

1 **High sea surface temperatures in tropical warm pools during the Pliocene**

2 Charlotte L. O'Brien^{1,2,3*}, Gavin L. Foster⁴, Miguel A. Martínez-Botí⁴, Richard

3 Abell⁵, James W. B. Rae⁶ and Richard D. Pancost^{1,2}

4

5 *¹Organic Geochemistry Unit, School of Chemistry, University of Bristol, Bristol, BS8*

6 *ITS, UK*

7 *²Cabot Institute, University of Bristol, Bristol, BS8 1UJ, UK*

8 *³Department of Earth Sciences, University of Oxford, Oxford, OX1 3AN, UK*

9 *⁴Ocean and Earth Science, National Oceanography Centre Southampton, University*
10 *of Southampton, Southampton, SO14 3ZH, UK*

11 *⁵Scottish Marine Institute, Oban, Argyll, PA37 1QA, UK*

12 *⁶Department of Earth Sciences, Irvine Building, University of St Andrews, St*
13 *Andrews, KY16 9AL, UK*

14

15 *email: charlotte.obrien@earth.ox.ac.uk

16 **The western warm pools of the Atlantic and Pacific Oceans are a critical store of**
17 **heat and power for the tropical climate system, such that accurately**
18 **reconstructing past tropical sea surface temperatures is essential for**
19 **understanding global climate history. Current low latitude Pliocene-to-recent**
20 **climate reconstructions indicate that sea surface temperatures in the tropical**
21 **warm pools have remained stable since the early Pliocene, despite 3-4 °C of**
22 **global cooling. This is commonly thought to imply the operation of some sort of**
23 **thermostatic regulation. An alternative possibility, that we explore here, is that**
24 **this apparent stability is the result of the inability of certain geochemical proxy**
25 **methods to accurately resolve sea surface temperatures in the Pliocene warm**
26 **pool. We use both inorganic- and organic-proxies to reconstruct sea surface**
27 **temperatures from the South China Sea, Caribbean and Western Equatorial**
28 **Pacific. This new multi-proxy reconstruction indicates that in contrast to earlier**
29 **findings, the western Pacific and western Atlantic warm pools during the**
30 **Pliocene were ~2 °C warmer than today. Consequently, no thermostat**
31 **mechanism limited the temperature of the warm pools of the Pliocene equatorial**
32 **ocean.**

33

34 The Western Pacific Warm Pool, comprising the warmest surface waters (>28 °C) of
35 the global oceans, is the main source area of heat and water vapour export to high
36 latitudes¹ (Fig. 1). Similarly, the equatorial Atlantic warm pool, although substantially
37 smaller (Fig. 1), represents another important source of moisture and heat to the
38 Northern Hemisphere². Variations in the size and intensity of these warm pool
39 regions, on intra-annual through to geological timescales, influence Walker and
40 Hadley circulations and likely played a major role in the evolution of global climate

41 since at least the Pliocene, the last time the Earth was significantly warmer than
42 today³. Both modelling and proxy-based studies suggest much greater warmth at
43 higher latitudes during the Pliocene⁴. Yet, despite an expansion of the warm pools,
44 current Pliocene to recent sea surface temperature (SST) reconstructions indicate that
45 SSTs in these tropical regions have remained stable for at least the last 5 Myr^{5,6} (Fig.
46 2c), implying the operation of some sort of thermostatic regulation^{7,8}. Ocean
47 thermostat hypotheses generally invoke one or a combination of evaporative feedback
48 processes, cloud-SST feedbacks and ocean heat transport mechanisms to restrict
49 maximum tropical ocean SSTs^{7,8}; however, recent studies have demonstrated the
50 concept of a strict SST upper limit to be false^{9,10}. Although stable tropical SSTs and
51 reduced pole-equator temperature gradients in the Pliocene may imply the existence
52 of an ocean thermostat^{6,11}, modelling studies and Quaternary palaeo-records^{12,13}
53 indicate that temperatures in the warm pool scale with both cooler and warmer global
54 temperatures. We therefore explore an alternative hypothesis here, that Pliocene warm
55 pool SST ‘stability’ may be the result of inherent proxy-bias¹¹.

56

57 Most Pliocene SST estimates depend on either the alkenone unsaturation temperature
58 proxy ($U^{k'}_{37}$) or Mg/Ca ratios in planktic foraminiferal calcite^{6,14}. However, both of
59 these proxy systems have significant limitations when applied to the Pliocene warm
60 pool. An advantage of the $U^{k'}_{37}$ -SST proxy is that the values are not directly
61 controlled by seawater chemistry¹⁵, which may vary over time. However, application
62 of the $U^{k'}_{37}$ -SST proxy for the Pliocene is restricted, as this proxy is insensitive to
63 temperatures $>29\text{ }^{\circ}\text{C}$ ¹⁵ and is therefore incapable of resolving SSTs in the warmest
64 ocean regions. Under these conditions, the Mg/Ca-SST proxy is more commonly
65 applied, although this technique also suffers weaknesses, including a sensitivity to

66 salinity, $[\text{CO}_3^{2-}]$, dissolution, and diagenesis (see Supplementary Information for
67 relevant references and discussion). Of particular importance on million-year
68 timescales is the fact that accurate conversion of foraminiferal Mg/Ca ratios to SST
69 requires secular changes in seawater composition to be taken into account (e.g. ref.
70 16). The residence times of Mg, ~ 13 Myr, and Ca, ~ 1 Myr, in seawater imply that
71 $\text{Mg}/\text{Ca}_{\text{sw}}$ is likely to have varied on timescales >1 Myr. Indeed, both model and proxy
72 data suggest $\text{Mg}/\text{Ca}_{\text{sw}}$ during the Pliocene was broadly lower than today, with
73 estimates ranging from 2.68 to 5.46 mol mol^{-1} compared to the modern value of
74 5.17 mol mol^{-1} (refs 17-21). Correction for changes in $\text{Mg}/\text{Ca}_{\text{sw}}$ has a significant
75 influence on reconstructions of thermal-stasis in the warm pool, yet significant debate
76 exists about the magnitude of this correction, or even if it is required at all (e.g. refs
77 16,22).

