Applicability of the Long-chain Diol Index (LDI) as a sea surface temperature proxy in the Arabian Sea

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November 24, 2022

Abstract

The long-chain diol index (LDI) is a relatively new proxy for sea surface temperature (SST) which has been rarely applied in upwelling regions. Here, we evaluated its application by comparison with other SST records obtained by commonly used proxies, i.e. the Mg/Ca ratio of the planktonic foraminifera species $_{37}$ and Mg/Ca_{*G*,ruber} SST records revealed an increase of 0.6-3.4°C from the Last Glacial Maximum to the late Holocene with somewhat higher amplitude in the northern part of the Arabian Sea than compared to the western part. In contrast, the LDI SSTs did not reveal major changes during the last glacial-interglacial transition which was followed by a decreasing trend during the Holocene. The LGM vs the Holocene LDI SSTs ranged between -0.2 and -2.7°C. Particularly at one record, offshore Oman, the SST decrease from during the Holocene was high in amplitude, suggesting a potential cold bias, possibly related to changes in upwelling intensity during the Holocene. This indicates that care has to be taken when applying the LDI for annual mean SST reconstruction in upwelling regions.

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17 Key Points:

- We applied the LDI as a paleothermometer to sedimentary records from the Arabian Sea focusing on the last glacial interglacial transition.
- The sea surface temperature records showed decreasing values with the onset of the deglaciation, different from other proxy records.
- Strong upwelling and high nutrient input may cause this cold bias, which was observed particularly at one record, offshore Oman.

25 Abstract

- 26 The long-chain diol index (LDI) is a relatively new proxy for sea surface temperature (SST)
- 27 which has been rarely applied in upwelling regions. Here, we evaluated its application by
- 28 comparison with other SST records obtained by commonly used proxies, i.e. the Mg/Ca ratio of
- 29 the planktonic foraminifera species *Globigerinoides ruber* and the alkenone paleothermometer
- $U_{37}^{K'}$. We focused on the last glacial-interglacial transition of four different sedimentary
- 31 archives from the western and northern Arabian Sea, which are currently under the influence of
- 32 monsoon-induced upwelling and the associated development of an oxygen minimum zone. The U_{k}^{K}
- U^{K'}₃₇ and Mg/Ca_{*G.ruber*} SST records revealed an increase of 0.6-3.4°C from the Last Glacial Maximum to the late Holocene with somewhat higher amplitude in the northern part of the
- Arabian Sea than compared to the western part. In contrast, the LDI SSTs did not reveal major
- changes during the last glacial-interglacial transition which was followed by a decreasing trend
- during the Holocene. The LGM vs the Holocene LDI SSTs ranged between -0.2 and -2.7° C.
- Particularly at one record, offshore Oman, the SST decrease from during the Holocene was high
- in amplitude, suggesting a potential cold bias, possibly related to changes in upwelling intensity
- 40 during the Holocene. This indicates that care has to be taken when applying the LDI for annual
- 41 mean SST reconstruction in upwelling regions.

43 **1 Introduction**

Reconstructing past ocean temperature is essential for understanding past climate change, 44 its drivers and responsible mechanisms. Several proxies were established over the past decades 45 46 in order to reconstruct sea surface temperature (SST) and changes therein. Planktonic foraminiferal assemblages (by transfer function; (Imbrie and Kipp, 1971; Pflaumann et al., 47 1996), stable oxygen isotopes (δ^{18} O) (Erez and Luz, 1983; Urey et al., 1954) and Mg/Ca ratios of 48 planktonic foraminifera species (Elderfield and Ganssen, 2000; Nürnberg et al., 1996) and 49 organic proxies, such as the $U^{K'}_{37}$ index (Brassell et al., 1986; Prahl and Wakeham, 1987) based 50 on the long chain alkenones synthesized by haptophyte algae, have been widely applied as paleo-51 thermometers. However, discrepancies between various SST proxy records as well as with SST 52 reconstructions based on climate model simulations have been observed. This is particularly the 53 case concerning the reconstructed Last Glacial Maximum (LGM) SSTs reported in the tropical 54 55 oceans and the upwelling regions where proxy records and models show disagreement with each other as well as with global estimates (e.g., Kucera et al., 2005; Mix et al., 2001; Shakun et al., 56 2012; Waelbroeck et al., 2009). Accordingly, there is a need for an increased fundamental 57 understanding of the processes that control the imprint of temperature on these proxies as well as 58 59 the processes underlying the observed offsets.

60 In the last decade, the LDI (Long-chain Diol Index; Rampen et al., 2012), which is based on the distribution of certain long-chain diols (LCDs), has been developed. The LDI is based on 61 the relative abundances of 1,13- and 1,15-diols of which culture studies showed that they are 62 produced by freshwater and marine eustigmatophyte algae. However, in the marine realm, it is 63 still uncertain what the source organisms are (e.g., Balzano et al., 2018; Rampen et al., 2014; 64 65 Volkman et al., 1999; Volkman et al., 1992). The number of studies of late Quaternary LDI applications has been rapidly increasing recently (Dauner et al., 2019; de Bar et al., 2018; Häggi 66 et al., 2019; Jonas et al., 2017; Lattaud et al., 2018; Lopes dos Santos et al., 2013; Rodrigo-67 Gámiz et al., 2015; Warnock et al., 2018; Zhu et al., 2018) giving broader information on global 68 69 SST variations in the past. Recently, a more extended calibration for the LDI became available, providing further insight into the main constraints on its applicability (de Bar et al., 2020). 70 Overall, the new calibration dataset was in line with downcore applications but also showed that 71 i) the LDI has limitations in certain regions, such as in the front of river mouths, in low salinity 72 regions, and at high latitudes; ii) the abundance of LCDs other (e.g., 1,12 and 1,14-diols) than 73 those used for the LDI may indicate a cold bias of LDI-derived SST estimations. It was, 74 therefore, suggested to use other LCD-based indices (e.g., diol upwelling index (DI) and the 75 relative abundance of C_{28} 1,12-diol (FC₂₈ 1,12-diol)) prior to LDI applications to constrain 76 potential biases (de Bar et al., 2020). However, many uncertainties with respect to the application 77 78 of the LDI still remain, such as those related to changing nutrient regimes, seasonality, and other potential changes in the water column (e.g., mixed layer depth, oxygenation). Moreover, SST 79 reconstructions from (sub)tropical upwelling regions indicated discrepancies and uncertainties 80

