



Peer review status:

This is a non-peer-reviewed preprint submitted to EarthArXiv.

# 1 **Warm deep ocean temperatures from clumped isotopes suggest high climate** 2 **sensitivity in early Cenozoic hothouse**

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17

## 18 **Abstract**

19 The early Cenozoic was characterized by the warmest climates and highest atmospheric CO<sub>2</sub> levels of the past 85  
20 Myrs. Reconstructions of deep ocean temperatures based on benthic foraminiferal oxygen isotope records are  
21 typically used to infer Earth's global climate state during this hothouse world. However, this approach requires  
22 uncertain assumptions, regarding the seawater isotope composition and pH, and species-specific vital effects. Here  
23 we use clumped isotope thermometry, a proxy not complicated by non-thermal influences, to reconstruct early  
24 Cenozoic deep ocean temperatures on million-year time scales from the South Atlantic Ocean. We find on average  
25 warmer temperatures than previously derived from oxygen isotopes, consistent with clumped isotope  
26 reconstructions from the North Atlantic. These results challenge our understanding of seawater isotope composition  
27 in an ice-free world and invoke potential pH effects on the benthic oxygen isotopes. Deep ocean temperatures  
28 reached maximum values of up to 20 °C during the Early Eocene Climatic Optimum, which is >5 °C warmer than  
29 previously thought. These findings imply that (past) climate sensitivity to pCO<sub>2</sub> forcing was much higher (6 to 8 °C)  
30 than currently used in climate models that simulate future warming scenarios of the IPCC (2.5 to 4.0 °C).

31

## 32 **Introduction**

33 The ocean is responsible for most of the heat transport from the equator to the polar latitudes and is an important

34 reservoir of carbon available in the climate system (Trenberth & Caron, 2001; Rose & Ferreira, 2013). Changes in  
35 the strength and patterns of ocean circulation influence the heat distribution and ocean carbon storage capacity  
36 (Anderson et al., 2009; Srokosz et al., 2012). The deep ocean is therefore considered to represent a key factor in  
37 regulating the state and evolution of Earth's global climate and the global carbon cycle through time (Clark et al.,  
38 2002; Anderson et al., 2009; Sexton et al., 2011; Burke & Robinson, 2012; Kostov et al., 2014). Reconstruction of  
39 deep ocean temperatures, or basically bottom water temperatures (BWT), is hence essential to investigate climate  
40 states in the geological past. A time when ocean temperature conditions were fundamentally different from today is  
41 the early Cenozoic, and particularly the late Paleocene to early Eocene (59–48 Ma). Proxy reconstructions show  
42 that this period experienced the warmest climates of the Cenozoic associated with highly elevated atmospheric CO<sub>2</sub>  
43 levels (~800–2500 ppm) (Penman et al., 2014; Anagnostou et al., 2016, 2020; Gutjahr et al., 2017; Harper et al.,  
44 2020; Rae et al., 2021; CenCO2PIP, 2023) with no continental ice sheets on both hemispheres and a strongly  
45 reduced equator to pole surface temperature gradient (Tripathi et al., 2003; Sluijs et al., 2006, 2009, 2011; Pearson  
46 et al., 2007; Zachos et al., 2008; Bijl et al., 2009, 2013; Hollis et al., 2012, 2019; Frieling et al., 2014, 2018; Inglis  
47 et al., 2015; Cramwinckel et al., 2018; Evans et al., 2018a; Harper et al., 2018; Gaskell et al., 2022; Fokkema et al.,  
48 2024a; Fokkema et al., 2024b; Kegel, Fokkema et al., 2025). Hence, the early Cenozoic is considered the most  
49 recent analogue for experiencing scenarios of high future CO<sub>2</sub> concentrations and associated global warming.  
50 Temperature reconstructions of this time may therefore provide important constraints on the sensitivity of the Earth's  
51 climate to elevated CO<sub>2</sub> levels (Burke et al., 2018; Inglis et al., 2020). In addition, these temperature estimates can  
52 be used to assess the performance of climate model simulations (Lunt et al., 2021).

53  
54 Over the past three decades, records of oxygen isotopes (Zachos et al., 2001, 2008; McCarren et al., 2008; Stap  
55 et al., 2010; Littler et al., 2014; Lauretano et al., 2015, 2016, 2018; Barnet et al., 2019; Thomas et al., 2018; Westerhold  
56 et al., 2018, 2020) and Mg/Ca ratios (Lear et al., 2000, 2010, 2015; Tripathi & Elderfield, 2005; Cramer et al., 2011)  
57 obtained from the fossil shells of benthic foraminifera have been widely used to estimate BWT across the Cenozoic.  
58 Since recent years, measurements of clumped isotopes (or “multiply substituted isotopologues”) have emerged as  
59 a new tool to reconstruct ocean temperatures (Rodríguez-Sanz et al., 2017; Evans et al., 2018a; Leutert et al.,  
60 2019, 2020, 2021; Modestou et al., 2020; Agterhuis et al., 2022; Meckler et al., 2022; Braaten et al., 2023; Hou et  
61 al., 2023; Taylor et al., 2023; Kocken et al., 2024). Carbonate clumped isotope thermometry ( $\Delta_{47}$ ) builds on the  
62 temperature dependent abundance of bonds between the heavy carbon and heavy oxygen isotopes (<sup>13</sup>C–<sup>18</sup>O)  
63 within carbonate ions, with more “clumping” of these rare heavier isotopes occurring at lower temperatures (Gosh  
64 et al., 2006; Schauble et al., 2006; Eiler et al., 2007, 2011; Huntington & Petersen, 2023). Analytical advances over  
65 the past decade have significantly reduced sample size requirements and have enabled the reproducibility of  
66 measurements across different laboratories (Huntington et al., 2009; Schmid & Bernasconi, 2010; Dennis et al.,  
67 2011; He et al., 2012; Bernasconi et al., 2013, 2018, 2021; Hu et al., 2014; Meckler et al., 2014; Müller et al., 2017).

68 Importantly, unlike the traditional  $\delta^{18}\text{O}$  and Mg/Ca proxies, clumped isotopes have the advantage that they are not  
69 affected by factors other than temperature. This clumping is independent of the isotope composition of the source  
70 water (Gosh et al., 2006; Schauble et al., 2006; Eiler et al., 2007, 2011; Huntington & Petersen, 2023). Several  
71 studies have furthermore shown that species-specific physiological differences (vital effects) in clumped isotope  
72 fractionation in foraminifera are small or non-existent (Tripathi et al., 2010; Grauel et al., 2013; Breitenbach et al.,  
73 2018; Peral et al., 2018, 2022; Piasecki et al., 2019; Meinicke et al., 2020) and experiments and models have not  
74 found significant pH effects on  $\Delta_{47}$  (Hill et al., 2014; Tang et al., 2014; Tripathi et al., 2015; Kelson et al., 2017;  
75 Watkins & Hunt, 2015; Guo et al., 2020; Watkins & Devriendt, 2022).

76  
77 Recently, the first clumped isotopes analysis on benthic foraminifera from Newfoundland, North Atlantic has  
78 revealed a new picture of BWT evolution across the early Cenozoic, with on average warmer temperatures than  
79 estimated from benthic oxygen isotopes ( $\delta^{18}\text{O}_b$ ), as well as surprisingly large temperature fluctuations on what seem  
80 to be million-year time scales (Meckler et al., 2022). However, the reported temperature variations might to some  
81 extent represent a regional signal unique to the small North Atlantic basin instead of global BWT changes. To  
82 answer this question, here we present and discuss a late Paleocene-early Eocene  $\Delta_{47}$ -based BWT record of the  
83 South Atlantic, a region that constitutes a major part of Cenozoic  $\delta^{18}\text{O}_b$  compilations (Cramer et al., 2011;  
84 Westerhold et al., 2020). For this purpose, we measured paired stable ( $\delta^{18}\text{O}_b$  and  $\delta^{13}\text{C}_b$ ) and clumped ( $\Delta_{47}$ ) isotopes  
85 on several benthic foraminiferal species from ODP (Ocean Drilling Program) Sites 1262 and 1263 (Walvis Ridge)  
86 (Zachos et al., 2004, 2005) to produce multiple new BWT bins in the period 60–48 Ma (see Supplementary Figure  
87 S1 for paleogeographic map). Each of these individual temperature bins represent the background climate states  
88 (thereby excluding hyperthermal events) and are based on numerous replicate  $\Delta_{47}$  measurements obtained from  
89 neighbouring samples, thereby each reflecting average conditions of 100–200 kyr intervals (see Methods).

90  
91 From clumped isotopes, we find similarly warm BWT in the South Atlantic compared to the North Atlantic (Meckler  
92 et al., 2022). However, temperatures appear more stable than in the North Atlantic, suggesting that the deep South  
93 Atlantic captures more of a global signal. These warmer BWT from  $\Delta_{47}$  than previously inferred from  $\delta^{18}\text{O}_b$  challenge  
94 longstanding assumptions on the oxygen isotope composition of the seawater ( $\delta^{18}\text{O}_{sw}$ ) in the early Cenozoic ice-  
95 free climate state. Potential pH effects on  $\delta^{18}\text{O}_b$  are required to explain the temperature discrepancy between the  
96 two proxies. Clumped isotopes show a major warming in the entire deep Atlantic at the onset of Early Eocene  
97 Climatic Optimum (~52 Ma), which is accompanied by elevated atmospheric  $\text{CO}_2$  levels. These higher BWT  
98 estimates from clumped isotopes suggest higher climate sensitivity to  $\text{pCO}_2$  forcing across the early Cenozoic than  
99 previously appreciated.

100

## 101 **Results and Discussion**

102

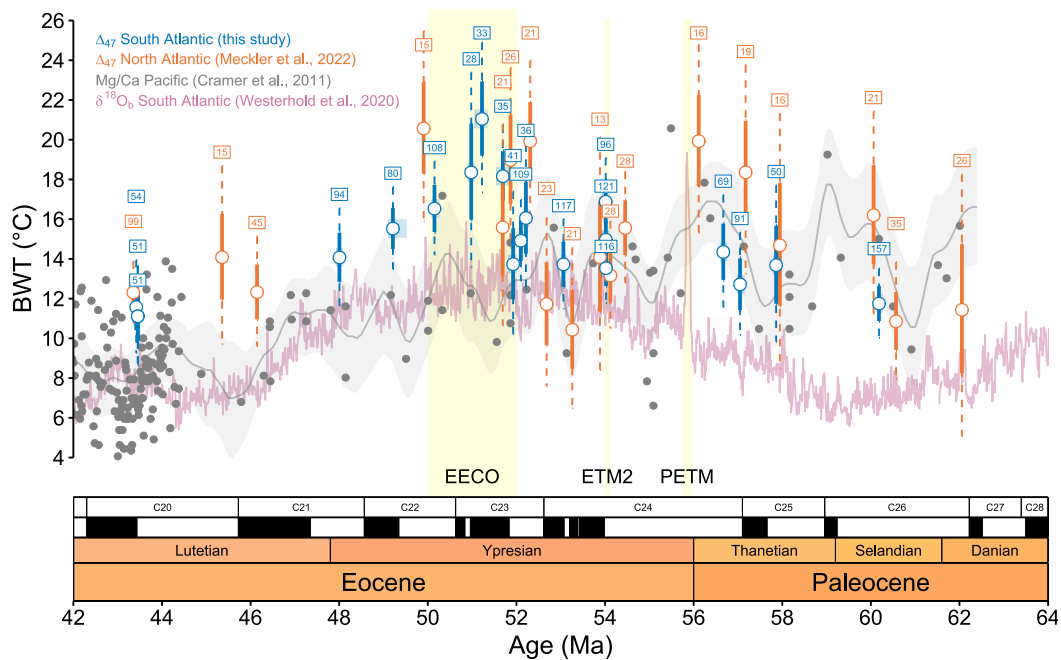
### 103 **Deep ocean temperatures**

104 Our new  $\Delta_{47}$ -based BWT from the South Atlantic are, like those from the North Atlantic (Meckler et al., 2022), overall  
105 warmer than the temperatures calculated from  $\delta^{18}\text{O}_b$  compiled for the South Atlantic (McCarren et al., 2008; Stap  
106 et al., 2010; Littler et al., 2014; Lauretano et al., 2015, 2016, 2018; Barnet al., 2019; Thomas et al., 2018; Westerhold  
107 et al., 2020) (Figure 1). The North Atlantic  $\Delta_{47}$ -data follows the new age model for IODP Site U1409 (Kirtland Turner  
108 et al., 2024), which changes the age of some data points up to 0.5 Myr compared to the original publication (Meckler  
109 et al., 2022). One might consider potential post depositional alteration of the  $\Delta_{47}$  signal as cause for the temperature  
110 discrepancy with the oxygen isotopes. However, previous studies comparing sites with different sedimentation rates  
111 have not found a relationship between  $\Delta_{47}$ -based temperatures and burial depth, which challenges this explanation  
112 (Meckler et al., 2022). The high-resolution composite  $\delta^{18}\text{O}_b$  record suggests that a gradual warming trend started  
113 from the late Paleocene onwards that culminated in a sustained period of peak global warmth, known as the EECO  
114 (~52–50 Ma) (Figure 1) (Westerhold et al., 2020). The clumped isotopes do not indicate a clear warming trend from  
115 the Paleocene into the early Eocene, though they reveal the warmest BWT at the EECO reaching up to exceptional  
116 values of ~20 °C. After this peak warmth, both the  $\Delta_{47}$  and  $\delta^{18}\text{O}_b$  data show a long-term cooling for the remainder  
117 of the Eocene. In comparison to the North Atlantic, our South Atlantic BWTs show less large amplitude variations  
118 and are on average cooler in the late Paleocene (~18 °C vs. 14 °C) and warmer in the early Eocene (~11 °C vs. 15  
119 °C). These differences might point to periodically local sources of deep water in the North Atlantic (Hohbein et al.,  
120 2012; Cramwinckel et al., 2020; Vickers et al., 2020), while the South Atlantic and Pacific were bathed by water  
121 masses primarily formed in the southern high latitudes (Thomas et al., 2003, 2014; Via & Thomas, 2006; Huck et  
122 al., 2017; Batenburg et al., 2018; Zhang et al., 2020, 2022).

123

124 Early Cenozoic BWT derived from Mg/Ca appear to be different from both oxygen and clumped isotope  
125 reconstructions (Figure 1). In the Eocene, our  $\Delta_{47}$ -based BWT are both warmer than inferred from Mg/Ca and  $\delta^{18}\text{O}_b$ .  
126 The major warming during the EECO also does not appear in the Mg/Ca record. The  $\Delta_{47}$  and Mg/Ca-based  
127 temperatures seem to be more consistent to each other in the Paleocene, being both warmer than estimated  
128 from  $\delta^{18}\text{O}_b$ . Unlike the  $\delta^{18}\text{O}_b$  record, the Mg/Ca-based BWTs do not exhibit a warming trend towards the early  
129 Eocene. In fact, the warmest Mg/Ca-based temperatures occur in the Paleocene and show a long-term cooling  
130 trend afterwards. In addition, there is high variability and 1–4 Myr oscillations in the Mg/Ca data that are not  
131 observed in the  $\delta^{18}\text{O}_b$  record (the clumped isotope record being of too low resolution to make a comparison).  
132 However, the longer-term oscillations are probably an artifact because of aliasing higher frequency variability  
133 (Cramer et al., 2011). Like oxygen isotopes, foraminiferal Mg/Ca is also affected by seawater chemistry.  
134 Reconstructions of BWT before 48 Ma have been considered to be unreliable (Miller et al., 2020) because of large  
135 uncertainties in the Mg/Ca composition of the past seawater (Lowenstein et al., 2001; Horita et al., 2002; Coggon

136 et al., 2010; Broecker & Yu, 2011; Evans & Müller, 2012; Lear et al., 2015; Evans et al., 2016; Evans et al., 2018b)  
 137 This might explain the apparent cooling trend in the early Cenozoic Mg/Ca-based BWT. In addition, other non-  
 138 thermal influences that complicate the Mg/Ca proxy might play a role, such as the carbonate saturation state  
 139 (Elderfield et al., 2006; Yu & Elderfield, 2008; Lear et al., 2010; Kender et al., 2014; Evans et al., 2018b; Gray et  
 140 al., 2018), and vital effects (Lear et al., 2002; Marchitto et al., 2007).  
 141



142  
 143 **Figure 1.** Comparison of early Cenozoic BWTs based on  $\delta^{18}\text{O}_6$  from the Walvis Ridge, South Atlantic (ODP Sites 1262/1263/1265)  
 144 (McCarren et al., 2008; Stap et al., 2010; Littler et al., 2014; Lauretano et al., 2015, 2016, 2018; Thomas et al., 2018; Barnet al.,  
 145 2019; Westerhold et al., 2020), Mg/Ca with trend and shaded 90% confidence intervals from Cramer et al., 2011 calibrated  
 146 following Lear et al., 2010, and  $\Delta_{47}$  from the Walvis Ridge, South Atlantic (ODP Sites 1262/1263) (this study; Leutert et al., 2019;  
 147 Agterhuis et al., 2022) and Newfoundland, North Atlantic (IODP Sites U1407/U1409) (Leutert et al., 2019; Meckler et al., 2022).  
 148 The Mg/Ca-based temperatures are primarily derived from Shatsky Rise, Western Pacific (ODP Site 1209) (Dutton et al., 2005a,  
 149 2005b) with additional data around ~55 Ma from the Weddell Sea, Southern Ocean (ODP Site 689) (Lear et al., 2000; Billups &  
 150 Schrag, 2003). The two South Atlantic clumped isotope temperature bins ( $n = 28$  and  $n = 33$ ) in the middle part of the EECO  
 151 originate from a single bin published in Meckler et al., 2022, which was separated into two parts in our study because of the  
 152 relatively long duration of the bin. The North Atlantic  $\Delta_{47}$  data is plotted following the new age model for IODP Site U1409 (Kirtland  
 153 Turner et al., 2024). The error bars on the  $\Delta_{47}$ -based temperatures indicate 68% (solid) and 95% (dashed) confidence intervals,  
 154 representing fully propagated analytical and calibration uncertainties. Numbers above  $\Delta_{47}$  data bins represent the number of  
 155 (replicate) measurements. The  $\Delta_{47}$ -derived temperatures were calculated using the foraminiferal clumped isotope calibration by  
 156 Meinicke et al., 2020, 2021 (see Methods). The effect of using an alternative clumped isotope calibration on the temperature  
 157 estimates is shown in Supplementary Figure S5. The  $\delta^{18}\text{O}_6$  data were corrected to *Cibicidoides* values (seawater equilibrium)  
 158 before calculation of BTW using the calibration of Marchitto et al., 2014 (see Methods). The record represents a 5 pts LOESS  
 159 smoothing of data averaged in 5 kyr time steps.

