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1 Southern high latitude warmth during the Jurassic–Cretaceous:  
2 New evidence from clumped isotope thermometry

3 **Madeleine L. Vickers<sup>1</sup>, David Bajnai<sup>2</sup>, Gregory D. Price<sup>3</sup>, Jolien Linckens<sup>2</sup>, Jens Fiebig<sup>2</sup>**

4 <sup>1</sup> Department of Geosciences and Natural Resource Management, University of Copenhagen, 1350  
5 Copenhagen, Denmark

6 <sup>2</sup> Institute of Geosciences, Goethe University Frankfurt, 60438 Frankfurt am Main, Germany

7 <sup>3</sup> School of Geography, Earth & Environmental Sciences, University of Plymouth, PL4 8AA  
8 Plymouth, United Kingdom

9 **ABSTRACT**

10 In order to understand the climate dynamics of the Mesozoic greenhouse world, it is vital to  
11 determine paleotemperatures from higher latitudes. For the Jurassic and Cretaceous climate, there  
12 are significant discrepancies between different proxies and between proxy data and climate models.  
13 We determined paleotemperatures from Late Jurassic and Early Cretaceous belemnites using the  
14 carbonate clumped isotope paleothermometer and compared these values to temperatures derived  
15 from TEX<sub>86</sub> and other proxies. From our analyses, we infer an average temperature of ca. 25 °C for  
16 the upper part of the water column of the Southern Atlantic Ocean. Our data imply that for mid to  
17 high latitudes, climate models underestimate marine temperatures by >5 °C and, therefore, the  
18 amount of warming that would accompany an increase in atmospheric CO<sub>2</sub> of more than 4x pre-  
19 industrial levels, as is projected for the near future.

20 **INTRODUCTION**

21 Modern anthropogenic CO<sub>2</sub> production has resulted in rapid climate change, with near-  
22 surface air temperatures in the high latitude regions rising at ca. twice the global average rate  
23 (Screen and Simmonds, 2010). Predictions of how global and polar temperatures will change over

24 the next few decades in response to continued CO<sub>2</sub> release may be improved by studying past  
25 climate response to elevated CO<sub>2</sub> levels. The Late Jurassic to Early Cretaceous (164 to 100 million  
26 years ago) was characterized by extremely high but variable levels of atmospheric CO<sub>2</sub> (from ca. 2x  
27 to 8x pre-industrial levels; Wang et al., 2014; Foster et al., 2017), yet reconstructions of marine  
28 temperatures, particularly for the high latitudes, are contradictory (e.g., Huber et al., 1995; Price and  
29 Gröcke, 2002; Bice et al., 2003; Poulsen, 2004; Jenkyns et al., 2012; Price and Passey, 2013;  
30 O'Brien et al., 2017).

31         The stable oxygen isotope composition of the carbonate remains of marine organisms is the  
32 most extensively used temperature proxy, yet high-latitude sea-surface temperatures (SST) derived  
33 from independent organic geochemical paleothermometers, i.e., TEX<sub>86</sub>, may be ca. 10 °C warmer  
34 than δ<sup>18</sup>O-based temperature reconstructions (e.g., Mutterlose et al., 2010; O'Brien et al., 2012) and  
35 up to 6 °C warmer than general circulation model (GCM) predictions (Price and Passey, 2013).  
36 These differences have led some authors to suggest that the high TEX<sub>86</sub> SST estimates are too  
37 warm (Hollis et al., 2009; Meyer et al., 2018), and there is an ongoing debate as to which  
38 calibration is appropriate for applications of the TEX<sub>86</sub> proxy at specific regions and different  
39 intervals of the geologic record (Kim et al., 2012; Taylor et al., 2013). Conversely, δ<sup>18</sup>O-based  
40 paleotemperature reconstructions rely on several assumptions, among which is the oxygen isotope  
41 composition of the seawater (δ<sup>18</sup>O<sub>sw</sub>; Huber et al., 1995; Price and Gröcke, 2002; Bice et al., 2003),  
42 and the accuracy of these assumptions still needs to be verified. If the interpretation of warm sub-  
43 polar paleo-ocean temperatures can be confirmed, they imply that past and future polar warming  
44 may be much greater (i.e., >5 °C) than indicated by climate models. Furthermore, such warm  
45 temperatures test the veracity of claims of Early to mid-Cretaceous polar ice, in particular from  
46 those studies deriving data from locations distal to the poles (Miller, 2009).

