Lower Cretaceous (Ryazanian-Barremian) marine connections and
- 669 cephalopod migrations between the Tethyan and Boreal Realms, in: Casey, R., Rawson,
- 670 P.F. (Eds.), The Boreal Lower Cretaceous. Seel House Press, Liverpool, pp. 131-144.
- 671 Reboulet, S., Szives, O., Aguirre-Urreta, B., Barragán, R., Company, M., Frau, C., Kakabadze,
- 672 M.V., Klein, J., Moreno-Bedmar, J.A., Lukeneder, A., Pictet, A., Ploch, I., Raisossadat, S.N.,
- 673 Vašíček, Z., Baraboshkin, E.J., Mitta, V.V., 2018. Report on the 6th International Meeting
- of the IUGS Lower Cretaceous Ammonite Working Group, the Kilian Group (Vienna,
- 675 Austria, 20th August 2017). Cretac. Res. 91, 100-110.
- 676 https://doi.org/10.1016/j.cretres.2018.05.008
- 677 Reicherter, K., Wiedmann, J., Herbin, J.P., 1996. Distribution of organic-rich sediments in
- 678 Subbetic sections during the Aptian-Turonian (Betic Cordillera, Southern Spain). Rev. Soc.679 Geol. Esp. 9, 75-88.
- 680 Rogov, M.A., Ershova, V.B., Shchepetova, E.V., Zakharov, V.A., Pokrovsky, B.G., Khudoley, A.K.,
- 681 2017. Earliest Cretaceous (late Berriasian) glendonites from Northeast Siberia revise the
- timing of initiation of transient Early Cretaceous cooling in the high latitudes. Cretac. Res.
- 683 71, 102-112. https://doi.org/10.1016/j.cretres.2016.11.011
- 684 Ryb, U., Eiler, J.M., 2018. Oxygen isotope composition of the Phanerozoic ocean and a possible
- solution to the dolomite problem. Proc. Natl. Acad. Sci. U.S.A. 115, 6602-6607.
- 686 https://doi.org/10.1073/pnas.1719681115
- 687 Sælen, G., 1989. Diagenesis and construction of the belemnite rostrum. Palaeontology 32, 765688 797.
- 689 Sagoo, N., Valdes, P., Flecker, R., Gregoire, L.J., 2013. The Early Eocene equable climate
- 690 problem: Can perturbations of climate model parameters identify possible solutions?
- 691 Philos. T. R. Soc. A 371, 20130123. https://doi.org/10.1098/rsta.2013.0123

- 692 Schmidt, G.A., Mysak, L.A., 1996. Can increased poleward oceanic heat flux explain the warm
- 693 Cretaceous climate? Paleoceanography 11, 579-593. https://doi.org/10.1029/96pa01851
- van de Schootbrugge, B., Föllmi, K.B., Bulot, L.G., Burns, S.J., 2000. Paleoceanographic changes
- 695 during the early Cretaceous (Valanginian-Hauterivian): evidence from oxygen and carbon
- 696 stable isotopes. Earth Planet. Sci. Lett. 181, 15-31. https://doi.org/10.1016/S0012-
- 697 821X(00)00194-1
- 698 Scotese, C.R., 2014. Atlas of Early Cretaceous Paleogeographic Maps, PALEOMAP Atlas for
- ArcGIS, volume 2, The Cretaceous, Maps 23-31, Mollweide Projection, Evanston, IL, USA.
- 700 Shackleton, N.J., Kennett, J.P., 1975. Paleotemperature history of the Cenozoic and the
- initiation of antarctic glaciation: oxygen and carbon isotope analyses in DSDP sites 277,
- 702 279, and 281. Deep Sea Drilling Project Initial Reports 29, 743-755.
- 703 https://doi.org/10.2973/dsdp.proc.29.117.1975
- 704 Shulgina, N.I., Burdykina, M.D., Basov, V.A., Arhus, N., 1994. Distribution of ammonites,
- foraminifera and dinoflagellate cysts in the Lower Cretaceous reference sections of the
- 706 Khatanga Basin, and Boreal Valanginian biogeography. Cretac. Res. 15, 1-16.
- 707 https://doi.org/10.1006/cres.1994.1001
- 708 Słowakiewicz, M., Tucker, M.E., Vane, C.H., Harding, R., Collins, A., Pancost, R.D., 2015. Shale-
- gas potential of the mid-Carboniferous Bowland-Hodder Unit in the Cleveland Basin
- 710 (Yorkshire), central Britain. J. Pet. Geol 38, 59-75. https://doi.org/10.1111/jpg.12598
- 711 Spicer, R.A., Ahlberg, A., Herman, A.B., Hofmann, C.-C., Raikevich, M., Valdes, P.J., Markwick,
- 712 P.J., 2008. The Late Cretaceous continental interior of Siberia: A challenge for climate
- 713 models. Earth Planet. Sci. Lett. 267, 228-235. https://doi.org/10.1016/j.epsl.2007.11.049
- 514 Spicer, R.A., Herman, A.B., 2010. The Late Cretaceous environment of the Arctic: A quantitative
- reassessment based on plant fossils. Palaeogeogr. Palaeoclimatol. Palaeoecol. 295, 423-
- 716 442. https://doi.org/10.1016/j.palaeo.2010.02.025