78

79 **Revised estimates of tropical warmth**

80 Here we shed new light on Plio-Pleistocene warm pool evolution, by employing a
81 multiple SST-proxy approach at two warm pool sites: South China Sea ODP Site
82 1143 and Caribbean Sea ODP Site 999 (Fig. 1). These sites are well suited for warm
83 pool SST reconstruction, being located within the western Pacific Warm Pool and
84 western Atlantic Warm Pool regions, respectively. Furthermore, these warm pool
85 sites exhibit little intra-annual variability today (<2.7 °C), and have deep mixed layers
86 (>30 m), reducing the likelihood of SST proxy discrepancies due to seasonality or
87 changes in habitat depths. We present a new $\text{TEX}_{86}^{\text{H}}$ -SST record for Site 1143 and
88 new Mg/Ca-SST data for Sites 1143 and 999 for the Pliocene to recent, and we then
89 compare these with existing U^{k}_{37} - and Mg/Ca-SST records from the same locations²³⁻
90 ²⁶. The $\text{TEX}_{86}^{\text{H}}$ (TetraEther index of tetraethers consisting of 86 carbon atoms) proxy

91 is a relatively new palaeo-SST technique and thus far has only been applied to
92 reconstruct Pliocene SSTs in a few locations (e.g. ref. 27). In comparison with $U^{k'}_{37}$ -
93 SST estimates, the TEX^H_{86} proxy is not subject to a warm temperature limit until
94 ocean temperatures exceed ~ 38 °C, nor does this proxy suffer from changes in ocean
95 chemistry or preservation. The TEX^H_{86} proxy is not without its own limitations: in
96 particular, TEX^H_{86} -derived temperatures can reflect subsurface conditions in some
97 settings²⁷ and for the Eocene TEX^H_{86} -SSTs at high latitudes appear to have a high
98 temperature bias²⁸. However, because its limitations are very different from those of
99 the Mg/Ca and $U^{k'}_{37}$ proxies, TEX^H_{86} palaeothermometry is a useful independent
100 technique for reconstructing warm Pliocene SSTs.

101

102 We find that in the southern South China Sea the $U^{k'}_{37}$ and TEX^H_{86} proxies yield
103 similar SSTs throughout the Pleistocene. Moreover, $U^{k'}_{37}$ - and TEX^H_{86} -SSTs from
104 Holocene samples yield temperatures of ~ 28 °C^{23,29}, which agree well with modern
105 mean annual SSTs at Site 1143 (28.4 °C; WOA09)³⁰. These observations suggest that
106 both proxies accurately record surface water conditions during the Pleistocene, and
107 likely also on longer timescales, in the southern South China Sea (Fig. 2;
108 Supplementary Figure 3). Furthermore, TEX^H_{86} may serve as an accurate SST
109 recorder at temperatures above 29 °C, when the $U^{k'}_{37}$ proxy becomes unresponsive.

110

111 For the past ~ 2 Myr, South China Sea SST-reconstructions from TEX^H_{86} and $U^{k'}_{37}$
112 exhibit similar absolute values, and both show a ~ 1 -2 °C cooling trend (Fig. 2a),
113 clearly arguing against a tropical thermostat at this site. During the Pliocene, ~ 5.0 to
114 2.6 Myr, TEX^H_{86} -SST estimates indicate even warmer conditions, varying between
115 27.3 and 30.9 °C. This yields an overall cooling of ~ 2.2 °C for the Pliocene to recent

116 (Fig. 2a). These SSTs are slightly warmer than $U^{k'}_{37}$ -SST estimates (Fig. 2a), which
117 remain approximately constant at ~ 28.8 °C. Therefore, the apparent ‘stabilisation’ of
118 $U^{k'}_{37}$ -derived temperature at Site 1143 during the Pliocene appears to be a
119 consequence of its temperature limit (~ 29 °C), rather than the operation of a
120 thermostat. Thus, the TEX^H_{86} - and $U^{k'}_{37}$ -SST²³ estimates together confirm that the
121 southern South China Sea warm pool was ~ 2 °C warmer in the Pliocene relative to
122 today, with cooling occurring from the early-mid Pliocene.

123

124 In contrast to TEX^H_{86} - and $U^{k'}_{37}$ -SST estimates, Pliocene *G. sacculifer* Mg/Ca-SST
125 estimates at Site 1143 are significantly cooler than today, offset by ~ 2.8 °C relative to
126 TEX^H_{86} -SSTs, and remaining stable for the interval ~ 4.8 to 2.6 Myr, before displaying
127 a warming trend of ~ 1 °C for the period 2.6 to 1.7 Myr (Fig. 2a). A high-resolution
128 Plio-Pleistocene *G. ruber* Mg/Ca-SST record³¹ for the same site also yields cooler
129 (>1 °C) temperatures relative to TEX^H_{86} and $U^{k'}_{37}$ for the interval 3.3-2.5 Myr
130 (Fig. 2a). For the past 1.5 Myr, however, *G. sacculifer* Mg/Ca-SST estimates yield
131 similar absolute values to TEX^H_{86} - and $U^{k'}_{37}$ -SST estimates, as well as displaying a
132 similar subtle cooling trend through this interval (Fig. 2a).

133

134 At the tropical Caribbean Sea Site 999, Mg/Ca-SST estimates from surface-dwelling
135 foraminifera *G. ruber*^{25,32} and *G. sacculifer* also exhibit good agreement with $U^{k'}_{37}$ -
136 SST estimates²⁵ for the past 2 Myr (Fig. 2b). Similar to Site 1143, *G. sacculifer*
137 Mg/Ca-SSTs record conditions ~ 1 °C cooler than those indicated by *G. ruber* Mg/Ca-
138 SSTs, reflecting the deeper mixed layer habitat of *G. sacculifer* (Fig. 2b). Prior to
139 2.6 Myr, however, Site 999 *G. ruber* and *G. sacculifer* Mg/Ca indicate significantly

140 cooler Pliocene SSTs, by ~1.2 to 3 °C, than those derived from comparable U^k₃₇-SST
141 records^{25,26} (Fig. 2b).