81 between proxies as well as modelling approaches (e.g., Otto-Bliesner et al., 2009). Multi-proxy

approaches can, therefore, be helpful to constrain these uncertainties (Kucera et al., 2005; Mix et
 al., 2001; Waelbroeck et al., 2009) as well as to better our understanding of past climate in

84 tropical upwelling regions.

Here, for the first time, we applied the LDI to generate four sedimentary records from 85 different locations in the Arabian Sea focusing on the last glacial-interglacial period. The 86 Arabian Sea is characterised by strong upwelling conditions dependent on monsoon activity, 87 88 particularly in the west, with relatively warm surface waters during the year (24-27°C Arabian Sea (Locarnini et al., 2013)). The Arabian Sea has been the focus of studies on past SST 89 reconstructions for more than two decades (e.g., Böll et al., 2015; Doose-Rolinski et al., 2001; 90 Emeis et al., 1995; Gaye et al., 2018; Huguet et al., 2006; Ivanochko et al., 2005; Rostek et al., 91 1997; Schulz et al., 1998; Sonzogni et al., 1998). These studies have revealed contrasting trends 92 and magnitudes of SST changes as reconstructed by various proxies as well as simulated using 93 state-of-the-art climate models, particularly concerning the last glacial-interglacial transition. 94 Application of the foraminifera transfer function suggested that the western Arabian Sea 95 96 experienced almost no cooling during the LGM (CLIMAP Project Members, 1988), whereas the alkenone paleothermometer indicated 1-4°C warming between LGM and the late Holocene 97 (Sonzogni et al., 1998). Moreover, modeling approaches reported a variable LGM SST range (1-98 3°C cooler compared to modern-day) for the Arabian Sea (Mix et al., 2001; Otto-Bliesner et al., 99 2009; Waelbroeck et al., 2009). The disagreement between proxy-based estimations have been 100 101 related to organisms' habitats as well as to regional environmental changes (e.g., Dahl and Opp, 2006; Rosell-Melé et al., 2004; Sonzogni et al., 1998) and has been recognized as a common 102 issue in the SST reconstruction of the LGM-Holocene warming in tropical regions (e.g., 103 Waelbroeck et al., 2009). In this study, our aim is to test the applicability of the LDI using four 104 105 sedimentary records recovered from the western and northern Arabian Sea by comparing the obtained reconstructed SST records with other SST proxy estimates from the same records and 106 evaluate the potential application of the LDI in a tropical upwelling region. 107

108 2 Research Setting

In the Arabian Sea, the seasonal cycle is regulated by the Indian monsoon, which is 109 driven by the pressure gradient between the Tibet Plateau and the South Indian Ocean (Rixen et 110 al., 2000; Webster et al., 1998; Wyrtki, 1973). Low temperatures over the Tibetan Plateau and 111 the Himalayas in boreal winter (January – March) causes a high-pressure system over Central 112 Asia and hence a strong pressure gradient towards the low-pressure cell located in the Indian 113 Ocean. During this period, dry and cold northeasterly winds prevail over the Arabian Sea, 114 resulting in cooler surface waters (Webster et al., 1998), particularly in the north of the Arabian 115 Sea (Figure 1a). During boreal summer (July – September), a strong pressure gradient between 116 the Indian-Tibetan low-pressure cell and a high-pressure belt over the Southern Ocean results in 117 powerful southwesterly winds. During this southwest (SW) monsoon period, the Intertropical 118 Convergence Zone (ITCZ) is positioned in the north (Figure 1b). As a result of these strong, 119 warm and humid SW winds, upwelling of nutrient-rich waters occurs along the margin of Oman 120

to Somalia, leading to lower SSTs (24-25°C) in the western Arabian Sea in comparison with the

- rest of the region and annual mean SST (e.g., (Haake et al., 1993; Locarnini et al., 2013;
- 123 Wakeham et al., 2002). During the NE monsoon the upwelling is surprised and waters above the
- thermocline are convectively mixed until the top of the oxygen minimum zone (Wakeham et al.,
- 125 2002), as northernmost Arabian Sea exhibits 3-4°C cooling in the surface waters (Dahl and
- 126 Oppo, 2006).