- 717 Stevens, K., Mutterlose, J., Schweigert, G., 2014. Belemnite ecology and the environment of the
- 718 Nusplingen Plattenkalk (Late Jurassic, southern Germany): Evidence from stable isotope
- 719 data. Lethaia 47, 512-523. https://doi.org/10.1111/let.12076
- 720 Super, J.R., Chin, K., Pagani, M., Li, H., Tabor, C., Harwood, D.M., Hull, P.M., 2018. Late
- 721 Cretaceous climate in the Canadian Arctic: Multi-proxy constraints from Devon Island.
- 722 Palaeogeogr. Palaeoclimatol. Palaeoecol. 504, 1-22.
- 723 https://doi.org/10.1016/j.palaeo.2018.03.004
- 724 Tarduno, J.A., Brinkman, D.B., Renne, P.R., Cottrell, R.D., Scher, H., Castillo, P., 1998. Evidence
- for extreme climatic warmth from Late Cretaceous Arctic vertebrates. Science 282, 2241-
- 726 2244. https://doi.org/10.1126/science.282.5397.2241
- 727 Tierney, J.E., Tingley, M.P., 2014. A Bayesian, spatially-varying calibration model for the TEX<sub>86</sub>
- 728 proxy. Geochim. Cosmochim. Acta 127, 83-106.
- 729 https://doi.org/10.1016/j.gca.2013.11.026
- 730 Upchurch, G.R., Kiehl, J., Shields, C., Scherer, J., Scotese, C., 2015. Latitudinal temperature
- 731 gradients and high-latitude temperatures during the latest Cretaceous: Congruence of
- 732 geologic data and climate models. Geology 43, 683-686.
- 733 https://doi.org/10.1130/g36802.1
- 734 Veizer, J., 1974. Chemical diagenesis belemnite shells possible consequences for
- paleotemperature determinations. Neues Jahrb. Geol. Palaontol. Abhand. 147, 91-111.
- 736 Veizer, J., Prokoph, A., 2015. Temperatures and oxygen isotopic composition of Phanerozoic
- 737 oceans. Earth-Sci. Rev. 146, 92-104. https://doi.org/10.1016/j.earscirev.2015.03.008
- 738 Vickers, M.L., Price, G.D., Jerrett, R.M., Watkinson, M., 2016. Stratigraphic and geochemical
- 739 expression of Barremian–Aptian global climate change in Arctic Svalbard. Geosphere 12,
- 740 1594-1605. https://doi.org/10.1130/ges01344.1

- 741 Vickers, M.L., Bajnai, D., Price, G.D., Linckens, J., Fiebig, J., 2019. Southern high latitude warmth
- 742 during Jurassic–Cretaceous: New evidence from clumped isotope thermometry. Geology
- 743 47, 724-728. https://doi.org/10.1130/G46263.1
- 744 Voigt, S., Wilmsen, M., Mortimore, R.N., Voigt, T., 2003. Cenomanian palaeotemperatures
- 745 derived from the oxygen isotopic composition of brachiopods and belemnites: evaluation
- of Cretaceous palaeotemperature proxies. Int. J. Earth Sci. 92, 285-299.
- 747 https://doi.org/10.1007/s00531-003-0315-1
- 748 Wacker, U., Fiebig, J., Tödter, J., Schöne, B.R., Bahr, A., Friedrich, O., Tütken, T., Gischler, E.,
- Joachimski, M.M., 2014. Empirical calibration of the clumped isotope paleothermometer
- vsing calcites of various origins. Geochim. Cosmochim. Acta 141, 127-144.
- 751 https://doi.org/10.1016/j.gca.2014.06.004
- 752 Wallmann, K., 2004. Impact of atmospheric CO<sub>2</sub> and galactic cosmic radiation on Phanerozoic
- 753 climate change and the marine  $\delta^{18}$ O record. Geochem. Geophys. Geosyst. 5, 1-29.
- 754 https://doi.org/10.1029/2003gc000683
- 755 Wang, Y., Huang, C., Sun, B., Quan, C., Wu, J., Lin, Z., 2014. Paleo-CO<sub>2</sub> variation trends and the
- 756 Cretaceous greenhouse climate. Earth-Sci. Rev. 129, 136-147.
- 757 https://doi.org/10.1016/j.earscirev.2013.11.001
- 758 White, T., Gonzalez, L., Ludvigson, G., Poulsen, C., 2001. Middle Cretaceous greenhouse
- hydrologic cycle of North America. Geology 29, 363-366. https://doi.org/10.1130/0091-
- 760 7613(2001)029<0363:Mcghco>2.0.Co;2
- 761 Wierzbowski, H., Rogov, M.A., Matyja, B.A., Kiselev, D., Ippolitov, A., 2013. Middle–Upper
- 762 Jurassic (Upper Callovian–Lower Kimmeridgian) stable isotope and elemental records of
- the Russian Platform: Indices of oceanographic and climatic changes. Glob. Planet.
- 764 Change 107, 196-212. https://doi.org/10.1016/j.gloplacha.2013.05.011