160

## 161 **Oxygen isotope composition of the seawater**

162 A major implication of the warmer BWT derived from clumped isotopes in comparison to  $\delta^{18}\text{O}_b$  is that they suggest  
163 that longstanding assumptions on the  $\delta^{18}\text{O}_{sw}$  in the early Cenozoic hothouse are not valid and require a re-  
164 assessment. Benthic oxygen isotope records represent a combined signal of BWT and  $\delta^{18}\text{O}_{sw}$  (Ravelo & Hillaire-  
165 Marcel, 2007; Pearson, 2012; Raymo et al., 2018). For the early Cenozoic, a constant  $\delta^{18}\text{O}_{sw}$  value of  $-1\text{‰}$  based  
166 on the absence of ice sheets is commonly used in the calculation of  $\delta^{18}\text{O}_b$ -derived BWT (Shackleton, 1986).  
167 Seawater isotope composition can be calculated when we combine the clumped isotope-derived temperatures with  
168 the oxygen isotope data of our measurements (see Methods). Our simultaneously obtained  $\delta^{18}\text{O}_b$  and  $\delta^{13}\text{C}_b$  data  
169 are consistent with previous studies (Supplementary Figure S2) (Littler et al., 2014; Lauretano et al., 2015, 2016,  
170 2018; Westerhold et al., 2020).

171

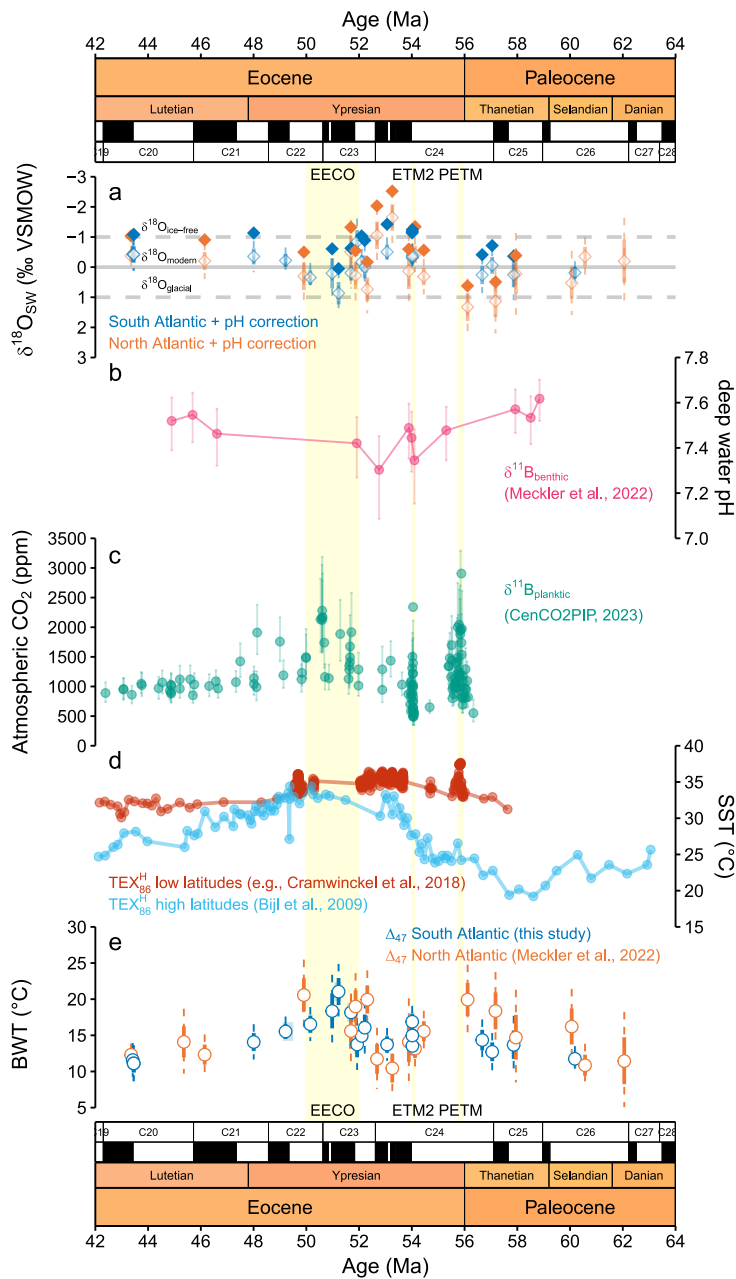
172 We find that the inferred  $\delta^{18}\text{O}_{sw}$  is much higher than the assumed composition based on an ice-free world (Figure  
173 2a). A first explanation would be that large ice sheets like present-day existed in the Paleocene and Eocene, which  
174 however seems highly unlikely given the evidence for subtropical temperatures and fossil evidence of palm trees  
175 and crocodiles in the polar regions (Sluijs et al., 2006, 2009; Bijl et al., 2009; Pross et al., 2012). Furthermore,  
176 records of ice-rafted debris only support the existence of small ice caps starting in the middle Eocene on Antarctica  
177 (Carter et al., 2017; Gulick et al., 2017; Barr et al., 2022) and the northern high-latitudes (Eldrett et al., 2007; St.  
178 John, 2008; Stickley et al., 2009; Darby, 2014; Tripathi & Darby, 2018; Spray et al., 2019), only eventually culminating  
179 millions later in large-scale Antarctic glaciation at the Eocene-Oligocene Transition (Ehrmann & Mackensen, 1992;  
180 Zachos et al., 1992; Scher et al., 2011; Galeotti et al., 2016; Passchier et al., 2017; Klages et al., 2024). Other  
181 factors have been proposed to influence the  $\delta^{18}\text{O}_{sw}$  on a global scale, such as isotope exchange between seawater  
182 and ocean crust at mid-ocean ridges, and ground water storage on land. Changes in mid-ocean ridge spreading  
183 rates may be able to influence the seawater isotope budget on multi-million-year timescales (Wallmann, 2001;  
184 Jaffrés et al., 2007), however, the global rates in the early Cenozoic were not different from today (Conrad &  
185 Lithgow-Bertelloni, 2007; Müller et al., 2008). Discharging and charging of continental aquifers has been invoked to  
186 explain large fluctuations in reconstructed sea level in the Cretaceous hothouse climate (Sames et al., 2020),  
187 however direct evidence for this is not available (Davies et al., 2020). Changes in deep ocean salinity is another  
188 factor that can alter  $\delta^{18}\text{O}_{sw}$ , but only on local/regional scales as the global ocean water isotope budget is constant  
189 (Ravelo & Hillaire-Marcel, 2007; Pearson, 2012). Deep ocean salinity reflects the evaporation-precipitation regime  
190 in the source regions of the deep water (Ravelo & Hillaire-Marcel, 2007; Pearson, 2012), and changes in  $\delta^{18}\text{O}_{sw}$   
191 could therefore indicate shifts in the distribution of different water masses (changes in ocean overturning circulation)  
192 (Meckler et al., 2022).

193

194 **pH effects on the oxygen isotopes**

195 Alternatively, instead of an underestimation of  $\delta^{18}\text{O}_{\text{sw}}$ , it could be that we are observing an effect of lower ocean pH  
196 on the incorporation of the oxygen isotopes in the foraminiferal tests (Spero et al., 1997; Uchikawa & Zeebe, 2010).  
197 Theory predicts this pH ( $\text{CO}_3^{2-}$ ) effect, suggesting that the oxygen isotope values of foraminifera should become  
198 higher with decreasing pH with a slope of  $-1.42$  ‰/unit pH (Zeebe, 1999, 2001) based on results from inorganic  
199 calcite precipitation experiments (McCrea, 1950; Usdowski & Hoefs, 1993). Oxygen isotope-based temperatures  
200 are calculated using calibrations established at modern ocean pH (e.g. Marchitto et al., 2014). Low-resolution  
201 reconstructions based on boron isotopes indicate that deep ocean was more acidic in the early Cenozoic, with pH  
202 on average about 0.5 units lower than present-day (pH of  $\sim 7.5$  vs.  $\sim 8.0$ , respectively) (Lauvset et al., 2020; Meckler  
203 et al., 2022) (Figure 2b), which can be attributed to the elevated atmospheric  $\text{CO}_2$  levels (Figure 2c). If not corrected  
204 for this lower pH, elevated foraminiferal  $\delta^{18}\text{O}$  values would be interpreted as apparent cooler temperatures. Note  
205 that there is only direct evidence for a pH effect on the oxygen isotopes of planktic foraminifera from culture  
206 experiments, which show different slopes for this effect between species (Spero et al., 1997). At present, it is unclear  
207 from sediment core top studies whether this effect also exists for benthic foraminifera (Rathmann & Kuhnert, 2008;  
208 Marchitto et al., 2014). Nonetheless, if we correct the  $\delta^{18}\text{O}_b$  measurements for a pH effect (using the theoretical  
209 slope of  $1.42$  ‰/unit pH), it brings the reconstructed  $\delta^{18}\text{O}_{\text{sw}}$  closer to the assumed  $-1$ ‰ value (Figure 2a). Thus, a  
210 large part of the BWT mismatch (approximately  $2$  to  $3^\circ\text{C}$ ) between the clumped- and oxygen isotopes might be  
211 explained by a so far neglected pH effect on the  $\delta^{18}\text{O}_b$  (Meckler et al., 2022; Evans et al., 2024; Rohling et al.,  
212 2024). Changes in the salinity of the deep water might then explain the residual variability in  $\delta^{18}\text{O}_{\text{sw}}$ , or there are  
213 changes in deep ocean pH that are not captured in the low-resolution deep ocean pH reconstruction used for our  
214 corrections (Fig. 2b).





216

217 **Figure 2. a)** inferred  $\delta^{18}\text{O}_{\text{sw}}$  composition from the combined  $\Delta_{47}$ -based BWT and  $\delta^{18}\text{O}_b$  data (corrected to *Cibicidoides* values)  
 218 from the Walvis Ridge, South Atlantic (ODP Sites 1262/1263) (this study; Leutert et al., 2019; Agterhuis et al., 2022) and  
 219 Newfoundland, North Atlantic (IODP Sites U1407/U1409) (Leutert et al., 2019; Meckler et al., 2022) (see Methods). The data  
 220 represented with a closed fill indicate the  $\delta^{18}\text{O}_{\text{sw}}$  values corrected for an assumed pH effect on the  $\delta^{18}\text{O}_b$ . **b)** deep water pH based  
 221 on boron isotopes of benthic foraminifera from the North Atlantic (ODP Sites 1258/1260 and IODP Site U1409) (Meckler et al.,  
 222 2022). **c)** atmospheric  $\text{CO}_2$  level reconstructions based on boron isotopes on planktic foraminifera (Penman et al., 2014;  
 223 Anagnostou et al., 2016, 2020; Gutjahr et al., 2017; Harper et al., 2020; Rae et al., 2021; CenCO2PIP, 2023). **d)** sea surface  
 224 temperature reconstructions based on  $\text{TEX}_{86}$  from the equatorial Atlantic (ODP Site 959) (Cramwinckel et al., 2018; Frieling et al.,  
 225 2018; Fokkema et al., 2024a; Kegel, Fokkema et al., 2025) and the Southern Ocean (ODP Site 1172) (Bijl et al., 2009). **e)**  $\Delta_{47}$ -  
 226 based BWTs from the Walvis Ridge, South Atlantic (ODP Sites 1262/1263) (this study; Leutert et al., 2019; Agterhuis et al., 2022)  
 227 and Newfoundland, North Atlantic (IODP Sites U1407/U1409) (Leutert et al., 2019; Meckler et al., 2022).

228

### 229 **High climate sensitivity**

230 At the start of the EECO around 52 Ma, a major warming (~5 °C) is recorded in the deep Atlantic, reaching  
231 exceptional peak temperatures of up to ~20 °C (Figures 1 and 2e). This rise in BWT coincides with elevated  
232 atmospheric CO<sub>2</sub> levels up to ~2000 ppm, as reconstructed from boron isotopes (Figure 2c), which approach peak-  
233 PETM values (Penman et al., 2014; Anagnostou et al., 2016, 2020; Gutjahr et al., 2017; Harper et al., 2020; Rae  
234 et al., 2021; CenCO2PIP, 2023). This co-occurrence could suggest a global pCO<sub>2</sub> forcing of these very warm  
235 temperatures, implying a rise in global temperatures. This warming seems however absent in current sea surface  
236 temperature reconstructions (Figure 2d) (Tripathi et al., 2003; Bijl et al., 2009, 2013; Frieling et al., 2014; Inglis et al.,  
237 2015; Cramwinckel et al., 2018; Fokkema et al., 2024a), which might be because of a geographical bias (Judd et  
238 al., 2020). The rise in CO<sub>2</sub> levels during the EECO may be related to an increase in volcanic activity in several  
239 igneous provinces (Storey et al., 2007; Lee et al., 2013; Reagan et al., 2013; Brune et al., 2017; Zhang et al., 2023),  
240 decreased marine primary productivity (weaker biological pump) (Hilting et al., 2008), and/or ventilation of dissolved  
241 inorganic carbon as proposed for the short-lived early Eocene hyperthermal events (Sexton et al., 2011).  
242 Interestingly, the onset of highly elevated BWT occurs before a global positive shift in carbon isotope records  
243 (Zachos et al., 2010; Kirtland Turner et al., 2014; Lauretano et al., 2016, 2018; Westerhold et al., 2018)  
244 (Supplementary Figure S2), suggesting that the warming may indirectly have affected the global carbon cycle.

245

246 For a long time now, BWT have intuitively been used to track the evolution of the global climate state over the  
247 Cenozoic, as the deep ocean constitutes the largest heat reservoir and represents a relatively stable component in  
248 the climate system (Zachos et al., 2001; Hansen et al., 2013; Westerhold et al., 2020). Recently, two studies that  
249 analysed climate simulation results from an ensemble of models have shown that BWT changes correlate with  
250 global mean surface temperature (GMST) changes in an approximate 1:1 ratio (Goudsmit-Harzevoort et al., 2023;  
251 Evans et al., 2024), consistent with early arguments by Hansen et al., 2013. In other words, the global average BWT  
252 change equals the global surface temperature change. Thus, a peak BWT of ~19 °C during the EECO would  
253 translate to a GMST of ~33 °C (considering modern BWT of ~0 °C and GMST of ~14 °C) (Goudsmit-Harzevoort et  
254 al., 2023; Evans et al., 2024). Such highly elevated GMST is also found for the Paleocene-Eocene Thermal  
255 Maximum (PETM; 56 Ma) based on sea surface temperature reconstructions (Tierney et al., 2022). Our new South  
256 Atlantic BWT estimates from clumped isotopes can be placed into a broader perspective of global climate. For this,  
257 we need to assume that the reconstructed South Atlantic BWT are representative for the global deep ocean, i.e., a  
258 homogeneous global deep ocean. While awaiting clumped isotope early Cenozoic BWT reconstructions from the  
259 Pacific, small interbasinal isotopic differences ( $\delta^{13}\text{C}_b$  and  $\delta^{18}\text{O}_b$ ) found between the South Atlantic and Pacific during  
260 this time support this assumption (Cramer et al., 2009; Lauretano et al., 2018; Westerhold et al., 2018). Clumped  
261 isotope records from the Pacific are available for the Eocene-Oligocene Transitions (~34 Ma) and show BWT of

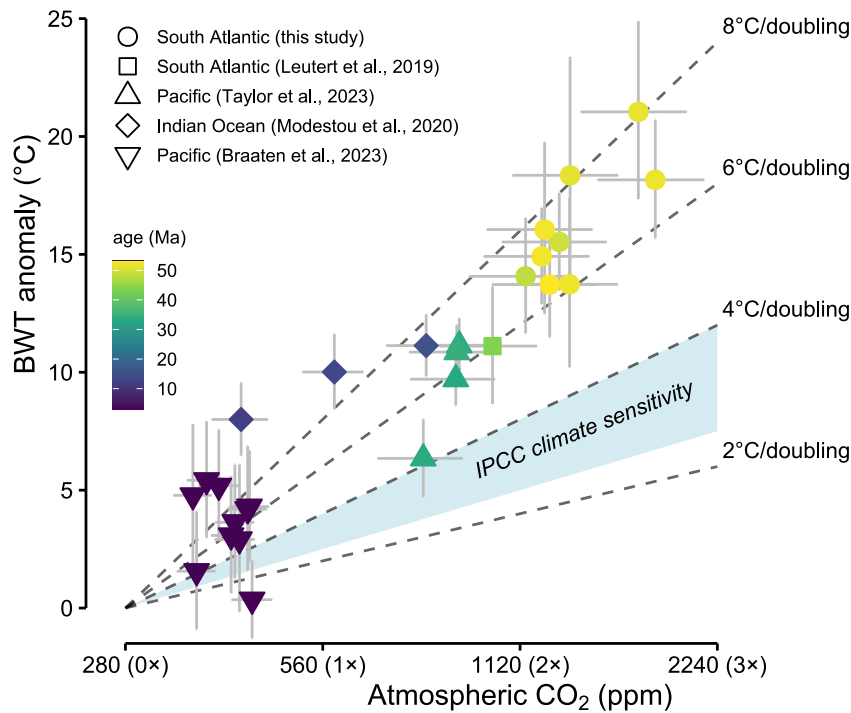
262 ~11 °C during the latest Eocene (Taylor et al., 2023), which are very similar to  $\Delta_{47}$ -based Atlantic BWT  
263 reconstructions for a time slice in the middle Eocene (~43 Ma) (Leutert et al., 2019). In addition, climate model  
264 simulations of the early Eocene also show little variation in BWT (typically <1°C) around the globe (Goudsmit-  
265 Harzevoort et al., 2023).

266

267 Using our new BWT in conjunction with atmospheric CO<sub>2</sub> level reconstructions allows for the opportunity to reassess  
268 climate sensitivity through the Cenozoic. The most used form of climate sensitivity in future climate projections is  
269 Equilibrium Climate Sensitivity, defined as the equilibrium GMST increase in response to a doubling in atmospheric  
270 CO<sub>2</sub> levels (PALAEOSENS, 2012). This only includes fast feedback processes (e.g., clouds, lapse rate, snow, sea  
271 ice). Our early Cenozoic BWT are however not only determined by CO<sub>2</sub> and short-term climate responses, but also  
272 incorporate effects of slower geological feedback processes such as changing paleogeography and growth/decay  
273 of continental ice sheets. Hence, we can only interpret our temperatures into the frame of so-called Earth System  
274 Sensitivity (Lunt et al., 2010; Pagani et al., 2010; PALAEOSENS, 2012; Royer et al., 2012; Feng et al., 2020; Ring  
275 et al., 2022).

276

277 The coevolution of BWT (relative changes are representative for similar change in GMST) and atmospheric CO<sub>2</sub>  
278 through the Cenozoic is displayed in Figure 3. The Paleocene data is absent in this compilation because no CO<sub>2</sub>  
279 level reconstructions have been published yet for this epoch. In addition to our Eocene clumped isotope data from  
280 the South Atlantic, we have added other  $\Delta_{47}$ -based BWT reconstructions in different ocean basins across younger  
281 intervals in the Cenozoic (Figure 3). We exclude Cenozoic  $\Delta_{47}$ -based temperatures from the relatively smaller North  
282 Atlantic basin (Meckler et al., 2022; Braaten et al., 2023) because it periodically exhibits temperature offsets  
283 compared to other ocean basins. In addition to the North-South Atlantic temperature differences observed in our  
284 early Cenozoic study (Figure 1), BWT reconstructions from the more recent mid-Pliocene indicate that the North  
285 Atlantic was >4 °C warmer than the Pacific during this period (Braaten et al., 2023). These findings suggest that  
286 additional factors, such as changes in ocean circulation, influenced North Atlantic BWTs beyond the global forcing  
287 of pCO<sub>2</sub> levels.