142

143 Temporal trends in Mg/Ca- and organic-SST estimates clearly diverge during the
144 Pliocene at Sites 1143 and 999, although it should be noted that these data do lie
145 within calibration error (Fig. 2). In this instance, however, the determination of
146 absolute temperature estimates is not as important as the temporal trends we
147 reconstruct for the different proxies, which are, in each case, greater than the
148 associated analytical uncertainty.

149

150 **Causes of sea surface temperature discrepancies**

151 The magnitude and direction of offsets in Pliocene Mg/Ca-SSTs relative to organic-
152 proxy estimates cannot simply be explained by seasonality. These sites are located in
153 warm pool regions with little seasonal variability³³, and today both species (*G. ruber*
154 and *G. sacculifer*) record mean annual SSTs everywhere between 20° N and 20° S
155 (*G. ruber* within ± 1 °C of mean annual SST and *G. sacculifer* the same or slightly
156 cooler than *G. ruber*)³⁴. Similarly, the depth habitat of these species is unlikely to
157 vary significantly, since both *G. sacculifer* and *G. ruber* are symbiont bearing; for
158 both to record temperatures lower than U^k₃₇ would require migration out of the mixed
159 layer, which is inconsistent with their physiology³⁵. We also judge the influence of
160 salinity change, [CO₃²⁻], partial dissolution and/or diagenesis to be minor (see
161 Supplementary Information for full discussion). Instead, the similarity in the Mg/Ca
162 records from our two widely separated sites and for both species of foraminifera,
163 together with the observed temporal deviation from the organic proxy records,
164 suggests a universal driver. In combination with the documented dependence of

165 foraminiferal Mg/Ca on Mg/Ca_{sw} (e.g. ref. 36 and references therein) and the likely
166 change of this parameter over the last 5 million years¹⁹, we suggest that the
167 underestimation of Pliocene Mg/Ca-SST estimates in the southern South China Sea
168 and tropical Caribbean Sea relative to organic SST proxy estimates is at least in part a
169 consequence of lower Mg/Ca_{sw} in the Pliocene.

170

171 **Exploring the effect of seawater Mg/Ca changes on Mg/Ca-SSTs**

172 To investigate the effect of secular changes in Mg/Ca_{sw} on Pliocene Mg/Ca-SST
173 records from warm pool regions, we adjust our Mg/Ca-SST estimates for changes in
174 Mg/Ca_{sw} (MgCa_{Cor}; following the approach of ref. 36) using a best fit of data-based
175 estimates^{17,18,21,37} (DBF) and also for a variety of different Mg/Ca_{sw} model predictions
176 (FD06¹⁹, HS12³⁸, SH98²⁰ and WA89³⁹; Fig. 3b, Supplementary Figure 7; for details
177 see Supplementary Information). Adjusting foraminiferal calcite Mg/Ca values for
178 changes in Mg/Ca_{sw} raises Pliocene Mg/Ca-SST estimates at Sites 1143 and 999 by
179 varying degrees, depending on the magnitude of Mg/Ca_{sw} change in the different
180 models/data estimates (Fig. 3b). The FD06¹⁹ correction gives the highest Mg/Ca-
181 SST_{cor} values, while other model estimates (HS12³⁸, SH98²⁰ and WA89³⁹; Fig. 3b)
182 and the DBF reconstruction (Fig. 3b) are lower and more similar to each other.
183 Nonetheless, accounting for lower Mg/Ca_{sw} clearly reduces the offset between
184 Mg/Ca- and organic-SST estimates in the Pliocene. Even with the most dramatic
185 correction Mg/Ca-SSTs are still somewhat lower (~0.8 °C relative to TEX₈₆^H-SSTs at
186 Site 1143 with the Mg/Ca_{sw} of FD06¹⁹; Fig. 3b), perhaps reflecting other
187 environmental controls, but still display a clear cooling trend similar to TEX₈₆^H-SSTs
188 for the past 5 Myr, albeit with a smaller magnitude. An alternative approach to using
189 model predictions of Mg/Ca_{sw} is to assume that all of the discrepancy between

190 $\text{TEX}^{\text{H}}_{86}$ and Mg/Ca at Site 1143 is due to $\text{Mg}/\text{Ca}_{\text{sw}}$ and generate a record of $\text{Mg}/\text{Ca}_{\text{sw}}$
191 through ‘back-calculating’ this parameter from paired foraminiferal Mg/Ca and
192 $\text{TEX}^{\text{H}}_{86}$ measurements. This record gives slightly larger $\text{Mg}/\text{Ca}_{\text{sw}}$ changes than the
193 FD06¹⁹ model but is largely consistent with the available data constraints
194 (Supplementary Figure 8).