47 Deep Sea Drilling Project Site 511, on the Falkland Plateau (51°00.28'S, 46°58.30'W), is  
48 particularly well suited for studying Jurassic and Cretaceous climate due to its abundant,  
49 exceptionally preserved macrofossils, including belemnites (Jeletzky, 1983; Price and Sellwood,  
50 1997; Price and Gröcke, 2002). The Falkland Plateau was located at approximately 53 °S during the  
51 Late Jurassic–Early Cretaceous (Scotese, 2014; Fig. 1). Mean annual temperatures derived from  
52 GCMs for the Late Jurassic and Early Cretaceous indicate that the temperatures of the Falkland  
53 Plateau region (avg. 10–22 °C) are representative of similar southern hemisphere paleolatitudes  
54 (Lunt et al., 2016). Earlier research at Site 511 used the TEX<sub>86</sub><sup>H</sup> paleotemperature proxy to suggest  
55 that warm sea-surface conditions (26–35 °C) existed during the Late Jurassic–Early Cretaceous  
56 interval (Jenkyns et al., 2012). These paleotemperatures are consistently warmer than  
57 paleotemperature estimates based on  $\delta^{18}\text{O}_{\text{belemnite}}$ , assuming a  $\delta^{18}\text{O}_{\text{sw}}$  of -1‰ SMOW (11–21 °C;  
58 Price and Gröcke, 2002). Another study, undertaken on Barremian to Aptian sediments from two  
59 outcrops in northern Germany, also shows that  $\delta^{18}\text{O}_{\text{belemnite}}$ -derived paleotemperatures (12–16 °C)  
60 are consistently cooler than TEX<sub>86</sub>-based estimates (26–32 °C; Mutterlose et al., 2010). Jenkyns et  
61 al. (2012) argue that the offset is due to TEX<sub>86</sub> recording sea surface temperatures, whereas  
62 belemnites record temperatures from deeper water, possibly from below the thermocline.

63 In this study, we apply the carbonate clumped isotope paleothermometer to exceptionally  
64 well-preserved belemnite rostra from Site 511. This proxy provides seawater temperature estimates  
65 independent of  $\delta^{18}\text{O}_{\text{sw}}$  (Price and Passey, 2013; Wierzbowski et al., 2018). In addition to  
66 constraining high latitude temperatures, we set out to resolve the uncertainties associated with  
67 previous  $\delta^{18}\text{O}$ -based belemnite temperature reconstructions.

## 68 MATERIALS AND METHODS

### 69 Stratigraphy and samples

70 The lithology of the sampled section of Site 511 consists of grey-black, thinly laminated  
71 mudstones and soft, grey claystones, which were deposited in a periodically anoxic, low-energy,  
72 shallow (< 400 m) basin (Basov and Krasheninnikov, 1983; Jeletzky, 1983).

73 A geothermal gradient of 7.4 °C/100 m has been determined (Langseth and Ludwig, 1983)  
74 at Site 511, thus, for the samples analyzed in this study, we can estimate a maximum burial  
75 temperature of ca. 50 °C. At elevated temperatures, diffusion of carbon and oxygen isotopes in the  
76 carbonate mineral lattice may reset the initial bond-ordering (e.g., Henkes et al., 2014). However,  
77 theoretical calculations based on laboratory experiments provide evidence that solid-state diffusion,  
78 even in wet and high-pressure conditions, is insignificant below 100 °C burial temperatures on a  
79 timescale of 100–160 Ma (Passey and Henkes, 2012). Thus, it is unlikely that the belemnite rostra  
80 analyzed in this study were affected by solid-state reordering.

81 Eleven belemnites (*Belemnopsis* sp.) were selected for maximum stratigraphic coverage and  
82 were geochemically screened to include the best-preserved samples, as indicated by available trace  
83 element concentrations (i.e., low Fe and Mn; high Sr and Mg concentrations; Price and Gröcke,  
84 2002; [Supplemental Information](#)) and cathodoluminescence analyses (Figure 5 of Price and  
85 Sellwood, 1997). Subsamples were derived avoiding the margins and apical zone, as these areas are  
86 much more susceptible to diagenetic overgrowth and cementation, respectively than the rest of the  
87 belemnite (e.g., Ullmann et al., 2015). In addition, we made electron backscatter diffraction (EBSD)  
88 analyses and secondary electron microscopy (SEM-BSE) images of selected rostra at the Goethe  
89 University Frankfurt ([Supplemental Information](#)).

