

Multiproxy reconstruction of late quaternary upper ocean temperature in the subtropical southwestern Atlantic

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1	Multiproxy reconstruction of late Quaternary upper ocean temperature in the
2	Subtropical Southwestern Atlantic
3	
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14	
15	ABSTRACT
16	Paleoceanographic studies addressing the oceanographic variability in the western sector
17	of the subtropical South Atlantic - especially those focused on the Brazil Current (BC)
18	and on a time scale that reaches marine isotope stage (MIS) 5 - are still rare when
19	compared with equivalent studies carried out in the Northern Hemisphere. In order to
20	close the data gap prior to the last 75 ka, in an unprecedented approach in this region, we
21	reconstructed the upper temperature variations in the Subtropical Southwestern Atlantic
22	(SSWA) between late MIS 6 and the onset of MIS 4 from organic proxies, using a marine
23	sediment core (GL-1090). Sea temperature records derived from alkenone-based $U_{37}^{K'}$ and
24	isoprenoid glycerol dialkyl glycerol tetraethers (isoGDGTs)-based TEX_{86}^{H} proxies were
25	compared with those previously obtained from the same core via Globigerinoides

ruber (G. ruber) Mg/Ca and planktonic foraminifera Modern Analog Technique (MAT). 26 The temporal variations of the temperature estimates derived from the $U_{37}^{K'}$ and TEX_{86}^{H} 27 indexes showed similar patterns, even though the absolute $U_{37}^{K'}$ temperatures were 28 systematically lower than those derived from TEX^H₈₆. Such a difference was related to the 29 different habitat depths of alkenones and isoGDGTs source organisms of – haptophyte 30 algae and marine *Thaumarchaeota*, respectively. The temperature estimates from TEX_{86}^{H} 31 match the range of Mg/Ca and MAT-derived temperatures between 0 and 10 m depth, 32 suggesting that these proxies reflect mixed layer temperatures. In contrast, the 33 temperature estimates derived from $U_{37}^{K'}$ were close to the MAT values at between 0 and 34 100 m and to those derived from TEX_{86}^{H} between 0 and 200 m depth, demonstrating that 35 the $U_{37}^{K'}$ proxy recorded temperatures from the upper thermocline. During MIS 5e, the 36 difference in temperature estimates from TEX_{86}^{H} and $U_{37}^{K'}$ was reduced due to more 37 prominent warming, probably related to a change in the thermal structure of the photic 38 zone. Comparison of our data with studies of intensity and salinity anomalies of the 39 Agulhas Current indicates a connection between the intensification of the Agulhas 40 Leakage and the heat storage in the upper thermocline in the SSWA during MIS 5e. Our 41 data suggest that the joint use of TEX_{86}^{H} and $U_{37}^{K'}$ is a promising approach to estimating 42 paleoceanographic changes in the upper thermocline. 43

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45 KEYWORDS: Alkenones; GDGTs; Subtropical Southwestern Atlantic; Last Interglacial46

47 1. INTRODUCTION

Paleoclimate studies based on geochemical data contribute to climate modeling by
providing a record of past natural climate oscillations beyond instrumental periods
(Hansen et al., 2016; Otto-Bliesner et al., 2016). In this context, studies focusing on the

reconstitution of past climate variability help to understand changes that occurred in a climate similar to the present. The Marine Isotope Stage (MIS) 5e (129 - 116 thousand of years BP, hereafter – "ka"), also known as the Last Interglacial (LIG), has been widely studied in climate change investigation because it is the most recent period in which the planet was warmer than it is in the present-day and due to its similarity to the preindustrial atmospheric greenhouse gas levels and high sea level (Turney and Jones, 2010; Capron et al., 2014; Govin et al., 2015; Otto-Bliesner et al., 2016; PAGES, 2016).

Paleoceanographic studies addressing the oceanographic variability in the western 58 sector of the subtropical South Atlantic - especially those focused on the Brazil Current 59 60 (BC) and on a time scale that reaches MIS 5 - are still rare when compared with equivalent studies conducted in the Northern Hemisphere. Most of the sea surface temperature (SST) 61 62 reconstructions from the BC focus on the last 75 ka (Lourenco et al., 2016; Pereira et al., 63 2018; Dauner et al., 2019; Luz et al., 2020) and/or the Holocene (Pivel et al., 2013; Chiessi et al., 2014; Cordeiro et al., 2014; Evangelista et al., 2014; Lessa et al., 2014; 64 65 Wainer et al., 2014; Chiessi et al., 2015; Lessa et al., 2016; Luz et al., 2020). The few temperature reconstructions for the BC that include MIS 5 were obtained from single 66 proxies, such as planktonic foraminifera transfer function and Mg/Ca ratio (Portilho-67 68 Ramos et al., 2015; Lessa et al., 2017; Santos et al., 2017a; Santos et al., 2017b).

Since the reconstruction of sea paleotemperatures is based on proxies derived from marine organisms, SST estimates may be affected by the ecological preferences of these organisms. The most common organic geochemical proxies used to reconstruct SSTs are (i) alkenones synthesized by haptophyta algae (Brassell et al., 1986), through the $U_{37}^{K'}$ index (Prahl and Wakeham, 1987), and (ii) isoprenoid glycerol dialkyl glycerol tetraethers (isoGDGTs) from marine *Thaumarchaeota*, through the TEX₈₆ index (Schouten et al., 2002). A multiproxy SST approach can help to assess the individual

proxy responses and can provide more confidence in the interpretations of how climate 76 signals are being recorded (Mann et al., 1998; Leduc et al., 2010). Moreover, applying a 77 multiproxy reconstruction in the same sediment core will reflect conditions from the same 78 79 time period without chronological uncertainties (Huguet et al., 2011; Ausín et al., 2019). This study is the first reconstruction of temperature variations at the upper ocean in 80 the Subtropical Southwestern Atlantic (SSWA) using organic proxies from late -MIS 6 81 82 to the onset of MIS 4. Here, we investigated possible discrepancies in temperatures reconstructed by organic proxies, what factors may have caused such differences and we 83 evaluated the responses of these proxies to the regional dynamics during the LIG. Sea 84 temperatures were reconstructed from the same sediment record using the $U_{37}^{K'}$ and TEX₈₆ 85 indexes, respectively derived from alkenones and isoGDGTs. The corresponding results 86 were compared with studies of intensity and salinity anomalies of the Agulhas Current. 87