127 The Arabian Sea is one of the most productive open marine systems in the world today (Qasim, 1982; Smith et al., 1998). Whilst primary productivity has its annual maximum during 128 the SW monsoon, particularly in the west due to enhanced upwelling, it is substantially less 129 during the NE monsoon (Haake et al., 1993; Honjo et al., 1999; Wakeham et al., 2002). The 130 combination of high productivity, subsequent mineralization of organic matter as it settles 131 through the water column, and consumed dissolved oxygen together with sluggish ventilation of 132 intermediate waters in the Arabian Sea results in one of the strongest OMZs in the world (e.g., 133 (Helly and Levin, 2004; Paulmier and Ruiz-Pino, 2009; Wyrtki, 1971). The OMZ, defined as 134 135 waters with oxygen concentrations <0.5 ml/l ($\sim 22 \mu$ M), is located in the Arabian Sea at water depths of ca. 150-1200 m (Figure 1c) (Acharya and Panigrahi, 2016; Helly and Levin, 2004; 136 Olson et al., 1993; Sarma, 2002; Wyrtki, 1973). Despite the higher primary productivity and 137 organic matter export to the deep sea in the western part of the region, the OMZ is much more 138 pronounced in the northeast east (Acharya and Panigrahi, 2016; Naqvi, 1991; Rixen et al., 2014). 139 This is mainly caused by the prevailing subsurface currents and intermediate water masses in the 140 region, which is strongly influenced by the lack of an opening to the north. Ventilation of OMZ 141 waters is facilitated by three water masses. Firstly, high salinity Persian Gulf Water (PGW) in 142 the north flowing south and eastwards (Prasad et al., 2001), secondly, less saline but denser Red 143 144 Sea Water (RSW) flowing along the Oman coast (Shankar et al., 2005) and, thirdly, oxygenated intermediate depth Indian Central Water (ICW) entering the Arabian Sea from the south. The 145 ICW is initially rich in oxygen but by the time it reaches the Arabian Sea, it is oxygen depleted 146 and nutrient-rich (Olson et al., 1993). Recently it was shown that the influence of ICW in the 147 148 region is observed predominantly during the SW Monsoon (Schmidt et al., 2020). The intense OMZ causes denitrification within the water column (Wyrtki, 1973) with strongest rates 149 observed in the northeast - east Arabian Sea (Gaye-Haake et al., 2005), where the maximum 150 expansion of the OMZ is observed (Figure 1c). 151

152 Sedimentary archives from the Arabian Sea suggest a teleconnection between the Indian

monsoon and Northern Hemisphere (NH) climate variability (e.g., Böning and Bard, 2009;

154 Clemens and Prell, 2003; Deplazes et al., 2013; Deplazes et al., 2014; Reichart et al., 1998;

- Reichart et al., 2002; Schulte and Müller, 2001; Schulz et al., 1998; Sirocko et al., 1996).
- 156 Interstadials are generally characterized by an intensified Arabian Sea OMZ, while during
- 157 stadials the strength of the OMZ is substantially reduced (Altabet et al., 2002; Gaye et al., 2018;
- 158 Pichevin et al., 2007; Reichart et al., 1998; Schulz et al., 1998). Meanwhile, proxy evidence has
- suggested contrasting differences in the west and east of Arabian Sea in terms of upwelling
- 160 intensity and surface water productivity (e.g., Emeis et al., 1995; Schulte et al., 1999). Moreover,

161 with the onset of the last deglaciation with interruptions during the cold periods, stronger SW

162 Monsoon, intensified upwelling and enhanced productivity were reported in the records from the

western Arabian Sea (Gaye et al., 2018; Marcantonio et al., 2001; Rampen et al., 2008; Singh et al., 2011; Siraelya et al., 1006)

164 al., 2011; Sirocko et al., 1996).

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Figure 1. Maps of the Arabian Sea with sediment core locations showing a) SST during Jan – Mar (NE Monsoon) and b) SST during Jul – Sep (SW Monsoon). c) A cross section of dissolved oxygen concentrations in the water column along the transect indicated by red box in b. Dashed lines indicate the ITCZ position and arrows show the wind direction. Data was obtained from the World Ocean Atlas (Garcia et al., 2013; Locarnini et al., 2013) and the figure was prepared using ODV (Schlitzer, 2011).

193**3** Materials and Methods

194 3.1 Sediment cores and age models

Four sediment cores were studied. They were collected from different areas during different expeditions; SO42-74KL (in 1986; Kasten core) and NIOP905 (in 1993; piston core) from western Arabian Sea, Oman - Somali upwelling zone; SO130-289KL (in 1998; Kasten core) and PASOM3 (in 2009; gravity core) from northern Arabian Sea within the OMZ from offshore Pakistan and the Murray Ridge, respectively (Figure 1, Table 1). The age models of cores NIOP905 and 74KL were published by Huguet et al. (2006) and of core 289KL by 201 Deplazes et al. (2013). We tuned the age model of core 74KL by fine-tuning of total organic

- carbon (TOC) to reflectance (L*) profile of core 289KL (Supp. Info. Figure S1). The age model
- of core PASOM3 is primarily based on fine-tuning of L* data to the NGRIP (Andersen et al.,
- 204 2004) and to L* profile of core 289KL (Supp. Info. Text S1). In addition, three AMS
- radiocarbon ages, based on mixed planktonic foraminifera species (predominantly that belong to genus *Orbulina*) were determined (Beta Analytic Inc., USA). Calibrated ages, (cal kyr BP; 0 BP
- equivalent to 1950 AD), were calculated using the conventional radiocarbon ages and the
- Marine 13 calibration curve (Reimer et al., 2013). A regional reservoir age of 232 ± 26 years
- were applied according to the CALIB 7.1 database (Stuiver et al., 2017). The final correlation
- was based on a total of 41 tie points and the age model was constructed by linear interpolation
- 211 between these control points. The abundance of the deep-dwelling planktonic foraminifera
- 212 Globorotalia truncatulinoides and G. crassaformis were used as an independent verification of
- the age model, and was based on the existence of so-called *Globorotalia* events (Reichart et al.,
- 214 1998).

Table 1. Metadata of the sediment cores and references. ^{*}age model is tuned (see Supp. Info.