## 90 **Clumped Isotope Analyses**

91 Carbonate digestion (90 °C), CO<sub>2</sub> purification (cryotrap and GC) and subsequent  
92 measurement procedures (ThermoFisher MAT 253) are identical to the techniques described in  
93 Wierzbowski et al. (2018). Raw isotope values were calculated using the IUPAC isotopic

94 parameters, and are projected to the CO<sub>2</sub> reference frame ( $\Delta_{47}(\text{RFAC})$ ; Petersen et al., 2019). To  
95 verify the consistency and precision of the clumped isotope measurements, six carbonate standards  
96 (ETH1–4, MuStd, Carrara) were analyzed along the samples (Data S1). We used the in-house  
97 Wacker et al. (2014) calibration to convert  $\Delta_{47}(\text{RFAC})$  values to temperatures (Supplemental  
98 Information; Petersen et al. 2019). Temperature uncertainties are based on external 1SE (including  
99 *t*-value) that is always larger than or identical to the best attainable internal precision as represented  
100 by the shot noise limit (0.004–0.005‰).

## 101 RESULTS

### 102 Electron Microscopy

103 All investigated rostra, excluding the areas adjacent to the apical line and the surface, are  
104 made up of optical calcite and the c-axis of the calcite grains point radially outwards (Figs. S1-S4).  
105 The distribution of the crystallographic a-axes also follows a pattern. This is analogous to pristinely  
106 preserved rostra (Stevens et al., 2017). Our EBSD and SEM-BSE analyses suggest that  
107 recrystallization, which would change the original orientation of the biogenic calcite grains, did not  
108 occur in the sampled areas.

### 109 Clumped Isotope Analyses

110 The  $\Delta_{47}(\text{RFAC})$  values range between 0.690( $\pm 0.011$ )‰ and 0.707( $\pm 0.015$ )‰. The 1SE  
111 uncertainty for the clumped isotope measurements, calculated from 4–6 replicate analyses are  
112 between 0.004‰ and 0.015‰ (mean 0.010‰). The  $\Delta_{47}(\text{RFAC})$  values yield seawater temperatures  
113 ranging between 21 °C and 28 °C (mean 25 °C) and show no significant stratigraphic trend (Fig. 2).  
114 The average uncertainty for the reconstructed temperatures is  $\pm 4$  °C. Steeper-sloped calibrations  
115 yield indistinguishable temperatures within  $\pm 1SE$  (Data S1).

## 116 DISCUSSION

117 The  $\Delta_{47}$ -derived temperature range (21–28 °C, mean 25 °C) for the entire section is higher  
118 than those temperatures reconstructed via stable oxygen isotope paleothermometry (11–19 °C,  
119 mean 16 °C, assuming  $\delta^{18}\text{O}_{\text{sw}} = -1\text{‰}$  SMOW; Price and Gröcke, 2002), and cooler, and rarely  
120 within error, of SST estimates derived from  $\text{TEX}_{86}$  (25–31 °C; Fig. 2; Jenkyns et al., 2012). In this  
121 study, as in Jenkyns et al. (2012), we calculate  $\text{TEX}_{86}$  temperatures using the  $\text{TEX}_{86}^{\text{H}}$  calibration  
122 (Kim et al., 2010). Given the shallow-water and high latitude setting of Site 511  $\text{TEX}_{86}^{\text{H}}$  may yield  
123 maximum SST estimates (Schouten et al., 2013; Taylor et al., 2013). In contrast to  $\text{TEX}_{86}^{\text{H}}$ , the  
124 linear calibration used of O'Brien et al. (2017) yield ca. 2–3 °C warmer temperatures, whereas the  
125 calibrations that assume a non-surface export depth of GDGTs (Kim et al., 2012; Schouten et al.,  
126 2013) yield ca. 5–6 °C cooler estimates (Fig. 2). Although the  $\text{TEX}_{86}^{\text{H}}$  proxy is likely the most  
127 appropriate for a high latitude setting such as Site 511, there is ongoing discussion and revision of  
128 the various calibrations, and ongoing debate as to which calibration should be applied (e.g., Ho et  
129 al., 2014; Inglis et al., 2015). The difference between the  $\text{TEX}_{86}^{\text{H}}$  and the  $\Delta_{47}$ -derived temperatures  
130 for Site 511 may be partially resolved by considering a seasonal bias in either proxy. It has been  
131 postulated that belemnites, as nektonic cephalopods, reflect mean annual temperatures (MAT; Price  
132 and Sellwood, 1997; Mutterlose et al., 2010), while  $\text{TEX}_{86}$  may indicate summer temperatures,  
133 rather than MAT (Leider et al., 2010; Hollis et al., 2012). Nevertheless, our  $\Delta_{47}$  temperatures  
134 suggest that belemnites were calcifying their rostra in the upper part of the water column (<200 m  
135 depth), and are broadly consistent with  $\text{TEX}_{86}$ -derived SSTs, given the uncertainties listed above.  
136 Such an interpretation is in alignment with an assumed predator lifestyle in the photic zone for  
137 belemnites (Klug et al., 2016).

