Impact of global cooling on Early Cretaceous high *p*CO₂ world during the Weissert Event
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3 SUPPLEMENTARY INFORMATION

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5 1. Chronostratigraphy

6 The Weissert Event is Late Valanginian in age and Supplementary Fig. 1 illustrates its 7 chronostratigraphy within the Berriasian-Barremian time interval. At low latitudes, integrated nannofossil biostratigraphy, magnetostratigraphy and C-isotopic stratigraphy has been obtained for a number of 8 9 Tethyan sections, providing the direct intercalibration of events. At higher latitudes, magnetostratigraphy 10 has not been resolved for Lower Cretaceous sections, and chronostratigraphy has been derived from ammonite and calcareous nannofossil biostratigraphy calibrated against chemostratigraphy. It is worth 11 12 noting that both ammonite and calcareous nannofossil assemblages are, however, affected by marked paleoprovincialism, hampering a direct correlation of bioevents from lower and higher latitudes. As a 13 14 consequence of such differences in stratigraphic instruments, the only common dating tool is the positive carbon isotopic excursion (CIE) in the δ^{13} C record associated with the Weissert Event. 15 Numerical ages of onset and termination - as well as phases within - of the Weissert Event, and 16 stage and sub-stage boundaries depend on the adopted timescale. Currently, there are two groups of 17 18 available geochronologies constructed using different approaches, namely the geologic timescale of Gradstein et al. $(2012)^1$ revised by Ogg et al. $(2016)^2$ and recently updated by Gradstein et al. $(2020)^3$, 19 and the timescale of Channell et al. (1995)⁴ revisited by Malinverno et al. (2012)⁵ (Supplementary Fig. 1). 20 21 The backbone of both timescales consists of polarity chrons directed dated by calcareous nannofossils. 22 The position of stage (and sub-stage) boundaries has been revised here following subsequent ad/or 23 implemented and/or revised chronostratigraphy including (when available) ammonite biozones. In Fig. 1, we report the position of stage boundaries as documented in the original papers^{4,1,5,2,3}. Previous work⁶ 24 25 documented ammonite and calcareous nannofossil biostratigraphy in a composite section also yielding magnetostratigraphy and chemostratigraphy, and re-calibrated the Valanginian/Hauterivian boundary. 26 Specifically, the base of the A. radiatus ammonite zone and, thus, the base of the Hauterivian was found 27

to correspond to the minor carbon isotope anomaly within magnetic chron CM 10N and nannofossil

NC4a subzone. This substantial chronostratigraphic revision was not adopted in^{1, 3 and 5} but it was
incorporated in the timescale of Ogg et al. (2016)².

In this work we adopt the Malinverno et al. (2012)⁵ timescale revised according to Ogg et al.
(2016)² for the position of the Valanginian/Hauterivian boundary relative to polarity chrons
(Supplementary Fig. 1).

In the chronostratigraphic scheme (Supplementary Fig. 1) the calcareous nannofossil zonations are
reported for the lower⁷ and higher latitudes⁸. The stratigraphic position of two calcareous nannofossil
events has been revised as follows: i) the FO of *R. wisei*, previously reported before the positive CIE⁷,
correlates with the ramp of the positive CIE of the Weissert Event as documented in some section in the
Vocontian Basin^{9,10}, in the Central Atlantic¹¹ and SE Spain¹²; ii) the the last occurrence (LO) of *T. verenae*, previously coinciding with the highest value of the positive Weissert CIE⁷, is now placed

40 slightly after the termination of the Weissert Event as reported in several sites $^{9, 11, 13, 10}$.

The Boreal zonation takes into account a revision¹⁴ that places the LO of *M. speetonensis* in the topmost
part of the positive Weissert CIE.

43 In the chronostratigraphic scheme we additionally reported those calcareous nannofossil events (in blue),

44 which have been used to stratigraphically constrain the age of Site 692 (Supplementary Figs. 1 and Fig.2).

- 45 The Boreal calcareous nannofossil BC4–BC7 zones have been calibrated against the carbon isotopic
- 46 curve considering the dataset from the Rødryggen section in Greenland^{15, 14}, the Wawal section in
- 47 Poland¹⁶, the BGS 81/43 Site in the North Sea¹⁷ and the revision¹⁴; while the age of Zones BC1–BC3 and
- 48 BC7–BC10 is based on the Boreal ammonites inter-calibrated with the Tethyan biochronology as
- 49 specified in¹⁴.

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51 2. Calcareous Nannofossils

52 Calcareous nannofossils were investigated in the Valanginian–Early Hauterivian interval, from
53 78.61 to 93 mbsf (cores 113–692–10R and 113–692–12R), consisting of a calcium carbonate-rich and
54 overall finely laminated black shale section. A high-resolution sampling at 10 to 20 cm was carried out,

leading to a set of 69 samples. In this work, we also revised the originally studied¹⁸ calcareous 55 56 nannofossil biostratigraphy of Site 692 that assigned a Valanginian age to the interval from 93 mbsf 57 (113-692-12R CC) to 53.6 mbsf (113-692-7R 1, 44 cm). Calcareous nannofossil assemblages are dominated by high latitude taxa, but cosmopolitan species are also common and a few typically Tethyan 58 59 species were observed. A biozonation for high latitudes of the southern hemisphere is not available and, 60 therefore, biostratigraphy is assigned with reference to the standard zonation scheme for the Boreal Realm (BC⁸ zonation) and the Tethys (NC⁷ zonation). Previous nannofossil investigations of Site 692^{18} adopted 61 62 the NC¹⁹ zonation.