289

290 **Figure 3.** Earth System Sensitivity across the Cenozoic based on clumped isotope-based BWTs. The compilation includes BWTs  
 291 from the Eocene in the South Atlantic (ODP Sites 1262/1263) ([this study](#), [Leutert et al., 2019](#)), the Eocene-Oligocene Transition  
 292 in the Eastern Pacific (ODP Site 1218 and IODP Sites U1333/U1334) ([Taylor et al., 2023](#)), the Miocene in the Indian Ocean (ODP  
 293 Site 761) ([Modestou et al., 2020](#)), and the Pliocene in the Eastern Pacific (ODP Site 849) ([Braaten et al., 2023](#)). The pre-industrial  
 294 BWT is set at 0 °C. The lightblue shading indicates the climate sensitivity used by the IPCC ([Collins et al., 2013](#); [Sherwood et al.,](#)  
 295 [2020](#); [Forster et al., 2021](#)).

296

297 The Cenozoic data compilation shows a strong relationship between atmospheric CO<sub>2</sub> and BWT on long time  
 298 scales. The CO<sub>2</sub> is plotted on a logarithmic scale, and the slopes of the dashed lines therefore represent different  
 299 magnitudes of Earth System Sensitivity. Our inferred Earth System Sensitivity across the Cenozoic generally falls  
 300 within the range of 6 to 8 °C, a similar result to previous modelling work ([Zhu et al., 2019](#)) and sea surface  
 301 temperature proxy data ([Tierney et al., 2022](#); [CenCO2PIP, 2023](#)). This is considerably higher than the estimated  
 302 range in present-day Equilibrium Climate Sensitivity, recently narrowed to 2.5 to 4.0 °C (best estimate 3.0 °C) in  
 303 AR6 of the Intergovernmental Panel on Climate Change (IPCC) ([Collins et al., 2013](#); [Sherwood et al., 2020](#); [Forster](#)  
 304 [et al., 2021](#)). During the early Cenozoic, when continental ice was absent, high Earth System Sensitivity might have  
 305 been controlled by fast cloud feedbacks or non-CO<sub>2</sub> greenhouse gasses that are stronger in hothouse worlds than  
 306 they are our modern colder climate system ([Zhu et al., 2019](#)). In other words, these additional processes appear to  
 307 play a key role in amplifying CO<sub>2</sub>-induced warmth, supporting a climate state dependency of climate sensitivity.  
 308 Such state dependency of climate sensitivity may have major implications for the IPCC projections of future global  
 309 warming, as these currently follow the typically lower estimated climate sensitivity.

310

## 311 **Methods**

312

### 313 **Approach for BWT reconstruction from $\Delta_{47}$**

314 A downside of measuring clumped isotopes in comparison to other proxies is that it suffers from analytical  
315 uncertainty arising from the extremely low natural abundance of  $^{13}\text{C}$ – $^{18}\text{O}$  bonds within carbonate ions and the low  
316 temperature sensitivity of this proxy ( $\sim 0.0045\text{‰}/^\circ\text{C}$ ) (Ghosh et al., 2006; Schmid & Bernasconi, 2010). Numerous  
317 replicate measurements of the same sample need to be averaged to obtain the precision required for  
318 paleotemperature reconstructions (Huntington et al., 2009; Meckler et al., 2014; Fernandez et al., 2017; de Winter  
319 et al., 2021). Therefore, clumped isotope analysis demands much larger sample sizes in comparison to  $\delta^{18}\text{O}$  and  
320  $\delta^{13}\text{C}$  (Zachos et al., 2001, 2008; Littler et al., 2014; Lauretano et al., 2015, 2016, 2018; Westerhold et al., 2018,  
321 2020), and Mg/Ca measurements (Lear et al., 2000, 2010, 2015; Tripathi & Elderfield, 2005; Cramer et al., 2011),  
322 which is inconvenient when working with ocean sediments that contain limited quantities of a given foraminiferal  
323 species.

324

325 While foraminiferal  $\delta^{18}\text{O}$  and Mg/Ca can be used to generate high resolution records, our clumped isotope-based  
326 temperatures represent the mean of  $\Delta_{47}$  measurements obtained from multiple neighbouring samples, resulting in  
327 averaging (binning) of data in intervals of 100–400 kyrs. Using this approach, we were able to generate 12 new  
328 BWT bins across the studied interval at the Walvis Ridge. The Paleocene and Eocene isotope data are derived  
329 from ODP Site 1262 (paleowater depth  $\sim 3600$  m) and ODP Site 1263 (paleowater depth  $\sim 1500$  m), respectively  
330 (Zachos et al., 2004, 2005).

331

332 As well documented, the early Eocene hothouse also knew periodical occurrences of multiple short-lived global  
333 warming events, the so-called hyperthermals (Lourens et al., 2005; Tripathi & Elderfield, 2005; Zachos et al., 2005,  
334 2010; Sluijs et al., 2006, 2009, 2011; Stap et al., 2010; Sexton et al., 2011; Kirtland Turner et al., 2014; Frieling et  
335 al., 2018; Lauretano et al., 2015, 2016, 2018; Harper et al., 2018; Westerhold et al., 2018; Fokkema et al., 2024a;  
336 Fokkema et al., 2024b; Kegel, Fokkema et al., 2025). To primarily capture changes in background climate state,  
337 we sampled intervals for our clumped isotope temperature bins that exhibit on average relatively high  $\delta^{18}\text{O}_b$  and  
338 high  $\delta^{13}\text{C}_b$  (background-related) values. In contrast, the hyperthermal events are recorded by negative excursions  
339 in high-resolution  $\delta^{18}\text{O}_b$  and  $\delta^{13}\text{C}_b$  records of Sites 1262 and 1263 (Stap et al., 2010; Littler et al., 2014; Lauretano  
340 et al., 2015, 2016, 2018). Note that early Eocene hyperthermal BWTs are expected to be approximately  $3^\circ\text{C}$  warmer  
341 than the background conditions (Agterhuis et al., 2022).

342

### 343 **Sample preparation**

344 Samples of each approximately 12 CC were first freeze-dried. Hereafter, they were washed over sieves to separate  
345 the sediment into three size fractions ( $>38\ \mu\text{m}$ ,  $>63\ \mu\text{m}$  and  $>150\ \mu\text{m}$ ) and subsequently oven-dried at  $40\ ^\circ\text{C}$   
346 overnight. The largest fraction ( $>150\ \mu\text{m}$ ) was then dry sieved to  $>212\ \mu\text{m}$  from which the benthic foraminiferal tests  
347 were picked. We picked several species or genera, specifically *Nuttallides truempyi*, *Oridorsalis umbonatus*,  
348 *Cibicidoides* spp, and additionally *Hanzawaia* spp. for some samples in the  $\sim 48$  Ma bin (Supplementary Figure S3).  
349 We generated Scanning Electron Microscope (SEM) images of a few benthic foraminiferal specimens to assess the  
350 preservation state (Supplementary Figure S4). Clearly, there are some signs of recrystallization, such as crystals  
351 of secondary calcite growing on the foraminiferal tests. However, studies have not found an impact of diagenetic  
352 overprinting on the stable and clumped isotope temperature signal of benthic foraminifera, probably because most  
353 of the recrystallization occurs during early burial at the seafloor and would therefore record the same temperatures  
354 as the original calcite (Edgar et al., 2013; Voigt et al., 2015, 2016; Stolper et al., 2018; Leutert et al., 2019; Modestou  
355 et al., 2020).

356  
357 Prior to isotope analysis, the benthic foraminifera were cleaned to remove any potential adhering particles and  
358 infillings (calcareous nannofossils, organic matter and clays). For each species, the specimens were gently cracked  
359 between two glass slides to open the test chambers. In case of low abundance, foraminifers (same species/genera)  
360 of neighbouring samples were combined to obtain sufficient material for an isotope measurement (10–20  
361 individuals). Hereafter, the foraminiferal fragments were ultrasonicated at least two times for 60 seconds in  
362 deionised water. After each ultrasonication step, the test fragments were rinsed with deionized water for at least  
363 two times until the solute was clear and no longer cloudy and the fragments displayed a glassy look under the  
364 microscope. Subsequently, after cleaning, the samples were dried at room temperature for two days. Finally, the  
365 monospecific samples were weighed and then measured for their  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ , and  $\Delta_{47}$  composition.

366

### 367 **Stable and clumped isotope analysis**

368 In total, we carried out 987 successful stable and clumped isotope measurements of foraminifer samples between  
369 April 2021 and August 2023. The setup and procedures are the same as in Agterhuis et al., 2022, which generally  
370 follows previous studies (Meckler et al., 2014; Müller et al., 2017).

371

372 A detailed description of the analytical methods and data processing can be found in the Supplementary  
373 Information. All isotope analyses ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ,  $\Delta_{47}$ ) were performed using a *Thermo Fisher Scientific MAT 253 Plus*  
374 gas source isotope mass spectrometer coupled to a *Thermo Fisher Scientific Kiel IV* carbonate preparation device  
375 (Thermo Fisher Scientific, Bremen, Germany) (Schmid & Bernasconi, 2010) at Utrecht University. The Kiel device  
376 has been equipped with a Porapak trap to capture organic contaminants (Schmid et al., 2012).

377

378 Replicate measurements of individual samples, weighed in between 70 and 90  $\mu\text{g}$ , were spread out randomly for  
379 several weeks or months. Furthermore, we measured three carbonate standards (ETH-1,-2, and -3), which differ in  
380 bulk isotopic composition and ordering state of isotopes (Bernasconi et al., 2018, 2021), to correct the stable and  
381 clumped isotope measurements of the samples. In addition, two check standards (IAEA-C2 and Merck) were used  
382 to monitor the long-term reproducibility of the instrument. Every run on the instrument included a similar number of  
383 samples and total carbonate standards, with ETH-3 being the dominant standard that was measured. External  
384 reproducibility in  $\Delta_{47}$  of the IAEA-C2 standard after correction was 0.042‰ (1 standard deviation). The final  $\delta^{13}\text{C}$   
385 and  $\delta^{18}\text{O}$  values (reported relative to the VPDB scale) of IAEA-C2 showed external reproducibility of 0.09‰ and  
386 0.14‰ (1 standard deviation), respectively.

387

### 388 $\Delta_{47}$ -based BWT calculations

389 As the relationship between  $\Delta_{47}$  and temperature is nonlinear (Anderson et al., 2021; Meinicke et al., 2020, 2021),  
390 mean  $\Delta_{47}$  values were first determined for each bin before the calculation of temperature. To achieve the necessary  
391 precision, we averaged ~30–150 individual final corrected  $\Delta_{47}$  measurements for each temperature estimate  
392 (Schmid & Bernasconi, 2010; Hu et al., 2014; Meckler et al., 2014; Fernandez et al., 2017; Müller et al., 2017; de  
393 Winter et al., 2021). As there seem to be no indications for foraminiferal species-specific effects in clumped isotopes  
394 (Peral et al., 2018, 2022; Piasecki et al., 2019; Meinicke et al., 2020), we grouped and averaged the  $\Delta_{47}$  values  
395 from different species together to generate one temperature estimate. Due to low benthic foraminiferal abundance,  
396 we pooled the  $\Delta_{47}$  data of multiple neighbouring samples together to obtain this number of measurements. This  
397 approach creates a high-resolution  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  time series for each clumped isotope bin.

398

399 To determine BWT from the mean  $\Delta_{47}$  values, we applied a foraminifer-based calibration (Meinicke et al., 2020)  
400 recalculated to the InterCarb-Carbon Dioxide Equilibrium Scale (I-CDES) in Meinicke et al., 2021 using the updated  
401 values of the carbonate standards (Bernasconi et al., 2021) (equation 1). This composite calibration is based on  
402 various planktic and benthic foraminiferal  $\Delta_{47}$  datasets derived from sediment core tops (Peral et al., 2018; Piasecki  
403 et al., 2019; Meinicke et al., 2020) and has been applied in many paleoceanographic studies (Leutert et al., 2020,  
404 2021; Modestou et al., 2020; Agterhuis et al., 2022; Meckler et al., 2022; Hou et al., 2023; Taylor et al., 2023;  
405 Braaten et al., 2024). We prefer this equation over the foraminifer-based calibration by Däeron & Gray, 2023. Their  
406 regression yields BWT approximately 2–3 °C lower across the Cenozoic, resulting in absolute values as low as  
407 –3°C during the Pleistocene, which are physically implausible. These outcomes might suggest potential issues in  
408 their approach for estimating calcification temperatures from planktic foraminifera in core tops. Therefore, we  
409 consider the calibration by Meinicke et al., 2020, 2021 to be more accurate.

410

$$\Delta_{47(I-CDES90^{\circ}C)} = (0.0397 \pm 0.0011) \times 10^6 / T^2 + (0.1518 \pm 0.0128) (T \text{ in K}) \quad (1)$$

412 ([Meinicke et al., 2020](#), recalculated to I-CDES in [Meinicke et al., 2021](#))

413

414 For comparison, we have also plotted BWT according to the combined inorganic-biogenic calibration by [Anderson](#)  
415 [et al., 2021](#) (equation 2) (Supplementary Figure S5), which spans a very wide temperature range of more than 1000  
416 °C.

417

$$\Delta_{47(I-CDES90^{\circ}C)} = (0.0391 \pm 0.0004) \times 10^6 / T^2 + (0.154 \pm 0.004) (T \text{ in K}) \quad (2)$$

419 ([Anderson et al., 2021](#))

420

421 Note that our reconstructed BWT are a little lower (~1.9 °C cooler) when using this calibration instead of the  
422 foraminifer-based regression from [Meinicke et al., 2020, 2021](#). For our study, we favour the foraminifer-based  
423 calibration because it has a large data density in the range of ocean temperatures. Furthermore, it avoids the  
424 influence of a few high temperature data points on the calibration slope ([Anderson et al., 2021](#)) that seem to suggest  
425 that the  $\Delta_{47}$ -temperature relationship might not follow a linear regression (with  $1/T^2$ ) over a large temperature range  
426 ([Guo et al., 2009; Meckler et al., 2022](#)).

427

#### 428 $\delta^{18}O_b$ -based BWT and $\delta^{18}O_{sw}$ calculations

429 To check if our  $\delta^{18}O_b$  and  $\delta^{13}C_b$  measurements are consistent with previous work (Supplementary Figure S2), we  
430 first compiled continuous high-resolution Paleocene and Eocene  $\delta^{18}O_b$  and  $\delta^{13}C_b$  records solely based on sites  
431 from the Walvis Ridge (South Atlantic) from published studies. The CENOGRID composite  $\delta^{18}O_b$  and  $\delta^{13}C_b$  records  
432 ([Westerhold et al., 2020](#)) are composed for a large part of these sites. The Paleocene to middle Eocene interval is  
433 entirely based on ODP Sites 1262 ([Stap et al., 2010; Littler et al., 2014; Barnet et al., 2019](#)) and 1263 ([McCarren et](#)  
434 [al., 2008; Stap et al., 2010; Lauretano et al., 2015, 2016, 2018; Thomas et al., 2018; Westerhold et al., 2020](#)), except  
435 for the period ~50–48 Ma which contains data from ODP Site 1258 (Demerara Rise, western tropical Atlantic)  
436 ([Sexton et al., 2011](#)). We removed the  $\delta^{18}O_b$  and  $\delta^{13}C_b$  data from Site 1258 and replaced it with Walvis Ridge data  
437 from Site 1263 ([Lauretano et al., 2016, 2018](#)) and Site 1265 ([Westerhold et al., 2020](#)). The high-resolution  $\delta^{18}O_b$   
438 and  $\delta^{13}C_b$  measurements from these studies are all based *N. truempyi*, while we also measured additional species.  
439 The oxygen isotopes of *Cibicidoides* are regarded to be close to seawater equilibrium ([Marchitto et al., 2014](#)). As  
440 such, we first corrected the isotope values of our study and the previously published records for inter-species offsets  
441 (vital effects). The isotopes of *N. truempyi* and *O. umbonatus* were converted towards *Cibicidoides* using the  
442 correction factors from [Katz et al., 2003](#) [ $\delta^{18}O_{Cib} = (\delta^{18}O_{Nutt} + 0.10)/0.89$ ;  $\delta^{13}C_{Cib} = \delta^{13}C_{Nutt} + 0.34$ ;  $\delta^{18}O_{Cib} = \delta^{18}O_{Orid}$   
443  $- 0.28$ ;  $\delta^{13}C_{Cib} = \delta^{13}C_{Orid} + 0.72$ ]. Our  $\delta^{18}O_b$  and  $\delta^{13}C_b$  measurements that are based on *Cibicidoides* obviously do



444 not require correction. Only few  $\delta^{18}\text{O}_b$  and  $\delta^{13}\text{C}_b$  measurements were derived from *Hanzawaia spp.*, which is a  
445 benthic species not commonly measured. Hence, we did not use these values for further calculations.

446

447 We calculated BWT for the compiled high-resolution South Atlantic  $\delta^{18}\text{O}_b$  composite record (Figure 1).  
448 Temperatures were obtained using the  $\delta^{18}\text{O}$ -temperature calibration for *Cibicidoides* of Marchitto et al., 2014  
449 (equation 3), which has been applied in previous reconstructions (Cramer et al., 2011; Agterhuis et al., 2022) (see  
450 discussions in Cramer et al., 2011 and Marchitto et al., 2014). A fixed value of  $-1\text{‰}$  VSMOW was employed for the  
451  $\delta^{18}\text{O}_{\text{sw}}$  based on the assumption of absence of ice sheets in the early Cenozoic (Shackleton, 1986). This regression  
452 shows good correspondence with calibrations derived from inorganic calcite (Kim & O'Neil et al., 1997; Bemis et  
453 al., 1998).

454

455  $\delta^{18}\text{O}_b(\text{‰ VPDB}) - \delta^{18}\text{O}_{\text{sw}}(\text{‰ VSMOW}) + 0.27 = (-0.245 \pm 0.005) \times T + (0.0011 \pm 0.0002) \times T^2 + (3.58 \pm 0.02)$  ( $T$  in  $^{\circ}\text{C}$ )  
456 (3)

457 (Marchitto et al., 2014)

458

459 Finally,  $\delta^{18}\text{O}_{\text{sw}}$  values were calculated for the bins, which allows us to test the traditional assumptions on  $\delta^{18}\text{O}_{\text{sw}}$   
460 under ice-free conditions. We used the average  $\delta^{18}\text{O}_b$  (corrected to *Cibicidoides*) of each bin in combination with  
461 the mean  $\Delta_{47}$ -based temperatures in equation 3 to determine the corresponding  $\delta^{18}\text{O}_{\text{sw}}$  values.