195

196 This treatment of our SST proxy comparisons at Sites 1143 and 999 implies that not
197 only are $U^{\text{k}^2}_{37}$ -SSTs in other warm regions (>28 °C) likely to be biased to too low
198 temperatures, but also that the Mg/Ca-SST proxy also could be underestimating SSTs
199 during the Pliocene at other locations. We discuss the impacts of this $\text{Mg}/\text{Ca}_{\text{sw}}$
200 correction on other Mg/Ca records in the Supplementary Information, but focus here
201 on ODP Site 806⁵, which is located in the heart of the modern Western Pacific warm
202 pool (Fig. 1) and has Pliocene Mg/Ca-SSTs similar to or lower than $U^{\text{k}^2}_{37}$ estimates
203 (Fig. 2c). The $\text{Mg}/\text{Ca}_{\text{sw}}$ correction increases Pliocene Mg/Ca-SSTs into consistency
204 with the $U^{\text{k}^2}_{37}$ -SST proxy (i.e. >29 °C) regardless of whether our back-calculated
205 $\text{Mg}/\text{Ca}_{\text{sw}}$ is used or the modelled values of FD06¹⁹. Furthermore, when corrected for
206 $\text{Mg}/\text{Ca}_{\text{sw}}$ changes, Site 806 SSTs are ~ 0.7 - 1.8 °C warmer than the $\text{TEX}^{\text{H}}_{86}$ proxy for
207 the southern South China Sea (Fig. 3c). The existence of this temperature gradient is
208 also evident from the raw *G. sacculifer* Mg/Ca data for the two sites (Mg/Ca of
209 ~ 3.2 mmol mol⁻¹ versus ~ 3.5 mmol mol⁻¹; equivalent to ~ 1 °C difference;
210 Supplementary Figures 12 and 13), supporting the veracity of the $\text{Mg}/\text{Ca}_{\text{sw}}$ correction.
211 It is important to note that, whilst we have demonstrated here that secular changes in
212 $\text{Mg}/\text{Ca}_{\text{sw}}$ has likely had dramatic implications for the Mg/Ca-SST proxy in the
213 Pliocene, future work is required to better empirically and directly determine past
214 variations in $\text{Mg}/\text{Ca}_{\text{sw}}$. Moreover, it does not preclude the influence of other factors

215 on the Mg/Ca records from Sites 999, 1143 or elsewhere, and additional studies on
216 the partitioning of Mg into foraminiferal calcite as a function of Mg/Ca_{sw}, and further
217 quantification of the secondary effects on Mg/Ca in foraminifer shells (e.g. salinity,
218 diagenesis, [CO₃²⁻]) are required.

219

220 **Climate forcing of tropical temperatures**

221 The potential operation of a tropical thermostat for the warmest regions of the ocean
222 can be explored by examining the response of the warm pool temperature to climate
223 forcing over the last 5 Myr (following the approach of ref. 13). Over the Pleistocene
224 glacial cycles the temperature evolution of the Pacific Warm Pool is largely a function
225 of climate forcing by CO₂ and changes in global albedo due to the waxing and waning
226 of the continental ice sheets^{13,40}. Given the Warm Pool SST response to climate
227 forcing (from ice albedo and CO₂) over Pleistocene glacial cycles, a Pliocene CO₂
228 range of 350 to 450 ppm²⁵ and sea-level +10 to +30 m higher than today⁴¹, SSTs in
229 the Pliocene at Site 1143 would be expected to be +1-2 °C compared to the modern,
230 and at Site 806 to be +1.5-2.5 °C (Supplementary Figure 14). Our new SST estimates
231 suggest a ~2-3 °C warming at both sites such that Pliocene temperatures are similar to
232 but slightly warmer than expected. This provides further evidence that there is no
233 ‘thermostatic’ control limiting SSTs in the warmest ocean regions, at least for SSTs
234 up to 32-34 °C.

235

236 These new warm pool Pliocene SST reconstructions support the view³⁶ that pre-
237 Pleistocene Mg/Ca based SST estimates are compromised, possibly by changes in the
238 Mg/Ca ratio of seawater, and indicate that the role of ocean warm pool regions in
239 generating Pliocene warmth has previously^{5,6} been underestimated. This recognition

240 also resolves the discrepancy between previous SST reconstructions^{6,42} and the recent
241 Pliocene Model Intercomparison Project results, which predict 2-3 °C warmer warm
242 pool temperatures in the Pliocene than existing data. Moreover, a ~2-3 °C warmer
243 warm pool in the Pliocene implies no mechanism will operate to limit the degree of
244 warmth of the equatorial ocean in coming centuries as the Earth approaches Pliocene-
245 like conditions.

246

247 **METHODS**

248 **Sampling strategy.** Sediments from Ocean Drilling Program (ODP) Site 1143
249 (9°22'N, 113°17'E, water depth 2772 m) were divided such that ca. 10 g of each
250 sample were used for organic biomarker analyses and the rest of the material was
251 used for *Globigerinoides sacculifer* (*G. sacculifer*) foraminiferal calcite analyses. For
252 ODP Site 999 (12°45'N, 78°44'W, 2828 m water depth), *Globigerinoides ruber*
253 (*G. ruber*) trace element analyses were performed on the same sample set as those
254 analysed for alkenones by an earlier study²⁶ and *G. sacculifer* trace element analyses
255 were carried out on the same sample set as those analysed for alkenones (and in some
256 cases also *G. ruber*) by Seki et al. (2010)²⁵.

257

258 **GDGT biomarker analysis.** Relative glycerol dibiphytanyl glycerol tetraether
259 (GDGT) biomarker abundances were used to derive TEX₈₆ sea surface temperatures
260 (SSTs). Sediments were freeze-dried and manually ground prior to extraction. Total
261 lipid extracts were obtained via 24 h Soxhlet extraction using
262 dichloromethane:methanol (2:1, v/v). Total lipid extracts were then separated into
263 apolar (which were archived) and polar fractions using alumina column
264 chromatography. Polar fractions were dissolved in hexane:propanol (99:1, v/v),

265 filtered through 0.45 μm PTFE filters, and then analysed for GDGT compounds using
266 High Performance Liquid Chromatography/Atmospheric Pressure Chemical
267 Ionisation-Mass Spectrometry (HPLC/APCI-MS). Filtered polar fractions were
268 analysed at the University of Bristol using a Thermo Scientific TSQ Quantum Access
269 equipped with Accela Autosampler, Accela Pump and Xcalibur software fitted with
270 an Alltech Prevail Cyano column (150 mm x 2.1 mm; 3 μm stationary phase
271 thickness). The injection volume was 20 μl in partial loop-no waste injection setting.
272 GDGTs were eluted isocratically with 99 % A and 1 % B v/v for the first 7 min, and
273 then a linear gradient to 1.6 % v/v B in 43 min, where A = hexane and B = *iso*-
274 propanol under a flow rate of 0.2 ml min⁻¹. Detection was achieved using atmospheric
275 pressure positive ion chemical ionisation-mass spectrometry (APCI-MS) analysis of
276 the eluent. Specific conditions were: corona discharge current 4 μA , vaporiser
277 temperature 355 °C, capillary temperature 280 °C and sheath gas 0.15 L min⁻¹. Ion
278 detection was performed in selective ion monitoring (SIM) mode with selected *m/z*
279 values relating to the $[\text{M}+\text{H}]^+$ (protonated molecular ion) of the isoprenoidal and
280 branched GDGT analytes⁴³. The reproducibility of the $\text{TEX}_{86}^{\text{H}}$ values was determined
281 to be ± 0.02 (from 37 duplicate analyses, n=116), which is equivalent to ± 0.62 °C⁴⁴.

