

1 **SUPPLEMENTAL INFORMATIONS**

2
3 **Atmospheric CO₂ estimates for the Miocene to Pleistocene based on foraminiferal $\delta^{11}\text{B}$**
4 **at Ocean Drilling Program Sites 806 and 807 in the Western Equatorial Pacific**

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19 Supplemental Methods

20 S1. Potential contamination

21 We found no evidence for contamination of TE (including Mg/Ca) arising from the
22 presence of silicate minerals or Mn-Fe-Oxide coatings. Contamination of samples by silicate
23 minerals was monitored using Fe/Mg ratios. Samples with Fe/Mg > 0.1 mol/mol are typically
24 rejected due to potential contamination by silicate minerals (Barker et al., 2003). Our samples
25 have an average Fe/Mg of 0.034 ± 0.07 mol/mol (2 SD, n=106), indicating that silicate
26 minerals have been efficiently removed during our cleaning. Contamination by clays was
27 monitored using Ti/Ca no correlations were found between Ti/Ca and Mg/Ca ($R^2=0.0066$) or
28 with B/Ca ($R^2=0.0237$). Contamination by Mn-Fe oxides is detected using Mn/Ca ratios and
29 Fe/Ca ratios. Our samples have Mn/Ca ratios of 0.12 ± 0.11 mmol/mol (2 SD, n=108)
30 consistent with previous published data of cleaned samples (Wara et al., 2005). No
31 correlations was observed between Mg/Ca and Fe/Ca ($R^2=0.0841$) or between Mg/Ca and
32 Mn/Ca ($R^2=0.0161$). No significant correlation was observed between B/Ca and Mn/Ca
33 ($R^2=0.0011$) or B/Ca and Fe/Ca ($R^2=0.0132$) ratios.

34

35 S2. Calculations of temperature, salinity, pH, and pCO_2

36 Analyses of $\delta^{11}B$, $\delta^{18}O$ and elemental ratios (eg., Mg/Ca, B/Ca) were used to
37 reconstruct the chemical and physical properties of seawater over the last 17 My of the
38 Western Equatorial Pacific (Fig. 2).

39

40 S2.1. Salinity reconstruction

41 Salinity was reconstructed using the relative sea level (RSL) reconstruction from Stap
42 et al. (2017) and equation S1:

43

$$44 \quad S = S_{\text{modern}}/3800 * (3800 + \text{RSL}) \quad \text{eq. S1}$$

45

46 S_{modern} is the modern salinity corresponding to the depth habitat of the foraminifera at the site
47 of interest. The depths used were 125 m for *T. sacculifer* and 80m for *G. ruber* (Rickaby et
48 al., 2005; Guillermic et al., 2020). At Site 806, values for S_{modern} of 35.38 was used for *T.*
49 *sacculifer* and 35.01 was used for *G. ruber*. At Site 807, a value of 35.05 was used for *T.*
50 *sacculifer*.

51

52 **S2.2. Temperature**

53 Paleotemperatures were calculated using Mg/Ca ratios of planktic foraminifera. A
54 number of factors have been shown to impact Mg/Ca ratios and calculated paleotemperature.
55 Factors identified in prior studies include salinity and pH effects on Mg/Ca, seawater Mg/Ca
56 ratios, cleaning methodology, dissolution, and basin-specific equations, as discussed in more
57 detail below. Below we describe some of the prior work that was factored into the regional
58 mono-specific equations we used for calculating temperature from Mg/Ca.