462

### 463 **Uncertainties and error propagation**

464 Uncertainties on the  $\Delta_{47}$ -based temperatures and calculated  $\delta^{18}\text{O}_{\text{sw}}$  values are reported as 68% and 95% CI. The  
465 error bars on the temperatures represent fully propagated analytical (scatter in the group of  $\Delta_{47}$  measurements) and  
466 calibration uncertainties. Errors were propagated following the conventional error propagation procedure in  
467 Huntington et al., 2009 (see the supporting information in their paper for a description of the mathematics), thereby  
468 using Matlab scripts that calculate a variance-covariance matrix of the slopes and intercepts of the foraminifer-  
469 based calibration (Meinicke et al., 2020; see Agterhuis et al, 2022 for detailed information). Note that most of the  
470 uncertainty in the  $\Delta_{47}$ -based temperatures stems from the low analytical precision of the measurements, while the  
471 effect of the calibration uncertainty is very small ( $\sim 0.11^{\circ}\text{C}$  in our error bars) (Huntington et al., 2009; Peral et al.,  
472 2018; Leutert et al., 2021). To calculate uncertainties on  $\delta^{18}\text{O}_{\text{sw}}$ , we used the  $\Delta_{47}$ -based temperatures at 68% and  
473 95% CI in equation 3 (Modestou et al., 2020; Agterhuis et al., 2022).

474

### 475 **Data availability**

476 All replicate-level raw isotope data of samples and standards will be provided upon publication in the EarthChem  
477 database (<https://www.earthchem.org/>) including information regarding the correction procedures (similar to

478 [Agterhuis et al., 2022](#) and [Meckler et al., 2022](#)). The final sample-averaged isotope data, temperatures and  $\delta^{18}\text{O}_{\text{sw}}$   
479 values are reported in Supplementary Data 1.

480

## 481 **References**

- 482 1. Agterhuis, T., Ziegler, M., de Winter, N. J. & Lourens, L. J. Warm deep-sea temperatures across Eocene  
483 Thermal Maximum 2 from clumped isotope thermometry. *Commun. Earth Environ.* **3**, 1–9 (2022).
- 484 2. Anagnostou, E. et al. Changing atmospheric CO<sub>2</sub> concentration was the primary driver of early Cenozoic  
485 climate. *Nature* **533**, 380–384 (2016).
- 486 3. Anagnostou, E. et al. Proxy evidence for state-dependence of climate sensitivity in the Eocene greenhouse.  
487 *Nat. Commun.* **11**, 1–9 (2020).
- 488 4. Anderson, R. F. et al. Wind-driven upwelling in the Southern Ocean and the deglacial rise in atmospheric  
489 CO<sub>2</sub>. *Science* **323**, 1443–1448 (2009).
- 490 5. Anderson, N. T. et al. A unified clumped isotope thermometer calibration (0.5–1,100 °C) using carbonate-based  
491 standardization. *Geophys. Res. Lett.* **48**, e2020GL092069 (2021).
- 492 6. Barnett, J. S. et al. A high-fidelity benthic stable isotope record of late Cretaceous–early Eocene climate change  
493 and carbon-cycling. *Paleoceanogr. Paleoclimatol.* **34**, 672–691 (2019).
- 494 7. Barr, I. D. et al. 60 million years of glaciation in the Transantarctic Mountains. *Nat. Commun.* **13**, 5526 (2022).
- 495 8. Batenburg, S. J. et al. Major intensification of Atlantic overturning circulation at the onset of Paleogene  
496 greenhouse warmth. *Nat. Commun.* **9**, 1–8 (2018).
- 497 9. Bemis, B. E., Spero, H. J., Bijma, J. & Lea, D. W. Reevaluation of the oxygen isotopic composition of planktonic  
498 foraminifera: Experimental results and revised paleotemperature equations. *Paleoceanography* **13**, 150–160  
499 (1998).
- 500 10. Bernasconi, S. M. et al. Background effects on Faraday collectors in gas-source mass spectrometry and  
501 implications for clumped isotope measurements. *Rapid Commun. Mass Spectrom.* **27**, 603–612 (2013).
- 502 11. Bernasconi, S. M. et al. Reducing uncertainties in carbonate clumped isotope analysis through consistent  
503 carbonate-based standardization. *Geochem. Geophys. Geosyst.* **19**, 2895–2914 (2018).
- 504 12. Bernasconi, S. M. et al. InterCarb: A community effort to improve interlaboratory standardization of the  
505 carbonate clumped isotope thermometer using carbonate standards. *Geochem. Geophys. Geosyst.* **22**,  
506 e2020GC009588 (2021).
- 507 13. Bijl, P. K. et al. Early Palaeogene temperature evolution of the southwest Pacific Ocean. *Nature* **461**, 776–779  
508 (2009).
- 509 14. Bijl, P. K. et al. Eocene cooling linked to early flow across the Tasmanian Gateway. *Proc. Natl Acad. Sci.*  
510 *USA* **110**, 9645–9650 (2013).

- 511 15. Billups, K. & Schrag, D. P. Application of benthic foraminiferal Mg/Ca ratios to questions of Cenozoic climate  
512 change. *Earth Planet. Sci. Lett.* **209**, 181–195 (2003).
- 513 16. Braaten, A. H. *et al.* Limited exchange between the deep Pacific and Atlantic oceans during the warm mid-  
514 Pliocene and MIS M2 "glaciation". *Clim. Past* **19**, 2109–2125 (2023).
- 515 17. Breitenbach, S. F. *et al.* Coupled Mg/Ca and clumped isotope analyses of foraminifera provide consistent water  
516 temperatures. *Geochim. Cosmochim. Acta* **236**, 283–296 (2018).
- 517 18. Broecker, W. & Yu, J. What do we know about the evolution of Mg to Ca ratios in seawater? *Paleoceanography*  
518 **26** (2011).
- 519 19. Brune, S., Williams, S. E. & Müller, R. D. Potential links between continental rifting, CO<sub>2</sub> degassing and climate  
520 change through time. *Nat. Geosci.* **10**, 941–946 (2017).
- 521 20. Burke, A. & Robinson, L. F. The Southern Ocean's role in carbon exchange during the last  
522 deglaciation. *Science* **335**, 557–561 (2012).
- 523 21. Burke, K. D. *et al.* Pliocene and Eocene provide best analogs for near-future climates. *Proc. Natl Acad. Sci.*  
524 *USA* **115**, 13288–13293 (2018).
- 525 22. Carter, A., Riley, T. R., Hillenbrand, C. & Rittner, M. Widespread Antarctic glaciation during the late  
526 Eocene. *Earth Planet. Sci. Lett.* **458**, 49–57 (2017).
- 527 23. Cenozoic CO<sub>2</sub> Proxy Integration Project (GenCO<sub>2</sub>PIP) Consortium. Toward a Cenozoic history of atmospheric  
528 CO<sub>2</sub>. *Science* **382**, eadi5177 (2023).
- 529 24. Clark, P. U., Pisias, N. G., Stocker, T. F. & Weaver, A. J. The role of the thermohaline circulation in abrupt  
530 climate change. *Nature* **415**, 863–869 (2002).
- 531 25. Coggon, R. M., Teagle, D. A., Smith-Duque, C. E., Alt, J. C. & Cooper, M. J. Reconstructing past seawater  
532 Mg/Ca and Sr/Ca from mid-ocean ridge flank calcium carbonate veins. *Science* **327**, 1114–1117 (2010).
- 533 26. Collins, M. *et al.* Long-term climate change: projections, commitments and irreversibility. *Climate Change 2013:*  
534 *The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the*  
535 *Intergovernmental Panel on Climate Change* Ch. 12, 1029–1136 (Cambridge Univ. Press, 2013).
- 536 27. Conrad, C. P. & Lithgow-Bertelloni, C. Faster seafloor spreading and lithosphere production during the mid-  
537 Cenozoic. *Geology* **35**, 29–32 (2007).
- 538 28. Cramer, B. S., Toggweiler, J. R., Wright, J. D., Katz, M. E. & Miller, K. G. Ocean overturning since the Late  
539 Cretaceous: Inferences from a new benthic foraminiferal isotope compilation. *Paleoceanography* **24**, PA4216  
540 (2009).
- 541 29. Cramer, B. S., Miller, K. G., Barrett, P. J. & Wright, J. D. Late Cretaceous–Neogene trends in deep ocean  
542 temperature and continental ice volume: Reconciling records of benthic foraminiferal geochemistry ( $\delta^{18}\text{O}$  and  
543 Mg/Ca) with sea level history. *J. Geophys. Res.* **116**, C12023 (2011).

- 544 30. Cramwinckel, M. J. et al. Synchronous tropical and polar temperature evolution in the Eocene. *Nature* **559**,  
545 382–386 (2018).
- 546 31. Cramwinckel, M. J. et al. A warm, stratified, and restricted Labrador Sea across the Middle Eocene and its  
547 climatic optimum. *Paleoceanogr. Paleoclimatol.* **35**, e2020PA003932 (2020).
- 548 32. Daëron, M. & Gray, W. R. Revisiting oxygen-18 and clumped isotopes in planktic and benthic  
549 foraminifera. *Paleoceanogr. Paleoclimatol.* **38**, e2023PA004660 (2023).
- 550 33. Darby, D. A. Ephemeral formation of perennial sea ice in the Arctic Ocean during the middle Eocene. *Nat.*  
551 *Geosci.* **7**, 210–213 (2014).
- 552 34. Davies, A. et al. Assessing the impact of aquifer-eustasy on short-term Cretaceous sea-level. *Cretac. Res.*  
553 **112**, 104445 (2020).
- 554 35. Dennis, K. J., Affek, H. P., Passey, B. H., Schrag, D. P. & Eiler, J. M. Defining an absolute reference frame for  
555 'clumped' isotope studies of CO<sub>2</sub>. *Geochim. Cosmochim. Acta* **75**, 7117–7131 (2011).
- 556 36. Dutton, A., Lohmann, K. & Leckie, R. Data report: stable isotope and Mg/Ca of Paleocene and Eocene  
557 foraminifers, ODP Site 1209, Shatsky Rise. *Proc. ODP, Sci. Results* **198**, 1–19 (Ocean Drilling Program,  
558 2005a).
- 559 37. Dutton, A., Lohmann, K. C. & Leckie, R. M. Insights from the Paleogene tropical Pacific: Foraminiferal stable  
560 isotope and elemental results from Site 1209, Shatsky Rise. *Paleoceanography* **20** (2005b).
- 561 38. Edgar, K. M., Pälike, H. & Wilson, P. A. Testing the impact of diagenesis on the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of benthic  
562 foraminiferal calcite from a sediment burial depth transect in the equatorial Pacific. *Paleoceanography* **28**, 468–  
563 480 (2013).
- 564 39. Ehrmann, W. U. & Mackensen, A. Sedimentological evidence for the formation of an East Antarctic ice sheet  
565 in Eocene/Oligocene time. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **93**, 85–112 (1992).
- 566 40. Eiler, J. M. "Clumped-isotope" geochemistry—The study of naturally-occurring, multiply-substituted  
567 isotopologues. *Earth Planet. Sci. Lett.* **262**, 309–327 (2007).
- 568 41. Eiler, J. M. Paleoclimate reconstruction using carbonate clumped isotope thermometry.  
569 *Quat. Sci. Rev.* **30**, 3575–3588 (2011).
- 570 42. Elderfield, H., Yu, J., Anand, P., Kiefer, T. & Nyland, B. Calibrations for benthic foraminiferal Mg/Ca  
571 paleothermometry and the carbonate ion hypothesis. *Earth Planet. Sci. Lett.* **250**, 633–649 (2006).
- 572 43. Eldrett, J. S., Harding, I. C., Wilson, P. A., Butler, E. & Roberts, A. P. Continental ice in Greenland during the  
573 Eocene and Oligocene. *Nature* **446**, 176–179 (2007).
- 574 44. Evans, D. & Müller, W. Deep time foraminifera Mg/Ca paleothermometry: Nonlinear correction for secular  
575 change in seawater Mg/Ca. *Paleoceanography* **27**, PA4205 (2012).

- 576 45. Evans, D., Brierley, C., Raymo, M. E., Erez, J. & Müller, W. Planktic foraminifera shell chemistry response to  
577 seawater chemistry: Pliocene–Pleistocene seawater Mg/Ca, temperature and sea level change. *Earth Planet.*  
578 *Sci. Lett.* **438**, 139–148 (2016).
- 579 46. Evans, D. et al. Eocene greenhouse climate revealed by coupled clumped isotope-Mg/Ca thermometry. *Proc.*  
580 *Natl Acad. Sci. USA* **115**, 1174–1179 (2018a).
- 581 47. Evans, D., Müller, W. & Erez, J. Assessing foraminifera biomineralisation models through trace element data  
582 of cultures under variable seawater chemistry. *Geochim. Cosmochim. Acta* **236**, 198–217 (2018b).
- 583 48. Evans, D., Brugger, J., Inglis, G. N. & Valdes, P. The temperature of the deep ocean is a robust proxy for global  
584 mean surface temperature during the Cenozoic. *Paleoceanogr. Paleoclimatol.* **39**, e2023PA004788 (2024).
- 585 49. Feng, R., Otto-Bliesner, B. L., Brady, E. C. & Rosenbloom, N. Increased climate response and Earth system  
586 sensitivity from CCSM4 to CESM2 in mid-Pliocene simulations. *J. Adv. Model. Earth Syst.* **12**, e2019MS002033  
587 (2020).
- 588 50. Fernandez, A. et al. A reassessment of the precision of carbonate clumped isotope measurements:  
589 Implications for calibrations and paleoclimate reconstructions. *Geochem. Geophys. Geosyst.* **18**, 4375–4386  
590 (2017).
- 591 51. Fokkema, C. D. et al. Polar amplification of orbital-scale climate variability in the early Eocene greenhouse  
592 world. *Clim. Past* **20**, 1303–1325 (2024a).
- 593 52. Fokkema, C. D., Brinkhuis, H., Peterse, F. & Sluijs, A. Orbital (hydro)climate variability in the ice-free early  
594 Eocene Arctic. *Paleoceanogr. Paleoclimatol.* **39**, e2024PA004907 (2024b).
- 595 53. Frieling, J. et al. Paleocene–Eocene warming and biotic response in the epicontinental West Siberian  
596 Sea. *Geology* **42**, 767–770 (2014).
- 597 54. Frieling, J. et al. Tropical Atlantic climate and ecosystem regime shifts during the Paleocene–Eocene Thermal  
598 Maximum. *Clim. Past* **14**, 39–55 (2018).
- 599 55. Forster, P. et al. The Earth's energy budget, climate feedbacks, and climate sensitivity. *Climate Change 2021:*  
600 *The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the*  
601 *Intergovernmental Panel on Climate Change* Ch. 7, 923–1054 (Cambridge Univ. Press, 2021).
- 602 56. Galeotti, S. et al. Antarctic Ice Sheet variability across the Eocene-Oligocene boundary climate  
603 transition. *Science* **352**, 76–80 (2016).
- 604 57. Gaskell, D. E. et al. The latitudinal temperature gradient and its climate dependence as inferred from  
605 foraminiferal  $\delta^{18}\text{O}$  over the past 95 million years. *Proc. Natl Acad. Sci. USA* **119**, e2111332119 (2022).
- 606 58. Ghosh, P. et al.  $^{13}\text{C}$ – $^{18}\text{O}$  bonds in carbonate minerals: A new kind of paleothermometer. *Geochim. Cosmochim.*  
607 *Acta* **70**, 1439–1456 (2006).
- 608 59. Goudsmit-Harzevoort, B. et al. The relationship between the global mean deep-sea and surface temperature  
609 during the early Eocene. *Paleoceanogr. Paleoclimatol.* **38**, e2022PA004532 (2023).

- 610 60. Grauel, A. et al. Calibration and application of the 'clumped isotope' thermometer to foraminifera for high-  
611 resolution climate reconstructions. *Geochim. Cosmochim. Acta* **108**, 125–140 (2013).
- 612 61. Gray, W. R. et al. The effects of temperature, salinity, and the carbonate system on Mg/Ca in Globigerinoides  
613 ruber (white): A global sediment trap calibration. *Earth Planet. Sci. Lett.* **482**, 607–620 (2018).
- 614 62. Gulick, S. P. et al. Initiation and long-term instability of the East Antarctic Ice Sheet. *Nature* **552**, 225–229  
615 (2017).
- 616 63. Guo, W., Mosenfelder, J. L., Goddard III, W. A. & Eiler, J. M. Isotopic fractionations associated with phosphoric  
617 acid digestion of carbonate minerals: Insights from first-principles theoretical modeling and clumped isotope  
618 measurements. *Geochim. Cosmochim. Acta* **73**, 7203–7225 (2009).
- 619 64. Guo, W. Kinetic clumped isotope fractionation in the DIC-H<sub>2</sub>O-CO<sub>2</sub> system: patterns, controls, and implications.  
620 *Geochim. Cosmochim. Acta* **268**, 230–257 (2020).
- 621 65. Gutjahr, M. et al. Very large release of mostly volcanic carbon during the Palaeocene–Eocene Thermal  
622 Maximum. *Nature* **548**, 573–577 (2017).
- 623 66. Hansen, J., Sato, M., Russell, G. & Kharecha, P. Climate sensitivity, sea level and atmospheric carbon  
624 dioxide. *Philos. Trans. R. Soc. A* **371**, 20120294 (2013).
- 625 67. Harper, D. T. et al. Subtropical sea-surface warming and increased salinity during Eocene Thermal Maximum  
626 2. *Geology* **46**, 187–190 (2018).
- 627 68. Harper, D. T. et al. The magnitude of surface ocean acidification and carbon release during Eocene Thermal  
628 Maximum 2 (ETM-2) and the Paleocene-Eocene Thermal Maximum (PETM). *Paleoceanogr. Paleoclimatol.* **35**,  
629 e2019PA003699 (2020).
- 630 69. He, B., Olack, G. A. & Colman, A. S. Pressure baseline correction and high-precision CO<sub>2</sub> clumped-isotope  
631 ( $\Delta_{47}$ ) measurements in bellows and micro-volume modes. *Rapid Commun. Mass Spectrom.* **26**, 2837–2853  
632 (2012).
- 633 70. Hill, P. S., Tripathi, A. K. & Schauble, E. A. Theoretical constraints on the effects of pH, salinity, and temperature  
634 on clumped isotope signatures of dissolved inorganic carbon species and precipitating carbonate  
635 minerals. *Geochim. Cosmochim. Acta* **125**, 610–652 (2014).
- 636 71. Hilting, A. K., Kump, L. R. & Bralower, T. J. Variations in the oceanic vertical carbon isotope gradient and their  
637 implications for the Paleocene-Eocene biological pump. *Paleoceanography* **23** (2008).
- 638 72. Hohbein, M. W., Sexton, P. F. & Cartwright, J. A. Onset of North Atlantic Deep Water production coincident  
639 with inception of the Cenozoic global cooling trend. *Geology* **40**, 255–258 (2012).
- 640 73. Hollis, C. J. et al. Early Paleogene temperature history of the Southwest Pacific Ocean: Reconciling proxies  
641 and models. *Earth Planet. Sci. Lett.* **349**, 53–66 (2012).