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89 2. STUDY AREA

The Santos Basin is located on the southeastern Brazilian continental margin, limited 90 to the north by the Campos Basin and to the south by the Pelotas Basin. The upper ocean 91 circulation (0 - 600 m) in this region is controlled by the BC, which originates from the 92 southern branch of the South Equatorial Current (SEC) (10 - 14 °S) (Peterson and 93 Stramma, 1991) and flows southward along the Brazilian margin (Stramma and England, 94 95 1999) (Fig. 1a). The upper layer of the BC (0 - 100 m depth) carries Tropical Water (TW) – a warm (> 20 °C), saline (> 36) and oligotrophic water mass influenced by high 96 97 solar radiation, the wind field and excessive evaporation (Peterson and Stramma, 1991; Campos et al., 1995; Stramma and England, 1999; Silveira et al., 2000). The South 98 Atlantic Central Water (SACW) corresponds to the bottom layer of the BC (100 – 600m 99 depth; Fig. 1c) and is colder (~ 6 - 20 °C), less saline (34.6 – 36) and richer in nutrients 100

101 than the TW. The SACW flows in the thermocline layer and is formed in two sites: (i) in 102 the Brazil-Malvinas Confluence (BMC) region, where the BC encounters the northward-103 flowing Malvinas Current (MC) (Peterson and Stramma, 1991) (Fig. 1a) and (ii) in the eastern region, via the Agulhas Leakage, bringing Indian Ocean Central Water into the 104 105 South Atlantic (Richardson, 2007). The water masses that compose the deepest layers of the region are the Antarctic Intermediate Water (AAIW) (600 – 1200 m depth, northward 106 direction), the Upper Circumpolar Deep Water (UCDW) (1200 - 1500 m depth, 107 108 northward direction) and the North Atlantic Deep Water (NADW) (1500 - 2000 m depth, 109 southward direction) (Stramma and England, 1999; Campos et al., 1995; Campos et al., 110 2000; Piola et al., 2000; Piola and Matano, 2001; Schmid, 2014; Silveira et al., 2000; Fig. 1c). 111



113

Fig. 1: Oceanographic setting of the study area and location of sediment core GL-1090. 114 (a) South Atlantic surface circulation with the main currents of the South Atlantic 115 subtropical gyre: (BC) Brazil Current; (BMC) Brazil-Malvinas Confluence; (MC) 116 Malvinas (Falkland) Current; (NBC) North Brazil Current; (SAC) South Atlantic Current; 117 and (SEC) South Equatorial Current (modified from Stramma and England, 1999). (b) 118 119 Zoom of the study area (gray rectangle in a) with the position of core GL-1090 (this study) 120 and cores used in the discussion: downcore NAP63-1 (Dauner et al., 2019) and core-top A11 (Ceccopieri et al., 2018). (c) Vertical section of the first 3000 m water depth of the 121 122 Santos Basin (highlighted red section in b) showing the cores mentioned above and the 123 water masses that compose the region: (TW) Tropical Water, (SACW) South Atlantic

Central Water, (AAIW) Antarctic Intermediate Water; (UCDW) Upper Circumpolar
Deep Water and (NADW) North Atlantic Deep Water. This figure was partly created with
the software Ocean Data View (Schlitzer, 2003). (For interpretation of the references to
color in this figure legend, the reader is referred to the web version of this article.)
Instrumental data show that the annual mean SST of the TW (0 m depth) is 24 °C, with

129 Instrumental data show that the annual mean SST of the Tw (O in depth) is 24°C, with
130 the lowest SST (22.2 °C) during austral winter and the highest SST (25.8 °C) during
131 austral summer (Locarnini et al., 2013). The difference in temperature between summer
132 and winter is most pronounced in the upper 20 m of the water column (Fig. 2).

133



134

Fig. 2: Vertical profiles of the present-day temperatures in the upper 200 m of the study area provided by the World Ocean Atlas 2013 (Locarnini et al., 2013): annual mean (black), winter (blue), spring (green), autumn (yellow) and summer (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

141 3. MATERIAL AND METHODS

142 3.1. Sediment sampling and age model

The marine sediment core GL-1090 (24.92 °S, 42.51 °W, 2225 m water depth, 1914 143 cm length) was collected by Petrobras on the continental slope of the Santos Basin (Fig. 144 1) and stored in a refrigerated container at 4 °C. The age model, shown for the first time 145 in Santos et al. (2017a), was based on radiocarbon dating and visual alignment of δ^{18} O 146 from benthic foraminifera with two reference curves, MD95-4042 (Govin et al., 2014) 147 148 and LR04 δ^{18} O global stack (Lisiecki and Raymo, 2005). The final age model was built using Bacon software v.2.2 (Blaauw and Christeny, 2011). Recently, Ballalai et al. (2019) 149 and Santos et al. (2020) implemented several improvements over the original age model. 150 Ballalai et al. (2019) chose one of the 230Th ages of the Sanbao cave as the connection 151 point for the abrupt transition observed in the corrected ice volume δ^{18} O at the end of 152 153 Termination II. This modification, with assumes a coupling between the movements of the Intertropical Convergence Zone and the bifurcation of the South Equatorial Current 154 155 in the tropical Atlantic, reduced age uncertainties from \pm 3.87 to \pm 1.51 ka close to the transition to the LIG. Santos et al. (2020) derived more benthic δ^{18} O tie- points between 156 GL-1090 and the Iberian Margin MD95-2042 (Govin et al., 2014) on the AICC2012 time 157 scale (Bazin et al., 2013; Veres et al., 2013). The success of the new tie-points can be 158 159 seen through a precise alignment between the variability on the δ^{18} O millennial scale of Globorotalia inflata and NGRIP (Santos et al., 2020). Core GL-1090 spans the last 185 160 ka. This study is focused on the age interval from 150 to 65 ka, corresponding to the depth 161 162 interval from 1591 to 689 cm. Each subsample is 2 cm thick with average collection intervals of 5 cm, corresponding to an average sampling resolution of approximately 400 163 164 years.

166 3.2. Lipid biomarker extraction and fractionation

Lipids were extracted from dry-frozen sediments (2 - 5 g) via three ultrasonication cycles using a solvent mixture of dichloromethane/methanol, 3:1 (v:v). The total lipid extracts were further separated into three fractions by silica gel chromatography using solvent mixtures of increasing polarity: 4 mL of hexane (elution of *n*-alkanes - not discussed in this study); 2 mL of hexane/ethyl acetate 95:5 (v:v) and then, in sequence, 2 mL of hexane/ethyl acetate 90:10 (v:v) (elution of alkenones); and 5 mL of hexane/ethyl acetate 70:30 (v:v) (elution of GDGTs).