59

60 **S2.2.1. Prior work showing evidence for salinity and pH effects on Mg/Ca-T**

61 Studies have found that Mg/Ca ratios in foraminifera are impacted by salinity
62 (Nürnberg et al., 1996; Hönisch et al., 2013) and pH or $[\text{CO}_3^{2-}]$ (Russell et al., 2004;
63 Kisakürek et al., 2008; Evans et al., 2016; Gray et al., 2018; Gray and Evans, 2019). Based
64 on culture experiments, Gray and Evans (2019) reported impacts of both salinity and pH on
65 *G. ruber* but only a salinity effect on *T. sacculifer*, and derived the following equations:

$$66 \quad \text{SST } (T. \textit{sacculifer}) = (\text{Ln}(\frac{\text{Mg}}{\text{Ca}} \textit{test}) - 0.054 * (S - 35) + 0.24)/0.062 \quad \text{eq. S2}$$

$$67 \quad \text{SST } (G. \textit{ruber}) = (\text{Ln}(\frac{\text{Mg}}{\text{Ca}} \textit{test} - 0.036 * (S - 35) + 0.87 * (\text{pH} - 8) + 0.03)/0.064 \quad \text{eq. S3}$$

68

69 **S2.2.2. Prior work showing evidence for variations in Mg/Ca ratios of seawater**

70 Over timescales of 10^6 - 10^7 years, $\text{Mg}/\text{Ca}_{\text{sw}}$ can vary. Evidence from evaporites,
71 carbonate veins, fossil corals and models suggests that seawater $\text{Mg}/\text{Ca}_{\text{sw}}$ ratios have varied
72 through time with variations of ~ 3 mol/mol (Horita et al., 2002; DeFante and Paolo, 2006;
73 Coggon et al., 2011; Brennan et al., 2013; Gothman et al., 2015). These studies do not agree
74 on the timing of changes in $\text{Mg}/\text{Ca}_{\text{sw}}$. Gothman et al. (2015) made measurements of corals
75 and also compiled different seawater archives including carbonate veins, gastropods,
76 brachiopods, fish teeth, and found that values of $\text{Mg}/\text{Ca}_{\text{sw}}$ of 2.5 mol/mol occurred ~ 25 My.
77 To correct for secular variations in $\text{Mg}/\text{Ca}_{\text{sw}}$ we used the approach of O'Brien et al. (2014),
78 theoretical work from Evans and Muller, (2012), and the $\text{Mg}/\text{Ca}_{\text{sw}}$ record of Gothman et al.
79 (2015). The equations we utilized are adapted from Dekens et al. (2002):

80

$$81 \quad \text{SST } (T. \textit{sacculifer}) = (\text{Ln}(\frac{\text{Mg}}{\text{Ca}} \textit{test} * \frac{\text{Mg}^H}{\text{Ca}} \textit{sw}_{t0}) - \text{Ln}(0.37 * \frac{\text{Mg}^H}{\text{Ca}} \textit{sw}_t))/0.09 + 0.36 * C + D$$

82

eq. S4

83

$$84 \quad SST (G. ruber) = \left(\ln \left(\frac{Mg}{Ca} test * \frac{Mg^H}{Ca} sw_{t0} \right) - \ln \left(0.37 * \frac{Mg^H}{Ca} sw_t \right) \right) / 0.09 + 0.61 * C + D \quad \text{eq. S5}$$

85

86 Specifically H refers to the power components of the power law relationship between the Mg
 87 partition coefficient and Mg/Ca_{sw}, with a value of 0.41 for *T. sacculifer* (Delaney et al., 1985)
 88 which we also assume is the same for *G. ruber*. C is the depth of the site. D refer to a basin-
 89 specific offset, which is 2 °C for *T. sacculifer* and 2.9 °C for *G. ruber* for the Pacific Ocean,
 90 (Table S1).

91

92 **S2.2.3. Prior work on reductive cleaning effects on Mg/Ca**

93 The use of a reductive step in cleaning has been shown to lower Mg/Ca_{test} ratios in
 94 planktic (Barker et al., 2003; Bian et al., 2010; Johnstone et al., 2016) and benthic
 95 foraminifera (Yu et al., 2007a), and contribute to offsets between studies using different
 96 methodologies. A decrease in Mg/Ca_{test} of 6-9% was reported for *T. sacculifer* by Bian et al.
 97 (2010), and of 5% by Johnstone et al. (2016). A decrease of 4% was reported for *G. ruber* by
 98 Johnstone et al. (2016).