- 642 74. Hollis, C. J. et al. The DeepMIP contribution to PMIP4: methodologies for selection, compilation and analysis  
643 of latest Paleocene and early Eocene climate proxy data, incorporating version 0.1 of the DeepMIP database.  
644 *Geosci. Model Dev.* **12**, 3149–3206 (2019).
- 645 75. Horita, J., Zimmermann, H. & Holland, H. D. Chemical evolution of seawater during the Phanerozoic:  
646 Implications from the record of marine evaporites. *Geochim. Cosmochim. Acta* **66**, 3733–3756 (2002).
- 647 76. Hou, S. et al. Reconciling Southern Ocean fronts equatorward migration with minor Antarctic ice volume  
648 change during Miocene cooling. *Nat. Commun.* **14**, 7230 (2023).
- 649 77. Hu, B. et al. A modified procedure for gas-source isotope ratio mass spectrometry: The long-integration dual-  
650 inlet (LIDI) methodology and implications for clumped isotope measurements. *Rapid Commun. Mass*  
651 *Spectrom.* **28**, 1413–1425 (2014).
- 652 78. Huck, C. E., van de Flierdt, T., Bohaty, S. M. & Hammond, S. J. Antarctic climate, Southern Ocean circulation  
653 patterns, and deep water formation during the Eocene. *Paleoceanography* **32**, 674–691 (2017).
- 654 79. Huntington, K. W. et al. Methods and limitations of ‘clumped’ CO<sub>2</sub> isotope ( $\Delta_{47}$ ) analysis by gas-source isotope  
655 ratio mass spectrometry. *J. Mass Spectrom.* **44**, 1318–1329 (2009).
- 656 80. Huntington, K. W. & Petersen, S. V. Frontiers of carbonate clumped isotope thermometry. *Annu. Rev. Earth*  
657 *Planet. Sci.* **51**, 611–641 (2023).
- 658 81. Jaffrés, J. B., Shields, G. A. & Wallmann, K. The oxygen isotope evolution of seawater: A critical review of a  
659 long-standing controversy and an improved geological water cycle model for the past 3.4 billion years. *Earth-*  
660 *Sci. Rev.* **83**, 83–122 (2007).
- 661 82. Judd, E. J., Bhattacharya, T. & Ivany, L. C. A dynamical framework for interpreting ancient sea surface  
662 temperatures. *Geophys. Res. Lett.* **47**, e2020GL089044 (2020).
- 663 83. Katz, M. E. et al. Early Cenozoic benthic foraminiferal isotopes: Species reliability and interspecies correction  
664 factors. *Paleoceanography* **18**, 1024 (2003).
- 665 84. Kegel, A. H. et al. Global warming and equatorial Atlantic paleoceanographic changes during early Eocene  
666 carbon cycle perturbation V. *Paleoceanogr. Paleoclimatol.* **40**, e2024PA004913 (2025).
- 667 85. Kelson, J. R., Huntington, K. W., Schauer, A. J., Saenger, C. & Lechler, A. R. Toward a universal carbonate  
668 clumped isotope calibration: Diverse synthesis and preparatory methods suggest a single temperature  
669 relationship. *Geochim. Cosmochim. Acta* **197**, 104–131 (2017).
- 670 86. Kender, S., Yu, J. & Peck, V. L. Deep ocean carbonate ion increase during mid Miocene CO<sub>2</sub> decline. *Sci. Rep.*  
671 **4**, 4187 (2014).
- 672 87. Kim, S. & O’Neil, J. R. Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochim.*  
673 *Cosmochim. Acta* **61**, 3461–3475 (1997).
- 674 88. Kirtland Turner, S., Sexton, P. F., Charles, C. D. & Norris, R. D. Persistence of carbon release events through  
675 the peak of early Eocene global warmth. *Nat. Geosci.* **7**, 748–751 (2014).

- 676 89. Kirtland Turner, S. *et al.* Sensitivity of ocean circulation to warming during the Early Eocene greenhouse. *Proc.*  
677 *Natl Acad. Sci. USA* **121**, e2311980121 (2024).
- 678 90. Klages, J. P. *et al.* Ice sheet-free West Antarctica during peak early Oligocene glaciation. *Science* **385**, 322–  
679 327 (2024).
- 680 91. Kocken, I. J. *et al.* North Atlantic temperature change across the Eocene-Oligocene transition from clumped  
681 isotopes. *Paleoceanogr. Paleoclimatol.* **39**, e2023PA004809 (2024).
- 682 92. Kostov, Y., Armour, K. C. & Marshall, J. Impact of the Atlantic meridional overturning circulation on ocean heat  
683 storage and transient climate change. *Geophys. Res. Lett.* **41**, 2108–2116 (2014).
- 684 93. Inglis, G. N. *et al.* Descent toward the Icehouse: Eocene sea surface cooling inferred from GDGT  
685 distributions. *Paleoceanography* **30**, 1000–1020 (2015).
- 686 94. Inglis, G. N. *et al.* Global mean surface temperature and climate sensitivity of the EECO, PETM and latest  
687 Paleocene. *Clim. Past* **16**, 1953–1968 (2020).
- 688 95. Lauvset, S. K. *et al.* Processes driving global interior ocean pH distribution. *Global Biogeochem. Cycles* **34**,  
689 e2019GB006229 (2020).
- 690 96. Lauretano, V., Littler, K., Polling, M., Zachos, J. C. & Lourens, L. J. Frequency, magnitude and character of  
691 hyperthermal events at the onset of the Early Eocene Climatic Optimum. *Clim. Past* **11**, 1313–1324 (2015).
- 692 97. Lauretano, V., Hilgen, F. J., Zachos, J. C. & Lourens, L. J. Astronomically tuned age model for the early Eocene  
693 carbon isotope events: A new high-resolution  $\delta^{13}\text{C}_{\text{benthic}}$  record of ODP Site 1263 between ~49 and ~54  
694 Ma. *Newsl. Stratigr.* **49**, 383–400 (2016).
- 695 98. Lauretano, V., Zachos, J. C. & Lourens, L. J. Orbitally paced carbon and deep-sea temperature changes at the  
696 peak of the Early Eocene Climatic Optimum. *Paleoceanogr. Paleoclimatol.* **33**, 1050–1065 (2018).
- 697 99. Lear, C. H., Elderfield, H. & Wilson, P. A. Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca  
698 in benthic foraminiferal calcite. *Science* **287**, 269–272 (2000).
- 699 100. Lear, C. H., Rosenthal, Y. & Slowey, N. Benthic foraminiferal Mg/Ca-paleothermometry: A revised core-top  
700 calibration. *Geochim. Cosmochim. Acta* **66**, 3375–3387 (2002).
- 701 101. Lear, C. H., Mawbey, E. M. & Rosenthal, Y. Cenozoic benthic foraminiferal Mg/Ca and Li/Ca records: Toward  
702 unlocking temperatures and saturation states. *Paleoceanography* **25** (2010).
- 703 102. Lear, C. H. *et al.* Neogene ice volume and ocean temperatures: Insights from infaunal foraminiferal Mg/Ca  
704 paleothermometry. *Paleoceanography* **30**, 1437–1454 (2015).
- 705 103. Lee, C. A. *et al.* Continental arc-island arc fluctuations, growth of crustal carbonates, and long-term climate  
706 change. *Geosphere* **9**, 21–36 (2013).
- 707 104. Leutert, T. J. *et al.* Sensitivity of clumped isotope temperatures in fossil benthic and planktic foraminifera to  
708 diagenetic alteration. *Geochim. Cosmochim. Acta* **257**, 354–372 (2019).



- 709 105. Leutert, T. J., Auderset, A., Martínez-García, A., Modestou, S. & Meckler, A. N. Coupled Southern Ocean  
710 cooling and Antarctic ice sheet expansion during the middle Miocene. *Nat. Geosci.* **13**, 634–639 (2020).
- 711 106. Leutert, T. J., Modestou, S., Bernasconi, S. M. & Meckler, A. N. Southern Ocean bottom-water cooling and ice  
712 sheet expansion during the middle Miocene climate transition. *Clim. Past* **17**, 2255–2271 (2021).
- 713 107. Littler, K., Röhl, U., Westerhold, T. & Zachos, J. C. A high-resolution benthic stable-isotope record for the South  
714 Atlantic: Implications for orbital-scale changes in Late Paleocene–Early Eocene climate and carbon  
715 cycling. *Earth Planet. Sci. Lett.* **401**, 18–30 (2014).
- 716 108. Lourens, L. J. et al. Astronomical pacing of late Palaeocene to early Eocene global warming  
717 events. *Nature* **435**, 1083–1087 (2005).
- 718 109. Lowenstein, T. K., Timofeeff, M. N., Brennan, S. T., Hardie, L. A. & Demicco, R. V. Oscillations in Phanerozoic  
719 seawater chemistry: Evidence from fluid inclusions. *Science* **294**, 1086–1088 (2001).
- 720 110. Lunt, D. J. et al. Earth system sensitivity inferred from Pliocene modelling and data. *Nat. Geosci.* **3**, 60–64  
721 (2010).
- 722 111. Lunt, D. J. et al. DeepMIP: Model intercomparison of early Eocene climatic optimum (EECO) large-scale  
723 climate features and comparison with proxy data. *Clim. Past* **17**, 203–227 (2021).
- 724 112. Marchitto, T. M., Bryan, S. P., Curry, W. B. & McCorkle, D. C. Mg/Ca temperature calibration for the benthic  
725 foraminifer *Cibicides pachyderma*. *Paleoceanography* **22** (2007).
- 726 113. Marchitto, T. M. et al. Improved oxygen isotope temperature calibrations for cosmopolitan benthic foraminifera.  
727 *Geochim. Cosmochim. Acta* **130**, 1–11 (2014).
- 728 114. McCarren, H., Thomas, E., Hasegawa, T., Röhl, U. & Zachos, J. C. Depth dependency of the Paleocene-  
729 Eocene carbon isotope excursion: Paired benthic and terrestrial biomarker records (Ocean Drilling Program  
730 Leg 208, Walvis Ridge). *Geochem. Geophys. Geosyst.* **9** (2008).
- 731 115. McCrea, J. M. On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* **18**, 849–  
732 857 (1950).
- 733 116. Meckler, A. N., Ziegler, M., Millán, M. I., Breitenbach, S. F. & Bernasconi, S. M. Long-term performance of the  
734 Kiel carbonate device with a new correction scheme for clumped isotope measurements. *Rapid Commun.*  
735 *Mass Spectrom.* **28**, 1705–1715 (2014).
- 736 117. Meckler, A. N. et al. Cenozoic evolution of deep ocean temperature from clumped isotope  
737 thermometry. *Science* **377**, 86–90 (2022).
- 738 118. Meinicke, N. et al. A robust calibration of the clumped isotopes to temperature relationship for foraminifers.  
739 *Geochim. Cosmochim. Acta* **270**, 160–183 (2020).
- 740 119. Meinicke, N., Reimi, M. A., Ravelo, A. C. & Meckler, A. N. Coupled Mg/Ca and clumped isotope measurements  
741 indicate lack of substantial mixed layer cooling in the Western Pacific Warm Pool during the last ~5 million  
742 years. *Paleoceanogr. Paleoclimatol.* **36**, e2020PA004115 (2021).

- 743 120. Miller, K. G. et al. Cenozoic sea-level and cryospheric evolution from deep-sea geochemical and continental  
744 margin records. *Sci. Adv.* **6**, eaaz1346 (2020).
- 745 121. Modestou, S. E., Leutert, T. J., Fernandez, A., Lear, C. H. & Meckler, A. N. Warm middle Miocene Indian Ocean  
746 bottom water temperatures: comparison of clumped isotope and Mg/Ca-based estimates. *Paleoceanogr.*  
747 *Paleoclimatol.* **35**, e2020PA003927 (2020).
- 748 122. Müller, I. A. et al. Carbonate clumped isotope analyses with the long-integration dual-inlet (LIDI) workflow:  
749 Scratching at the lower sample weight boundaries. *Rapid Commun. Mass Spectrom.* **31**, 1057–1066 (2017).
- 750 123. Müller, R. D., Sdrolias, M., Gaina, C., Steinberger, B. & Heine, C. Long-term sea-level fluctuations driven by  
751 ocean basin dynamics. *Science* **319**, 1357–1362 (2008).
- 752 124. Pagani, M., Liu, Z., LaRiviere, J. & Ravelo, A. C. High Earth-system climate sensitivity determined from  
753 Pliocene carbon dioxide concentrations. *Nat. Geosci.* **3**, 27–30 (2010).
- 754 125. PALAEOSENS Project Members. Making sense of palaeoclimate sensitivity. *Nature* **491**, 683–691 (2012).
- 755 126. Passchier, S., Ciarletta, D. J., Miriagos, T. E., Bijl, P. K. & Bohaty, S. M. An Antarctic stratigraphic record of  
756 stepwise ice growth through the Eocene-Oligocene transition. *Geol. Soc. Am. Bull.* **129**, 318–330 (2017).
- 757 127. Pearson, P. N. et al. Stable warm tropical climate through the Eocene Epoch. *Geology* **35**, 211–214 (2007).
- 758 128. Pearson, P. N. Oxygen isotopes in foraminifera: overview and historical review. *Reconstructing Earth's Deep-*  
759 *Time Climate—The State of the Art in 2012. Paleontological Society Papers* **18**, 1–38 (Paleontological Society,  
760 2012).
- 761 129. Penman, D. E., Hönisch, B., Zeebe, R. E., Thomas, E. & Zachos, J. C. Rapid and sustained surface ocean  
762 acidification during the Paleocene-Eocene Thermal Maximum. *Paleoceanography* **29**, 357–369 (2014).
- 763 130. Peral, M. et al. Updated calibration of the clumped isotope thermometer in planktonic and benthic foraminifera.  
764 *Geochim. Cosmochim. Acta* **239**, 1–16 (2018).
- 765 131. Peral, M. et al. On the combination of the planktonic foraminiferal Mg/Ca, clumped ( $\Delta_{47}$ ) and conventional  
766 ( $\delta^{18}\text{O}$ ) stable isotope paleothermometers in palaeoceanographic studies. *Geochim. Cosmochim. Acta* **339**, 22–  
767 34 (2022).
- 768 132. Piasecki, A. et al. Application of clumped isotope thermometry to benthic foraminifera. *Geochem. Geophys.*  
769 *Geosyst.* **20**, 2082–2090 (2019).
- 770 133. Pross, J. et al. Persistent near-tropical warmth on the Antarctic continent during the early Eocene epoch. *Nature*  
771 **488**, 73–77 (2012).
- 772 134. Rae, J. W. et al. Atmospheric CO<sub>2</sub> over the past 66 million years from marine archives. *Annu. Rev. Earth Planet.*  
773 *Sci.* **49**, 599–631 (2021).
- 774 135. Rathmann, S. & Kuhnert, H. Carbonate ion effect on Mg/Ca, Sr/Ca and stable isotopes on the benthic  
775 foraminifera *Oridorsalis umbonatus* off Namibia. *Mar. Micropaleontol.* **66**, 120–133 (2008).

- 776 136. Ravelo, A. C. & Hillaire-Marcel, C. The use of oxygen and carbon isotopes of foraminifera in paleoceanography.  
777 *Proxies in Late Cenozoic Paleoceanography. Developments in Marine Geology* **1**, 735–764 (Elsevier, 2007).
- 778 137. Raymo, M. E., Kozdon, R., Evans, D., Lisiecki, L. & Ford, H. L. The accuracy of mid-Pliocene  $\delta^{18}\text{O}$ -based ice  
779 volume and sea level reconstructions. *Earth-Sci. Rev.* **177**, 291–302 (2018).
- 780 138. Reagan, M. K. et al. The geology of the southern Mariana fore-arc crust: Implications for the scale of Eocene  
781 volcanism in the western Pacific. *Earth Planet. Sci. Lett.* **380**, 41–51 (2013).
- 782 139. Ring, S. J., Mutz, S. G. & Ehlers, T. A. Cenozoic proxy constraints on Earth system sensitivity to greenhouse  
783 gases. *Paleoceanogr. Paleoclimatol.* **37**, e2021PA004364 (2022).
- 784 140. Rodríguez-Sanz, L. et al. Penultimate deglacial warming across the Mediterranean Sea revealed by clumped  
785 isotopes in foraminifera. *Sci. Rep.* **7**, 16572 (2017).
- 786 141. Rohling, E. J. et al. Reconciling the apparent discrepancy between Cenozoic deep-sea temperatures from  
787 proxies and from benthic oxygen isotope deconvolution. *Paleoceanogr. Paleoclimatol.* **39**, e2024PA004872  
788 (2024).
- 789 142. Rose, B. E. & Ferreira, D. Ocean heat transport and water vapor greenhouse in a warm equable climate: A  
790 new look at the low gradient paradox. *J. Clim.* **26**, 2117–2136 (2013).
- 791 143. Royer, D. L., Pagani, M. & Beerling, D. J. Geobiological constraints on Earth system sensitivity to  $\text{CO}_2$  during  
792 the Cretaceous and Cenozoic. *Geobiology* **10**, 298–310 (2012).
- 793 144. Sames, B., Wagreich, M., Conrad, C. P. & Iqbal, S. Aquifer-eustasy as the main driver of short-term sea-level  
794 fluctuations during Cretaceous hothouse climate phases. *Geol. Soc. Lond. Spec. Publ.* **498**, 9–38 (2020).
- 795 145. Schauble, E. A., Ghosh, P. & Eiler, J. M. Preferential formation of  $^{13}\text{C}$ – $^{18}\text{O}$  bonds in carbonate minerals,  
796 estimated using first-principles lattice dynamics. *Geochim. Cosmochim. Acta* **70**, 2510–2529 (2006).
- 797 146. Scher, H. D., Bohaty, S. M., Zachos, J. C. & Delaney, M. L. Two-stepping into the icehouse: East Antarctic  
798 weathering during progressive ice-sheet expansion at the Eocene–Oligocene transition. *Geology* **39**, 383–386  
799 (2011).
- 800 147. Schmid, T. W. & Bernasconi, S. M. An automated method for ‘clumped-isotope’ measurements on small  
801 carbonate samples. *Rapid Commun. Mass Spectrom.* **24**, 1955–1963 (2010).
- 802 148. Schmid, T. W., Radke, J. & Bernasconi, S. M. Clumped-isotope measurements on small carbonate samples  
803 with a Kiel IV carbonate device and a MAT 253 mass spectrometer. *Appl. Note* **30233**, (Thermo Fisher, 2012).
- 804 149. Sexton, P. F. et al. Eocene global warming events driven by ventilation of oceanic dissolved organic carbon.  
805 *Nature* **471**, 349–352 (2011).
- 806 150. Shackleton, N. J. Paleogene stable isotope events. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **57**, 91–102  
807 (1986).
- 808 151. Sherwood, S. C. et al. An assessment of Earth's climate sensitivity using multiple lines of evidence. *Rev.*  
809 *Geophys.* **58**, e2019RG000678 (2020).