Figure S1). n.a.: not available

Core Name	Core location		Water Depth	Metadata				
	Lat (N)	Long (E)	(m)	Age Model	$U^{K'}_{37}$	$\delta^{18}O_{\textit{G.ruber}}$	Mg/Ca _{G.ruber}	LDI
NIOP905	10°47.0′	51°56.0′	1586	Huguet et al. (2006)	Huguet et al. (2006)	Sirocko et al. (1993)	Anand et al. (2008)	this study
SO42-74KL	14°19.2'	57°20.8′	3212	Huguet et al. (2006) [*]	Huguet et al. (2006)	Jung et al. (2001)	Dahl and Oppo (2006)	this study
PASOM3	22°19.9′	63°36.0′	1172	this study	this study	this study	this study	this study
SO130-289KL	23°07.3'	66°29.8′	571	Deplazes et al. (2013)	n.a.	n.a.	n.a.	this study

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3.2 Globigerinoides ruber δ^{18} O and Mg/Ca analysis of core PASOM3

For elemental and isotopic analysis, 50 specimens of G. ruber were hand-picked per 219 sample from the 250-355 µm fraction. Picked material was later crushed and divided into two 220 parts; one third was saved for stable isotope analysis and the remaining part was used for 221 analyses of the elemental composition. The crushed foraminiferal specimens were cleaned 222 following the Barker protocol (Barker et al., 2003) without the reductive cleaning step. This 223 cleaning protocol includes removing clay particles using ultrapure water, ultrasonication and 224 methanol and removal of organic particles using an alkali buffered 1% H₂O₂ solution with 225 NH₄OH. Stable oxygen (δ^{18} O) isotope analyses were performed using an automated carbonate 226 device (Kiel IV, Thermo) connected to a Thermo Finnigan MAT 253 Dual Inlet IRMS. Values 227 are reported in permille relative to the Peedee belemnite (PDB) standard in δ notation. For 228 calibration we used NBS19 (limestone) and in-house standard for drift detection (NFHS-1; 229 (Mezger et al., 2016), showing a precision better than 0.1‰ for δ^{18} O. Measurements for 230

foraminiferal Mg/Ca composition were performed on an Element 2-ICPMS using low mass

- resolution. Samples were measured against four ratio calibration standards with a similar matrix
- and with a drift standard (NFHS-1) measured on every third sample. The monitor standards JCt-
- 1 and NFHS-1 were measured for quality control (Mezger et al., 2016; Okai et al., 2002).
- 235 3.3 Long Chain Diol and Alkenone analysis

For LCD analysis, we extracted sediments obtained from cores PASOM3 and 289KL. 236 For cores NIOP905 and 74KL we analyzed the polar fractions previously obtained by Huguet et 237 al. (2006). For PASOM3 and 289KL freeze-dried and homogenized sediments (9 to 18 g from 238 PASOM3 and 0.75 to 11 g from 289KL) were extracted using an Accelerated Solvent Extractor 239 350 (ASE 350, DIONEX; 100°C and 7.6 × 106 Pa) and subsequently separated over an activated 240 Al_2O_3 column into apolar, ketone and polar fractions. The solvents hexane:DCM 9:1 (v:v), 241 hexane:DCM 1:1 (v:v) and DCM:MeOH 1:1 (v:v) were used to elute the apolar, ketone and polar 242 fractions, respectively. Ketone fractions were used for alkenone analysis of PASOM3 that were 243 244 conducted on a Hewlett Packard 6890 gas chromatograph (GC) equipped with a flame ionization detector (FID) and helium as the carrier gas, with an autosampler and an injection volume of 1 245 μ L after re-dissolving the ketone fractions in 100 to 800 μ L ethyl acetate. Separation was 246 achieved on a fused silica column CP Sil-5 (50 m x 0.32 mm; film thickness 0.12µm). Initial 247 oven temperature of 70°C increased with 20°C per min to 200°C and subsequently with 3°C per 248 min to 320° C, a temperature which was held for 25 min. Peak areas of C_{37'2} and C_{37'3} alkenones 249 were determined by integration. The $U^{K'_{37}}$ values were calculated using the calibration of Müller 250 et al. (1998) and after the equation described by Prahl and Wakeham (1987): 251

252 with
$$U^{K'}_{37} = [C_{37:2}] / ([C_{37:2}] + [C_{37:3}])$$

For LCD analysis polar fractions were silvlated by the addition of 15 μ L pyridine and 15 253 µL BSTFA, followed by heating at 60 °C for 30 min. The analysis were carried out using an 254 Agilent 7990B GC coupled to an Agilent 5977A MS following de Bar et al. (2017). The GC was 255 equipped with an on-column injector and fused silica column (25 m x 0.32 mm) coated with CP 256 Sil-5 (film thickness 0.12 µm). Samples were re-dissolved in 300 - 600 µL ethyl acetate and the 257 injection volume was 1 µL. The oven temperature was 70°C at injection and was programmed to 258 increase to 130°C by 20°C/min, and subsequently to 320°C by 4°C /min, which was held for 25 259 min. Helium flow was held constant at 2 ml/min. The MS operated with an ionization energy of 260 70 eV and the temperature of the ion source was 250°C and of the interface was 320°C. The total 261 runtime was 75.5 min. Peak areas were defined using SIM of characteristic m/z ratios of LCD 262 ions: 299.3 (C₂₆ 1,12-diol and C₂₈ 1,14-diol), 313.3 (C₂₈ 1,13-diol and C₃₀ 1,15-diol), 327.3 (C₂₈ 263 1,12-diol and C₃₀ 1,14-diol) and 341.3 (C₃₀ 1,13-diol) (Rampen et al., 2012; Versteegh et al., 264 1997). Full-scan mode allowed for identity confirmation, since the different LCDs show 265 characteristic spectra of fragmentation (Versteegh et al., 1997). The LDI SST were calculated 266 following the calibration of de Bar et al. (2020), based on globally distributed marine surface 267 sediments and covers a temperature range from -1.8 to 30.3°C with a calibration error of 3°C 268