At date, there is no available intercalibration of low and high latitude nannofossil biozonations. However, the direct correlation of a few nannofossil biohorizons relative to chemostratigraphy exists for sections in a variety of basins (e.g.,^{20,21,6,9,11,15,22,10,14,12}) allowing indirect tie-points. Moreover, following the lower⁷ and higher⁸ latitude zonations, revised age assignments were documented for a few nannofossil events and such updates were incorporated in the chronostratigraphic framework applied in this work (Supplementary Fig. 1).

69 The majority of samples investigated at Site 692 contain relatively diverse and moderate to well 70 preserved nannofossils although the assemblages are dominated by few species, most prominently 71 Watznaueria barnesiae and, in the interval comprised between 91.87 mbsf (113-692-12R-3, 65-68 cm) and 80.52 mbsf (113–692–10R–2, 50–54 cm), by Biscutum constans and Crucibiscutum salebrosum. 72 73 Spare samples in core 113–692–12R (91.31, 90.57, 90.42, 89.4, 89.22, 88.93, 88.78 and 88.50 mbsf) are 74 barren of nannofossils. The lowermost studied sample (sample 113-692-12R-3, 112-115 cm) is 75 characterized by the presence of the Boreal taxon Crucibiscutum ryazanicum and the Tethyan taxon Percivalia fenestrata, which indicate an age not older than late Berriasian, within Zone BC2⁸ and subzone 76 NC2b⁷ (Supplementary Fig. 2). 77

The absence of Boreal *Triquetrorhabdulus shetlandensis* and Tethyan *Calcicalathina oblongata*marker species for the base of the Valanginian does not allow a more precise age determination of the
interval between 93 and 91.87 mbsf (sample 113–692–12R–3, 65–68 cm) that is attributed to the Late
Berriasian–Early Valanginian BC2–BC3 and NC2b Zone (Supplementary Fig. 2).

The first occurrence (FO) of *Zeugrhabdotus trivectis* was observed at 91.87 mbsf, shortly before the onset of the positive δ^{13} C isotopic CIE of the Weissert Event (Supplementary Fig. 2). This biohorizon has been documented in the lowermost part of Zone NC3 in sections from the Vocontian Basin^{9, 22, 10}, SE Spain¹² and DSDP Site 535 in the Gulf of Mexico¹⁷ (Supplementary Fig. 1). According to previous work⁸, the FO of *Z. trivectis* falls within zone BC4.

87 In well-dated sections from the Vocontian Basin (France) and Betic Cordillera (Spain), the LO of 88 *Eiffellithus primus* was found above the FO of *Z. trivectis*, and below the FO of *R. wisei* at the base of the 89 δ^{13} C isotopic positive CIE^{9, 10, 12}. At Site 692 the position of the LO of *E. primus* is comparable (sample 90 113–692–12R–2, 105–110 cm; 90.78 mbsf) (Supplementary Fig. 2).

91 The LO of the Tethyan species *Rucinolithus wisei* at 89.02 mbsf (sample 113–692–12R–1, 80–83 cm)

92 marks the base of subzone NC3b⁷ and is Late Valanginian in age as documented in several low latitudinal 93 sites^{9, 11, 22, 10, 12} (Supplementary Fig. 1). At Site 692, the LO of *R. wisei* corresponds to the early phase of 94 the δ^{13} C positive CIE (Supplementary Fig. 2).

At Site 692, disarticulated elements of possible *Micrantolithus speetonensis* occur in the interval
comprised between 84.03 mbsf (sample 113–692–10R–4, 101–104 cm) and 83.74 mbsf (sample 113–692
-10R–4, 73–75 cm) in correspondence of the topmost part of the δ¹³C isotopic positive CIE
(Supplementary Fig. 2). The LO of *M. speetonenesis*, marking the base of Zone BC5⁸, was originally
identified as latest Early Valanginian in age^{8, 23}, but a recent revision¹⁴ places this event in the Late
Valanginian, close to the topmost part of the positive carbon isotope excursion of the Weissert Event
(Supplementary Fig. 1). The stratigraphic position of disarticulated *M. speetonensis* at Site 692 is, thus,

102 consistent with the revision¹⁴.

103 At Site 692, the boundary between zones NC3 and NC4 cannot be determined because *Tubodiscus*

104 *verenae* is absent. However, the LO of *T. verenae* is calibrated with respect to the chemo- and

105 magnetostratigraphy and correlates with the topmost part of magnetochron CM11 and just above the

106 Weissert Event CIE. Consequently, at Site 692 we tentatively place the NC3/NC4 zonal boundary

107 between 82 mbsf and 83 mbsf (Supplementary Fig. 2).