99

100 **S2.2.4. Mg/Ca-SST equations used for this study**

101 Based on the above equations from Gray and Evans (2019) (eq. S2 and S3), we
 102 incorporated a term to account for changes in the Mg/Ca ratio of seawater, and based on
 103 results from Dekens et al., (2002) we incorporated two terms to account for dissolution (C)
 104 and basin-specific offsets (D), and used an iterative approach for our calculations to account
 105 for pH effect on *G. ruber* (Gray and Evans, 2019). The equations we used are:

$$106 \quad SST (T. sacculifer) = \frac{\ln \left(\left(\frac{Mg}{Ca} test * 1.05 * \frac{Mg^H}{Ca} sw_{t0} \right) - 0.054 * (S-35) + 0.24 \right)}{0.062} + 0.36 * C + 2.0 \quad \text{eq. S6}$$

107

108

$$109 \quad SST (G. ruber) = \frac{\ln \left(\left(\frac{Mg}{Ca} test * 1.05 * \frac{Mg^H}{Ca} sw_{t0} \right) - 0.036 * (S-35) + 0.87 * (pH-8) + 0.03 \right)}{0.064} + 0.61 * C + 2.9 \quad \text{eq. S7}$$

110

111 With H being the power components of the power relationship between the Mg partition
 112 coefficient and Mg/Ca_{sw}, 0.41 for *T. sacculifer* (Delaney et al., 1985). We use the same value
 113 for *G. ruber*. C is the depth of the core (km). In order to take the impact of reductive cleaning

114 into account we applied a decrease of 5% for *G. ruber* and *T. sacculifer* (Bian et al., 2010 and
115 Johnstone et al., 2016).

116 Given evidence for a pH effect on Mg/Ca-SST calibration for *G. ruber*, we used an
117 iterative approach for our calculations, following Gray and Evans, (2019). Up to 4 iterations
118 were needed to achieve a difference in SST with the previous iteration of <0.05°C and a
119 difference in pH of <0.001. For this iterative approach, we first calculate pH₁ from
120 foraminiferal δ¹¹B, then calculate SST₁ from pH₁, then calculate pH₂ with SST₁, and then
121 repeat.

122

123 **S2.3. δ¹¹B_{borate} from δ¹¹B_{carbonate}**

124 The use of δ¹¹B in foraminiferal carbonate to calculate seawater δ¹¹B_{borate}, and derived
125 pH and pCO₂ values, has been shown to accurately replicate pCO₂ records independently
126 determined from ice cores and using oceanographic data, if several factors are taken into
127 account (Chalk et al., 2017; Guillermic et al., 2020). These factors include mono-specific
128 calibrations, size fraction or shell weight, basin, and water depth. In order to accurately
129 reconstruct seawater pH (and pCO₂) from δ¹¹B of foraminifera, mono-specific calibrations
130 are needed to convert δ¹¹B_{carbonate} to δ¹¹B_{borate}. Recent culture and field-based calibrations
131 have refined the sensitivities of δ¹¹B_{carbonate} to δ¹¹B_{borate} for different foraminiferal species
132 (Henehan et al., 2016; Raitzsch et al., 2018; Guillermic et al., 2020). For *T. sacculifer* and *G.*
133 *ruber*, the sensitivities of δ¹¹B_{carbonate} to δ¹¹B_{borate} are 0.82 and 0.58, respectively (Raitzsch et
134 al., 2018; Guillermic et al., 2020). As with Mg/Ca, the intercepts are prone to large
135 uncertainties and are commonly adjusted based on core-top data, in order to yield the
136 expected pre-industrial pH or pCO₂ value at the site being examined (Chalk et al., 2017;
137 Sosdian et al., 2018). The rationale for this correction is the impact of the depth habitat on
138 microenvironment pH and subsequent δ¹¹B_{carbonate} (Hönisch and Hemming, 2004; Guillermic
139 et al., 2020) and/or preferential dissolution of gametogenic calcite (Ni et al., 2007). It is also
140 possible that these offsets may reflect observed size effects on *G. ruber* as well as *T.*
141 *sacculifer* (Henehan et al., 2013; Hönisch et al., 2019). For *T. sacculifer*, a relationship
142 between shell size and δ¹¹B_{carbonate} has been observed in the WEP (Hönisch and Hemming,
143 2004; Ni et al., 2007). Hönisch and Hemming, (2004) also reported that values for the 515-
144 865 μm size fraction yielded values of 21.76 ‰, and determined a size-fraction specific
145 relationship. Here, we modify this approach to develop a shell-weight specific relationship:

146
$$\text{Size offset (‰)} = 21.76 - (0.06522 * \text{Weight/shell (μg)} + 17.38) \quad \text{eq. S8}$$

147 We adapted the equation for *T. sacculifer* from Guillermic et al. (2020):

$$148 \quad \delta^{11}\text{B}_{\text{borate}} = [(\delta^{11}\text{B}_{T. \text{ sacculifer}} + \text{Size offset}) - 4.09 (\pm 0.86)] / 0.83 (\pm 0.48) \quad \text{eq. S9}$$

149 Due to the lack of coretop measurements for *G. ruber* from this study, we selected three
150 control points at Marine isotope stages (MIS) 30, 37 and 39 (Lisiecky and Raymo, 2005)
151 times when both *T. sacculifer* and *G. ruber* were measured to determine appropriate offsets
152 for both Mg/Ca and $\delta^{11}\text{B}$ that yield (Table S1 and S2) the best agreement between the
153 species. This was used to adapt the equation from Guillermic et al. (2020) for *G. ruber*:

154

$$155 \quad \delta^{11}\text{B}_{\text{borate}} = [(\delta^{11}\text{B}_{G. \text{ ruber}} + 2.0) - 9.11 (\pm 0.73)] / 0.58 (\pm 0.91) \quad \text{eq. S10}$$

156

157 **S2.4. Constants**

158 Temperature, salinity and pressure were used to calculate the different dissociation
159 constants and parameters. We used K_1 , K_2 from Lueker et al. (2000), K_B from Dickson,
160 (1990), KSO_4 from Dickson, (1990), KF from Peres and Fraga, (1987) and total boron from
161 Lee et al. (2010).

162

163 **S2.5. pH calculations**

164 The quantitative estimation of pH using downcore $\delta^{11}\text{B}_{\text{carbonate}}$ requires: 1) calculations
165 of the borate isotopic composition of seawater ($\delta^{11}\text{B}_{\text{borate}}$), 2) constraints on the secular
166 variation of the boron isotopic composition of seawater ($\delta^{11}\text{B}_{\text{seawater}}$), 3) the fractionation
167 factor (α) between $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ and 4) the calculations of acid/base equilibrium
168 constants based temperature, salinity and pressure. To translate our $\delta^{11}\text{B}$ measurements to pH,
169 we used the following relationship (Hemming and Hanson, 1992):

170

$$171 \quad \text{pH} = \text{pK}_B^* - \log \left(\frac{\delta^{11}\text{B}_{\text{seawater}} - \delta^{11}\text{B}_{\text{borate}}}{\delta^{11}\text{B}_{\text{seawater}} - \alpha * \delta^{11}\text{B}_{\text{borate}} - \epsilon} \right) \quad \text{eq. S11}$$

172

173 pK_B^* is the dissociation constant between the two boron species (8.5975 at 25 °C and a
174 salinity of 35 psu, Dickson, 1990). A fractionation between $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ (ϵ) of 27.2
175 ± 0.6 ‰ was empirically determined by Klochko et al. (2006) in seawater and confirmed
176 independently using a different method by Nir et al. (2015).