138 All three records from Site 511 show less than 7 °C variability across the entire Late  
139 Jurassic and Early Cretaceous interval, although the low sampling resolution means it is not  
140 possible to derive more detailed information on Jurassic and Cretaceous climate evolution. These

141 data confirm warm Late Jurassic–Early Cretaceous high latitude ocean temperatures, possibly  
142 precluding the likelihood of substantial land ice, and are consistent with estimated MATs from  
143 fossil plant assemblages from the Antarctic Peninsula (Francis and Poole, 2002). The most likely  
144 mechanism to account for such warmth observed at Site 511 is high atmospheric greenhouse gas  
145 concentrations and high polar heat transport. The shallow meridional temperature gradients of the  
146 past greenhouse climates pose a significant challenge to numerical climate models (Huber and  
147 Caballero, 2011), in that increased greenhouse gases may yield warm Polar Regions, but also  
148 overheat the Tropics. MATs for the Cretaceous derived from coupled ocean-atmosphere climate  
149 models provide estimates for 53 °S ranging from 12 °C to 21 °C (Zhou et al., 2008; Donnadieu et  
150 al., 2016). The higher of these estimates are generated with 2240 ppm  $p\text{CO}_2$  (8 x pre-industrial  
151 levels; Donnadieu et al., 2016). These atmospheric  $\text{CO}_2$  concentrations typically exceed estimates  
152 of Cretaceous  $p\text{CO}_2$  derived from fossil leaf stomatal index measurements, isotope-based or  
153 geochemical model estimates (Wang et al., 2014; Foster et al., 2017).

154         Furthermore, it is crucial to consider the magnitude of a non- $\text{CO}_2$  component of local  
155 climate change, before proxies from a single site are interpreted in a global context (Lunt et al.,  
156 2016). GCM output indicates warm conditions during the Cretaceous at Site 511 when compared to  
157 the Eocene (Lunt et al., 2016), with almost invariable modeled global mean temperatures over the  
158 same period, when  $p\text{CO}_2$  is kept constant. This suggests that contributions from other processes  
159 (e.g., paleogeography) may account for some of the observed warmth. Despite these findings and  
160 those of others (Donnadieu et al., 2016), the role of paleogeography in regulating climate remains  
161 less than clear.

162         Such warm temperatures at Site 511 challenge our understanding of how the ocean-  
163 atmosphere system operated in the past (Poulsen, 2004) and may also have important implications  
164 for the prediction of future climates as they imply we may be underestimating future climate change



165 in such regions (Spicer et al., 2008). Proposed mechanisms to increase the transfer of heat toward  
166 the poles (Schmidt and Mysak, 1996), including sensible and latent heat transfer via the atmosphere  
167 and heat transfer via the oceans (Hotinski and Toggweiler, 2003), are hence implied. As Site 511  
168 was situated in a seaway open to the southwest (Fig. 1), increased heat transfer via warm ocean  
169 currents can only be derived from the Pacific. Thus, other processes, including heat transfer via the  
170 atmosphere, might also be important for this region.

