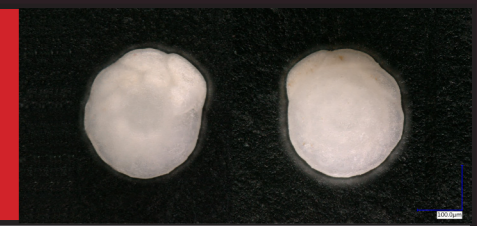


# Warm deep-sea temperatures across Eocene Thermal Maximum 2 from clumped isotope thermometry ( $\Delta_{47}$ )

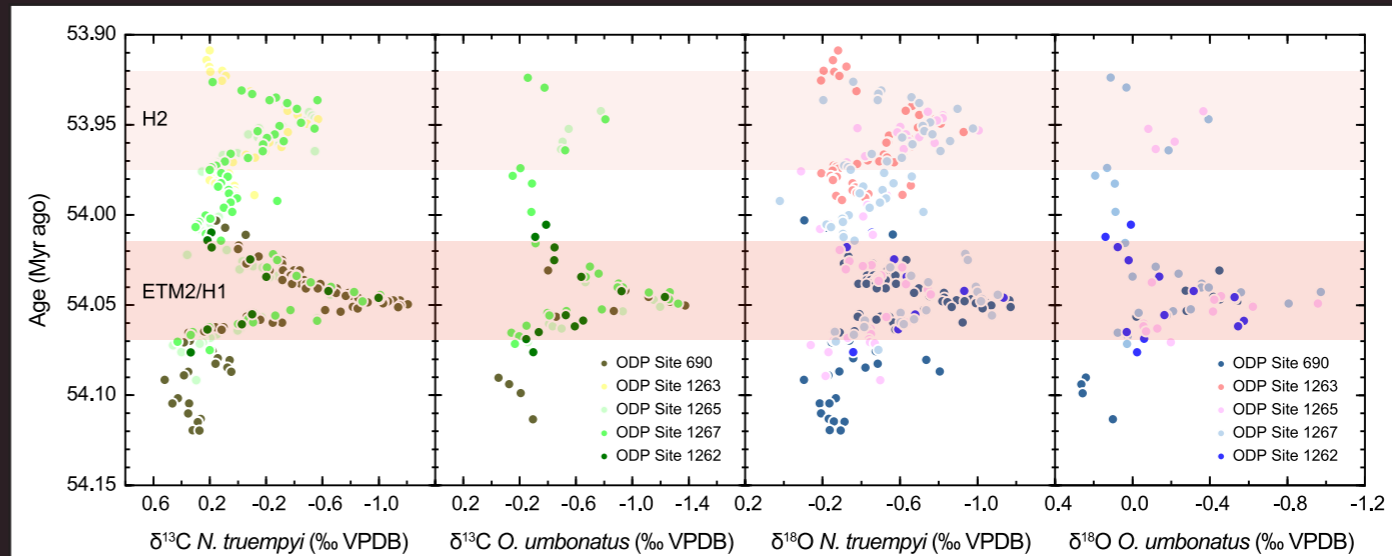
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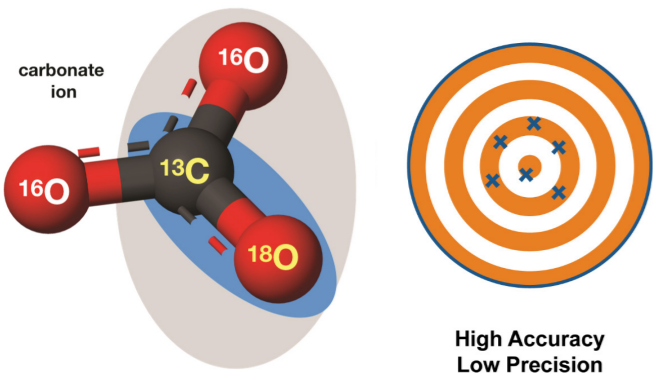


**Background:** A potential analogue for the future climate state is the ice-free hothouse climate of the early Eocene (56–48 Ma)<sup>1</sup>. This period experienced the highest CO<sub>2</sub> levels of the Cenozoic (~1000 ppm)<sup>2</sup>, as well as the occurrence of multiple transient (10–100 kyr) global warming events, so-called hyperthermals<sup>3</sup>. These events are recorded by negative excursions in carbon and oxygen isotopes ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) in deep-sea sediments, which reflect major short-lived perturbations of the carbon cycle and climate system (Figure 1)<sup>1,3</sup>.