177

178 A few studies have attempted to reconstruct secular variations of $\delta^{11}\text{B}_{\text{seawater}}$
(Lemarchand et al., 2000; Foster et al., 2012; Raitzsch and Hönisch, 2013; Greenop et al.,

179 2017). For our work, we first compared different scenarios (Fig. 3). These scenarios are
 180 modeled values of $\delta^{11}\text{B}_{\text{seawater}}$ based on constraints on the boron budget from Lemarchand et
 181 al. (2000), a second modeled history that assumed changes in seawater pH from Raitzsch and
 182 Hönisch (2013), and a third scenario that also considered constraints on pH gradients from
 183 $\delta^{13}\text{C}$ measurements published by Greenop et al. (2017).

184

185 **S2.6. pCO₂ calculations**

186 The carbonate system has two degrees of freedom, meaning that if two parameters of the
 187 carbonate system are known all the others can be calculated. For this study, we utilized pH
 188 calculated using $\delta^{11}\text{B}_{\text{borate}}$, and total alkalinity (TA) as a second parameter that are shown in
 189 Fig. 3-4. We used three different alkalinity scenarios for our calculations (Tyrell and Zeebe,
 190 2004; Ridgwell and Zeebe, 2005; and Caves et al. 2016). For all calculations, we used the MS
 191 excel program “CO₂sys” version 2.3 from Pierrot et al. (2006). pH and TA, temperature,
 192 salinity were used to determined pCO₂ in μatm .

193

194 **S2.7. Error propagation for temperature (T), pH and pCO₂**

195 The main source of uncertainty in reconstructed pCO₂ comes from the errors in pH.
 196 Table S3 summarizes the sensitivity of pH and pCO₂ to different variables. The individual
 197 uncertainties were propagated in quadrature to combined uncertainties for temperature (δT),
 198 pH (δpH) and pCO₂ (δpCO_2) (eq. S12, S13, S14, S15, S16 and S17). Minimum and
 199 maximum propagated uncertainties were derived separately for pH and pCO₂. δpCO_2 (A) is
 200 the full uncertainty propagation, δpCO_2 (B) is the uncertainty propagation without taking into
 201 account the $\delta^{11}\text{B}_{\text{sw}}$. Both are shown in the figures and discussed below.

202

$$203 \delta T_{G. \text{ruber}} = \sqrt{(\delta T_{\text{Mg/Ca}})^2 + (\delta T_{\text{Salinity}})^2 + (\delta T_{\text{pH}})^2} \quad \text{eq. S12}$$

204

$$205 \delta T_{T. \text{sacculifer}} = \sqrt{(\delta T_{\text{Mg/Ca}})^2 + (\delta T_{\text{Salinity}})^2} \quad \text{eq. S13}$$

206

207

$$208 \delta\text{pH (A)} = \sqrt{(\delta\text{pH}_{\text{Temperature}})^2 + (\delta\text{pH}_{\text{Salinity}})^2 + (\delta\text{pH}_{\delta^{11}\text{B}_{\text{sw}}})^2 + (\delta\text{pH}_{\delta^{11}\text{B}_{\text{carbonate}}})^2}$$

209 **eq. S14**

210

211 $\delta pH (B) = \sqrt{(\delta pH_{\text{Temperature}})^2 + (\delta pH_{\text{Salinity}})^2 + (\delta pH_{\delta^{11}B_{\text{carbonate}}})^2}$ **eq. S15**

212

213 $\delta pCO_2 (A) = \sqrt{\frac{(\delta pCO_2_{\text{Temperature}})^2 + (\delta pCO_2_{\text{Salinity}})^2 + (\delta pCO_2_{\delta^{11}B_{sw}})^2 + (\delta pCO_2_{\delta^{11}B_{\text{carbonate}}})^2 + (\delta pCO_2_{\text{Alkalinity}})^2}{}}$ **eq. S16**

214 $\delta pCO_2 (B) = \sqrt{\frac{(\delta pCO_2_{\text{Temperature}})^2 + (\delta pCO_2_{\text{Salinity}})^2 + (\delta pCO_2_{\delta^{11}B_{\text{carbonate}}})^2 + (\delta pCO_2_{\text{Alkalinity}})^2}{}}$ **eq. S17**

215

216 With for example, “ $\delta pCO_2_{\text{Temperature}}$ ” being the uncertainty in pCO_2 due to temperature.

217

218

219

220

221 **Tables**

222

223 **Table S1:** Control points for a 2‰ offset used for *G. ruber*.