108	At Site 692, the position of the Valanginian/Hauterivian boundary based on calcareous nannofossils is
109	not straightforward due to the absence of low and high latitude markers such as <i>Tubodiscus verenae</i> ⁷
110	and T. shetlandensis and/or Eprolithus antiquus ⁸ , respectively. However, the Valanginian/Hauterivian
111	boundary may be constrained using the last common occurrence (LCO) of C. deflandrei detected at
112	80.98 mbsf (sample 113–692–10R–2, 96–99 cm) (Supplementary Fig. 2). In fact, in Tethyan and low
113	latitude sections, the LCO of C. deflandrei was documented in the latest Valanginian after the LO of
114	<i>T. verenae</i> within subzone NC4a and close to the Valanginian/Hauterivian boundary ^{24, 19, 25.} With
115	respect to the carbon isotopic curve (δ^{13} C), the LCO of <i>C. deflandrei</i> is reported just above the
116	Weissert Event CIE ²⁵ with respect to the δ^{13} C record of ²⁰ ; Roth (1983) ¹⁹ with respect to the δ^{13} C curve
117	of Littler et al. $(2011)^{26}$ and Applegate & Bergen $(1988)^{27}$ with respect to the δ^{13} C curve of Kessels et
118	al. (2006) ¹⁷ . At Site 692, the LCO of <i>C. deflandrei</i> shortly precedes the minor carbon isotope anomaly
119	that was equated to the base of the Acanthodiscus radiatus ammonite zone and, thus, to the base of the
120	Hauterivian ⁶ , confirming the potentiality of this nannofossil event to place the
121	Valer sinisr /Henterinier henry dom

121 Valanginian/Hauterivian boundary.

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123 **2.1 Paleoecology of braarudosphaerids**

A braarudosphaerid increase in abundance is observed at Site 692 in the relative warming phase 124 following the cooling at the end of the Weissert Event and in the warmer interval following the cold 125 phase across the Valanginian/Hauterivian boundary (Supplementary Fig. 3). Coeval braarudosphaerid-126 enrichments are documented offshore Antarctica, at ODP Sites 766 and 765^{28, 29}, and at high latitudes in 127 the northern hemisphere, in the BGS 81/43¹⁷ and Rødryggen section in Greenland^{15, 14}, where 128 129 braarudosphaerids are mainly represented by Micrantholithus hoschulzii and Micrantholithus obtusus. Conversely, latest Valanginian braarudosphaerid blooms have not been recorded at low latitudes in 130 Tethyan sections, where discrete *Micrantholithus* enrichments are observed in upper lower Valanginian^{30,} 131 ³¹, upper Hauterivian^{32,31} and lower Aptian³¹ intervals. In the Vocontian Basin (Angels section³³) 132 braarudosphaerids (mostly M. hoschulzii and M. obtusus) are frequent before, during and after the 133 Weissert Event. In Romania³⁴, in the Galicia Margin (ODP Site 638^{27, 17}) and in the Proto North Atlantic 134

(DSDP Site 603³⁵) braarudosphaerids (*M. hoschulzii* and *M. obtusus*) enrichments are detected only after
the Weissert Event. Modern braarudosphaerids are often most abundant in low-salinity waters^{36, 37} and
fossil enrichments of *Braarudosphaera* have been referred to coastal low-salinity waters^{38, 39, 30}. The
specific occurrence of braarudosphaerid enrichments at high latitudes during the warmer interlude
separating the two cold periods and locally shortly after the Valanginian/Hauterivian boundary, suggests
seasonal salinity lowering possibly triggered by discharges of fresh deglacial melt water, supporting the
possibility of ice in coastal regions.

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143 **3. Benthic foraminifera**

Benthic foraminifera were studied in 31 samples from Site 692 (from 113-692-10R-1, 25-27 cm 144 to 113-692-12R-3, 112-115 cm) to reconstruct the paleowater depth during the Valanginian-Hauterivian. 145 The most abundant genus recorded at Site 692 is *Eoguttulina*, indicative of a shallow shelf (e.g.,^{40,41}) or 146 upper bathyal setting (e.g.,⁴²). Less abundant taxa such as *Laevidentalina*, *Lenticulina*, *Lagena*, 147 Saracenaria, and Nodosaria are characteristic for a wide paleobathymetric range, from inner neritic to 148 lower bathyal environments (e.g.,^{42, 43}). The genus Vaginulinopsis is reported as a bathyal indicator in the 149 Indian Ocean (e.g.,⁴⁴). Based on the benthic foraminiferal assemblage, an outer neritic-upper bathyal 150 (~200-500 m) paleodepth is suggested for the Valanginian-Hauterivian interval at Site 692. A published 151 paleobathymetric division^{45, 46} was applied. 152

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154 4. Anomalous GDGT distributions

155 The the fraction of crenarchaeol regio-isomer to total crenarchaeol, $f_{Cren':Cren' + Cren}$ (= 156 [Cren']/[Cren] + [Cren'];⁴⁷) is always <0.25 in all study samples, however we note an anomalous 157 isoprenoid-Glycerol Dialkyl Glycerol Tetraether (i-GDGT) distribution in samples from the restricted 158 Early Cretaceous proto-Weddell Sea and proto-North Atlantic. Supplementary Fig. 4 shows a cross-159 plot of $f_{Cren':Cren' + Cren}$ against TEX₈₆ that documents a systematic increase in the relative abundance of 160 crenarchaeol regio-isomer [Cren'] compared to crenarchaeol [Cren] in the Early Cretaceous Atlantic 161 Ocean (red dots in Supplementary Fig. 4;⁴⁷) and in the Weddell Sea (Site 692; green rectangles in