171 These new warm  $\Delta_{47}$ -derived temperature reconstructions also have implications for basin-  
172 scale hydrologies. In conjunction with the  $\delta^{18}\text{O}_{\text{belemnite}}$  data (Price and Sellwood, 1997; Price and  
173 Gröcke, 2002), we can estimate  $\delta^{18}\text{O}_{\text{sw}}$ , assuming the temperature dependence of oxygen isotope  
174 fractionation between belemnite calcite and seawater corresponds to Kim and O'Neil (1997). The  
175  $\delta^{18}\text{O}$ -temperature equation of Kim and O'Neil (1997) indicates that  $\delta^{18}\text{O}_{\text{sw}}$  may have averaged  
176  $+1.0\text{‰}$  SMOW ( $1SE = 0.7\text{‰}$ ; Fig. 2, Data S1), heavier than the global average for an ice-free world  
177 ( $-1\text{‰}$  SMOW; Shackleton and Kennett, 1975). This could suggest that the semi-enclosed basin in  
178 which Site 511 was located was dominated by evaporation; alternatively, it is quite possible that the  
179 Kim and O'Neil (1997) calcite equation is not applicable to belemnite calcite.

## 180 CONCLUSIONS

181 This proxy-to-proxy intercomparison reduces the uncertainty on temperature estimates for  
182 the Mesozoic high southern latitudes. Our  $\Delta_{47}$ -derived temperatures, although slightly cooler, are  
183 consistent with the  $\text{TEX}_{86}^{\text{H}}$  reconstructions for sea-surface temperatures. The new  $\Delta_{47}$  data, in  
184 conjunction with  $\delta^{18}\text{O}_{\text{belemnite}}$  data imply local  $\delta^{18}\text{O}_{\text{sw}}$  values of ca.  $1.0(\pm 0.7)\text{‰}$  SMOW, indicating a  
185 strong role of evaporation on the Falkland Plateau, which was a semi-enclosed basin during the Late  
186 Jurassic and Early Cretaceous. The warm reconstructed paleotemperatures, if extrapolated  
187 poleward, reinforce evidence of temperate polar conditions and lack of polar ice. If these warm  
188 ocean temperatures, occurring when  $p\text{CO}_2$  in Earth's atmosphere were also high, prove accurate,

189 they may indicate that greenhouse gases could have heated the oceans during the Jurassic and  
190 Cretaceous more than currently accepted. This suggests that future warming from elevated  
191 atmospheric CO<sub>2</sub> concentrations may be much greater than that predicted by models.

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339 **FIGURE CAPTIONS**

340 **Figure 1.** Paleogeographic setting of the Deep Sea Drilling Project Site 511. Early Cretaceous

341 paleogeographic reconstruction after Scotese (2014).



342 **Figure 2.** Jurassic and Early Cretaceous temperatures and seawater  $\delta^{18}\text{O}$  from DSDP Site 511. **(A)**  
 343 Clumped isotope seawater temperature reconstructions for Site 511 (this study) are compared to  
 344 those based on  $\delta^{18}\text{O}_{\text{belemnite}}$  (Price and Gröcke, 2002; Price and Sellwood, 1997; plotted using Kim  
 345 and O’Neil, 1997, with an assumed  $\delta^{18}\text{O}_{\text{sw}}$  of -1‰ SMOW) and  $\text{TEX}_{86}$  (Jenkyns et al., 2012).  
 346 Infilled green circles represent  $\delta^{18}\text{O}_{\text{belemnite}}$  temperatures from Price and Gröcke (2002), hollow  
 347 green circles are the belemnites that were also used for clumped isotopes analysis in this study. For  
 348  $\text{TEX}_{86}$  temperatures, dotted lines used  $\text{TEX}_{86}^{\text{H},0-200}$  (Kim et al. 2012., eq. 2), dashed used  $\text{TEX}_{86}^{\text{linear}}$   
 349 (O’Brien et al., 2017, eq. 4), and solid line and points used the  $\text{TEX}_{86}^{\text{H}}$  calibration (Kim et al. 2010,  
 350 eq.10). **(B)** Reconstructed  $\delta^{18}\text{O}_{\text{sw}}$  values (this study) using the equation of Kim and O’Neil (1997).  
 351 Error bars represent for  $\delta^{18}\text{O}_{\text{belemnite}}$  and  $\Delta_{47}$  the 1SE of multiple replicate analyses; for  $\text{TEX}_{86}^{\text{H}}$  the  
 352 calibration error; and for  $\delta^{18}\text{O}_{\text{sw}}$  the 1SE. corresponding to the  $\Delta_{47}$  measurements. Age model  
 353 construction is described in the [Supplemental Information](#), whereas data for this figure can be found  
 354 in [Data S1](#).

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