(1)

269 with $LDI = [C_{30} 1, 15 \text{-diol}] / ([C_{28} 1, 13 \text{-diol}] + [C_{30} 1, 13 \text{-diol}] + [C_{30} 1, 15 \text{-diol}])$ (2)

After calculation of the fractional abundances of the C_{28} and C_{30} 1,14-diols, C_{30} 1,15-diol and C_{28}

and C_{30} 1,13-diols, the Diol Index (DI) was calculated following Rampen et al. (2008)

272 with $DI = ([C_{28} 1, 14\text{-diol}] + [C_{30} 1, 14\text{-diol}]) / [C_{30} 1, 15\text{-diol}]$ (3)

273 The distribution of LCDs in core NIOP905 has been reported before (Rampen et al.,

274 2008) but LCDs were re-analyzed here using an improved GC-MS method (de Bar et al., 2017).

Comparisons showed that our results were similar with the previously published values (Supp.

Info. Figure S2).

277 **4 Results**

We compiled and generated SST records of cores 74KL and NIOP905 for 0-25 kyr and 278 of cores PASOM3 and 289KL 0-35 kyr (Table 1). Except for core PASOM3, we compiled data 279 from previous studies concerning $U^{K'_{37}}$, and the $\delta^{18}O$ and Mg/Ca ratio of the planktonic 280 foraminiferal species *Globigerinoides ruber*. We applied the same calibrations for all proxies 281 and, therefore, re-calculated the $U^{K'}_{37}$ and Mg/Ca_{G ruber}-derived SSTs (after Müller et al. (1998) 282 and Anand et al. (2003), respectively) for all records. We generated LDI-derived SST records for 283 all cores as well those obtained by $U^{K'_{37}}$, and $\delta^{18}O$ and Mg/Ca ratio data of G. ruber from the 284 PASOM3 core. Based on these records, we estimated average SSTs for the Last Glacial 285 286 Maximum (LGM; 19 - 22 kyr) and the late Holocene (0 - 5 kyr for NIOP905 and 74KL; 3 - 5kyr for PASOM3 and 2 – 5 kyr for 289KL) and calculated an approximate SST change Δ SST 287 (LGM-late Holocene) (Table 2). The downcore Mg/Ca ratio based SST estimations of core 74KL 288 is limited to four discrete specific time intervals (Dahl and Oppo, 2006). 289

290 The PASOM3 *G. ruber* oxygen isotopic record ($\delta^{18}O_{G.ruber}$) showed changes coinciding

with the glacial-interglacial transition with positive values during the glacial and negative values

during the Holocene (Figure 2a). The Mg/Ca_{G,ruber} SST in PASOM3 showed fluctuations</sub>

between 22°C and 27°C, showing substantial differences within relatively short time intervals,

294 particularly during the Glacial, while the Holocene SSTs were relatively stable at this core

location. The LGM – late Holocene difference (Δ SST) was 1.2°C at PASOM3 core (Table 2).



Figure 2. SST proxy records (b-d) for four Arabian Sea sediment cores together with oxygen 298 isotope records of G. ruber ($\delta^{18}O_{G,ruber}$) and, for reference, the Greenland ice core (GRIP; $\delta^{18}O$) 299 (a); see Table 1). Thick lines show the 5-point moving average. The late Holocene (0-5 kyr BP) 300 of core PASOM3 is not well represented due to low sedimentation rates during this period and 301 loss of the core top (first available data point is, therefore, from 3 kyr BP). The present-day mean 302 annual SST in the Arabian Sea is indicated on each scale bar. Specific periods are indicated by 303 grey shaded bars: i.e. Younger Dryas (YD), Heinrich Stadial 1 (H1) and LGM: Last Glacial 304 Maximum

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The $U_{37}^{K'}$ SST estimations of PASOM3 showed substantial fluctuations throughout the record. The SSTs during 29-35 kyr BP period were slightly lower than present day whereas during the following period SSTs were variable with minimum temperatures of 20.4°C during the LGM. The maximum estimated SST was 26.8°C during the Holocene (Figure 2c). The LGMlate Holocene $U_{37}^{K'}$ SST difference was 3.4°C (Table 2). This SST record showed continuous warming during the deglaciation and Holocene with interruptions during the Heinrich Stadial 1 (H1) and the Younger Dryas (YD; Figure 2c). The $U_{37}^{K'}$ -derived SST for the core top (ca. 3.1

314 kyr BP) was 25.8°C.

The LDI SST records of the northern cores, PASOM3 and 289KL, did not reveal major 315 fluctuations during the last 35 kyr, with minimum temperatures of 24.4°C and 24.8°C and 316 maximum temperatures of 26.3°C and 26.6°C, respectively (Figure 2d). The LDI SST records 317 from the cores in the western Arabian Sea, NIOP905 and 74KL, covering the last 25 kyr 318 319 indicated fluctuating SSTs from the LGM (19 - 22 kyr BP) and onwards with minimum SSTs of 25°C and 21°C, and maximum SSTs of 27°C and 26°C, respectively. Overall, all LDI-derived 320 SST records of NIOP905, 289KL and PASOM3 showed a small decreasing trend from H1 to the 321 late Holocene, with a major change observed at core 74KL. The difference in LDI SSTs from the 322 323 LGM to the late Holocene (0-5 cal kyr BP) was observed to be -1.6°C at PASOM3, -0.2°C at 289KL, -0.8°C at NIOP905 and -2.7°C at 74KL, respectively (Table 2). All cores revealed 324 higher reconstructed SSTs during the H1 and YD with the largest changes observed at 74KL. 325 Core top (0 kyr BP for NIOP905 and 74KL) LDI-derived SSTs in the western cores were 25.4°C 326 and 22.1°C, respectively, whereas those in the northern cores (ca. 3.1 kyr BP for PASOM3 and 327 ca. 2.2 kyr BP for 289KL) were 24.7°C and 26.1°C, respectively. 328