282

283 **Foraminiferal Calcite Trace Element Analysis.** Mg/Ca ratios in foraminiferal
284 calcite were used to derive Mg/Ca SSTs. Site 1143 and Site 999 *G. sacculifer*
285 (without sac) samples were prepared and analysed at the University of Bristol. Site
286 999 *G. ruber* (white) samples were prepared and analysed at the University of
287 Southampton. In all cases, aliquots of the sediment assigned for foraminiferal trace
288 element analyses were washed over a 63 μm sieve and dried. *G. sacculifer* (~10-20
289 individuals) and *G. ruber* (120-180 individuals, of which a 7 % aliquot was assigned

290 for trace element analysis in this study) tests were picked from the 300-355 μm size
291 fraction, gently crushed between two glass slides and transferred to clean vials. All
292 planktic foraminifer samples were cleaned using established oxidative cleaning
293 methods⁴⁵, no reductive step was carried out as this is known to dissolve foraminiferal
294 calcite⁴⁶. After cleaning, all samples were dissolved in $\sim 0.15\text{ M HNO}_3$, centrifuged
295 and transferred to a clean plastic centrifuge tube. *G. sacculifer* trace elements were
296 measured using a Thermo Scientific Element 2 single collector Inductively Coupled
297 Plasma-Mass Spectrometer (ICP-MS) at the University of Bristol, following methods
298 outlined in Foster (2008)⁴⁷. An aliquot was taken and measured for [Ca] in order to
299 matrix-match samples and bracketing standards, and then the remaining solution was
300 diluted to a known Ca concentration, typically 4 mmol l^{-1} , and analysed for trace
301 element composition. Long-term analytical reproducibility for Mg/Ca is $\pm 1.8\%$
302 (2 s.d.) based on replicate analysis of consistency standards matched in concentration
303 to dissolved foraminifera solutions. *G. ruber* trace elements were measured using a
304 Thermo Scientific Element 2 single collector ICP-MS at the University of
305 Southampton, following the same approach as outlined for *G. sacculifer*⁸. Final
306 analyses were typically run at $2\text{ mmol l}^{-1}\text{ Ca}$. Over the period 2012-2013, analytical
307 reproducibility for Mg/Ca was $\pm 2.7\%$ (2 s.d.).

308

309 **ADDITIONAL INFORMATION**

310 Correspondence and requests for materials should be addressed to C.L.O.B.

311

312 **ACKNOWLEDGEMENTS**

313 This work was supported by a NERC studentship awarded to C.L.O.B. and a NERC
314 standard grant NE/H006273/1 awarded to R.D.P (Principal Investigator) and G.L.F.

315 (Co-Investigator). R.D.P. also acknowledges the Royal Society Wolfson Research
316 Merit Award. We would like to thank Kirsty Edgar for helpful discussions on
317 diagenesis of foraminifera.

318

319 **AUTHOR CONTRIBUTIONS**

320 C.L.O.B. collected all the data (except where otherwise noted), interpreted results,
321 and prepared the manuscript and figures. G.L.F. and R.D.P. supervised the project,
322 and aided in interpretation, figure making and editing the manuscript. M.A.M.-B.
323 generated the *G. ruber* Mg/Ca data for Site 999. R.A. and G.L.F. generated the
324 *G. sacculifer* Mg/Ca data for Site 999. J.W.B.R. aided in the collection of
325 *G. sacculifer* Mg/Ca data for Site 1143, figure making and editing the manuscript.

326

327 **COMPETING FINANCIAL INTERESTS**

328 The authors declare no competing financial interests.

329

330 **REFERENCES**

- 331 1 Pierrehumbert, R. Climate change and the tropical Pacific: The sleeping
332 dragon wakes. *Proc. Nat. Acad. Sci.* **97**, 1355-1358 (2000).
- 333 2 Wang, C. & Enfield, D. B. The tropical Western Hemisphere warm pool.
334 *Geophys. Res. Lett.* **28**, 1635-1638 (2001).
- 335 3 Herbert, T. D., Peterson, L. C., Lawrence, K. T. & Liu, Z. Tropical ocean
336 temperatures over the past 3.5 million years. *Science* **328**, 1530-1534 (2010).
- 337 4 Brierley, C. M. *et al.* Greatly expanded tropical warm pool and weakened
338 Hadley circulation in the early Pliocene. *Science* **323**, 1714-1718 (2009).

- 339 5 Wara, M. W., Ravelo, A. C. & Delaney, M. L. Permanent El Niño-like
340 conditions during the Pliocene warm period. *Science* **309**, 758-761 (2005).
- 341 6 Fedorov, A. *et al.* Patterns and mechanisms of early Pliocene warmth. *Nature*
342 **496**, 43-49 (2013).
- 343 7 Ramanathan, V. & Collins, W. Thermodynamic regulation of ocean warming
344 by cirrus clouds deduced from observations of the 1987 El Niño. *Nature* **351**,
345 27-32 (1991).
- 346 8 Newell, R. E. Climate and the Ocean: Measurements of changes in sea-surface
347 temperature should permit us to forecast certain climatic changes several
348 months ahead. *Am. Sci.* **67**, 405-416 (1979).
- 349 9 Williams, I. N., Pierrehumbert, R. T. & Huber, M. Global warming,
350 convective threshold and false thermostats. *Geophys. Res. Lett.* **36**, L21805
351 (2009).
- 352 10 van Hoodonk, R. & Huber, M. Equivocal evidence for a thermostat and
353 unusually low levels of coral bleaching in the Western Pacific Warm Pool.
354 *Geophys. Res. Lett.* **36** (2009).
- 355 11 Medina-Elizalde, M. & Lea, D. W. Late Pliocene equatorial Pacific.
356 *Paleoceanography* **25**, PA2208 (2010).
- 357 12 Lea, D. W., Pak, D. K. & Spero, H. J. Climate Impact of Late Quaternary
358 Equatorial Pacific Sea Surface Temperature Variations. *Science* **289**, 1719-
359 1724 (2000).
- 360 13 Rohling, E., Medina-Elizalde, M., Shepherd, J., Siddall, M. & Stanford, J. Sea
361 surface and high-latitude temperature sensitivity to radiative forcing of climate
362 over several glacial cycles. *J. Climate* **25**, 1635-1656 (2012).