174

175 3.3. Alkenone analysis and temperature estimations

The fractions containing alkenones were analyzed on an Agilent 6890 Plus gas 176 chromatograph coupled with a flame ionization detector (GC-FID), and equipped with a 177 178 CPSIL-5 CB column (50 m long \times 0.32 mm internal diameter \times 0.25 µm film thickness). Helium gas was used as carrier gas (2.0 mL/min). The oven was programmed with an 179 180 initial temperature of 50 °C, which was then increased to 140 °C at 30 °C/min, then to 181 280 °C at 20 °C/min, and finally to 305 °C at 0.5 °C/min. Di- and tri-unsaturated C₃₇ alkenones (C_{37:2} and C_{37:3}, respectively) were quantified by comparing their peak area 182 183 with that of an internal standard (5α -cholestane, added prior to analysis).

The alkenone unsaturation index $U_{37}^{K'}$ was calculated according to Prahl and Wakeham (1987; Equation 1) and converted into temperature values using the Bayesian B-spline regression model, BAYSPLINE, for the $U_{37}^{K'}$ paleothermometer (Tierney and Tingley, 2018), with a standard error of ± 1.0 °C.

188

189
$$U_{37}^{K'} = \frac{C_{37:2}}{C_{37:2} + C_{37:3}}$$
 (1)

191 3.4. GDGT analysis and temperature estimations

192	GDGT analyses were performed on a Shimadzu LCMS-2020 high-performance liquid
193	chromatography-mass spectrometry (HPLC-MS) system, as recently described by
194	Huguet et al. (2019). The semi-quantification of the GDGTs was performed by comparing
195	the peak area of the internal standard $C_{46}GDGT$ with those of the compounds (cf. Huguet
196	et al., 2013).
197	The TEX $_{86}$ index was calculated according to Schouten et al. (2002) (Equation 2). The
198	numbering of the isoGDGTs refers to the publication by Kim et al. (2010).
199	
200	$TEX_{86} = \frac{isoGDGT-2 + isoGDGT-3 + Crenarchaeol regioisomer}{isoGDGT-1 + isoGDGT-2 + isoGDGT-3 + Crenarchaeol regioisomer} $ (2)
201	
202	The annual mean sea surface temperatures (0 m) were estimated from the TEX_{86}^{H} index
203	(Equation 3) using the calibration by Kim et al. (2010) adapted for temperatures between
204	$15-30$ °C, with a given uncertainty of ± 2.5 °C (Equation 4).
205	
206	$TEX_{86}^{\rm H} = \log(TEX_{86}) \tag{3}$
207	
208	Temp-TEX ₈₆ ^H (°C) = 68.4 (TEX ₈₆ ^H) + 38.6 (4)
209	
210	The annual mean depth-integrated temperatures (0 to 200m water depth) were
211	calculated from the global calibration by Kim et al. (2012; Equation 5), with an
212	uncertainty of ± 2.2 °C.
213	
214	Temp-TEX ₈₆ ^H (0-200) (°C) = 54.7 (TEX ₈₆ ^H) + 30.7 (5)
215	

216	The Branched and Isoprenoid Tetraether (BIT) index is suggested to represent
217	terrestrial organic matter inputs into aquatic environments (Hopmans et al., 2004). In
218	order to evaluate if TEX_{86}^{H} values were biased by terrigenous input at our core site, the
219	BIT index was calculated from Hopmans et al. (2004) (Equation 6). The numbering of
220	the branched GDGTs (brGDGTs) refer to the publication by Hopmans et al. (2004). High
221	BIT values (> 0.4) may lead to anomalously high TEX_{86}^{H} -derived temperatures (Weijers
222	et al., 2006).
223	
224	$BIT index = \frac{brGDGT-I + brGDGT-II + brGDGT-III}{brGDGT-I + brGDGT-II + brGDGT-III + Crenarchaeol} $ (6)
225	

226 4. RESULTS

4.1. Alkenone-derived temperatures (Temp- $U_{37}^{K'}$)

During the period between 150 and 65 ka, the mean Temp-U₃₇^{K'} was 20.8 °C \pm 1.4 and 228 ranged from 17.6 °C (ca. 146.4 ka ka, MIS 6) to 26.8 °C (ca. 126.6 ka, MIS 5e) (Fig. 3a). 229 230 The alkenone temperature estimates were mainly below the mean value from 150 to 140 ka (MIS 6 / T II). An abrupt warming of 6.1 °C marked the Termination II (T II), reaching 231 a peak during MIS 5e (~127 ka), followed by a gradual cooling until mid-MIS 5d (ca. 112 232 ka). The MIS 5e, 5c, and 5a substages generally showed warmer temperatures than MIS 233 5d and 5b substages. The periods between ca. 82 - 79 ka and ca. 77 - 75 ka were marked 234 by a decrease in temperature. 235

- 4.2. GDGT-derived temperatures (Temp-TEX $_{86}^{\text{H}}$, Temp-TEX $_{86}^{\text{H}}$ (0-200)
- The mean Temp-TEX^H₈₆ from 140 to 65 ka was 25.4 °C \pm 1.4, ranging from 21.1 °C
- 239 (ca. 68.4 ka, MIS 4) to 28.5 °C (ca. 123.8 ka, MIS 5e) (Fig. 3a). The T II was marked by
- an abrupt warming of 5.7 °C. Throughout the substages MIS 5d to MIS 5a, the

temperatures remained roughly stable, except for two abrupt decreases in temperature during MIS 5a. The minimum temperature was recorded at the MIS 5a / 4 (21.1 °C at 69 ka). Regarding the depth-integrated temperatures, Temp-TEX^H₈₆ (0-200) oscillated between 16.7 °C (ca. 68.4 ka, MIS 4) and 22.7 °C (ca. 123.8 ka, MIS 5e), with an average of 20.1 °C \pm 1.2 (Fig. 4).

246

247 5. DISCUSSION

248 5.1. Comparison of the TEX_{86}^{H} and $U_{37}^{K'}$ temperature estimates

In core GL-1090, similar trends were generally observed for temperatures derived 249 from alkenones and isoprenoid GDGTs (Temp- $U_{37}^{K'}$ and Temp-TEX₈₆^H), with a high 250 amplitude during LIG (Fig. 3). Nevertheless, the two organic proxies provided different 251 absolute temperature estimates. $U_{37}^{K'}$ -derived temperatures were systematically lower than 252 those provided by TEX₈₆^H (Fig. 3a). The peaks of Temp-U₃₇^{K'} and Temp-TEX₈₆^H were 26.8 253 °C (126.6 ka, MIS 5e) and 28.5 °C (123.8 ka, MIS 5e), respectively, which are 2.8 °C and 254 4.5 °C higher than the current annual mean surface temperature (0 m depth) near the GL-255 256 1090 site (Fig. 3a).