Supplementary Fig. 4; this study and 12 other Early Cretaceous data from this site²⁶). Therefore, the 162 Early Cretaceous Atlantic Ocean and Weddell Sea samples, similarly to the present-day deep 163 restricted basins of the Mediterranean and Red Sea (yellow rectangles in Supplementary Fig. 4;^{48,49}), 164 document a considerable deviation from values observed in the modern core-top dataset (empty grey 165 circles in Supplementary Fig. 4;⁵⁰) and the rest of Cretaceous data (black dots in Supplementary Fig. 166 4;⁴⁷). Moreover, we also document high [GDG-2]/[GDGT-3] ratios at Site 692 that range between 4 167 and 8.5, similar to deeper sediments from the modern Mediterranean Sea (see^{49 and 51}). To date, a 168 169 possible explanation for these distinct sedimentary i-GDGT distribution documented in the proto-North and South Atlantic⁵¹ and Southern Ocean Basin (proto- Weddell Sea^{this study}) might be peculiar 170 of young and restricted Mesozoic ocean basins, leading to a different TEX₈₆-temperature relation⁵¹, as 171 documented in the modern Mediterranean and Red Sea⁴⁹. 172 It is important to note that the paleoceanographic setting and resulting circulation of the 173 Valanginian Weddell Sea are different from the present-day Eastern Mediterranean and Red Sea. The 174 paleolatitude of ~54 °S is consistent with an overall more humid climate based on modern day climate 175 176 zonation. While this is clearly different to the modern evaporative Mediterranean Sea, we argue that the increased surface freshwater input combined with deoxygenated bottom waters is a better analogue to 177 times of sapropel formation in the Mediterranean Sea. Importantly, a downcore study⁵² showed that 178 regional TEX₈₆-SSTs are consistently warmer (up to 15 °C) than U^{K}_{37} -derived temperatures, both inside 179 180 and outside of Pleistocene sapropels. This is clear evidence that the occurrence of endemic

Thaumarchaeota populations in the restricted basin can change the local TEX₈₆-SST relation independent
of large swings in water column stratification and oxygenation. We therefore argue that the young and

restricted basins of the Early Cretaceous, in analogue to the modern Mediterranean and Red Sea, might

also provide special environmental conditions enabling specific Thaumarchaeota community structures and potentially different TEX_{86} export dynamics than commonly considered in the present-day global core-top calibrations.

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188 5. Organic matter quality and thermal maturation

189 Carbon isotope and TEX₈₆ analysis was supplemented by analysis of thermal maturity 190 characteristics by Rock-Eval pyrolysis and GC-MS analysis of the aliphatic hydrocarbon fraction in 191 order to determine the quality of the organic matter in the studied stratigraphic interval (cores 113-192 692–10R and 113–692–12R) of Site 692. The aliphatic fraction (purified as described above) was 193 performed on a Thermo Scientific Trace 1310 GC fitted with a split splitless injector (at 280 °C) and 194 linked to a Single Quadrupole Mass Spectrometer using electron ionization (electron voltage 70eV, source temperature 230 °C, quadrupole temperature 150 °C, multiplier voltage 1800V, interface 195 temperature 310 °C). Data acquisition and processing was carried out using Thermo Chromeleon 7 196 197 software. Samples were analysed in full scan acquisition mode (50-600 amu/sec) and in selected ion monitoring (SIM) mode. Samples were diluted in hexane and injected onto a Thermo fused silica 198 199 capillary column (60 m x 0.25 mm i.d) coated with 0.25 µm 5 % phenylmethylpolysiloxane phase using an auto sampler. The GC temperature was increased from 50 to 310 °C at a rate of 5 °C/min. 200 The final temperature was held for 10 minutes. Helium was used as the carrier gas (flow rate of 1 201 202 ml/min, initial inlet pressure of 50 kPa, split at 30 ml/min).

203 Our samples yielded consistently high $\beta\beta/(\beta\beta+\alpha\beta+\beta\alpha)$ -C₃₁-homohopane ratios of ~0.5–0.6 204 indicating the presence of immature organic matter⁵³, consistent with previous work²⁶ on thermal 205 maturity assessment of Early Cretaceous samples from Site 692.

206Rock-Eval pyrolysis was performed on aliquots of ~100 mg of powdered core samples, with207each sample analysed in duplicate and a standard sample analysed after every 10 samples. The208samples were heated at 100 °C for three minutes, during which free volatile hydrocarbons (gas) were209released (S₀). The temperature was then increased from 100 °C to 300 °C and held for three minutes210to allow the expulsion of free hydrocarbons (oil) from the sample (S1). The furnace temperature was211then ramped from 300 °C to 550 °C at a rate of 25 °C /minutes and held at 550 °C for 2 minutes; the212S2 peak and the T_{max} (°C) were recorded at this stage.

213 Results indicates mainly Type II/III kerogen (HI ~400, OI ~65) with low thermal maturity 214 $(T_{max} \text{ values } \sim 420 \text{ °C})$. These additional data are consistent with published data from Site 692¹⁸ and 215 further support a low thermal maturity, which had a negligible impact on TEX₈₆ values.