- 363 14 Dowsett, H. J. *et al.* Assessing confidence in Pliocene sea surface
364 temperatures to evaluate predictive models. *Nature Clim. Change* **2**, 365-371
365 (2012).
- 366 15 Müller, P. J., Kirst, G., Ruhland, G., Von Storch, I. & Rosell-Melé, A.
367 Calibration of the alkenone paleotemperature index UK'37 based on core-tops
368 from the eastern South Atlantic and the global ocean (60 N-60 S). *Geochim.*
369 *Cosmochim. Acta* **62**, 1757-1772 (1998).
- 370 16 Medina-Elizalde, M., Lea, D. W. & Fantle, M. S. Implications of seawater
371 Mg/Ca variability for Plio-Pleistocene tropical climate reconstruction. *Earth*
372 *Planet. Sci. Lett.* **269**, 585-595 (2008).
- 373 17 Coggon, R. M., Teagle, D. A. H., Smith-Duque, C. E., Alt, J. C. & Cooper, M.
374 J. Reconstructing past seawater Mg/Ca and Sr/Ca from mid-ocean ridge flank
375 calcium carbonate veins. *Science* **327**, 1114-1117 (2010).
- 376 18 Lowenstein, T. K., Timofeeff, M. N., Brennan, S. T., Hardie, L. A. &
377 Demicco, R. V. Oscillations in Phanerozoic seawater chemistry: Evidence
378 from fluid inclusions. *Science* **294**, 1086-1088 (2001).
- 379 19 Fantle, M. S. & DePaolo, D. J. Sr isotopes and pore fluid chemistry in
380 carbonate sediment of the Ontong Java Plateau: Calcite recrystallization rates
381 and evidence for a rapid rise in seawater Mg over the last 10 million years.
382 *Geochim. Cosmochim. Acta* **70**, 3883-3904 (2006).
- 383 20 Stanley, S. M. & Hardie, L. A. Secular oscillations in the carbonate
384 mineralogy of reef-building and sediment-producing organisms driven by
385 tectonically forced shifts in seawater chemistry. *Palaeogeogr.*,
386 *Palaeoclimatol.*, *Palaeoecol.* **144**, 3-19 (1998).

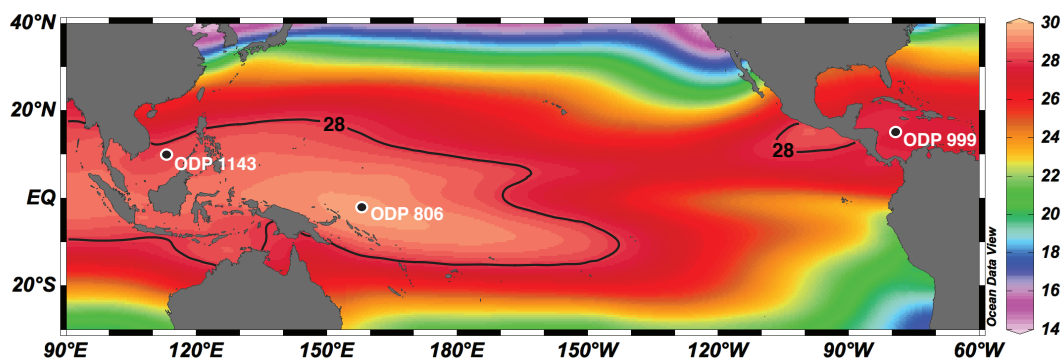
- 387 21 Rausch, S., Böhm, F., Bach, W., Klügel, A. & Eisenhauer, A. Calcium
388 carbonate veins in ocean crust record a threefold increase of seawater Mg/Ca
389 in the past 30 million years. *Earth Planet. Sci. Lett.* **362**, 215-224 (2013).
- 390 22 Dekens, P. S., Ravelo, A. C., McCarthy, M. D. & Edwards, C. A. A 5 million
391 year comparison of Mg/Ca and alkenone paleothermometers.
392 *Geochem. Geophys. Geosyst.* **9**, Q10001 (2008).
- 393 23 Li, L. *et al.* A 4-Ma record of thermal evolution in the tropical western Pacific
394 and its implications on climate change. *Earth Planet. Sci. Lett.* **309**, 10-20
395 (2011).
- 396 24 Groeneveld, J. *Effect of the Pliocene closure of the Panamanian Gateway on*
397 *Caribbean and east Pacific sea surface temperatures and salinities by*
398 *applying combined Mg/Ca and $\delta^{18}O$ measurements (5.6-2.2 Ma)* PhD thesis,
399 University of Kiel, (2005).
- 400 25 Seki, O. *et al.* Alkenone and boron-based Pliocene pCO₂ records. *Earth*
401 *Planet. Sci. Lett.* **292**, 201-211 (2010).
- 402 26 Badger, M. P., Schmidt, D. N., Mackensen, A. & Pancost, R. D. High-
403 resolution alkenone palaeobarometry indicates relatively stable pCO₂ during
404 the Pliocene (3.3–2.8 Ma). *Phil. Trans. R. Soc. A* **371** (2013).
- 405 27 Seki, O. *et al.* Paleooceanographic changes in the Eastern Equatorial Pacific
406 over the last 10 Myr. *Paleoceanography* **27**, PA3224 (2012).
- 407 28 Hollis, C. J. *et al.* Early Paleogene temperature history of the Southwest
408 Pacific Ocean: Reconciling proxies and models. *Earth Planet. Sci. Lett.* **349**,
409 53-66 (2012).