- 810 152.Sluijs, A. et al. Subtropical Arctic Ocean temperatures during the Palaeocene/Eocene Thermal Maximum.  
811 *Nature* **441**, 610–613 (2006).
- 812 153.Sluijs, A. et al. Warm and wet conditions in the Arctic region during Eocene Thermal Maximum 2. *Nat.*  
813 *Geosci.* **2**, 777–780 (2009).
- 814 154.Sluijs, A. et al. Southern ocean warming, sea level and hydrological change during the Paleocene-Eocene  
815 thermal maximum. *Clim. Past* **7**, 47–61 (2011).
- 816 155.Spero, H. J., Bijma, J., Lea, D. W. & Bemis, B. E. Effect of seawater carbonate concentration on foraminiferal  
817 carbon and oxygen isotopes. *Nature* **390**, 497–500 (1997).
- 818 156.Spray, J. F. et al. North Atlantic evidence for a unipolar icehouse climate state at the Eocene-Oligocene  
819 Transition. *Paleoceanogr. Paleoclimatol.* **34**, 1124–1138 (2019).
- 820 157.Srokosz, M. et al. Past, present, and future changes in the Atlantic meridional overturning circulation. *Bull. Am.*  
821 *Meteorol. Soc.* **93**, 1663–1676 (2012).
- 822 158.St. John, K. Cenozoic ice-rafting history of the central Arctic Ocean: Terrigenous sands on the Lomonosov  
823 Ridge. *Paleoceanography* **23** (2008).
- 824 159.Stap, L. et al. High-resolution deep-sea carbon and oxygen isotope records of Eocene Thermal Maximum 2  
825 and H2. *Geology* **38**, 607–610 (2010).
- 826 160.Stickley, C. E. et al. Evidence for middle Eocene Arctic sea ice from diatoms and ice-rafted debris. *Nature* **460**,  
827 376–379 (2009).
- 828 161.Stolper, D. A., Eiler, J. M. & Higgins, J. A. Modeling the effects of diagenesis on carbonate clumped-isotope  
829 values in deep-and shallow-water settings. *Geochim. Cosmochim. Acta* **227**, 264–291 (2018).
- 830 162.Storey, M., Duncan, R. A. & Tegner, C. Timing and duration of volcanism in the North Atlantic Igneous Province:  
831 Implications for geodynamics and links to the Iceland hotspot. *Chem. Geol.* **241**, 264–281 (2007).
- 832 163.Tang, J., Dietzel, M., Fernandez, A., Tripathi, A. K. & Rosenheim, B. E. Evaluation of kinetic effects on clumped  
833 isotope fractionation ( $\Delta_{47}$ ) during inorganic calcite precipitation. *Geochim. Cosmochim. Acta* **134**, 120–136  
834 (2014).
- 835 164.Taylor, V. E., Wilson, P. A., Bohaty, S. M. & Meckler, A. N. Transient Deep Ocean Cooling in the Eastern  
836 Equatorial Pacific Ocean at the Eocene-Oligocene Transition. *Paleoceanogr. Paleoclimatol.* **38**,  
837 e2023PA004650 (2023).
- 838 165.Thomas, D. J., Bralower, T. J. & Jones, C. E. Neodymium isotopic reconstruction of late Paleocene–early  
839 Eocene thermohaline circulation. *Earth Planet. Sci. Lett.* **209**, 309–322 (2003).
- 840 166.Thomas, D. J., Korty, R., Huber, M., Schubert, J. A. & Haines, B. Nd isotopic structure of the Pacific Ocean  
841 70–30 Ma and numerical evidence for vigorous ocean circulation and ocean heat transport in a greenhouse  
842 world. *Paleoceanography* **29**, 454–469 (2014).

843 167.Thomas, E. *et al.* Early Eocene thermal maximum 3: Biotic response at Walvis ridge (SE Atlantic  
844 ocean). *Paleoceanogr. Paleoclimatol.* **33**, 862–883 (2018).

845 168.Tierney, J. E. et al. Spatial patterns of climate change across the Paleocene–Eocene Thermal Maximum. *Proc.*  
846 *Natl Acad. Sci. USA* **119**, e2205326119 (2022).

847 169.Trenberth, K. E. & Caron, J. M. Estimates of meridional atmosphere and ocean heat transports. *J. Clim.* **14**,  
848 3433–3443 (2001).

849 170.Tripati, A. K. et al. Tropical sea-surface temperature reconstruction for the early Paleogene using Mg/Ca ratios  
850 of planktonic foraminifera. *Paleoceanography* **18** (2003).

851 171.Tripati, A. & Elderfield, H. Deep-sea temperature and circulation changes at the Paleocene-Eocene Thermal  
852 Maximum. *Science* **308**, 1894–1898 (2005).

853 172.Tripati, A. K. et al.  $^{13}\text{C}$ – $^{18}\text{O}$  isotope signatures and ‘clumped isotope’ thermometry in foraminifera and  
854 coccoliths. *Geochim. Cosmochim. Acta* **74**, 5697–5717 (2010).

855 173.Tripati, A. K. et al. Beyond temperature: Clumped isotope signatures in dissolved inorganic carbon species and  
856 the influence of solution chemistry on carbonate mineral composition. *Geochim. Cosmochim. Acta* **166**, 344–  
857 371 (2015).

858 174.Tripati, A. & Darby, D. Evidence for ephemeral middle Eocene to early Oligocene Greenland glacial ice and  
859 pan-Arctic sea ice. *Nat. Commun.* **9**, 1–11 (2018).

860 175.Uchikawa, J. & Zeebe, R. E. Examining possible effects of seawater pH decline on foraminiferal stable isotopes  
861 during the Paleocene-Eocene Thermal Maximum. *Paleoceanography* **25**, PA2216 (2010).

862 176.Usdowski, E. & Hoefs, J. Oxygen isotope exchange between carbonic acid, bicarbonate, carbonate, and water:  
863 a re-examination of the data of McCrea (1950) and an expression for the overall partitioning of oxygen isotopes  
864 between the carbonate species and water. *Geochim. Cosmochim. Acta* **57**, 3815–3818 (1993).

865 177.Via, R. K. & Thomas, D. J. Evolution of Atlantic thermohaline circulation: Early Oligocene onset of deep-water  
866 production in the North Atlantic. *Geology* **34**, 441–444 (2006).

867 178.Vickers, M. L. et al. Cold spells in the Nordic Seas during the early Eocene Greenhouse. *Nat. Commun.* **11**, 1–  
868 12 (2020).

869 179.Voigt, J., Hathorne, E. C., Frank, M., Vollstaedt, H. & Eisenhauer, A. Variability of carbonate diagenesis in  
870 equatorial Pacific sediments deduced from radiogenic and stable Sr isotopes. *Geochim. Cosmochim. Acta* **148**,  
871 360–377 (2015).

872 180.Voigt, J., Hathorne, E. C., Frank, M. & Holbourn, A. Minimal influence of recrystallization on middle Miocene  
873 benthic foraminiferal stable isotope stratigraphy in the eastern equatorial Pacific. *Paleoceanography* **31**, 98–  
874 114 (2016).

875 181.Wallmann, K. The geological water cycle and the evolution of marine  $\delta^{18}\text{O}$  values. *Geochim. Cosmochim. Acta*  
876 **65**, 2469–2485 (2001).

- 877 182. Watkins, J. M. & Hunt, J. D. A process-based model for non-equilibrium clumped isotope effects in  
878 carbonates. *Earth Planet. Sci. Lett.* **432**, 152–165 (2015).
- 879 183. Watkins, J. M. & Devriendt, L. S. A combined model for kinetic clumped isotope effects in the CaCO<sub>3</sub>-DIC-H<sub>2</sub>O  
880 system. *Geochem. Geophys. Geosyst.* **23**, e2021GC010200 (2022).
- 881 184. Westerhold, T., Röhl, U., Donner, B. & Zachos, J. C. Global extent of early Eocene hyperthermal events: A  
882 new Pacific benthic foraminiferal isotope record from Shatsky Rise (ODP Site 1209). *Paleoceanogr.*  
883 *Paleoclimatol.* **33**, 626–642 (2018).
- 884 185. Westerhold, T. et al. An astronomically dated record of Earth's climate and its predictability over the last 66  
885 million years. *Science* **369**, 1383–1387 (2020).
- 886 186. de Winter, N. J., Agterhuis, T. & Ziegler, M. Optimizing sampling strategies in high-resolution paleoclimate  
887 records. *Clim. Past* **17**, 1315–1340 (2021).
- 888 187. Yu, J. & Elderfield, H. Mg/Ca in the benthic foraminifera *Cibicides wuellerstorfi* and *Cibicides mundulus*:  
889 Temperature versus carbonate ion saturation. *Earth Planet. Sci. Lett.* **276**, 129–139 (2008).
- 890 188. Zachos, J. C., Breza, J. R. & Wise, S. W. Early Oligocene ice-sheet expansion on Antarctica: Stable isotope  
891 and sedimentological evidence from Kerguelen Plateau, southern Indian Ocean. *Geology* **20**, 569–573 (1992).
- 892 189. Zachos, J., Pagani, M., Sloan, L., Thomas, E. & Billups, K. Trends, rhythms, and aberrations in global climate  
893 65 Ma to present. *Science* **292**, 686–693 (2001).
- 894 190. Zachos, J. C. et al. Early Cenozoic extreme climates: Walvis Ridge transect. *Proc. ODP Init. Rep.* **208**, 1–112  
895 (2004).
- 896 191. Zachos, J. C. et al. Rapid acidification of the ocean during the Paleocene-Eocene thermal  
897 maximum. *Science* **308**, 1611–1615 (2005).
- 898 192. Zachos, J. C., Dickens, G. R. & Zeebe, R. E. An early Cenozoic perspective on greenhouse warming and  
899 carbon-cycle dynamics. *Nature* **451**, 279–283 (2008).
- 900 193. Zachos, J. C., McCarren, H., Murphy, B., Röhl, U. & Westerhold, T. Tempo and scale of late Paleocene and  
901 early Eocene carbon isotope cycles: Implications for the origin of hyperthermals. *Earth Planet. Sci. Lett.* **299**,  
902 242–249 (2010).
- 903 194. Zeebe, R. E. An explanation of the effect of seawater carbonate concentration on foraminiferal oxygen isotopes.  
904 *Geochim. Cosmochim. Acta* **63**, 2001–2007 (1999).
- 905 195. Zeebe, R. E. Seawater pH and isotopic paleotemperatures of Cretaceous oceans. *Palaeogeogr.*  
906 *Palaeoclimatol. Palaeoecol.* **170**, 49–57 (2001).
- 907 196. Zhang, Y. et al. Early Eocene vigorous ocean overturning and its contribution to a warm Southern Ocean. *Clim.*  
908 *Past* **16**, 1263–1283 (2020).
- 909 197. Zhang, Y. et al. Early Eocene ocean meridional overturning circulation: The roles of atmospheric forcing and  
910 strait geometry. *Paleoceanogr. Paleoclimatol.* **37**, e2021PA004329 (2022).

911 198.Zhang, S., Ji, W., Chen, H., Kirstein, L. A. & Wu, F. Linking rapid eruption of the Linzizong volcanic rocks and  
912 Early Eocene Climatic Optimum (EECO): Constraints from the Pana Formation in the Linzhou and Pangduo  
913 basins, southern Tibet. *Lithos* **446**, 107159 (2023).

914 199.Zhu, J., Poulsen, C. J. & Tierney, J. E. Simulation of Eocene extreme warmth and high climate sensitivity  
915 through cloud feedbacks. *Sci. Adv.* **5**, eaax1874 (2019).

916

#### 917 **Acknowledgements**

918 This research was performed under the program of the Netherlands Earth System Science Centre (NESSC), being  
919 financially supported by the Ministry of Education, Culture, and Science (OCW) of the Netherlands. M.Z.  
920 acknowledges additional funding from the Dutch Research Council (NWO), research grant 016.161.365. This study  
921 used samples and data provided by the International Ocean Discovery Program (IODP). We thank Arnold E. van  
922 Dijk and Desmond D. Eefting (Geolab of Utrecht University) for technical support in the lab.

923

#### 924 **Author contributions**

925 T.A., M.Z., and L.J.L. designed the study. T.A., B.O., S.K., B.L.P.K., L.V., M.K., S.P., and A.R. generated and  
926 analysed the stable and clumped isotope data. All authors contributed to data interpretation. T.A. wrote the article  
927 with input from all authors.

928

#### 929 **Competing interests**

930 The authors declare no competing interests.

931

932 **Correspondence** and requests for materials should be addressed to Tobias Agterhuis

933

## 934 **Supplementary Information**

935

### 936 **Mass spectrometry and clumped isotope data processing**

937 Samples were measured in 73 runs over a period of approximately two years. Each run typically contained a mix  
938 of 22 samples (sometimes including samples from other projects) and 24 carbonate standards and lasted ~30  
939 hours. The individual replicate measurements for the samples were distributed randomly over different runs and  
940 long periods. This approach was chosen in order to prevent possible biases in the obtained data due to short-term  
941 and long-term changes in the mass spectrometer performance. The relative proportion of the measured standards  
942 ETH-1, ETH-2, and ETH-3 was approximately 1:1:5, respectively. Measuring more of a standard that has a  
943 temperature close to the sample target (ETH-3 in this case) significantly reduces the uncertainty in the  $\Delta_{47}$  sample  
944 data (Kocken et al., 2019).

945

946 Glass vials with small samples and standards, weighed in between 70 and 90  $\mu\text{g}$ , were first loaded in an automatic  
947 carousel of the *Thermo Fisher Scientific Kiel IV* device. After this, the carbonates were individually dissolved with  
948 nominally anhydrous phosphoric acid (103%  $\text{H}_3\text{PO}_4$ ) at 70 °C (Schmid & Bernasconi, 2010). The generated  $\text{CO}_2$   
949 gas from this reaction was purified using several steps in the instrument. First, the sample gas was captured in a  
950 first cryogenic liquid nitrogen ( $\text{LN}_2$ ) trap at  $-196$  °C. Here,  $\text{CO}_2$  was separated from water and non-condensable  
951 gases. Subsequently, the gas was passed through a Porapak-Q trap kept at  $-50$  °C used to remove organic  
952 compounds, such as halo-, hydrocarbons and sulphides (Schmid et al., 2012). To prevent contamination, the  
953 Porapak was cleaned by heating it to 150 °C for 1.5 hours before starting a new run. After these steps, the sample  
954 gas entered a second liquid nitrogen trap for one more purification step.

955

956 Eventually, a near pure  $\text{CO}_2$  gas was transferred into a *Thermo Fisher Scientific MAT 253 Plus* instrument for  
957 isotope analysis. The mass spectrometer is equipped with Faraday cups for  $m/z$  44–49, representing the different  
958 isotopologues of  $\text{CO}_2$  (Gosh et al., 2006; Eiler et al., 2007; Schmid & Bernasconi, 2010). The  $m/z$  48 and 49 signals  
959 were used to trace the presence of contaminants, as natural  $\text{CO}_2$  gas is characterized by very low amounts of these  
960 two masses (Ghosh et al., 2006; Eiler et al., 2007; Bernasconi et al., 2013). The sample gas was measured against  
961 a reference gas of known isotopic composition ( $\delta^{13}\text{C} = -2.82\text{‰}$ ;  $\delta^{18}\text{O} = -4.67\text{‰}$ ) in order to obtain the necessary  
962 accuracy of the measurements (Huntington et al., 2009; Müller et al., 2017). The samples were measured in micro-  
963 volume mode using the long-integration dual-inlet (LIDI) workflow (Hu et al., 2014; Müller et al., 2017). This method  
964 first measures all sample gas before starting with the reference gas, to minimize the waste of gas. Pressure baseline  
965 effects were corrected during every run preparation by performing background scans using the reference gas at  
966 varying acceleration voltages (9.38–9.54 kV) and five  $m/z$  44 intensities (5, 10, 15, 20, and 25 V) (Bernasconi et al.,  
967 2013; He et al., 2012; Meckler et al., 2014).



968

969 Subsequently, the three carbonate standards ETH-1, ETH-2, and ETH-3 were used to convert the raw  $\Delta_{47}$  data of  
970 the samples into absolute values, to correct for drift in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , and to correct for scale compression/stretching  
971 in  $\delta^{18}\text{O}$ . First, the  $\Delta_{47}$  values of the measured samples and (check)standards were corrected using the offset  
972 between the measured  $\Delta_{47}$  values of the ETH-3 standards and their accepted  $\Delta_{47}$  values (see values below in this  
973 section). Only the neighbouring ETH-3 standards around the samples were used for this correction to account for  
974 trends in the mass spectrometer performance during the run. Next, the offset-corrected measured raw  $\Delta_{47}$  values  
975 were normalized into the absolute reference frame (Dennis et al., 2011). Empirical transfer functions (ETF) were  
976 established, which represent linear regressions between the measured raw  $\Delta_{47}$  and the internationally accepted  
977 (true)  $\Delta_{47}$  values of all the three ETH standards (ETH-1:  $\Delta_{47} = 0.2052 \pm 0.0016\text{‰}$  (1SE); ETH-2:  $\Delta_{47} =$   
978  $0.2085 \pm 0.0015\text{‰}$  (1SE); ETH-3:  $\Delta_{47} = 0.6132 \pm 0.0014\text{‰}$  (1SE) (Bernasconi et al., 2021). These ETFs transfer the  
979 raw  $\Delta_{47}$  values into the InterCarb-Carbon Dioxide Equilibrium Scale (I-CDES90°C), which enables inter-laboratory  
980 comparison (Dennis et al., 2011; Bernasconi et al., 2018, 2021). The ETFs were constructed based on the ETH  
981 standards contained within a moving window of 250 measurements before and 250 measurements after (total,  
982 including both standards and sample measurements) each measurement. In practice, this implied that  
983 approximately 180 ETH-3 and 35 ETH-1 and ETH-2 measurements were used to establish the linear regression of  
984 the ETF. Subsequently, the final  $\Delta_{47}$  values (as I-CDES90°C) of the samples were determined using the slope and  
985 intercept of the regression lines. To determine final  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the samples, the raw values were  
986 corrected using the offset between the measured and accepted values of all the measured ETH standards in the  
987 same run (ETH-1:  $\delta^{13}\text{C}_{\text{VPDB}} = 2.02 \pm 0.03\text{‰}$ ,  $\delta^{18}\text{O}_{\text{VPDB}} = -2.19 \pm 0.04\text{‰}$ ; ETH-2:  $\delta^{13}\text{C}_{\text{VPDB}} = -10.17 \pm 0.06\text{‰}$ ,  $\delta^{18}\text{O}_{\text{VPDB}}$   
988  $= -18.69 \pm 0.11\text{‰}$ ; ETH-3:  $\delta^{13}\text{C}_{\text{VPDB}} = 1.71 \pm 0.02\text{‰}$ ,  $\delta^{18}\text{O}_{\text{VPDB}} = -1.78 \pm 0.06\text{‰}$ ) (Bernasconi et al., 2018).

989

990 The check standards (IAEA-C2 and Merck) were treated like samples and their final  $\Delta_{47}$  values were used to monitor  
991 the corrections applied to the isotope data and to trace the instrument performance. Furthermore, the long-term  
992 averages of the final  $\Delta_{47}$  values of ETH-1 and ETH-2 were monitored to verify the accuracy of the pressure baseline  
993 correction. This correction should result in these standards having the same  $\Delta_{47}$  values (Bernasconi et al., 2018).