**MOTIVATION:** The deep ocean constitutes a stable and vast heat reservoir in the climate system, and is therefore assumed to represent a setting to estimate past global mean temperatures<sup>4</sup>. However, available deep-sea temperature estimates from foraminiferal  $\delta^{18}\text{O}$  and Mg/Ca rely on uncertain assumptions, such as estimation of the chemical composition of the ancient seawater, pH and biological factors<sup>5,6</sup>. Here, we apply for the first time the carbonate clumped isotope paleothermometer ( $\Delta_{47}$ ), a proxy independent of these non-thermal factors<sup>7,8</sup>, to reconstruct early Eocene deep-sea temperatures across two hyperthermal events.

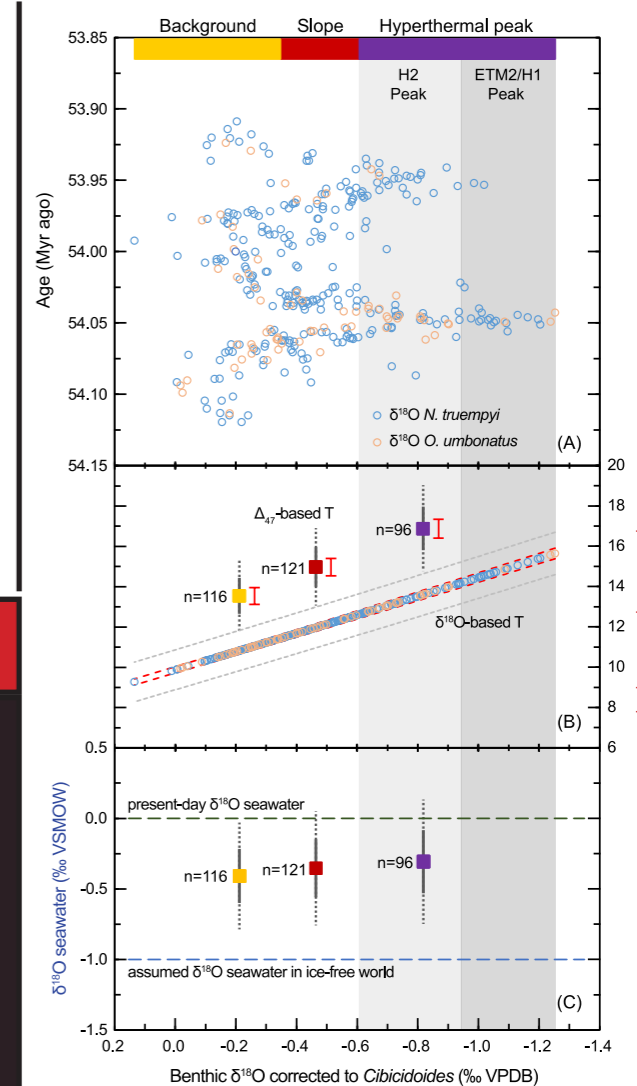


**Figure 1.** Benthic foraminiferal  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  records across ETM2 and H2 from multiple sites in the South Atlantic measured on *Nutallides truempyi* and *Oridorsalis umbonatus*. The offset in the stable isotopes between the two species indicate species-specific vital effects.



## METHODS

- Paired stable ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) and clumped isotope ( $\Delta_{47}$ ) analysis across the ETM2/H1 and H2 hyperthermals on benthic foraminifera from ODP Sites 690, 1262, 1263, 1265, and 1267 in the South Atlantic Ocean.
- *Nutallides truempyi* and *Oridorsalis umbonatus* were measured on a Thermo 253+ with Kiel-IV instrument in the geolab of Utrecht University<sup>9,10</sup>. For each replicate measurement (80  $\mu\text{g}$ ) about 25 specimens were picked and ultrasonically cleaned.
- Clumped isotope analysis is characterized by a low analytical precision due to the sporadic natural abundance of  $^{13}\text{C}$ – $^{18}\text{O}$  bonds in carbonate ions<sup>7</sup>. Averaging multiple  $\Delta_{47}$  measurements is required to obtain precise temperature estimates<sup>11</sup>. Here, we compiled  $\Delta_{47}$  temperature bins for the average background, slope, and average hyperthermal peak state based on the  $\delta^{18}\text{O}$  values corresponding to these measurements (optimal bin sizes determined using t-test)<sup>11</sup>.