Table 2. Modern annual mean SST observed at the site location (Locarnini et al., 2013), SST ranges and SST changes (Δ SST) between the Last Glacial Maximum (19 – 22 kyr) and late Holocene (0 – 5 kyr; ca. 3 – 5 kyr for PASOM3, and 2 – 5 kyr for 289KL) calculated for each core for each proxy. *The values of Δ SST from the Mg/Ca ratio for core 74KL was calculated for time intervals of 24.3-24.5 kyr and 0.5-1.5 kyr after Dahl and Oppo (2006) considering the core depths reported in their study and the new age model reported in this study. Continuous downcore record of 74KL is not available. n.a.: not available.

	Annual mean SST	U ^{K′} ₃₇ (°C)		LDI (°C)		Mg/Ca _{G.ruber} (°C)	
Core Name	modern	Range	ΔSST	Range	ΔSST	Range	ΔSST
NIOP905	26.2	24.8 - 26.3	0.6	25.0 - 26.5	-0.5	22.7 - 25.6	1.7
SO42-74KL	26.5	24.8 - 27.4	2.0	21.1 - 26.0	-2.7	21.4 - 24.4	2.5*
PASOM3	26.7	20.4 - 26.8	3.4	24.4 - 26.3	-1.6	22.3 - 26.8	1.2
SO130-289KL	26.9	n.a.	n.a.	24.8 - 26.6	-0.2	n.a.	n.a.

5 Discussion

339

5.1 Arabian Sea temperature records using established proxies.

Our newly generated PASOM3 $\delta^{18}O_{G,ruber}$ record is similar to other $\delta^{18}O_{G,ruber}$ Arabian 340 Sea records and they all show agreement with the Greenland ice core δ^{18} O trend (Johnsen et al., 341 2001), indicating that these records reflect global climate dynamics (Figure 2). The Mg/Ca ratio-342 derived SST record from the PASOM3 core shows a larger variability than that of NIOP905 but 343 shows a similar trend from LGM to late Holocene with an approximately $1-2^{\circ}C$ warming (Table 344 2). This is somewhat smaller than the 2.5°C warming reported for the 74Kl record (Dahl and 345 Oppo, 2006; Table 2) but it should be noted that that was only determined by a single data point 346 in the LGM. During the Holocene Mg/Ca ratio-derived SSTs of NIOP905 and PASOM3 follow 347 a relatively stable trend with only slight cooling during the late Holocene. Considering the 348 present day mean annual SST of the Arabian Sea (26-27°C; Locarnini et al., 2013) and the 349 calibration error of Mg/Ca_{G.ruber} (ca. 1.5°C; Anand et al., 2003) Mg/Ca ratio-derived SST 350 estimates of 24-25 °C from core tops of the western cores (NIOP905 and 74KL) are somewhat 351 352 low. Based on observations on the modern specimens of G. ruber and the Mg/Ca based - SST calibrations in the Arabian Sea (Conan and Brummer, 2000; Curry et al., 1992) SST estimates 353 were observed to be 1.7 ± 0.8 °C lower than annual mean SST (Peeters et al., 2002). This is 354 potentially due to the present-day habitat of G. ruber in the Arabian Sea, where this species was 355 observed living year around, calcifying in the uppermost part of the water column and with 356 blooms during both monsoon seasons in relatively cold surface waters (Curry et al., 1992; Dahl 357 and Oppo, 2006). 358

The newly obtained $U_{37}^{K'}$ -derived SST record of PASOM3 shows a high variability but 359 the 5-points running mean shows a similar trend as other previously published $U^{K'}_{37}$ -derived SST 360 records and follows the $\delta^{18}O_{G.ruber}$ as well as the global climate trend with lower SST values 361 during the LGM and increasing towards the Holocene (Figure 2). However, $U_{37}^{K'}$ -derived SSTs 362 for the LGM were substantially lower in our PASOM3 record from the Northern Arabian Sea 363 compared to other two U^{K'}₃₇-derived SST records from the western part and showed a much 364 larger LGM to Holocene change (i.e. 3.4°C; Table 2). This is in accordance with previous 365 observations based on $U_{37}^{K_{37}}$ SSTs from the region, suggesting such a north – west difference in 366 deglacial warming (e.g., Böll et al., 2015). This regional difference was interpreted as a result of 367 reduced impact of NE monsoon related cooling and/or strengthening SW monsoon induced 368 upwelling in the region after the Glacial (Dahl and Oppo, 2006; Emeis et al., 1995; Gaye et al., 369 2018; Rostek et al., 1997). With the onset of the deglaciation, the SW monsoon and upwelling in 370 371 the western Arabian Sea intensified and resulted in cooler SSTs in comparison with the northern Arabian Sea (e.g., Anand et al., 2008; Böll et al., 2015; Gaye et al., 2018). However, the U_{37}^{K} 372 derived SST record of NIOP905 shows even cooler surface water conditions during the 373 Holocene in comparison with those of the other western Arabian Sea core 74KL (Figure 2c). 374 375 This is potentially due to a local feature and circulation pattern observed in the region (Figure 1b; e.g., Sonzogni et al., 1998). Right above the core site, the so-called *Great Whirl* develops and remains stationary during the SW Monsoon, which has a major effect on the local SST and surface productivity (Fischer et al., 1996; Koning et al., 2001; Peeters et al., 1999). This local feature is potentially reflected in $U_{37}^{K'}$ SSTs from core NIOP905, particularly during the Holocene part of the record.