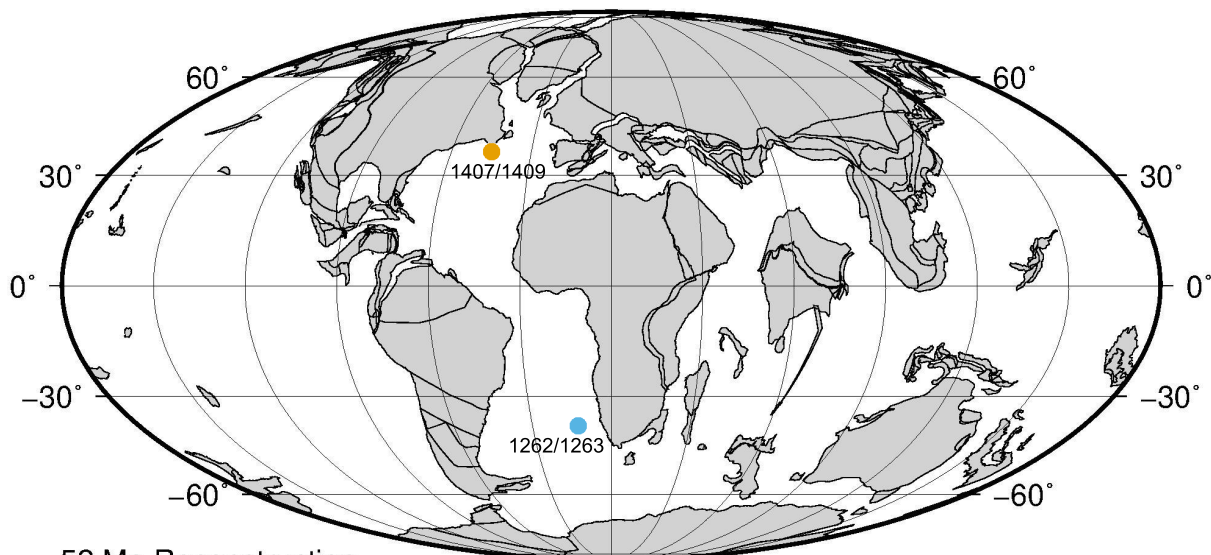
994

995 Some sample and standard measurements were excluded from the dataset based on criteria. First, sample and  
996 standard measurements with internal  $\Delta_{47}$  standard deviations of  $>0.150$  were considered bad measurements.  
997 Second, any contamination originating from impurities in the samples (and standards) were closely monitored by  
998 using the so-called '49 parameter' (John & Bowen, 2016). Measurements with a 49 parameter of  $>0.200$  were  
999 regarded significantly contaminated. Third, measurements with too low ( $<8$  V) or too high initial intensities ( $>40$  V),  
1000 and/or too big a difference between sample and reference gas intensity ( $>3$  V) were removed. Fourth, sample

1001 measurements with individual  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values that have a big offset from the average value of the bin (offset  
1002  $>2\%$ ) were considered unreliable, as these might contain contamination.

1003

1004 **Supplementary Figures**

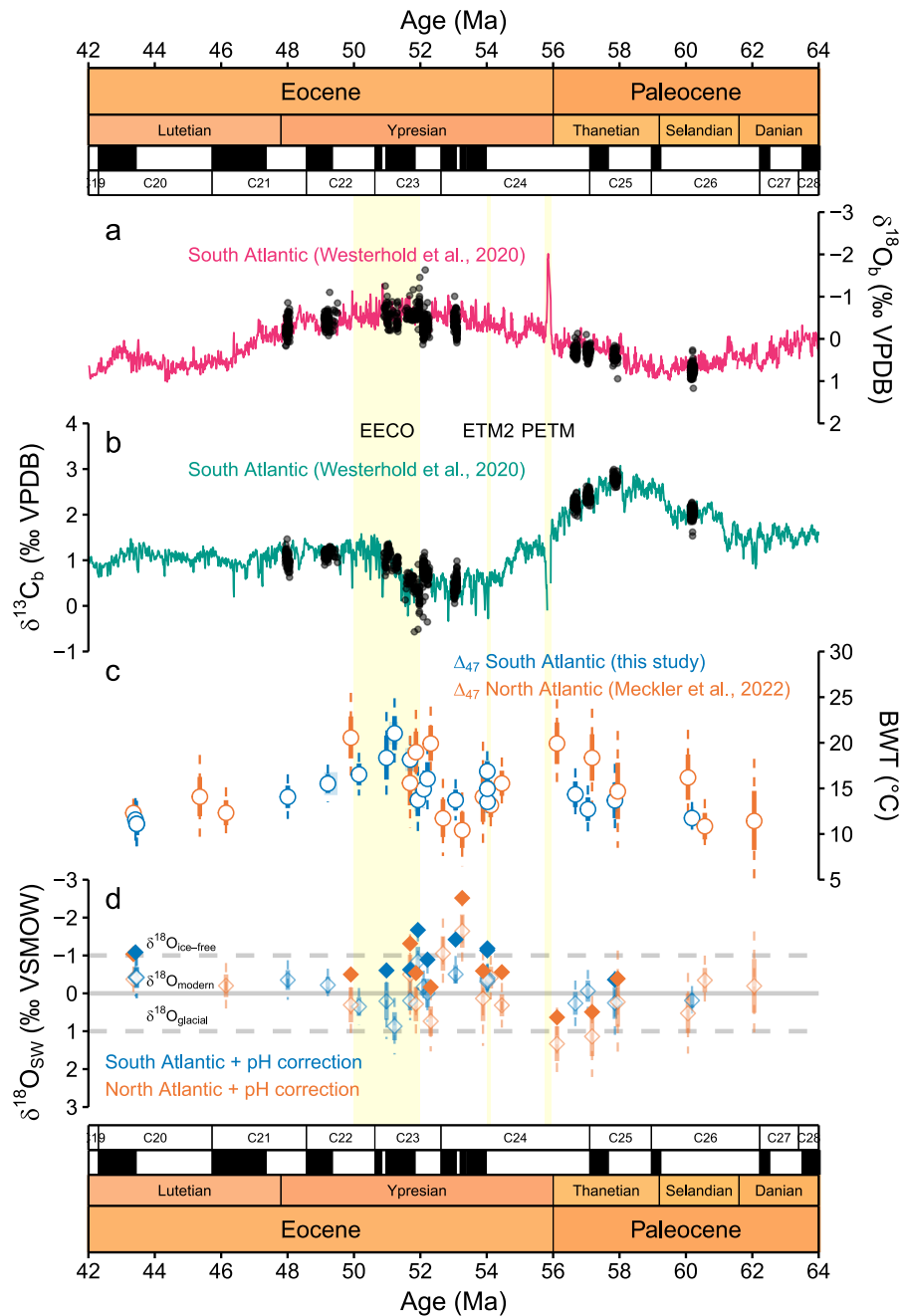


52 Ma Reconstruction

1005  
1006 **Figure S1.** Paleogeographic reconstruction (52 Ma) with the locations of the South Atlantic (ODP Sites 1262 and 1263) and the  
1007 North Atlantic (IODP Sites U1407 and U1409) sites. This map is generated from the plate tectonic reconstruction service of the  
1008 Ocean Drilling Stratigraphic Network (ODSN; <http://www.odsn.de>).

1009

1010

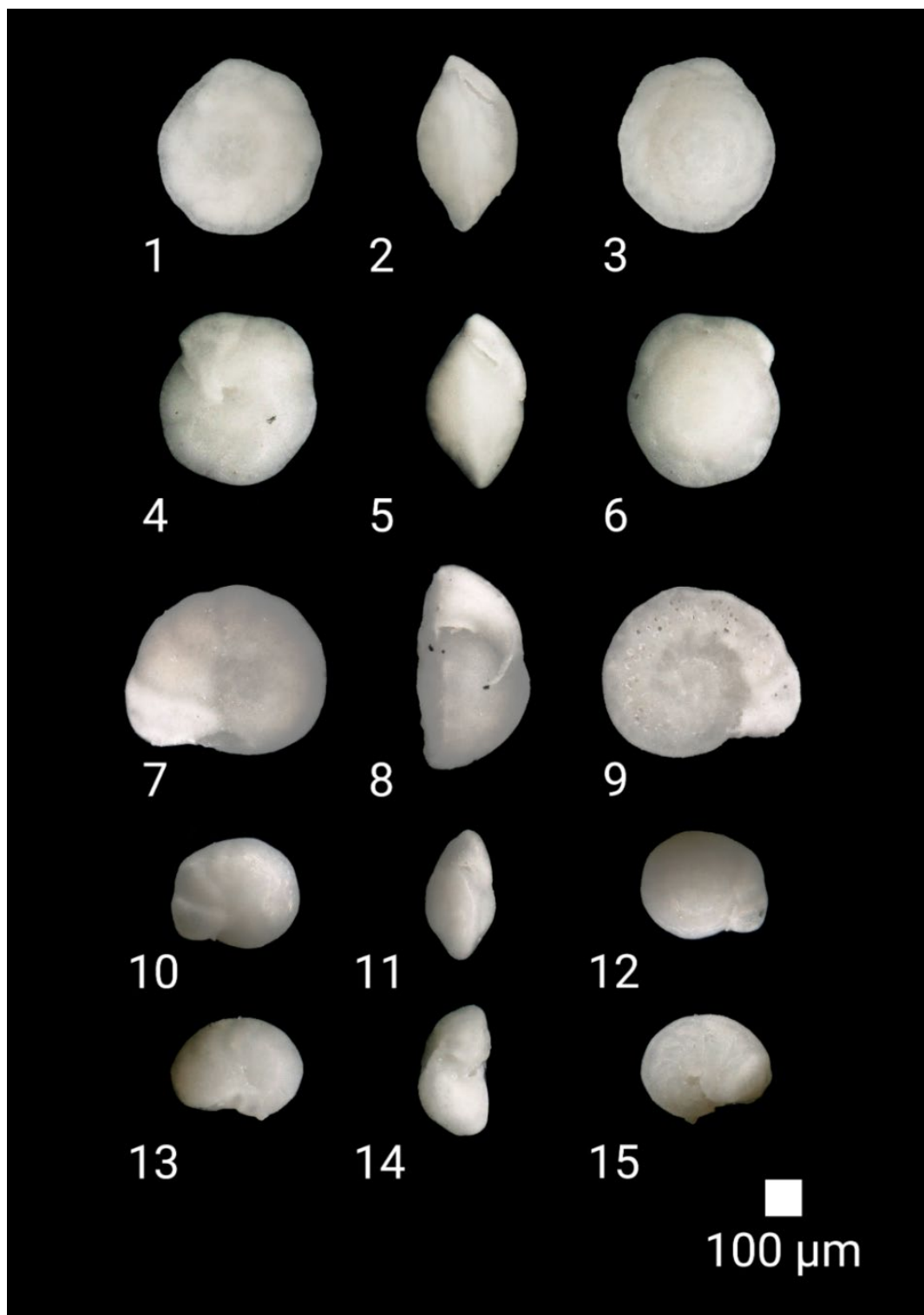


1011

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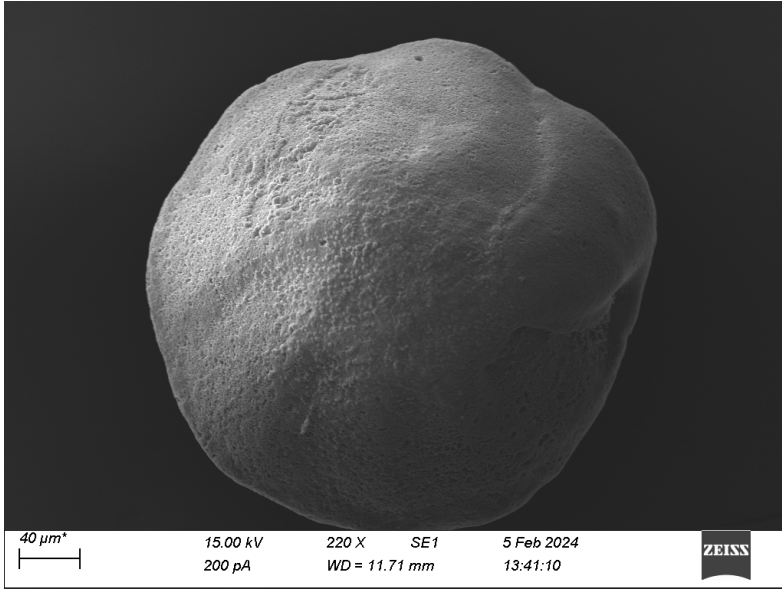
**Figure S2. a-b)** Comparison between our  $\delta^{18}\text{O}_b$  and  $\delta^{13}\text{C}_b$  measurements and published continuous high-resolution records of the Walvis Ridge, South Atlantic (ODP Sites 1262/1263/1265) (McCarren et al., 2008; Stap et al., 2010; Littler et al., 2014; Lauretano et al., 2015, 2016, 2018; Thomas et al., 2018; Barnett et al., 2019; Westerhold et al., 2020). All  $\delta^{18}\text{O}_b$  and  $\delta^{13}\text{C}_b$  data are corrected towards *Cibicidoides* values, considered to represent seawater equilibrium (Marchitto et al., 2014). The high-resolution composite record shows relatively less scatter in the isotope values because it represents a 5 pts LOESS smoothing of data averaged in 5 kyr time steps. **c)**  $\Delta_{47}$ -based BWTs from the Walvis Ridge, South Atlantic (ODP Sites 1262/1263) (this study; Leutert et al., 2019; Agterhuis et al., 2022) and Newfoundland, North Atlantic (IODP Sites U1407/U1409) (Leutert et al., 2019; Meckler et al., 2022). **d)** inferred  $\delta^{18}\text{O}_{sw}$  composition from the combined  $\Delta_{47}$ -based BWT and  $\delta^{18}\text{O}_b$  data from the Walvis Ridge, South Atlantic (ODP Sites 1262/1263) (this study; Leutert et al., 2019; Agterhuis et al., 2022) and Newfoundland, North Atlantic (IODP Sites U1407/U1409) (Leutert et al., 2019; Meckler et al., 2022). The data represented with a closed fill indicate the  $\delta^{18}\text{O}_{sw}$  values corrected for an assumed pH effect on the  $\delta^{18}\text{O}_b$ .

1022

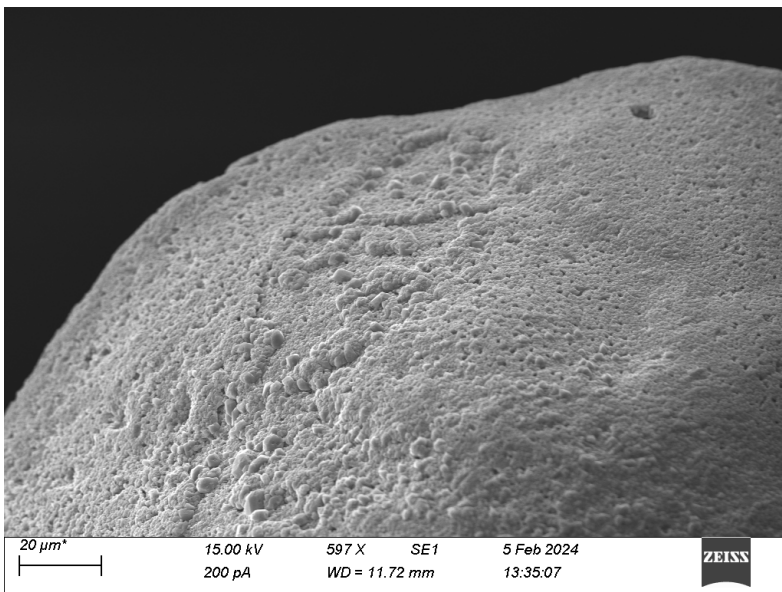


1024

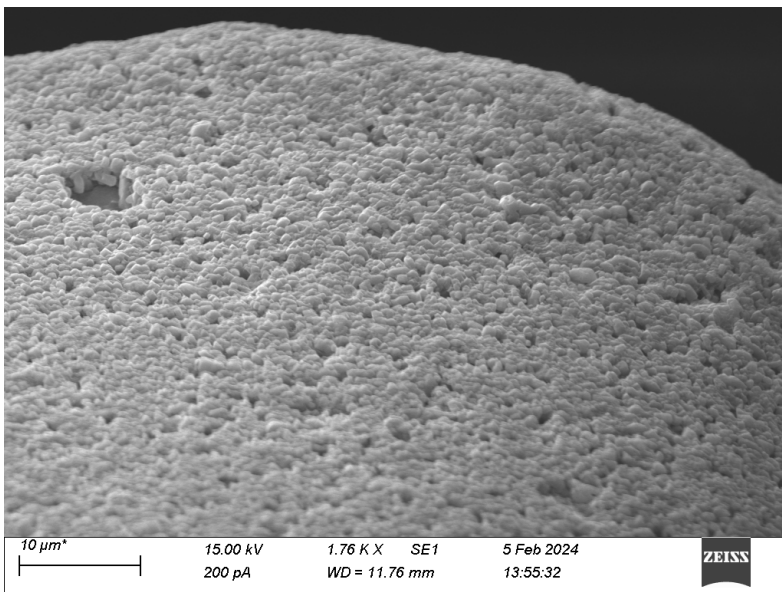
1025 **Figure S3.** Images of benthic foraminiferal species measured for stable and clumped isotopes in this study. Pictures were taken  
 1026 using a Nikon Keyence VHX-5000 series digital microscope. Plates: (1) *Nuttallides truempyi* umbilical view, (2) apertural view, (3)  
 1027 spiral view (1263B 16H1W 84-85 cm); (4) *Oridorsalis umbonatus* umbilical view, (5) apertural view, (6) spiral view (1263B 16H1W  
 1028 21-22 cm); (7) *Cibicoides eoceanus* umbilical view, (8) apertural view, (9) spiral view (1263B 23H4W 54-55 cm); (10) *Cibicoides*  
 1029 *mundulus* group umbilical view, (11) apertural view, (12) spiral view (1263B 23H4W 12-13 cm); (13) *Hanzawaia ammophila*  
 1030 umbilical view, (14) apertural view, (15) spiral view (1263B 23H4W 12-13 cm).