224

225 **Table S2:** Comparison of the control points reconstructions between *T. sacculifer* and *G. ruber* for
226 MIS 30, 37 and 39, using different offsets (see text).

227

228 **Table S3:** Sensitivity tests for reconstructed pH and pCO₂ (G17, Caves-16), all results are given as
229 the minimum and maximum variation (%) observed in our data.

230

231

232

Table S1: Control points for a 2‰ offset used for *G. ruber*

Species	Sample	mcid	mbsf	Shell Wt (µg)	Age (Ma)	SST (°C)	error (°C)	Salinity (psu)	TA (µmol/kg)	pH (total scale)	Error	pCO ₂ (µatm)	Error max (µatm)	Error min (µatm)			
MIS 30	<i>G. ruber</i>	806 B 3	5 6	8	22.06	22.06	16.1	1.046	26.4	1.8	35.3	2241	8.16	0.09	249	72	55
	<i>T. sacculifer</i>	806 B 3	5 31	33	22.31	22.31	18.2	1.048	25.9	0.9	35.6	2230	8.28	0.08	164	44	35
	<i>G. ruber</i>	806 B 4	1 71	73	26.21	26.21	17.0	1.240	26.6	1.9	35.1	2230	8.09	0.09	308	93	69
MIS 37	<i>T. sacculifer</i>	806 B 4	1 56	58	26.06	26.06	22.2	1.233	29.8	0.9	35.6	2228	8.08	0.09	295	87	66
	<i>G. ruber</i>	806 B 4	1 131	133	26.81	26.81	16.1	1.267	28.0	1.9	35.5	2228	8.09	0.09	308	92	69
MIS 39	<i>G. ruber</i>	806 B 4	1 146	148	26.96	26.96	24.0	1.274	27.8	0.9	35.6	2219	8.07	0.09	306	93	69
	<i>T. sacculifer</i>	806 B 4	1 146	148	26.96	26.96	24.0	1.274	27.8	0.9	35.6	2219	8.07	0.09	306	93	69

233
234
235
236

Table S2: Comparison of the control points reconstructions between *T. sacculifer* and *G. ruber* for MIS 30, 37 and 39, using different offsets (see text).

	1.8 ‰ offset			1.85 ‰ offset			2.0 ‰ offset			2.1 ‰ offset		
	MIS 30	MIS 37	MIS 39	MIS 30	MIS 37	MIS 39	MIS 30	MIS 37	MIS 39	MIS 30	MIS 37	MIS 39
ΔpCO_2 (μatm)	105	37	26	100	31	20	86	13	2	77	1	-10
ΔpH (tot scale)	-0.14	-0.02	-0.01	-0.14	-0.01	-0.003	-0.12	0.01	0.02	-0.11	0.02	0.03
ΔT ($^{\circ}C$)	-0.02	-3.75	-0.36	0.06	-3.65	-0.27	0.31	-3.39	-0.005	0.47	-3.21	0.17

Table S3: Sensitivity tests for reconstructed pH and pCO₂ (GI7, Caves-16), all results are given as the minimum and maximum variation (%) observed in our data

	Salinity	Temperature	$\delta^{11}\text{C}_{\text{Carbonate}}$	$\delta^{11}\text{C}_{\text{Seawater}}$	Alkalinity
pH (<i>G. ruber</i>)	0.07%	0.2-0.3%	0.2-0.5%	0.8-1.6%	x
pH (<i>T. sacculifer</i>)	0.07-0.08%	0.12-0.13%	0.1-0.5%	0.8-1.4%	x
pCO₂ (<i>G. ruber</i>)	0.8-1.5%	0.02-1.5%	5-11%	19-25%	5%
pCO₂ (<i>T. sacculifer</i>)	0.8-1.4%	0.02-0.7%	3-12%	19-27%	5-7%