257 Turney and Jones (2010) compiled a global dataset of annual temperatures from cores 258 spanning the LIG and deduced an increase in sea surface and terrestrial temperatures of 259 nearly 2.0 °C above pre-industrial levels over this period. However, such warming was 260 not uniform across the global oceans, and the SSWA was not included in the dataset. Model data performed by Otto-Bliesner et al. (2013) and sea surface temperature 261 reconstructions published by Hoffman et al. (2017) did not indicate a significant 262 263 difference in temperature during the LIG compared with the present in global tropical 264 regions. It should be noted that these authors did not present results near our sampling 265 site.



267

Fig. 3: Comparison of paleotemperatures reconstructed from isoGDGTs and alkenones: 268 a) Temp-TEX₈₆^H (green) and Temp-U₃₇^{K'} (red). The dashed line in violet marks the global 269 average increase during the LIG, approximately 2.0 °C relative to pre-industrial levels 270 (Turney and Jones, 2010). The blue dashed line marks the current annual mean sea surface 271 temperature in the study area (Locarnini et al., 2013); b) Temperature gradient ΔT (TEX₈₆^H 272 - $U_{37}^{K'}$). The black dashed line marks the average ΔT (4.1 °C). The marine isotopic stages 273 (MIS) are highlighted on the upper x-axis. (For interpretation of the references to color 274 275 in this figure legend, the reader is referred to the web version of this article.)

The peak of Temp- $U_{37}^{K'}$ from GL-1090 is consistent with the + 2.0 °C LIG surface temperature anomaly relative to the present-day mean (Turney and Jones, 2010), equivalent to 24 °C in the study area (Cordeiro et al., 2014; Locarnini et al., 2013). In contrast, Temp-TEX_{86}^{H} showed a very high LIG SST anomaly relative to the modern annual mean (4.5 °C), which does not seem plausible. In order to understand the similarities and divergences between the temperature estimates derived from $U_{37}^{K'}$ and

TEX $_{86}^{H}$, the different factors which may influence these organic proxies and their associated temperatures – choice of calibration equations, continental inputs, lateral transport of the alkenones and isoGDGTs, ecology and seasonality of the source organisms of these lipids – will be considered in detail below.

287

288 5.2. Potential factors influencing the $U_{37}^{K'}$ and TEX_{86}^{H} temperature estimates

289 5.2.1. Choice of the calibrations

290 The choice of the calibration has an influence on the absolute temperature estimates. We tested the Temp- $U_{37}^{K'}$ annual calibration for the global ocean from 60 °N to 60 °S 291 (Müller et al., 1998), the Temp- $U_{37}^{K'}$ SE Atlantic annual mean core top calibration (Müller 292 et al., 1998) and the new Bayesian B-spline regression model, BAYSPLINE, for the $U_{37}^{K'}$ 293 294 paleothermometer (Tierney and Tingley, 2018). The three calibrations resulted in highly similar temperatures (cf. Supp. Fig. 1). The annual calibration for the global ocean from 295 60 °N to 60 °S resulted in Temp-U_{37}^{K'} on average 0.8 °C warmer than the values obtained 296 297 with the SE Atlantic annual calibration equation proposed by Müller et al. (1998). The Temp-U₃₇^{K'} calibration by Tierney and Tingley (2018) resulted in Temp-U₃₇^{K'} on average 298 0.04 °C warmer than the values calculated with the SE Atlantic annual calibration 299 300 equation proposed by Müller et al. (1998).

Using 53 core-top sediments, Ceccopieri et al. (2018) tested on a regional scale in the SSWA (SE Brazilian continental margin) the applicability of Temp- $U_{37}^{K'}$ calibrations by Müller et al. (1998) for the SE Atlantic: annual mean core top calibration (for temperatures from 0 to 27 °C) and seasonal (austral) calibrations. These authors concluded that the Temp- $U_{37}^{K'}$ SE Atlantic annual calibration (Müller et al., 1998) is comparable to SSWA annual mean present-day temperatures. Due to the high similarity between the Temp- $U_{37}^{K'}$ SE Atlantic annual mean core top calibration (Müller et al., 1998) and Temp- $U_{37}^{K'}$ calibration by Tierney and Tingley (2018), both calibrations could be used interchangeably. In this work we adopt the most recent one.

Regarding GDGTs, we tested the Temp-TEX $_{86}^{H}$ calibration proposed by Kim et al. 310 (2010), the Temp-TEX₈₆^H(0-200) calibration by Kim et al. (2012), and the Temp-TEX₈₆^H 311 and Temp-TEX₈₆^H(0-200) calibrations by Tierney and Tingley (2014). The TEX₈₆^H and 312 TEX_{86}^{H} (0-200) calibrations by Tierney and Tingley (2014) resulted in a less pronounced 313 temperature oscillation over time, and the absolute surface and subsurface values were 314 closer to each other (cf. Supp. Fig. 2). The TEX^H₈₆ calibration by Tierney and Tingley 315 (2014) resulted in colder absolute temperatures than the TEX_{86}^{H} calibration by Kim et al. 316 (2010). The $\text{TEX}_{86}^{\text{H}}$ (0-200) calibration by Tierney and Tingley (2014) resulted in warmer 317 absolute temperatures than the TEX_{86}^{H} (0-200) calibration by Kim et al. (2012). 318

The applicability of the Temp-TEX₈₆^H calibration for regions with present-day temperatures from 15 to 30 °C proposed by Kim et al. (2010) was also tested by Ceccopieri et al. (2018) in the SSWA using the same core-top sediments as for the $U_{37}^{K'}$ investigation. Temp-TEX₈₆^H was found to reflect the annual temperature in the SSWA. Although the Temp-TEX₈₆^H by Tierney and Tingley (2014) are closer to the present-day temperature in GL-1090, we adopted Kim et al. (2010) calibration because its regional application in our study area was already validated by previous study.