- 410 29 Wei, Y. *et al.* Spatial variations in archaeal lipids of surface water and core-
411 top sediments in the South China Sea and their implications for paleoclimate
412 studies. *Appl. Environ. Microbiol.* **77**, 7479-7489 (2011).
- 413 30 Locarnini, R. A. *et al.* in *NOAA Atlas NESDIS 68* Vol. 1 (ed S. Levitus) 184
414 (U.S. Government Printing Office, 2010).
- 415 31 Tian, J. *et al.* Late Pliocene monsoon linkage in the tropical South China Sea.
416 *Earth Planet. Sci. Lett.* **252**, 72-81 (2006).
- 417 32 Schmidt, M. W., Vautravers, M. J. & Spero, H. J. Western Caribbean sea
418 surface temperatures during the late Quaternary. *Geochem. Geophys. Geosyst.*
419 **7**, Q02P10 (2006).
- 420 33 Wunsch, C. A perpetually running ENSO in the Pliocene? *J. Climate* **22**,
421 3506-3510 (2009).
- 422 34 Fraile, I., Mulitza, S. & Schulz, M. Modeling planktonic foraminiferal
423 seasonality: Implications for sea-surface temperature reconstructions. *Mar.*
424 *Micropaleontol.* **72**, 1-9 (2009).
- 425 35 Hemleben, C., Spindler, M. & Erson, O. *Modern planktonic foraminifera.*
426 (Springer, 1989).
- 427 36 Evans, D. & Müller, W. Deep time foraminifera Mg/Ca paleothermometry:
428 Nonlinear correction for secular change in seawater Mg/Ca.
429 *Paleoceanography* **27**, PA4205 (2012).
- 430 37 Horita, J., Zimmermann, H. & Holland, H. D. Chemical evolution of seawater
431 during the Phanerozoic: implications from the record of marine evaporites.
432 *Geochim. Cosmochim. Acta* **66**, 3733-3756 (2002).

- 433 38 Higgins, J. & Schrag, D. Records of Neogene seawater chemistry and
434 diagenesis in deep-sea carbonate sediments and pore fluids. *Earth Planet. Sci.*
435 *Lett.* **357**, 386-396 (2012).
- 436 39 Wilkinson, B. H. & Algeo, T. J. Sedimentary carbonate record of calcium-
437 magnesium cycling. *Am. J. Sci.* **289**, 1158-1194 (1989).
- 438 40 Köhler, P. *et al.* What caused Earth's temperature variations during the last
439 800,000 years? Data-based evidence on radiative forcing and constraints on
440 climate sensitivity. *Quat. Sci. Rev.* **29**, 129-145 (2010).
- 441 41 Rohling, E. J. *et al.* Sea-level and deep-sea-temperature variability over the
442 past 5.3 million years. *Nature* **508**, 477-482 (2014).
- 443 42 Dowsett, H. J. *et al.* Sea Surface Temperature of the mid-Piacenzian Ocean: A
444 Data-Model Comparison. *Sci. Rep.* **3** (2013).
- 445 43 Schouten, S., Hopmans, E. C., Schefuß, E. & Sinninghe Damsté, J. S.
446 Distributional variations in marine crenarchaeotal membrane lipids: a new tool
447 for reconstructing ancient sea water temperatures? *Earth Planet. Sci. Lett.* **204**,
448 265-274 (2002).
- 449 44 Kim, J. H. *et al.* New indices and calibrations derived from the distribution of
450 crenarchaeal isoprenoid tetraether lipids: Implications for past sea surface
451 temperature reconstructions. *Geochim. Cosmochim. Acta* **74**, 4639-4654
452 (2010).
- 453 45 Barker, S., Greaves, M. & Elderfield, H. A study of cleaning procedures used
454 for foraminiferal Mg/Ca paleothermometry. *Geochem. Geophys. Geosyst.* **4**,
455 8407 (2003).

- 456 46 Yu, J., Elderfield, H., Greaves, M. & Day, J. Preferential dissolution of
 457 benthic foraminiferal calcite during laboratory reductive cleaning. *Geochem.*
 458 *Geophys. Geosyst.* **8** (2007).
- 459 47 Foster, G. L. Seawater pH, pCO₂ and [CO₂-3] variations in the Caribbean
 460 Sea over the last 130 kyr: A boron isotope and B/Ca study of planktic
 461 foraminifera. *Earth Planet. Sci. Lett.* **271**, 254-266 (2008).
- 462 48 Schlitzer, R. Interactive analysis and visualization of geoscience data with
 463 Ocean Data View. *Comput. Geosci.* **28(10)**, 1211-1218 (2002).
- 464 49 Pagani, M., Liu, Z., LaRiviere, J. & Ravelo, A. C. High Earth-system climate
 465 sensitivity determined from Pliocene carbon dioxide concentrations. *Nature*
 466 *Geosci.* **3**, 27-30 (2009).
- 467 50 Lisiecki, L. E. & Raymo, M. E. A Pliocene-Pleistocene stack of 57 globally
 468 distributed benthic $\delta^{18}\text{O}$ records. *Paleoceanography* **20**, PA1003 (2005).