Overall, the SST records based on these proxies reveal relatively small SST change (1-381 2° C) from LGM to the Holocene, with the exception of PASOM3 (3.4°C). Besides the above-382 383 discussed reasons for specific proxy and core site, this is a well-known observation for SST reconstructions in the tropical regions (e.g., Mix et al., 2001; CLIMAP Project Members, 1981; 384 Rosell-Melé et al., 2004; Waelbroeck et al., 2009). Basin-wide proxy applications (Dahl and 385 Oppo, 2006; Rosell-Melé et al., 2004; Sonzogni et al., 1998) as well as model simulations (Mix 386 et al., 2001; Otto-Bliesner et al., 2009; Waelbroeck et al., 2009) showed that the Arabian Sea 387 SST warming from the LGM to the late Holocene ranged between 1-3.5°C, with higher 388 amplitude in the north. The new Mg/Ca ratio and $U^{K'}_{37}$ results from core PASOM3 are also in 389 line with previous observations and model simulations. 390

391 5.2 Arabian Sea temperature records using the LDI.

The overall trend observed for the LDI-derived SST records are consistent in three of the 392 four records (i.e. excepting the 75KL record) but surprisingly only reveal minor changes from 393 glacial to the Holocene (Figure 2d; Table 2) and a slight cooling trend during the Holocene 394 (except for the 289KL record). The small Holocene to LGM SST change and cooling during the 395 Holocene in the LDI records show similarities to the CLIMAP Project data based on planktonic 396 foraminifera SST approaches (modern analogue technique and transfer function), which revealed 397 relatively low LGM-Holocene warming or even cooling at sites in the Arabian Sea between 10-398 20°N interval (CLIMAP Project, 1981; Sonzogni et al., 1998). The LDI record of core 74KL is 399 clearly an exception to the other three (Figure 2d) in that it shows 1.5°C lower glacial SSTs prior 400 to H1 as well as a strong continuous decline in SST during the Holocene, arriving at SSTs of ca. 401 22°C in the upper Holocene. This clearly contrasts most other proxy records discussed above, 402 403 which show some degree of LGM to Holocene warming and is incompatible with the global climate trend (Figure 2; Table 2). Interestingly, SSTs estimated from planktonic foraminifera-404 based transfer functions for core 74KL (Schulz, 1995a, 1995b) also show decreasing values for 405 the Holocene and suggest cooler summer (SW monsoon) SSTs after the Heinrich Stadial 1 (H1) 406 and, in this way, are partly in agreement with the LDI-derived SST trend in the Holocene (Figure 407 3a). The decreasing trend of LDI SST observed in most of our records during the Holocene may 408 be a direct effect on SST due to intensified upwelling (e.g., Gaye et al., 2018; Marcantonio et al., 409 2001; Rampen et al., 2008; Sirocko et al., 1996) leading to a summer monsoon (i.e. cold) bias in 410 LDI SSTs. Therefore, the LDI is potentially reflecting SW summer monsoon SSTs rather than 411 412 annual mean temperatures in the Arabian Sea, particularly after the H1 event. Indeed, the deglacial decrease in LDI-based SSTs is lowest at core site 289KL (-0.2°C; Table 2), which is 413

also the furthest from the modern upwelling cell (Figure 1). Nevertheless, we cannot exclude thatother factors not related to SST have impacted the LDI.



416

Figure 3. Compilation of various records from core 74KL; a) SST reconstructions based on LDI
and planktonic foraminifera transfer functions for different seasons (light blue: winter, NE
monsoon; brown: summer, SW monsoon; (Schulz, 1995b), b) Diol upwelling index (DI) and C₂₈
1,12-diol factor showing potential influence of diatom productivity on the LDI. Largest
convergence between the LDI and the planktonic foraminifera transfer function SSTs coincide
with periods characterized by reduced upwelling. LDI SSTs show continuous decrease where DI
and 1,12-diol increase.

Sedimentary oxic degradation has been shown to impact LDI values in Arabian Sea 424 surface sediments due to different degradation rates of 1,13- and 1,15-diols leading to ca. 1.5-425 2.5°C cooler LDI-reconstructed SSTs in sediments deposited below the OMZ (Rodrigo-Gámiz 426 et al., 2016). Enhanced bottom water ventilation and a weaker OMZ has been inferred for cold 427 periods (e.g., Böning and Bard, 2009; Reichart et al., 1997; Reichart et al., 1998; Schulte et al., 428 1999), presumably leading to enhanced oxygen exposure times (OETs). This may have led to 429 lower LDI SST estimates during these colder times for the cores obtained from stations located 430 431 within the present-day OMZ (NIOP905, PASOM3 and 289KL; Figure 1). In contrast, our results actually indicate relatively warmer conditions, particularly during YD and H1, and cooler SSTs 432

during the Holocene (Figure 2). This suggests that the oxic degradation of the LCDs likely did
not significantly affect these LDI records. Being by far the deepest core site, 74KL has always
been below the OMZ (Figure 1) and the sediments deposited probably have been impacted by
much longer oxygen exposure times (OET) than the other sedimentary records studied. These
enhanced OET may have led to an overall cold bias compared to other cores, especially during
the Holocene when other sites may have been within the OMZ and therefore experienced lower
OET (Figure 2d).