326

327 5.2.2. Continental inputs

Temp-TEX^H₈₆ may be biased by isoprenoid GDGTs derived from terrigenous inputs and transported to the marine system by rivers and/or runoff (Schouten et al., 2013 and references therein). These inputs can notably be quantified by applying the BIT index (Hopmans et al., 2004), whose values close to 0 were generally associated with organic

332 material from open sea origin and those close to 1 (maximum value) with organic matter 333 from terrestrial origin. In marine settings, BIT values above 0.4 were suggested to cause a deviation of the TEX₈₆ temperature estimates greater than 2.0 °C (Weijers et al., 2006). 334 335 Nevertheless, care should be taken when interpreting the BIT values, as the two types of GDGTs used to calculate the BIT index - branched glycerol dialkyl glycerol tetraethers 336 (brGDGTs) (Peterse et al., 2009; Sinninghe Damsté et al., 2009; Tierney et al., 2010) and 337 crenarchaeol (Leininger et al., 2006; Weijers et al., 2006; Walsh et al., 2008) - can be 338 339 produced in both terrestrial and aquatic environments. Therefore, in aquatic settings, high BIT values, which reflect a higher relative abundance of brGDGTs than that of 340 341 crenarchaeol, could be associated with high terrestrial inputs of brGDGTs and/or in situ production of brGDGTs. 342

Along the core GL-1090, the BIT index varied between 0.11 and 0.92, with an average 343 344 of 0.45 ± 0.12 and higher values recorded during cold periods, from late MIS 6 to the 345 onset of MIS 5e and during the onset of MIS 4 (cf. Supp. Fig. 3). Considering that 346 previous studies have shown that no large river flows directly to the sea in this region 347 (Conti and Furtado, 2006; Pessenda et al., 2012), terrestrial inputs were not expected to be high in the study area. To better evaluate this hypothesis, the behavior of organic and 348 349 inorganic compounds from the same core was investigated, even though the latter are 350 transported from the continent to marine sediments by different particles. No similar trends were observed between the BIT values and the Fe/Ca ratio - an inorganic proxy 351 from continental runoff along the GL-1090 core (Figueiredo et al., 2020). The Fe/Ca 352 peaks were not even registered by the BIT index or by Temp-TEX $_{86}^{H}$ (cf. Supp. Fig. 3). 353 However, the calcium ratios are influenced by sea level in the study area, embedding 354

a very dominant low-frequency variability in the data. This sea level influence maysuggest that the null correlation between BIT and XRF may not be substantially strong

evidence. Recently, Mathias et al. (2021) performed a deep sedimentological analysis on 357 GL-1090 and they found very little river entry into the continental margin of southeastern 358 Brazil during the Late Pleistocene. Although there was some continental influence, the 359 360 results indicated the lowest terrigenous entries during MIS 5e and MIS 1. This suggests that the BIT values cannot be interpreted as recording high terrestrial inputs, since its 361 highest values were found during MIS 5e. The high BIT values would rather be due to in 362 363 situ production of brGDGTs at the GL-1090 sampling site, as observed in coastal regions (Crampton-Flood et al., 2019). 364

365

366 5.2.3. Lateral transport

The effect of lateral transport on $U_{37}^{K'}$ temperature estimates has been reported in 367 specific oceanic regions. Anomalously cold (by $2 \,^{\circ}\text{C} - 6 \,^{\circ}\text{C}$) U^{K'}₃₇ temperature values were 368 369 found in sediments located under the Brazil-Malvinas Confluence and Malvinas Current in the southwestern Atlantic (Benthien and Muller, 2000). In this area of peculiar 370 circulation, alkenone-bearing sediments are advected northwards carrying $U_{37}^{K'}$ signals of 371 372 their origin in cold waters. In the Campos Basin, SSWA, cold bias in Uk'37 derived 373 temperatures wre reported in core-top sediments close to the Cabo Frio Upwelling System 374 and they were ascribed to alkenones advected from adjacent colder (upwelled) waters.

Considering that alkenones are more susceptible to lateral transport than isoGDGTs (Mollenhauer et al., 2007; Shah et al., 2008), Ceccopieri et al. (2018) suggested that TEX^H₈₆-derived estimates better reflect local temperatures in this region in comparison with alkenones. In line with the conclusion of Ceccopieri et al. (2018), the lower absolute values of $U_{37}^{K'}$ compared with those of TEX^H₈₆ could be explained by intrusions of SACW into the photic zone identified in the GL-1090 during MIS 5e, 5c, and 5a substages due to the southward expansion of the Cabo Frio Upwelling System (Lessa et al. 2017).

Nevertheless, it should be noted that, while Lessa et al (2017) showed a vertical cooling 382 only during warm substages, here Temp- $U_{37}^{K'}$ presented lower values than Temp-383 TEX_{86}^{H} during the entire studied period (150 – 65 ka), indicating that the advection of cold 384 water alone cannot explain the differences in TEX_{86}^{H} and $U_{37}^{K'}$ -based temperature 385 estimates. Additionally, the similar pattern and the high correlation between temperatures 386 derived from the $U_{37}^{K'}$ and TEX^H₈₆ indices (r = 0.73, p < 0.05) suggest that either (i) the 387 signals from the alkenones and isoGDGTs were produced vertically in the same area, 388 probably at different depths in the water column, or (ii) the intensity of the lateral 389 transport might differ over the investigated period, affecting both types of lipids in the 390 391 same way during some periods. In any case, it means that lateral transport alone cannot explain the differences in absolute temperatures between $U_{37}^{K'}$ and TEX_{86}^{H} . 392

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394 5.2.4. Seasonality

In a number of studies disparities between paleotemperatures reconstructed with the $U_{37}^{K'}$ and TEX_{86}^{H} indexes have been attributed to seasonal patterns in the production of the organisms, hapophyte algae and marine Thaumarchaeota, respectively (eg Lopes dos Santos et al., 2013; Auderset et al., 2019) but a consistent, globally applicable, seasonal pattern has not emerged.

Furthermore, compilation of sediment trap time series data have shown that the maximum alkenone flux across the oceans displays seasonal variations depending on local/regional oceanographic conditions and sedimentation processes (Mele and Prahl 2013). However, apart from few locations close to major hydrographic fronts, sedimentation patterns for $U_{37}^{K'}$ in sediment trap time series appears provide a measure of annual mean SST.

The age of the GL-1090 core-top sample is 6.6 ka (Santos et al., 2017a), hampering 406 its use to compare the seasonality of alkenone and isoGDGT source organisms -407 hapophyte algae and marine Thaumarchaeota, respectively - in the present-day. 408 409 However, core-top studies in the SSWA shelf and slope (Cordeiro et al., 2014; Ceccopieri et al., 2018) have found that $U_{37}^{K'}$ -derived temperature estimates agreed well with 410 interpolated mean annual SST of ca. 24 °C. They also reported that, despite a likely most 411 efficient export of isoGDGT during austral summer, core-top Temp-TEX^H₈₆ values were 412 better correlated with the annual mean SST (Ceccopieri et al., 2018). In the regional 413 context, Mahiques et al. (2005) analyzed alkenones in box cores near GL-1090 and 414 considered Temp- $U_{37}^{K'}$ as reflecting mean annual temperatures over the last 700 years. A 415 similar conclusion was drawn by Dauner et al. (2019), who showed that the temperature 416 estimates derived from TEX_{86}^{H} and $U_{37}^{K'}$ over the last 75 ka reflected the mean annual 417 418 temperature in the SSWA.