- 765 Wierzbowski, H., Bajnai, D., Wacker, U., Rogov, M.A., Fiebig, J., Tesakova, E.M., 2018. Clumped
- isotope record of salinity variations in the Subboreal Province at the middle–late Jurassic
- transition. Glob. Planet. Change 167, 172-189.
- 768 https://doi.org/10.1016/j.gloplacha.2018.05.014
- 769 Witkowski, C.R., Weijers, J.W.H., Blais, B., Schouten, S., Sinninghe Damsté, J.S., 2018. Molecular
- fossils from phytoplankton reveal secular *p*CO<sub>2</sub> trend over the Phanerozoic. Sci. Adv. 4,

771 eaat4556. https://doi.org/10.1126/sciadv.aat4556

- Young, A., Flament, N., Maloney, K., Williams, S., Matthews, K., Zahirovic, S., Müller, R.D., 2019.
- Global kinematics of tectonic plates and subduction zones since the late Paleozoic Era.
- 774 Geosci. Front. 10, 989-1013. https://doi.org/10.1016/j.gsf.2018.05.011
- Zakharov, V.A., Bogomolov, Y.I., Il'ina, V.I., Konstantinov, A.G., Kurushin, N.I., Lebedeva, N.K.,
- 776 Meledina, S.V., Nikitenko, B.L., Sobolev, E.S., Shurygin, B.N., 1997. Boreal zonal standard
- and biostratigraphy of the Siberian Mesozoic. Russ. Geol. Geophys. 38, 965-993.
- Zeebe, R.E., 1999. An explanation of the effect of seawater carbonate concentration on
- foraminiferal oxygen isotopes. Geochim. Cosmochim. Acta 63, 2001-2007.
- 780 https://doi.org/10.1016/S0016-7037(99)00091-5
- 781 Zeebe, R.E., 2001. Seawater pH and isotopic paleotemperatures of Cretaceous ocean.
- 782 Palaeogeogr. Palaeoclimatol. Palaeoecol. 170, 49-57. https://doi.org/10.1016/S0031-
- 783 0182(01)00226-7
- 784 Zhou, J., Poulsen, C.J., Pollard, D., White, T.S., 2008. Simulation of modern and middle
- 785 Cretaceous marine  $\delta^{18}$ O with an ocean-atmosphere general circulation model.
- 786 Paleoceanography 23, PA3223. https://doi.org/10.1029/2008pa001596
- 787 Zhu, J., Poulsen, C.J., Tierney, J.E., 2019. Simulation of Eocene extreme warmth and high climate
- sensitivity through cloud feedbacks. Sci. Adv. 5, eaax1874.
- 789 https://doi.org/10.1126/sciadv.aax1874

# 791 Figures



**Fig. 1.** Early Cretaceous palaeogeographic reconstruction with locations of the discussed study sites. Map modified after Scotese (2014). Blue circles = data from this study; green squares = location of published Early Cretaceous TEX<sub>86</sub> data (Littler et al. 2011; Jenkyns et al. 2012). The locations of additional published  $\Delta_{47}$ -based temperature data are marked with a yellow square (Price and Passey, 2013) and a red square (Vickers et al. 2019). The palaeolatitude estimates are consistent with Young et al. (2019) that are used for Figs 3 and 4.