217 6. Global mean surface temperature and *p*CO₂ estimates

We compare the reconstructed Valanginian ocean temperatures with the simulated sea surface temperatures (SSTs) at the individual paleopositions (see Supplementary Table 1) to calculate global mean surface temperature (GMST) estimates for each site. We follow the approach described in⁵⁴ that assumes a linear relation between changes in local and global mean surface temperatures. We further assume that our model can capture this relation and we can therefore use our ×2 and ×4 CO₂ simulations to estimate the GMST (<T>^{inferred}) from a local proxy temperature (T^{proxy}) as

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$$< T > inferred = < T^{x2} > + (T^{proxy} - T^{x2}) \frac{< T^{x4} > - < T^{x2} >}{T^{x4} - T^{x2}}$$
 (3)

where $\langle T^{x^2} \rangle$ and $\langle T^{x^2} \rangle$ are the GMST of the $\times 2$ and $\times 4$ CO₂ simulations, respectively, and T^{x^2} and 225 T^{x4} are the local model SSTs from the same simulations. T^{x2} and T^{x4} are averaged over a horizontal 226 area of ± 1 grid point ($\pm 2.5^{\circ}$ latitude and $\pm -3.8^{\circ}$ longitude) around the rotated paleolocations to 227 account for paleogeographic uncertainties. $\langle T \rangle^{x^2}$ and $\langle T \rangle^{x^4}$ for the Valanginian are 17.28 °C and 228 21.03 °C, respectively. We note that any GMST estimate for a proxy temperature smaller than T^{x2} or 229 larger than T^{x4} is based on extrapolated instead of interpolated model temperatures and is therefore 230 more uncertain. Illustrations of the results of this method for all sites are shown in Supplementary Fig. 231 5. Proxy temperatures for locations 10 and 19 from Table S1 result in extreme GMST estimates above 232 30 °C and below 10 °C, respectively (Supplementary Figs. 5j and p). We note that the reconstructed 233 234 temperatures based on oxygen isotopes at location 10 might be influenced by diagenetic alterations (see discussion below), while the authors of the original publication of location 19⁵⁵ argue that the 235 236 absolute Mg/Ca-derived temperatures are highly uncertain. We therefore exclude GMST estimates from locations 10 and 19 from the calculation of the average GMSTs. Exclusion of both sites results 237 238 in virtually identical mean GMST estimates, but with a reduced standard error of the mean. We still include the relative temperature changes towards the Weissert CIE end at both sites (Supplementary 239 Table 1) to calculate the root-mean-square-errors between simulated and reconstructed surface 240 cooling (Figure 4c of the article, Supplementary Figs. 6e and f). Fig. 3 in main text indicates that most 241

242 available records show relatively stable temperatures across the Early-Late Valanginian transition and virtually no warming associated with the onset of the Weissert CIE. One contrasting observation 243 suggesting significant warming in the proto-North Atlantic and Tethys realm based on $\delta^{18}O_{carb}$ -based 244 temperature reconstructions⁵⁶. We note that this reconstruction is in stark contrast with other 245 temperature proxies from same locations (e.g., TEX₈₆;²⁶; δ^{18} O of belemnites^{57, 58}; Mg/Ca ratios⁵⁵), and 246 therefore conclude that the causes for these marked discrepancies are likely related to a diagenetic 247 alteration of the $\delta^{18}O_{carb}$ values, which were measured on bulk rock samples. We therefore focus our 248 249 model-data comparison on only two distinct temperature periods. The Weissert warm interval 250 includes Valanginian average temperature estimates older than the first Weissert CIE peak (red bars 251 below point B in Fig. 3 in the article). The cold Weissert end includes the coldest temperature reached 252 at the end of the Weissert CIE (dark blue color interval coincident with point C in Fig. 3 in the article). 253

We calculate mean GMST estimates $\langle T \rangle_{avg}^{inferred}$ as the average over all proxy locations for each period and derive uncertainty estimates as the respective standard error of the mean. We can then calculate a global mean scaling factor s by

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$$s = \frac{\langle T \rangle_{avg}^{inferred} - \langle T^{x2} \rangle}{\langle T^{x4} \rangle - \langle T^{x2} \rangle}$$
(4)

to linearly scale simulated surface temperatures to the estimated $\langle T \rangle_{avg}^{inferred}$ by

259 $T^{scaled} = T^{x2} + s * (T^{x4} - T^{x2})$ (5)

Temperature distributions for T^{scaled} are shown in Figs. 4 and 5 in the article as well as in
Supplementary Fig. 6. We further use T^{scaled} to calculate the root-mean-square-error (RMSE) between
best-fit model temperatures and local proxy data. The same scaling factor can also be used to derive
the associated best-fit model CO₂ concentration by

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$$CO_2^{inferred} = 560ppm * \left(\frac{1120ppm}{560ppm}\right)^3$$
 (6)

The shown temperature changes towards the Weissert CIE end (cooling) follow as the difference between T^{scaled} of both time intervals with uncertainties derived from the error propagation of both time periods. We perform the GMST estimation both using annual mean model temperatures at all sites (annual mean assumption) as well as using warmest 3-month means for mid to high-latitude (>45
°) sites (summer bias assumption) to assess the influence of a potential seasonal bias in the proxy
signal formation (see discussion in the article).