Based on the afore-mentioned studies we argue that seasonal bias in the Temp-TEX^H₈₆ and Temp-U^{K'}₃₇ estimates is of minor importance and that both TEX^H₈₆ and U^{K'}₃₇ indexes record the mean annual temperature in the study area.

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423 5.2.5. Water depth

Standard deviations of ± 1.0 °C for Temp-U^{K'}₃₇ (Müller et al., 1998) and ± 2.5 °C for Temp-TEX^H₈₆ (Kim et al., 2010) suggest that temperature differences of up to ± 3.5 °C between these proxies may be within the calibration error. The reconstructed mean temperature gradient (Δ T) of TEX^H₈₆ and U^{K'}₃₇ is 4.5 °C (Fig. 3b) and, therefore, higher than the calibration error. One explanation may be the difference of depth production between haptophytes and *Thaumarchaeota*.

Previous studies at the Campos Basin slope indicate that haptophyte algae, alkenone 430 producers, inhabit the photic zone between 6 - 50 m depth (predominantly the 20 °C 431 isotherm; Mahiques et al., 2009; Sousa et al., 2014; Rodrigues et al., 2014). This 432 433 temperature isotherm corresponds to the interface between TW and SACW at the Santos Basin slope. Dauner et al. (2019) concluded that the temperatures derived from $U_{37}^{K'}$ were 434 435 consistent with those at around 30 m depth in the SSWA. Similarly, Luz (2019) considered that the $U_{37}^{K'}$ signal reflected the temperature of the water column up to 25 m 436 in the same region. This is consistent with previous studies in other areas, such as the 437 Mediterranean Sea, the northern Arabian Sea, and in the tropical and subtropical Atlantic 438 439 Ocean, which reported the possibility of alkenones recording temperature conditions below the surface (Ternois et al., 1997; Andruleit et al., 2003; Poulton et al., 2017). 440

441 IsoGDGT-producing archea are generally more widely distributed in the water column 442 than haptophytes, presenting a greater abundance between 40 and 150 m water depth 443 (Lopes dos Santos et al., 2013; Kim et al., 2012; Schouten et al., 2002; Wuchter et al., 2006). In their study of the structure of the picoplankton community in a southern Atlantic 444 transect, Zubkov et al. (2000) indicated that heterotrophic prokaryotes (bacteria and 445 446 archea) mainly inhabit the surface layer. While Dauner et al. (2019) confirmed that the TEX_{86}^{H} signal represents the average annual temperature of the surface layer at the Santos 447 Basin, Luz (2019) considered that Temp-TEX^H₈₆ reflects those of the water depths around 448 100 - 200m, showing that there is no consensus on the depth of *Thaumarchaeota* growth 449 450 in the SSWA.

Assuming that the non-thermal factors investigated in the previous sections (5.2.1, 5.2.2, 5.2.3 and 5.2.4) do not cause significant deviations in temperature reconstructions, the results for the GL-1090 core suggest that the alkenones reflect temperatures at the 454 interface between the TW and the SACW, corresponding to the upper thermocline, and

455 the isoGDGTs reflect temperatures at the mixed layer of the Santos Basin slope.

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457 5.3. Multiproxy temperature reconstruction in the water column

In order to estimate the temperature gradient (Δ T) between the mixed layer and the upper thermocline from GL-1090, Temp-TEX^H₈₆(0-200) – for subsurface temperature – was calculated and compared with Temp-TEX^H₈₆ – for surface temperature. The average Δ T between Temp-TEX^H₈₆ and Temp-TEX^H₈₆(0-200) was 5.2 °C (Fig. 4a), while the average Δ T between Temp-TEX^H₈₆(0-200) and Temp-U^{K'}₃₇ was considerably smaller (less than 1.0 °C) (Fig. 4b).

464 Ceccopieri et al. (2018) also applied the Temp-TEX $_{86}^{H}$ (0-200) calibration by Kim et al. 465 (2012) to core-top samples. At station A11 (Fig. 1b,c), these authors obtained values close 466 to instrumental data from WOA13 (Locarnini et al., 2013) depth-integrated temperatures 467 at about 100 - 200 m depth throughout the Campos Basin slope (between 13.8 °C and 468 21.7 °C). This suggests that the $U_{37}^{K'}$ signal at the GL-1090 site reflects the upper 469 thermocline temperature in the SSWA.



Fig. 4: Comparison of depth-integrated $\text{TEX}_{86}^{\text{H}}(0\text{-}200)$ with $\text{TEX}_{86}^{\text{H}}$ and $U_{37}^{\text{K'}}$ -based temperatures, and their respective temperature gradients: a) $\text{TEX}_{86}^{\text{H}}$ (green), $\text{TEX}_{86}^{\text{H}}(0\text{-}200)$ (blue) and ΔT ($\text{TEX}_{86}^{\text{H}}\text{-}\text{TEX}_{86}^{\text{H}}(0\text{-}200)$) (black); b) $U_{37}^{\text{K'}}$ (red), $\text{TEX}_{86}^{\text{H}}(0\text{-}200)$ (blue) and ΔT ($U_{37}^{\text{K'}}\text{-}\text{TEX}_{86}^{\text{H}}(0\text{-}200)$) (black). Dashed lines mark the mean difference between the absolute temperatures derived from the organic proxies. Marine isotope stages (MIS) are highlighted on the upper x-axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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The sea temperature estimates derived from $U_{37}^{K'}$ and TEX_{86}^{H} were compared with those 480 inferred for the same core from Mg/Ca G. ruber (Santos et al., 2017a) and from Modern 481 Analog Technique (MAT) - a transfer function based on planktonic foraminiferal census 482 483 count (Lessa et al., 2017) - at 10m (MAT-10m) and at 100m (MAT-100m) water depth. The Mg/Ca values published in Santos et al. (2017a) were converted to temperatures 484 485 using the recent species-specific equation by Gray and Evans (2019). The calcification depth of G. ruber in the SSWA corresponds to the mixed layer (30 – 40m water depth), 486 as shown by sediment traps studies (Venancio et al., 2017). This supports the use of the 487 Mg/Ca proxy for reconstructing mixed layer temperatures in the region (eg Chiessi et al., 488 2007; Chiessi et al. 2014). Temp-TEX $_{86}^{H}$ values fall into the range of those derived from 489 490 Mg/Ca and are close to MAT-10m temperatures, suggesting that these proxies reflect mixed layer temperatures (Fig. 5a). 491