**Fig. 2.** Biostratigraphic correlation of the Early Cretaceous Tethyan (Reboulet et al., 2018) sub-Boreal and Boreal (Gradstein et al. 2012; Nunn et al. 2010; Shulgina et al., 1994; Zakharov et al., 1997; Baraboshkin, 2004) ammonite schemes. The green shaded area indicates the position of sampled Valanginian zones for Tethyan (Caravaca, Spain), Sub-Boreal (Speeton), and Boreal sites (Khatanga Basin and Pechora Basin). The ammonite range of additional Valanginian  $\Delta_{47}$ data from the Yatria River is shown (Price and Passey 2013). Early Cretaceous southern high latitude data shown on Figs 3 and 4 have less constrained biostratigraphy (Vickers et al., 2019).



806 **Fig. 3.** Early Cretaceous (Valanginian) meridional temperature reconstruction. Mean annual

- calibration (Kim et al., 2010). Dark blue circles show mean Δ<sub>47</sub>-based temperatures from this
- 810 study with ± uncertainties corresponding to the standard deviation from individual belemnites
- 811 (light blue circles). Additional  $\Delta_{47}$  data of Vickers et al., (2019) (for the Early Cretaceous) and
- 812 Price and Passey (2013) (Valanginian) were converted to temperatures using the synthetic
- 813 calcite calibration of Petersen et al. (2019). Early Cretaceous data are compared with sea
- 814 surface temperatures from the Early Cretaceous (Valanginian) GCM with 4x pre-industrial pCO<sub>2</sub>

surface temperature observations from the World Ocean Atlas (Locarnini et al., 2013).

<sup>808</sup> Valanginian TEX<sub>86</sub> temperatures (Littler et al., 2011) were recalculated using the TEX<sub>86</sub><sup>H</sup>

- 815 (Lunt et al., 2016) a mid-Cretaceous GCM with 12x pre-industrial *p*CO<sub>2</sub> (Poulsen et al., 2007) and
- a Late Cretaceous GCM with 8x pre-industrial *p*CO<sub>2</sub> (Donnadieu et al., 2016). Thermal gradients
- 817 of the simulations have been calculated from an average over the longitudes including the
- 818 South Atlantic sector and the Tethyan area (see Donnadieu et al., 2016). A version of this plot
- 819 where  $\Delta_{47}$ -based temperatures are calculated using the Wacker et al. (2014) equation is shown
- 820 in the Supplementary Information.



Fig. 4. Early Cretaceous (Valanginian) meridional seawater oxygen isotope gradient. Modern gridded mean annual  $\delta^{18}O_{sw}$  values from LeGrande and Schmidt (2006).  $\delta^{18}O_{sw}$  (‰ SMOW) calculated using the Kim and O'Neil (1997) equation (see Supplementary Figure 2 for Coplen (2007) equation) with additional Valanginian data derived from Price and Passey (2013) and Vickers et al. (2019). Dark blue circles are mean estimates and ± uncertainties are standard deviations. Light blue circles are estimates from individual belemnites. Modelled mid Cretaceous mean annual zonal average of  $\delta^{18}O_{sw}$  after Zhou, et al. (2008).

**Table 1.** Clumped and bulk isotopic composition of Early Cretaceous belemnites

Sample	Taxonomy	Location	N	δ <sup>13</sup> C (‰ VPDB)	δ <sup>18</sup> Ο (‰ VPDB)	∆47 (RFAC) (‰)	Temperature (°C)	δ <sup>18</sup> O <sub>sw</sub> (‰ SMOW) Coplen (2007)	$\delta^{18}O_{sw}$ (‰ SMOW) Kim and O'Neil (1997)
KH18-10.50	Acroteuthis sp.	Boyarka	5	0.22	-1.55	0.707 (±0.005)	19 (±1)	-2.1 (±0.3)	-0.6 (±0.3)
KH18-11.20	indet.	Boyarka	5	1.12	-0.48	0.701 (±0.006)	21 (±2)	-0.6 (±0.4)	0.8 (±0.4)
KH18-27.00	Lagonibelus sp.	Boyarka	6	0.96	0.03	0.713 (±0.006)	17 (±2)	-0.9 (±0.4)	0.5 (±0.4)
KH18-2.85	indet.	Boyarka	5	0.38	0.07	0.699 (±0.009)	21 (±3)	0.0 (±0.6)	1.5 (±0.6)
KH18-7.10	Pachyteuthis sp.	Boyarka	5	0.60	-2.19	0.709 (±0.007)	18 (±2)	-2.9 (±0.5)	-1.5 (±0.5)
YCL214-031	<i>Berriasibelus</i> sp.	Caravaca	6	-1.25	-0.57	0.670 (±0.012)	32 (±5)	1.4 (±0.9)	2.9 (±0.9)
YG14-015	<i>Duvalia</i> sp.	Caravaca	3	0.50	0.37	0.671 (±0.007)	31 (±3)	2.3 (±0.5)	3.8 (±0.5)
YP14-005	<i>Hibolithes</i> sp.	Caravaca	5	1.74	-0.41	0.691 (±0.013)	24 (±4)	0.1 (±0.9)	1.6 (±0.9)
YP14-001	Duvalia cf. lata	Caravaca	6	-0.29	-0.50	0.690 (±0.009)	25 (±3)	0.1 (±0.6)	1.6 (±0.7)
YP14-014	Duvalia binervia	Caravaca	4	0.95	-0.27	0.691 (±0.009)	24 (±3)	0.3 (±0.6)	1.7 (±0.6)
PC7-B1	Pachyteuthis sp.	Izhma	7	-0.49	0.21	0.735 (±0.004)	10 (±1)	-2.1 (±0.3)	-0.8 (±0.3)
PC7-B2	Pachyteuthis sp.	Izhma	6	0.19	0.56	0.700 (±0.003)	21 (±1)	0.5 (±0.2)	1.9 (±0.2)