We perform the analysis with five different variations of the proxy data to test how individual 271 272 proxy techniques and calibration choices influence the resulting GMST and pCO_2 estimates. First, we include all data for each time period but apply either the calibration for modern deep, restricted 273 basins⁴⁹ (min-TEX₈₆, Equation 2 in Methods section in the article) or the BAYSPAR calibration^{59, 50} 274 (max-TEX₈₆) to DSDP/ODP sites 534, 603 and 692. The higher T^{proxy} from the BAYSPAR calibration 275 (Supplementary Fig. 6) in turn leads to higher GMST estimates $\langle T \rangle$ ^{inferred} (Supplementary Equation 4) 276 for these sites than in min-TEX₈₆ and the overall average GMST for both time periods increases by 4– 277 6 °C (Supplementary Table 2). Associated model pCO₂ concentrations for the Weissert warm interval 278 279 would be above 2500 ppm - even for the summer bias assumption (Supplementary Fig. 6) - and therefore higher than the ~ 1700 ppm reported as the upper 95% confidence limit of a multi-proxy CO₂ 280 compilation⁶⁰. Furthermore, the scaled temperature distributions in the model at these high GMSTs 281 show higher RMSE scores (e.g., worse model-data fit) than in min-TEX₈₆ (Supplementary Fig. 6). 282 We further perform three different subsampling experiments where we only include estimates from single 283 proxy techniques (only-TEX₈₆, only- δ^{18} O and only- Δ 47) to test whether our results are consistent across 284 the different proxy archives. Note that subsampling experiment only- $\Delta 47$ has only been performed for the 285 Weissert warm interval due to the lack of Δ 47-derived temperatures for the Weissert cold CIE end. All 286 three subsampling experiments show similar results for the Weissert warm interval with GMST estimates 287 well within reported uncertainties of the mean (Supplementary Fig. 6). Sensitivity to the proxy method is 288 larger for the Weissert cold end with higher GMST estimates derived from TEX₈₆ than δ^{18} O samples. The 289 Experiment only-TEX₈₆ includes the respective minimum TEX₈₆ temperatures and shows overall highest 290 consistency to the scaled model temperatures (e.g., lowest RMSE), while we find largest uncertainties in 291 the comparison with the oxygen isotope record (experiment only- δ^{18} O) of both time intervals. 292





297 interval (this study). Detailed revised nannofossil biostratigraphy integrated, magneto- and

298 chemostratigraphy across the Valanginian-Hauterivian time interval are also provided. Numerical

ages of the Weissert ($\delta^{13}C_{carb}^{6}$) are based on the timescale⁵ revisited in this study.





301 Supplementary Figure 2. Calcareous nannofossil biostratigraphy of ODP Site 692 (this study).



303 zonation). The relative abundance of nannofossil species relevant for biostratigraphy are reported.

R=Rare, 1 specimen in >30 fields of view; F=Frequent, 1 specimen in 11–30 fields of view;

305 C=Common, 1 specimen in 2–10 fields of view. LCO=Last Common Occurrence. The dark grey lines

306 correspond to samples barren of nannofossils. The carbon isotopic curve is from this work. The grey

307 band corresponds to the Weissert Event interval.



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309 Supplementary Figure 3. Intervals of braarudosphaerid enrichments at higher and lower latitudinal

310 sites across the Weissert Event interval (this study). Numerical ages are based on the timescale⁵

311 revised in this work. Identification of the Weissert positive carbon isotope excursion (CIE) is based on the

312 carbon isotope record measured from bulk carbonate $(\delta^{13}C_{carb})^6$, which has been calibrated in the Southern

- Alps in the uppermost part of magnetic chron CM12 (A, CIE onset) and in the upper part of magnetic
- 314 chron CM11 (C–CIE end)²¹. Temperature intervals include the literature data and the new
- 315 paleotemperatures reconstructed in the current work as discussed in the article (see Fig.3 in the article).
- **316** Paraná–Etendeka timing after $(1)^{61}$, $(2)^{62}$ and $(3)^{63}$.



Supplementary Figure 4. Cross-plot of fractional abundances of crenarchaeol regio-isomer to 318 319 total crenarchaeol (f_{Cren':Cren' + Cren}) against TEX₈₆. Data show a modern global dataset of marine core-tops and surface sediments (empty grey circles;⁵⁰); present-day samples from deep (below 1000 320 m) restricted basins of the Mediterranean and Red Sea (yellow rectangles;^{48, 49}); a Cretaceous 321 compilation (black dots;⁴⁷) that also includes Early Cretaceous Atlantic Ocean samples (red dots;⁴⁷); 322 323 and the Early Cretaceous Weddell Sea dataset (ODP Site 692; green rectangles including new Valanginian data from this study and 12 other Early Cretaceous data from this site²⁶). All samples 324 with ring index $|\Delta RI| > 0.3$ and present-day samples with sea surface temperatures (SST_s) <5 °C are 325 excluded from this analysis for comparability to previous work⁵¹. 326 327



330 Supplementary Figure 5. Illustration of global mean surface temperatures (GMST) estimates for
331 all sites (Supplementary Table 1) calculated with Supplementary Equation 3. a – p Results from

- 333 Mg/Ca (p). The vertical line shows $\langle T \rangle^{inferred}$ for annual mean (bold line) and 3-month summer mean
- temperatures (stippled line) and the horizontal line shows T^{proxy} for sites covering the (red) Weissert
- warm interval and (blue) Weissert cold carbon isotope excursion end. The black dots show $\langle T^{2x} \rangle$ and
- 336 T^{2x} as well as $\langle T^{4x} \rangle$ and T^{4x} derived from the model (where $\langle T^{x2} \rangle$ and $\langle T^{x4} \rangle$ are the GMST of the $\times 2$

- and $\times 4$ CO₂ simulations). Calculations are repeated with 3-month summer mean temperatures for sites
- 338 poleward of 45 ° (grey circles) that lead to overall lower GMST estimates. Linear regression lines are
- 339 presented for annual mean (black) and 3-month summer mean temperatures (grey). Proxy
- temperatures for sites in shaded panels (j) and (p) result in extreme GMST estimates above 30 °C and
- below 10 °C and are excluded from the subsequent mean GMST estimates.