440 A cold bias in SSTs reconstructed with the LDI could also occur when groups of organisms, such as *Proboscia* diatoms, produce, in addition to their characteristic 1,14-diols, also 441 1,13- and 1,15-diols as has been observed around Iceland (Rodrigo-Gámiz et al., 2015). de Bar et 442 al. (2020) reported that such a bias in LDI could be assessed by the relative abundance of 1,12-443 diols, produced by certain *Proboscia* diatoms, expressed in the FC_{28} 1,12. However, in all of our 444 records, FC_{28} 1,12 remained below the threshold (<0.1), although Holocene values at core 74KL 445 were getting close to this value (Figure 3). Nevertheless, the Diol Index (DI), a proxy for 446 upwelling intensity and enhanced nutrient concentrations, does show increasing values in all 447 sites after the last deglaciation (Figures 3 and 4), as previously reported for core NIOP905 448 449 (Rampen et al., 2008), suggesting an overall increase in *Proboscia* diatom contributions However, except for core 74KL, the LDI SST estimates during the Holocene fit well with other 450 temperature proxies as well as modern day SST (Figure 2 and Figure 3), despite having relatively 451 high DI values. Hence, these changes in upwelling and concomitantly increasing nutrient 452 availability cannot explain the relatively high LDI-reconstructed SSTs during the glacial. 453

As discussed, LDI-reconstructed SSTs for core 74KL remain very unusual compared to 454 the other cores as they show the highest SSTs during cold intervals, the YD and H1, and a 455 continuously decreasing trend during the Holocene with the largest offset from the LGM to the 456 Holocene (Δ SST= -2.7°C; Table 2). Core 74KL was collected in an area where the SW monsoon 457 and related upwelling are much more pronounced today in comparison to the western part of the 458 Arabian Sea. Indeed, we observe strong correlation between the DI and LDI (r2=0.72) at core 459 74KL. Moreover, the OMZ is much stronger within the overlying waters of the 74KL core site, 460 in comparison to the other western Arabian Sea core NIOP905 (Figure 1; Garcia et al., 2013). 461 These local differences suggest that the extent of the OMZ in combination with enhanced 462 upwelling might have a pronounced impact on the LDI at the 74KL location. 463



Figure 4: Records for the Diol upwelling index (DI) for the four stations considered in thisstudy.

Finally, the strong enhanced upwelling and expanded OMZ at 74KL may also impact the 467 diol producers, which likely live in the photic zone (Rampen et al., 2012). Studies show that with 468 enhanced upwelling, surface productivity and an extended OMZ, there is enhanced nitrogen loss 469 (denitrification) in subsurface waters (Galloway et al., 2004). As a result of intensified 470 upwelling, oxygen and nitrate limited (denitrified) waters are brought to surface waters resulting 471 in enhanced N₂-fixation (Bange et al., 2005; Deutsch et al., 2007; White et al., 2013). This will 472 cause changes within the plankton community with a relative increase being expected in the 473 abundance of N₂ fixing organisms such as cyanobacteria or cyanobacterial symbionts of diatoms 474 (Zehr and Capone, 2020; and the references therein), due to changes in nutrient dynamics in the 475 upwelled waters (such as N:P ratio) (Bange et al., 2005; White et al., 2013). It is however unclear 476 how and what extent this will affect the LCD producers and their diol composition. In an early 477 478 study focusing on Baltic Sea, detection of LCDs during cyanobacterial bloom were reported suggesting some link with enhanced N₂ fixation (Morris and Brassell, 1988), although it is clear 479 that they are not derived from the cyanobacteria as these compounds are not detected in 480 cyanobacterial cultures (e.g., de Leeuw et al., 1992). Further research investigating the link 481 482 between nutrient dynamics and diol production as well as composition of diol producers is needed to clarify this. 483

484

485 **5 Conclusions**

A multi proxy application in series of cores from the western and northeastern part of the Arabian Sea emphasize the importance of application of different proxies and on several records to reconstruct regional climate dynamics. Our results show that LDI is likely to reflect in part summer monsoonal temperatures showing little change in SST from glacial to the Holocene and is not an ideally suited proxy to reconstruct annual mean SST in the Arabian Sea. The index may

- also be potentially biased by upwelling intensity and related nutrient input in regions of strong
- upwelling and extended OMZs. Results from LDI in upwelling regions should therefore be
- 493 interpreted carefully. However, other SST proxies such as $U_{37}^{K'}$ and Mg/Ca_{*G.ruber*} show also
- variable trends though they mostly document a relatively consistent overall SST increase from
- the Last Glacial Maximum (LGM) to the late Holocene of 1-2°C, with a larger amplitude in the
- 496 northern Arabian Sea in comparison with the west.
- 497

498 Acknowledgments, Samples, and Data

- 499 We would like to thank the crew and scientists aboard *R/V Pelagia* during PASOM expedition
- 500 64PE301 and Rick Hennekam for his support with the XRF data analysis. This research has been
- funded by the European Research Council (ERC) under the European Union's Seventh
- 502 Framework Program (FP7/2007-2013) ERC grant agreement [339206] to S.S. S.S and by
- 503 financial support from the Netherlands Earth System Science Centre (NESSC) through a
- gravitation grant from the Dutch Ministry for Education, Culture and Science to GJR, JSSD and
- 505 SS.
- 506 Datasets for this research are available in these in-text data citation references: Schulz, H.(1995):
- 507 <u>https://doi.pangaea.de/10.1594/PANGAEA.134165</u>, Huguet et al., (2006):
- 508 <u>https://doi.org/10.1594/PANGAEA.861247</u> and <u>https://doi.org/10.1594/PANGAEA.861245</u>,
- Dahl and Oppo (2006): <u>https://doi.org/10.1594/PANGAEA.834987</u>. New datasets are included
- in this paper's supplementary information files. They were also recently submitted to the same
- 511 platform (<u>www.pangaea.de</u>) and will be linked to existing datasets once they are publicly
- 512 available.
- 513
- 514

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