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Fig. 5: Comparison of paleotemperature ranges reconstructed from multiproxies at GL-1090, between 150 and 65 ka: temperature (°C) derived from Mg/Ca *G. ruber* (gray) (after Santos et al., 2017a); TEX^H₈₆ (green) (this study); MAT-10m (gray) (Lessa et al., 2017); $U_{37}^{K'}$ (red) (this study); TEX^H₈₆(0-200) (blue) (this study); and MAT-100m (gray) (Lessa et al., 2017). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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In contrast, the range of temperatures derived from $U_{37}^{K'}$ is similar to the ones from 501 $\mathrm{TEX}^{\mathrm{H}}_{86}(0\text{-}200)$ and MAT-100 m. The corresponding estimates are lower than Mg/Ca, 502 $\text{TEX}_{86}^{\text{H}}$ and MAT-10m-based temperatures, suggesting that, in core GL-1090, Temp-U₃₇^{K'} 503 recorded temperatures from the upper thermocline. This is consistent with the fact that, 504 505 in the SSWA, haptophytes reach their maximum abundance where the deep chlorophyll 506 maximum occurs, above the thermocline (Brandini et al., 2014; Rodrigues et al., 2014; 507 Ribeiro et al., 2016). Dauner et al. (2019) also attributed to the depth of the haptophyte habitat the lower Temp- $U_{37}^{K'}$ than Temp-TEX^H₈₆ over the last 75 ka in the SSWA, and this 508 condition seems to be the most likely to explain why the temperatures derived from $U_{37}^{K'}$ 509 are more similar to the temperatures from the upper thermocline than from the mixed 510 layer in GL-1090, between 150 and 65 ka (Fig. 5b). 511

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513 5.4. Regional dynamics in the water column in the SSWA during MIS 5e

During the MIS 5e (129-116 ka) and the onset of MIS 4 (71-65 ka), the ΔT between 514 TEX_{86}^{H} and $U_{37}^{K'}$ was lower than the average one over the whole core GL-1090 (Fig. 3b). 515 During the MIS 5e, the ΔT was reduced due to a more prominent warming of $U_{37}^{K'}$. In 516 contrast, during the onset of the MIS 4, this decrease could be explained by a more 517 pronounced cooling of TEX^H₈₆. If we assume that the source organisms of alkenones and 518 isoGDGTs live at different depths, then a change in the thermal structure of the photic 519 520 zone may explain the similar temperatures between the mixed layers and the upper thermocline during MIS 5e and the onset of MIS 4. The pronounced positive temperature 521 anomaly derived from $U_{37}^{K'}$ during MIS 5e (Fig. 6a) suggests greater heat storage at the 522 upper thermocline. 523





Fig. 6: Temperature anomalies normalized by the standard deviation of each proxy along
the core GL-1090 for three time intervals: (a) Last Interglacial (LIG/MIS 5e); (b) Glacial
inception (MIS 5d-a); (c) Glacials (MIS 6 and MIS 4), based on Mg/Ca *G. ruber* (gray)
(after Santos et al., 2017a); TEX^H₈₆ (green) (this study); MAT-10m (gray) (Lessa et al.,
2017); U^{K'}₃₇ (red) (this study); TEX^H₈₆(0-200) (blue) (this study); and MAT-100m (gray)

(Lessa et al., 2017). (For interpretation of the references to color in this figure legend, thereader is referred to the web version of this article.)

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During the LIG period (Figure 6a), $U_{37}^{K'}$ recorded a steep thermal gradient in the upper 534 535 thermocline, which decreased in the middle/end of the interglacial complex scenario (Figure 6b). The intensity of this thermal gradient was further reduced in the glacial 536 537 scenario (Figure 6c). The evaluation of these different water column temperature profiles over time suggests that alkenones are more strongly affected by changes in depth 538 conditions than isoGDGTs, the latter being directly affected by the vertical mixing 539 temperature oscillation. This explains why $U_{37}^{K'}$ -based temperatures are similar to those of 540 541 the surface layer during the LIG and close to the subsurface temperatures during the 542 glacials.



Figure 7: Comparison of temperature anomalies from core GL-1090 with other low/midpaleoclimate signals from 150 to 65 ka: a) ϵ Nd record of core ODP1063 (Böhm et al., 2015); b) Temperature anomalies from core GL-1090 based on TEX^H₈₆ (green) and U^{K'}₃₇ (red) (this study); c) Temperature gradient from core GL-1090 based on TEX^H₈₆ (this study) minus MAT-100m (Lessa et al., 2017; green), and U^{K'}₃₇ (this study) minus MAT-100m (Lessa et al., 2017; red); d) $\Delta\delta^{18}$ O (*Globorotalia inflata – Globigerinoides ruber*) (Santos et al.,

2017); e) Thermocline $\delta^{18}O_{IVC-SW}$ values from core GL-1090 (Ballalai et al., 2019) 551 552 estimated from Mg/Ca ratio-derived thermocline temperatures; f) Surface $\delta^{18}O_{IVC-SW}$ values from core 64PE- 174P13 (Walvis Ridge) (Scussolini et al., 2015) estimated from 553 554 *Globigerinoides ruber* δ^{18} O values; g) Thermocline δ^{18} O_{IVC-sw} values from core 64PE-174P13 (Walvis Ridge) (Scussolini et al., 2015) estimated from Globigerinoides 555 556 *truncatulinoides* δ^{18} O values. Marine isotope stages (MIS) are highlighted on the upper 557 x-axis. (For interpretation of the references to color in this figure legend, the reader is referred to 558 the web version of this article.)