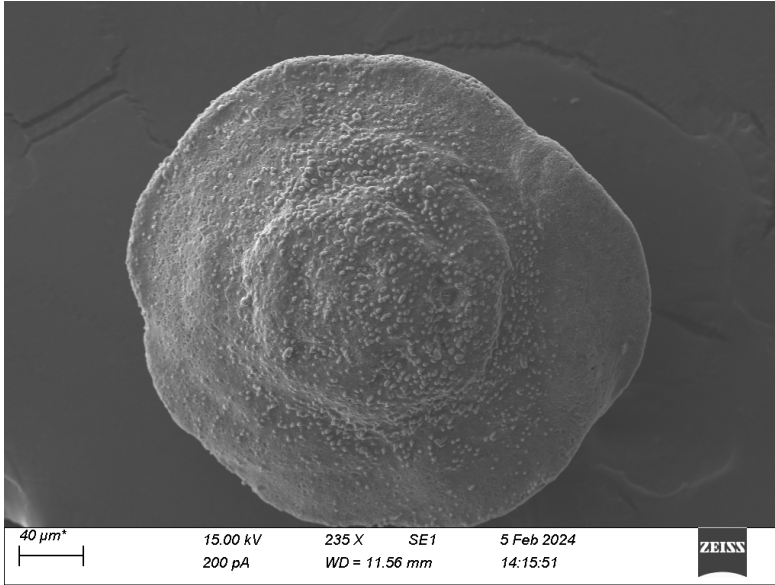
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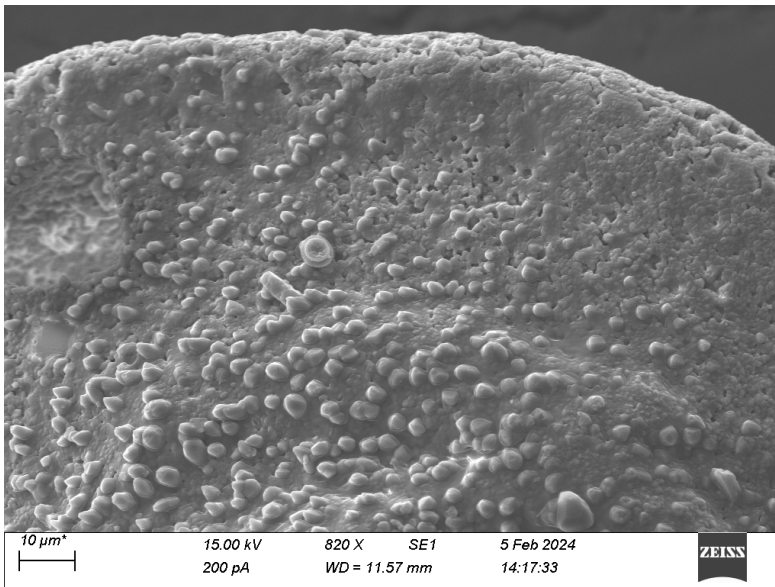
1032



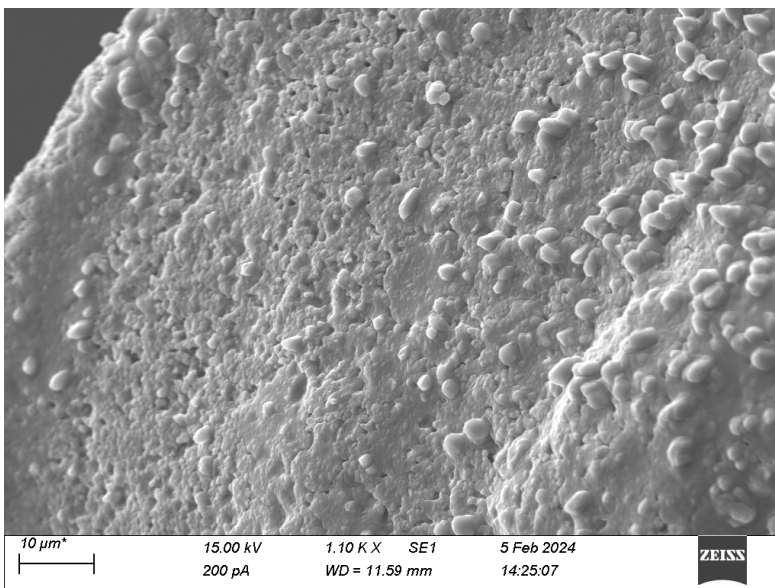
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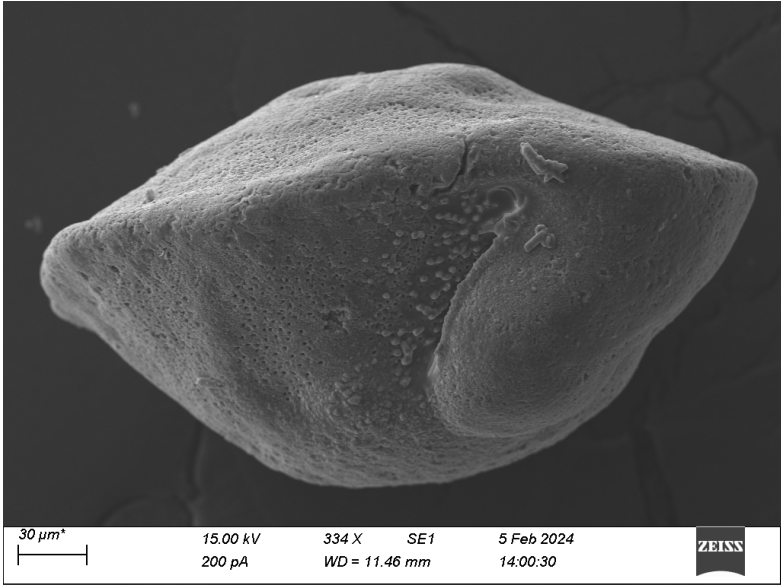
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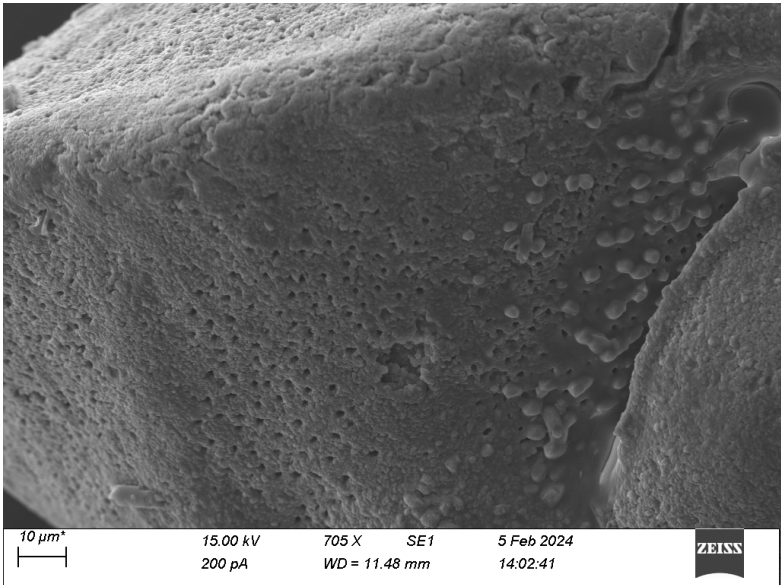
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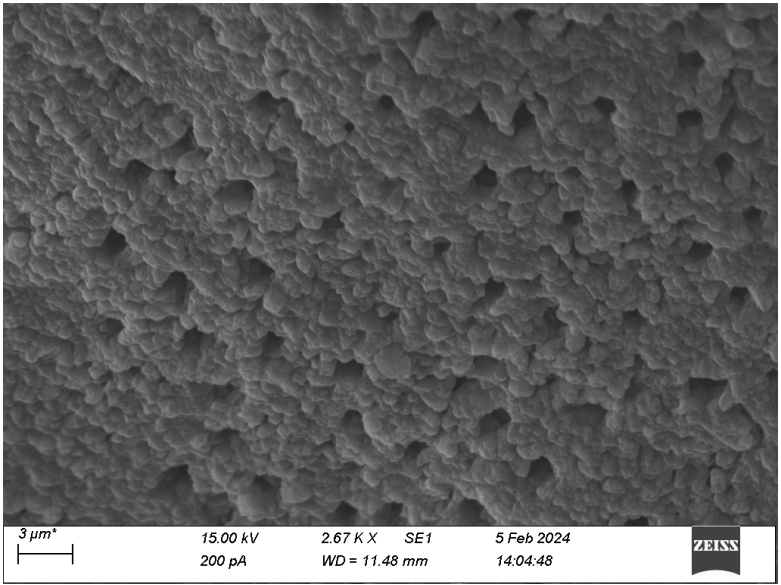
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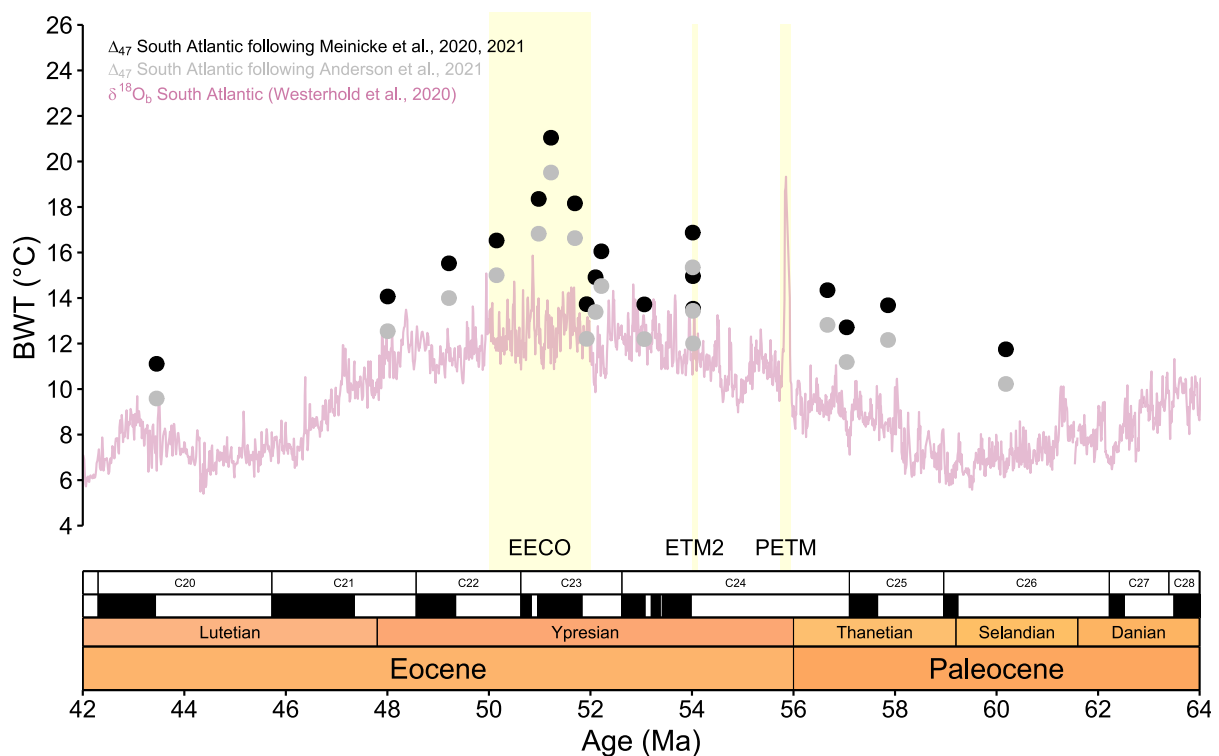


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1040 **Figure S4.** Scanning Electron Microscope (SEM) images of early Eocene *Nuttallides truempyi* specimens used in this study, from  
 1041 samples 1263B 20H3W 62-63 cm, 1263B 20H3W 79-80 cm, and 1263B 20H3W 94-95 cm (umbilical, spiral, and apertural view).  
 1042



1043 **Figure S5.** Comparison between  $\Delta_{47}$ -based BWTs of the South Atlantic (this study; Leutert et al., 2019; Agterhuis et al., 2022)  
 1044 following the foraminifer-based calibration by Meinicke et al., 2020, 2021 and the combined inorganic-biogenic calibration by  
 1045 Anderson et al., 2021. The  $\delta^{18}O_6$  composite record consists of sites from the South Atlantic (Walvis Ridge) (McCarren et al., 2008;  
 1046 Stap et al., 2010; Littler et al., 2014; Lauretano et al., 2015, 2016, 2018; Thomas et al., 2018; Barnet et al., 2019; Westerhold et al.,  
 1047 2020) and was corrected to *Cibicidoides* values (seawater equilibrium) before calculation of BWT using the calibration of Marchitto  
 1048 et al., 2014. The record represents a 5 pts LOESS smoothing of data averaged in 5 kyr time steps.  
 1049

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 1051 **Supplementary references**

- 1052 1. Agterhuis, T., Ziegler, M., de Winter, N. J. & Lourens, L. J. Warm deep-sea temperatures across Eocene  
 1053 Thermal Maximum 2 from clumped isotope thermometry. *Commun. Earth Environ.* **3**, 1–9 (2022).
- 1054 2. Anderson, N. T. et al. A unified clumped isotope thermometer calibration (0.5–1,100 °C) using carbonate-based  
 1055 standardization. *Geophys. Res. Lett.* **48**, e2020GL092069 (2021).
- 1056 3. Barnet, J. S. et al. A high-fidelity benthic stable isotope record of late Cretaceous–early Eocene climate change  
 1057 and carbon-cycling. *Paleoceanogr. Paleoclimatol.* **34**, 672–691 (2019).
- 1058 4. Bernasconi, S. M. et al. Background effects on Faraday collectors in gas-source mass spectrometry and  
 1059 implications for clumped isotope measurements. *Rapid Commun. Mass Spectrom.* **27**, 603–612 (2013).
- 1060 5. Bernasconi, S. M. et al. Reducing uncertainties in carbonate clumped isotope analysis through consistent  
 1061 carbonate-based standardization. *Geochem. Geophys. Geosyst.* **19**, 2895–2914 (2018).



- 1062 6. Bernasconi, S. M. et al. InterCarb: A community effort to improve interlaboratory standardization of the  
1063 carbonate clumped isotope thermometer using carbonate standards. *Geochem. Geophys. Geosyst.* **22**,  
1064 e2020GC009588 (2021).
- 1065 7. Dennis, K. J., Affek, H. P., Passey, B. H., Schrag, D. P. & Eiler, J. M. Defining an absolute reference frame for  
1066 'clumped' isotope studies of CO<sub>2</sub>. *Geochim. Cosmochim. Acta* **75**, 7117–7131 (2011).
- 1067 8. Eiler, J. M. "Clumped-isotope" geochemistry—The study of naturally-occurring, multiply-substituted  
1068 isotopologues. *Earth Planet. Sci. Lett.* **262**, 309–327 (2007).
- 1069 9. Ghosh, P. et al. <sup>13</sup>C–<sup>18</sup>O bonds in carbonate minerals: A new kind of paleothermometer. *Geochim. Cosmochim.*  
1070 *Acta* **70**, 1439–1456 (2006).
- 1071 10. He, B., Olack, G. A. & Colman, A. S. Pressure baseline correction and high-precision CO<sub>2</sub> clumped-isotope  
1072 ( $\Delta_{47}$ ) measurements in bellows and micro-volume modes. *Rapid Commun. Mass Spectrom.* **26**, 2837–2853  
1073 (2012).
- 1074 11. Hu, B. et al. A modified procedure for gas-source isotope ratio mass spectrometry: The long-integration dual-  
1075 inlet (LIDI) methodology and implications for clumped isotope measurements. *Rapid Commun. Mass*  
1076 *Spectrom.* **28**, 1413–1425 (2014).
- 1077 12. Huntington, K. W. et al. Methods and limitations of 'clumped' CO<sub>2</sub> isotope ( $\Delta_{47}$ ) analysis by gas-source isotope  
1078 ratio mass spectrometry. *J. Mass Spectrom.* **44**, 1318–1329 (2009).
- 1079 13. John, C. M. & Bowen, D. Community software for challenging isotope analysis: First applications of 'Easotope'  
1080 to clumped isotopes. *Rapid Commun. Mass Spectrom.* **30**, 2285–2300 (2016).
- 1081 14. Kocken, I. J., Müller, I. A. & Ziegler, M. Optimizing the use of carbonate standards to minimize uncertainties in  
1082 clumped isotope data. *Geochem. Geophys. Geosyst.* **20**, 5565–5577 (2019).
- 1083 15. Lauretano, V., Littler, K., Polling, M., Zachos, J. C. & Lourens, L. J. Frequency, magnitude and character of  
1084 hyperthermal events at the onset of the Early Eocene Climatic Optimum. *Clim. Past* **11**, 1313–1324 (2015).
- 1085 16. Lauretano, V., Hilgen, F. J., Zachos, J. C. & Lourens, L. J. Astronomically tuned age model for the early Eocene  
1086 carbon isotope events: A new high-resolution  $\delta^{13}\text{C}_{\text{benthic}}$  record of ODP Site 1263 between ~49 and ~54  
1087 Ma. *Newsl. Stratigr.* **49**, 383–400 (2016).
- 1088 17. Lauretano, V., Zachos, J. C. & Lourens, L. J. Orbitally paced carbon and deep-sea temperature changes at the  
1089 peak of the Early Eocene Climatic Optimum. *Paleoceanogr. Paleoclimatol.* **33**, 1050–1065 (2018).
- 1090 18. Leutert, T. J. et al. Sensitivity of clumped isotope temperatures in fossil benthic and planktic foraminifera to  
1091 diagenetic alteration. *Geochim. Cosmochim. Acta* **257**, 354–372 (2019).
- 1092 19. Littler, K., Röhl, U., Westerhold, T. & Zachos, J. C. A high-resolution benthic stable-isotope record for the South  
1093 Atlantic: Implications for orbital-scale changes in Late Paleocene–Early Eocene climate and carbon  
1094 cycling. *Earth Planet. Sci. Lett.* **401**, 18–30 (2014).

- 1095 20. Marchitto, T. M. et al. Improved oxygen isotope temperature calibrations for cosmopolitan benthic foraminifera.  
1096 *Geochim. Cosmochim. Acta* **130**, 1–11 (2014).
- 1097 21. McCarren, H., Thomas, E., Hasegawa, T., Röhl, U. & Zachos, J. C. Depth dependency of the Paleocene-  
1098 Eocene carbon isotope excursion: Paired benthic and terrestrial biomarker records (Ocean Drilling Program  
1099 Leg 208, Walvis Ridge). *Geochem. Geophys. Geosyst.* **9** (2008).
- 1100 22. Meckler, A. N., Ziegler, M., Millán, M. I., Breitenbach, S. F. & Bernasconi, S. M. Long-term performance of the  
1101 Kiel carbonate device with a new correction scheme for clumped isotope measurements. *Rapid Commun.*  
1102 *Mass Spectrom.* **28**, 1705–1715 (2014).
- 1103 23. Meckler, A. N. et al. Cenozoic evolution of deep ocean temperature from clumped isotope  
1104 thermometry. *Science* **377**, 86–90 (2022).
- 1105 24. Meinicke, N. et al. A robust calibration of the clumped isotopes to temperature relationship for foraminifers.  
1106 *Geochim. Cosmochim. Acta* **270**, 160–183 (2020).
- 1107 25. Meinicke, N., Reimi, M. A., Ravelo, A. C. & Meckler, A. N. Coupled Mg/Ca and clumped isotope measurements  
1108 indicate lack of substantial mixed layer cooling in the Western Pacific Warm Pool during the last ~5 million  
1109 years. *Paleoceanogr. Paleoclimatol.* **36**, e2020PA004115 (2021).
- 1110 26. Müller, I. A. et al. Carbonate clumped isotope analyses with the long-integration dual-inlet (LIDI) workflow:  
1111 Scratching at the lower sample weight boundaries. *Rapid Commun. Mass Spectrom.* **31**, 1057–1066 (2017).
- 1112 27. Schmid, T. W. & Bernasconi, S. M. An automated method for ‘clumped-isotope’ measurements on small  
1113 carbonate samples. *Rapid Commun. Mass Spectrom.* **24**, 1955–1963 (2010).
- 1114 28. Schmid, T. W., Radke, J. & Bernasconi, S. M. Clumped-isotope measurements on small carbonate samples  
1115 with a Kiel IV carbonate device and a MAT 253 mass spectrometer. *Appl. Note* **30233**, (Thermo Fisher, 2012).
- 1116 29. Stap, L. et al. High-resolution deep-sea carbon and oxygen isotope records of Eocene Thermal Maximum 2  
1117 and H2. *Geology* **38**, 607–610 (2010).
- 1118 30. Thomas, E. et al. Early Eocene thermal maximum 3: Biotic response at Walvis ridge (SE Atlantic  
1119 ocean). *Paleoceanogr. Paleoclimatol.* **33**, 862–883 (2018).
- 1120 31. Westerhold, T. et al. An astronomically dated record of Earth’s climate and its predictability over the last 66  
1121 million years. *Science* **369**, 1383–1387 (2020).