343 Supplementary Figure 6. Model-proxy comparison of upper ocean temperatures and model CO₂ 344 estimates. The model-data comparison is performed both with 3-month summer mean temperatures for sites poleward of 45° (summer bias assumption; first column) as well as annual mean model data 345 (annual mean assumption; second column). The results for each calculation are presented as a table in 346 the respective sub-figure. Global mean surface temperatures (GMSTs) and associated model CO₂ 347 levels are calculated for the whole data set and repeated for three different subsampling experiments 348 including only single proxy techniques (only-TEX₈₆, only- δ^{18} O and only- $\Delta 47$). Moreover, either the 349 calibration for modern deep, restricted basins (min-TEX₈₆) or the BAYSPAR calibration (max-TEX₈₆) 350 351 for DSDP/ODP sites 534, 603 and 692 are included. Model sea surface temperatures (SSTs) are 352 linearly scaled to the respective mean CO₂ estimates (Supplementary Equation 5) with root-mean-353 square-error (RMSE) between scaled model temperatures and local proxy data. Full symbols represent

- direct temperature reconstruction from proxy-data with error bars documenting 90% confidence
- 355 intervals for the TEX₈₆ calibration and uncertainties for other proxies as reported in Supplementary
- Table 1. Dashed symbols represent model SSTs at the proxy locations. Shading around the zonal
- 357 mean shows the range of annual mean SSTs at each latitude, for modern (grey) and Valanginian (red
- 358 for Weissert warm and blue for Weissert cold end). Modern SST range (HadISST,⁶⁴) is averaged for
- the period 1990–2019. $\mathbf{a} \mathbf{b}$ Weissert warm interval with CO₂ estimates of 1181 ppm. $\mathbf{c} \mathbf{d}$ Weissert
- 360 cold end with CO₂ estimates of 682 ppm. e f Model temperature and *p*CO₂ change from the Weissert
- 361 warm interval to Weissert cold end.



Supplementary Figure 7. Atmospheric CO₂ sensitivity of simulated Antarctic snow accumulation. a Model orography used for both simulations. b Integrated February snow mass poleward of 60 °S for the last 3000 model years. Absolute Antarctic snow masses increase throughout the simulations indicating a net freshwater transport onto Antarctica at both CO₂ levels. Calculated slopes show an increase of 58% in annual mass accumulation rates (from 126 to 200 Gt/year) for an atmospheric CO₂ reduction from ×4 to ×2 pre-industrial levels. $\mathbf{c} - \mathbf{d}$ Panels show regions with a positive mass balance where the snow accumulates.

Proxy	ODP DSDP Sites/ global sections	Location	Location in Fig.1 in the article	Model Latitude	Weissert warm interval [°C]	Weissert cold end [°C]	Cooling (ΔT)	Temp. calib.	Weissert carbon isotope excursion $(\delta^{13}C)$	Ref.	Notes
TEX ₈₆	DSDP 603	Proto North Atlantic	1	24°N	~41/ 28±1°C	~41/ 28±1°C	0	max/ min TEX ₈₆ calib.	\checkmark	26,47	
TEX ₈₆	DSDP 534	Proto North Atlantic	2	19°N	~43/ 28.5±1°C	~43/ 28.5±1°C	0	max/ min TEX ₈₆ calib.	\checkmark	26,47	
TEX ₈₆	ODP 766	Exmouth Plateau	3	52°S	-	-	~25.5	max TEX ₈₆ calib.	X	26,47	25.5=avg. temperatu- re calculated from the 8 lowermost data points at Site 766 that sits slightly above the Weissert CIE end
TEX ₈₆	ODP 692	Proto Weddell Sea	4	54°S	~30/ 22.7±1°C	~25.6/ 20.1±1°C	~3/4	max/ min TEX ₈₆ calib	√	this study	
Δ47	Caravaca	Spain	5	24°N	~27	-	-	calcite	Х	66	
Δ47	Speeton	Southern	6	36°N	~24	-	-	calcite	Х	66	
Δ47	Izhma	Arctic	7	53°N	~19	-	-	calcite	Х	66	
Δ47	Yatria River	Arctic	8	54°N	~16	-	-	calcite	Х	67; 66	
Δ47	Boyarka	Arctic	9	64°N	~19	-	-	calcite	Х	66	
δ ¹⁸ O bulk carbonate	DSDP 603 and 534	Proto North Atlantic	10	22°N	~37.4 (±0.9)	~35	~2.4	calib. ⁶⁸ using 0.5‰ δ ¹⁸ O seawater		56	37.4=avg. values from Late Val. transition to Late Val. interval in ¹³ . Trends may be bias due to large scattering and/or diagenetic overprint of the bulk carbonate signal.