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560 Furthermore, during MIS 5e and MIS 5c, the high ΔT between the organic proxies $U_{37}^{K'}$ /TEX₈₆ and MAT-100 (Fig. 7) suggests upper ocean stratification with the flattening 561 562 of the mixed layer, which may have reduced the downward diffusion of heat. This decrease in vertical mixing due to enhanced stratification is showed by $\Delta \delta^{18}$ O (G. inflata 563 - G. ruber) (Fig. 7d). Leonhardt et al. (2013) analyzed fossil assemblages of 564 565 coccolithophorids, Globigerinoides ruber and corresponding stable oxygen isotopes from a sediment core collected in the SSWA, covering the last 130 ka. The authors observed 566 567 lower surface productivity during MIS 5e, which was related to an increase in the nutricline depth, making surface water fertilization impossible. 568

During late MIS 6 / T II and the onset of MIS 4, sea temperature positive anomalies
(Fig. 7b) were associated with the weakening of the AMOC and consequent strengthening
of the BC due to changes in circulation structure (Broecker, 1998; Santos et al., 2017).
The εNd, a water mass provenance proxy used for interpretation of water mass geometry
from the Bermuda Rise (Böhm et al., 2015), corroborates this hypothesis (Fig. 7a).

It is known that warm and saline Subtropical Indian Ocean water is transported into the South Atlantic through the Indian-Atlantic oceanic gateway (Gordon, 1986; Lutjeharms, 2006; Beal et al., 2011). Marino et al. (2013) point that the salinity increase between 138 ka and 130 ka indicated by $\delta^{18}O_{SW}$ represents an interhemispheric coupling

once it is correlated with abrupt swings in the North Atlantic. According to Marino et al.
(2013), the Indian-to-Atlantic salt transport is a strong driver of the AMOC during the
abrupt climate changes of the Late Pleistocene.

581 Ballalai et al. (2019) analyzed thermocline Mg/Ca-derived temperatures and salinity from ice volume-corrected δ^{18} O seawater (δ^{18} O_{IVC-SW}) records in GL-1090 during 582 Termination II and early Late Interglacial (Fig. 7e). According to these authors, during 583 584 the intensification of the Agulhas Leakage, starting from ca. 142 ka BP (Fig. 7f; g), the 585 salt anomaly was recirculated within the South Atlantic subtropical gyre instead of being immediately transmitted to the North Atlantic due to a "barrier" caused by an ocean-586 atmosphere coupling that increased the BC flow and limited its equatorial crossing. Our 587 findings are consistent with those of Ballalai et al. (2019). In this sense, this study confirm 588 589 the connection between the intensification of the Agulhas Leakage and the heat storage 590 at the upper thermocline in the SSWA during MIS 5e.

591 In summary, our organic data from GL-1090 provided information on the applicability of the $U_{37}^{K'}$ and TEX^H₈₆ proxies in the SSWA and have enabled the identification of a 592 change in the thermocline structure in the SSWA from late MIS 6 to the onset of MIS 4. 593 594 Based on our results, we suggest that alkenones were more affected by warm temperatures 595 at the upper thermocline during the LIG period (MIS 5e), and isoGDGTs were more affected by cold temperatures at the mixed layer during glacials (MIS 6 and MIS 4). 596 597 However, more studies covering the same time range with atmospheric modeling and thermocline proxies in the South Atlantic must be considered in future research studies 598 599 in the region in order to better understand the mechanisms that led to these scenarios.

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601 6. CONCLUSIONS

This work presents the first temperature reconstruction based on alkenones and 602 isoGDGTs covering late MIS 6 to the onset of MIS 4 in the SSWA. A multiproxy 603 approach was developed, involving the organic proxies $U_{37}^{K'}$ and TEX_{86}^{H} , as well as 604 previously published data (Mg/Ca ratio and MAT derived from planktonic foraminifera). 605 606 Non-thermal factors, i.e. terrestrial inputs and lateral transport, were suggested to have minor influence on the temperature signal derived from alkenones/isoGDGTs. TEX^H₈₆ 607 and $U_{37}^{K'}$ temperature estimates were assumed to reflect different water depths, i.e. those 608 of the mixed layer and the upper thermocline, respectively. This was related to the 609 610 different habitat depths of the source organisms of isoGDGTs and alkenones - marine 611 Thaumarchaeota and hapophyte algae, respectively.

612 Our downcore record emphasizes the relevance of a multiproxy approach to bringing 613 insights into the interpretation of the response of each proxy in the same sediment core, leading to better understanding of the paleoceanographic changes from 150 ka to 65 ka, 614 615 mainly during the LIG, in the south-eastern Brazilian margin. Our results suggest that a steep thermal gradient in the upper thermocline exists during the LIG, as does a reduced 616 617 thermal gradient in the glacial scenario. Finally, our study demonstrates that the organic 618 proxies applied here are reliable for reconstructing paleoceanographic changes in the SSWA. 619

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621 CRediT AUTHORSHIP CONTRIBUTION STATEMENT

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Rodrigo A. Nascimento: writing – review & editing. Ioanna Bouloubassi, Arnaud Huguet:
formal analysis, review & editing. Marcelo C. Bernardes: supervision, formal analysis,
review & editing.

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628 DECLARATION OF COMPETING INTEREST

629 The authors declare that they have no known competing financial interests or personal

relationships that could have appeared to influence the work reported in this paper.

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1006 SUPPLEMENTARY MATERIAL



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Supp. Fig. 1: Temp- $U_{37}^{K'}$ Global calibration - annual average (Müller et al., 1998) (blue), Temp- $U_{37}^{K'}$ SE Atlantic calibration - annual average (Müller et al., 1998) (green), and Temp- $U_{37}^{K'}$ BAYSPLINE calibration (Tierney and Tingley, 2018) (red) - red shading represents the 95% confidence interval. Marine isotope stages (MIS) are highlighted on the upper x-axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



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Supp. Fig. 2: Temp-TEX^H₈₆ Global calibration - annual average (> 15 °C) (Kim et al.,
2010) (blue), Temp-TEX^H₈₆ (0-200) Global calibration - annual average (Kim et al., 2012)
(green), Temp-TEX^H₈₆ Bayesian calibration (Tierney and Tingler, 2014) (red) - red shading

1019 represents the 95% confidence interval, and SubTemp-TEX $_{86}^{H}$ Bayesian calibration 1020 (Tierney and Tingler, 2014) (orange) - orange shading represents the 95% confidence 1021 interval. Marine isotope stages (MIS) are highlighted on the upper x-axis. (For 1022 interpretation of the references to color in this figure legend, the reader is referred to the 1023 web version of this article.)

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Supp. Fig. 3: Comparison between (a) Temp-TEX^H₈₆ (green) (this study), (b) BIT index
(pink) (this study) and (c) Fe/Ca ratio (gray) (Figueiredo et. al, 2020). Gray bars indicate
peaks in Fe/Ca ratios. Marine isotope stages (MIS) are highlighted on the upper x-axis.
(For interpretation of the references to color in this figure legend, the reader is referred to
the web version of this article.)