PC9-G23	indet.	Izhma	5	-0.79	0.52	0.702 (±0.007)	20 (±2)	0.3 (±0.5)	1.7 (±0.5)
PC9-G8	Acroteuthis sp.	Izhma	7	1.16	0.98	0.688 (±0.005)	25 (±2)	1.7 (±0.3)	3.2 (±0.3)
D2E	Acroteuthis sp.	Speeton	2	-0.46	-0.36	0.690 (±0.007)	25 (±2)	0.3 (±0.5)	1.7 (±0.5)
D3D	Acroteuthis sp.	Speeton	2	-0.09	-0.21	0.680 (±0.020)	28 (±7)	1.1 (±1.4)	2.5 (±1.4)
D4A	Acroteuthis sp.	Speeton	6	0.51	0.41	0.683 (±0.004)	27 (±1)	1.5 (±0.3)	3.0 (±0.3)
SP 1181	Acroteuthis sp.	Speeton	5	-0.12	-0.60	0.711 (±0.004)	18 (±1)	-1.4 (±0.3)	0.0 (±0.3)
SP 1297	Acroteuthis sp.	Speeton	4	0.60	-0.89	0.699 (±0.005)	22 (±2)	-0.9 (±0.3)	0.5 (±0.3)
SP 1522C	Acroteuthis sp.	Speeton	5	0.60	-0.36	0.688 (±0.005)	25 (±2)	0.4 (±0.3)	1.9 (±0.3)

829 The standard error of the carbonate  $\delta^{13}$ C and  $\delta^{18}$ O values is 0.01‰. The ± uncertainty in the

830  $\Delta_{47 (RFAC)}$  values represents the (external) standard error of 2–7 replicate analyses, multiplied by

the *t*-value that corresponds to the number of replicates (68.2% confidence interval). The

832  $\Delta_{47 (RFAC)}$  values were converted to temperatures using synthetic calcite calibration (Petersen et

al., 2019) as discussed in the text (Data S1). The error in the calculated temperatures and  $\delta^{18}O_{sw}$ 

834 correspond to the standard error of the  $\Delta_{47 (RFAC)}$  values.

835	Table 2. Mean	seawater ten	peratures and	$\delta^{18} O_{sw}$ fo	r the location	ons in this study.
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Location	Palaeolatitude Number o		Mean seawater	Mean δ <sup>18</sup> Osw	Mean δ <sup>18</sup> Osw
		belemnites	temperature	(‰ SMOW)	(‰ SMOW) Kim
			(°C)	Coplen (2007)	and O'Neil
					(1997)
Caravaca	24° N	5	27 (±4)	0.8 (±1.1)	2.3 (±1.2)
Speeton	40° N	6	24 (±4)	0.1 (±1.2)	1.6 (±1.2)
Izhma	59° N	4	19 (±7)	0.1 (±1.7)	1.5 (±1.7)
Boyarka	74° N	5	19 (±2)	-1.3 (±1.4)	0.1 (±1.4)

836 The ± uncertainties for the mean temperatures are calculated using the standard deviation of

837 the  $\Delta_{47 (RFAC)}$  values of the individual belemnites (Table 1). This uncertainty was combined with

838 the standard deviation of the  $\delta^{18}$ O values of the individual belemnites to calculate the ±

839 uncertainties for the mean  $\delta^{18}O_{sw}$  values. Palaeolatitude estimates are from Young et al. (2019).