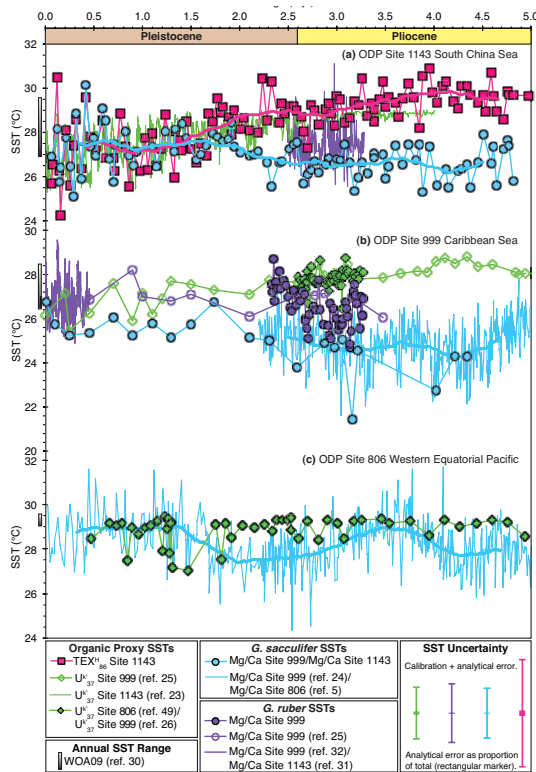
470 **FIGURE CAPTIONS**



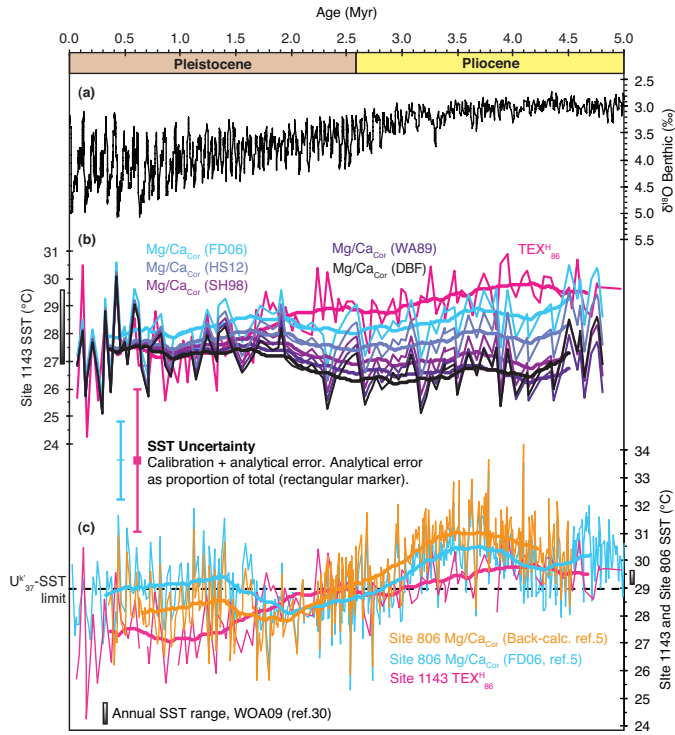
471

472 **Figure 1: Map of mean annual ocean surface temperatures and locations of the**
 473 **sediment cores discussed in this paper**^{30,48}. New palaeoceanographic proxy data
 474 were generated for ODP Site 1143 (9°22'N, 113°17'E, water depth 2772 m) and ODP
 475 Site 999 (12°45'N, 78°44'W, 2828 m water depth). ODP: Ocean Drilling

476 Program. Black line indicates the 28 °C isotherm defining the ocean warm pool
 477 regions.



478
 479 **Figure 2: Pliocene to recent warm pool SST estimates.** (a) Site 1143 $\text{TEX}_{86}^{\text{H}}$ -SSTs,
 480 *G. sacculifer* Mg/Ca-SSTs, *G. ruber* Mg/Ca-SSTs (ref. 31) and $U^{k'}$ ₃₇-SSTs (ref. 23).
 481 (b) Site 999 *G. ruber* Mg/Ca-SSTs (this study and refs 25,32), *G. sacculifer* SSTs
 482 (this study and ref. 24) and $U^{k'}$ ₃₇-SSTs (refs 25,26). (c) ODP Site 806 *G. sacculifer*
 483 Mg/Ca-SSTs (ref. 5) and $U^{k'}$ ₃₇-SSTs (ref. 49). Thick lines, where included, indicate
 484 600 kyr running average smoothing. SST proxy error bars (to scale) include both
 485 analytical error ($\sigma_{\text{Analytical}}$; $\sigma_{\text{Analytical}} = \sigma_{\text{Analytical}}^2 / (\sigma_{\text{Analytical}}^2 + \sigma_{\text{Calibration}}^2)$) and calibration
 486 error ($\sigma_{\text{Calibration}}$; $\sigma_{\text{Calibration}} = \sigma_{\text{Calibration}}^2 / (\sigma_{\text{Analytical}}^2 + \sigma_{\text{Calibration}}^2)$).



487

488 **Figure 3: Plio-Pleistocene warm pool evolution.** (a) Benthic oxygen isotope stack
 489 (ref. 50). (b) Site 1143 $\text{TEX}^{\text{H}}_{86}$ -SSTs and Mg/Ca-SSTs corrected for variable
 490 Mg/Ca_{sw} (Mg/Ca-SST_{cor}) for both data (DBF; refs 17,18,21,37) and Mg/Ca_{sw} model
 491 estimates; FD06 (ref. 19), HS12 (ref. 38), SH98 (ref. 20) and WA89 (ref. 39). (c) Site
 492 1143 $\text{TEX}^{\text{H}}_{86}$ -SSTs and Site 806 Mg/Ca-SSTs (ref. 5) corrected for variable Mg/Ca_{sw},
 493 Mg/Ca-SST_{cor}, using the FD06 (ref. 19) model and our back-calculated Mg/Ca_{sw}
 494 curve. Thick lines indicate 600 kyr running average smoothing. SST proxy error bars,
 495 analytical ($\sigma_{\text{Analytical}} = \sigma_{\text{Analytical}}^2 / (\sigma_{\text{Analytical}}^2 + \sigma_{\text{Calibration}}^2)$) and calibration ($\sigma_{\text{Calibration}} =$
 496 $\sigma_{\text{Calibration}}^2 / (\sigma_{\text{Analytical}}^2 + \sigma_{\text{Calibration}}^2)$), are to scale.