$\delta^{18}O$	Compila-	South East	11	26°N	-	-	~1-2	-	1	57; 58	Authors
belemnite	tion	France							•		suggest
											that the
											positive
											shift in
											δ ¹⁸ O is
											equivalent
											to a
											~1-2°C
											cooling
											but
											absolute
											tempera-
											tures are
											highly
											uncertain.
δ ¹⁸ O bulk	Compila-	North	12	26°N	~31.0	~28.9	~2.1	calib. 68;	\checkmark	56	31.0=avg.
carbonate	tion	West			(±0.9)	(±0.9)		avg. for			values
		Tethys						1‰ and			from Late
								$1.4\% \delta^{18}O$			Val.
								seawater			transition
											to Late
											Val.
											interval
											1n ¹³ .
											Trends
											may be
											bias due to
											large
											scattering
											and/or
											diagenetic
											overprint of the bulk
											of the bulk
											signal
δ ¹⁸ O	Compila-	Southern	13	38°N	_	_	~4	_	not clear	58	Authors
belemnite	tion	Boreal	15	50 11					not cicai		suggest
conciliance		Doreal									that the
											positive
											shift in
											δ^{18} O is
											equivalent
											to a ~4°C
											cooling
											but
											absolute
											tempera-
											tures are
											highly
											uncertain.
$\delta^{18}O$	Compila-	Southern	14	38°N	~16.0	~14	~2	calib.68;	not clear	56	
lenticuli-	tion	Boreal			(±0.9)	(±0.9)		avg. for			
na								0‰ and			
+bivalve								-0.5‰			
								$\delta^{18}O$			
10								seawater			
δ ¹⁸ O	Rio	Austral	15	51°S	~24.9	-	-	calib.68	not clear	69	
belemnite	Guanaco	Basin			(19-30)			using			
								-1.2 ‰			
								0°'6			
1		1		1		1	1	seawater		1	1

$\delta^{18}O$	Compila-	Arctic	16	65°N	-	-	~2	-	not clear	58	Authors
belemnite	tion	Boreal									suggest
											that the
											positive
											shift in
											δ^{10} O is
											equivalent
											to a $\sim 2^{\circ}C$
											cooling
											DUI absoluto
											tempera-
											tures are
											highly
											uncertain.
$\delta^{18}O$	Festnin-	Arctic	17	61°N	-	~5.5	-	calib. 68;	not clear	70	
belemnite	gen and	Svalbard				(4–7)		avg. for			
co-	Janusfjel-							-5.3‰			
occurring	let							and			
with								-6.1‰			
glendo-								δ18Ο			
nites	000.000	0 1	10	5000	144	1.7	2 (0 0)	seawater		56	
o ¹⁶ O bulk	ODP 765	Southern	18	52°S	~16.6	~15	~2 (±0.9)	calib. 00	\checkmark	50	
carbonate		Tethys			(±0.9)	(± 0.9)		using			
								-1.5%			
								0 U			
Belelem-	Compila-	SE	10	26°N	~21	~19	~?	calib for	1	55	
nite	tion	France-	17	20 11	(+0.6)	(+0.6)	(+0.6)	low Mg	v		
Mg/Ca	uon	Spain			(=0.0)	(=010)	(=0.0)	calcite			
ratio		~ 1						benthic			
								foraminif-			
								era ⁷¹			

371 Supplementary Table 1. Valanginian geochemical multi-proxy based ocean temperatures across

372 the Weissert Event. Average values document, when possible, i) the average temperature value

373 representing the Weissert warm interval that characterizes the initial phase of the event from the onset

of the Weissert carbon isotope excursion (CIE) (A, Fig. 3 in the article) to the first Weissert CIE peak

375 (B, Fig.3); ii) the cool temperature reached at the end of the Weissert CIE (C, Fig. 3), and iii) the

temperature change (cooling) that is calculated as the difference between the ocean temperatures of

both intervals. We point out that all literature records document a large scatter and thus the reported

378 uncertainties are probably minimum estimates. This may also apply to the relatively small calibration

uncertainty (e.g., 0.6/0.9) reported for oxygen isotope and Mg/Ca records.

			Summer bia	s assumption	Annual mean assumption		
	Time interval	Ν	Mean [°C]	SEM [°C]	Mean [°C]	SEM [°C]	
	Warm interval	12	21.3	1.2	24.4	1.8	
min-TEX ₈₆	Cold end	8	18.3	1.1	21.5	1.6	
	Cooling	/	3.0	1.7	2.9	2.4	
	Warm interval	12	25.5	2.7	28.7	2.8	
max-TEX ₈₆	Cold end	8	24.4	4.2	27.6	3.9	
	Cooling	/	1.1	5.0	1.0	4.7	
	Warm interval	3	21.7	0.6	23.7	2.6	
only-TEX ₈₆	Cold end	4	20.6	0.3	24.2	1.9	
	Cooling	/	1.1	0.7	-0.5	3.2	
	Warm interval	4	20.7	3.1	23.6	3.5	
only- $\delta^{18}O$	Cold end	4	16.1	1.6	18.7	1.9	
	Cooling	/	4.7	3.5	5.0	4.0	
	Warm interval	5	21.5	2.0	25.4	3.4	
only- $\Delta 47$	Cold end	0	/	/	/	/	
	Cooling	/	/	/	/	/	

Supplementary Table 2. Global mean surface temperature estimates (GMSTs) from model-proxy comparison of upper ocean temperatures in °C. Mean values and standard errors of the mean (SEM) are calculated for the whole data set including the restricted basin TEX₈₆ calibration for DSDP/ODP Sites 534, 603 and 692 (min-TEX₈₆), the same data but applying the BAYSPAR TEX₈₆ calibration for DSDP/ODP Sites 534, 603 and 692 (max-TEX₈₆), and different subsampling experiments including only single proxy techniques (only-TEX₈₆, only- δ^{18} O and only- Δ 47). The model-data comparison is performed both with annual mean model data (annual mean assumption) as well as with 3-month summer mean temperatures for sites poleward of 45 ° (summer bias assumption). The assumption of a potential bias towards summer temperatures in high-latitude proxy reconstructions always leads to lower GMST estimates due to the warmer local model temperatures (Supplementary Fig. 6).

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