**Figure 2.** (a) Benthic foraminiferal  $\delta^{18}\text{O}$  values across ETM2 and H2 corrected to *Cibicidoides* for assumed seawater equilibrium. (b) Deep-sea temperatures based on  $\Delta_{47}$  and  $\delta^{18}\text{O}$  (assuming ice-free world) including analytical (dark grey; 68% and 95% CI for  $\Delta_{47}$  and 2xSD of the IAEA-C2 standard for  $\delta^{18}\text{O}$ ) and calibration (red; 95% CI) uncertainties. (c) Calculated seawater  $\delta^{18}\text{O}$  is much higher than the assumed value based on ice-free conditions. Alternatively, this assumed seawater  $\delta^{18}\text{O}$  value may be correct when an effect of low bottom water pH on foraminiferal  $\delta^{18}\text{O}$  is taken into account<sup>12–14</sup>.

## TAKE HOME MESSAGES

- Our independent early Eocene deep-sea temperature reconstructions indicate **13.5±1.8 °C (95% CI) for the background conditions, and average hyperthermal peak temperatures of 16.9±2.2 °C (95% CI).**
- On average, absolute temperatures are **three degrees warmer** from clumped isotope thermometry **than from conventional benthic oxygen isotopes.**
- This finding implies a necessary **reassessment of the seawater isotope composition and pH in the deep ocean during the Eocene, and of a potential pH effect on benthic foraminiferal oxygen isotopes.**
- Future work: the clumped isotope proxy opens up new opportunities to investigate the distribution of different water masses in the ocean basins and test the existing views on the homogeneity/heterogeneity of the ocean over the Cenozoic<sup>15</sup>.

## References

(1) Zachos et al. (2008). An early Cenozoic perspective on greenhouse warming and carbon-cycle dynamics. *Nature*; (2) Anagnostou et al. (2016). Changing atmospheric CO<sub>2</sub> concentration was the primary driver of early Cenozoic climate. *Nature*; (3) Lauretano et al. (2018) Orbitally paced carbon and deep-sea temperature changes at the peak of the early Eocene climatic optimum. *Paleoceanography and Paleoclimatology*; (4) Hansen et al. (2013). Climate sensitivity, sea level and atmospheric carbon dioxide. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*; (5) Pearson (2012). Oxygen isotopes in foraminifera: Overview and historical review. *The Paleontological Society Papers*; (6) Evans & Müller (2012). Deep time foraminifera Mg/Ca paleothermometry: Nonlinear correction for secular change in seawater Mg/Ca. *Paleoceanography*; (7) Eiler (2011). Paleoclimate reconstruction using carbonate clumped isotope thermometry. *Quaternary Science Reviews*; (8) Meinicke et al. (2020). A robust calibration of the clumped isotopes to temperature relationship for foraminifera. *Geochim. Cosmochim. Acta*; (9) Meckler et al. (2014). Long-term performance of the Kiel carbonate device with a new correction scheme for clumped isotope measurements. *Rapid Communications in Mass Spectrometry*; (10) Bernasconi et al. (2018). Reducing uncertainties in carbonate clumped isotope analysis through consistent carbonate-based standardization. *Geochemistry, Geophysics, Geosystems*; (11) de Winter et al. (2020). Optimizing sampling strategies in high-resolution paleoclimate records. *Climate of the Past*; (12) Raitzsch & Hönisch (2013). Cenozoic boron isotope variations in benthic foraminifera. *Geology*; (13) Spero et al. (1997). Effect of seawater carbonate concentration on foraminiferal carbon and oxygen isotopes. *Nature*; (14) Uchikawa & Zeebe (2010). Examining possible effects of seawater pH decline on foraminiferal stable isotopes during the Paleocene-Eocene Thermal Maximum. *Paleoceanography*; (15) Cramer et al. (2009). Ocean overturning since the Late Cretaceous: Inferences from a new benthic foraminiferal isotope compilation. *Paleoceanography*.