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The impact of oxic degradation on long chain alkyl diol distributions in Arabian Sea surface sediments

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Abstract

1

2   Oxygen exposure has a large impact on lipid biomarker preservation in surface

3 sediments and may affect the application of organic proxies used for reconstructing past

4 environmental conditions. To determine its effect on long chain alkyl diol and keto-ol based

5 proxies, the distributions of these lipids was studied in nine surface sediments from the

6 Murray Ridge in the Arabian Sea obtained from varying water depths (900 to 3000 m) but in

7 close lateral proximity and, therefore, likely receiving a similar particle flux. Due to

8 substantial differences in bottom water oxygen concentration (<3 to 77 μmol/L) and

9 sedimentation rate, substantial differences exist in the time the biomarker lipids are exposed to

10 oxygen in the sediment. Long chain alkyl diol and keto-ol concentrations in the surface

11 sediments (0-0.5 cm) decreased progressively with increasing oxygen exposure time,

12 suggesting increased oxic degradation. The 1,15-keto-ol/diol ratio (DOXI) increased slightly

13 with oxygen exposure time as diols had apparently slightly higher degradation rates than keto-

14 ols. The ratio of 1,14- vs. 1,13- or 1,15-diols, used as upwelling proxies, did not show

15 substantial changes. However, the C_{30} 1,15-diol exhibited a slightly higher degradation rate

16 than C_{28} and C_{30} 1,13-diols, and thus the Long chain Diol Index (LDI), used as sea surface

17 temperature proxy, showed a negative correlation with the maximum residence time in the

18 oxic zone of the sediment, resulting in ca. 2-3.5 ºC change, when translated to temperature.

19 The $U^{K'}_{37}$ index did not show significant changes with increasing oxygen exposure. This

20 suggests that oxic degradation may affect temperature reconstructions using the LDI in oxic

21 settings and where oxygen concentrations have varied substantially over time.

22

23 **Keywords:** long chain alkyl diols, keto-ols, LDI, $U^{K'}_{37}$, upwelling indices, DOXI, oxygen

24 minimum zone, Arabian Sea, surface sediments, oxic degradation.

25

1. Introduction

Long chain alkyl diols and keto-ols are structurally related groups of lipids occurring widespread in Quaternary marine and lake sediments (e.g., Versteegh et al., 1997, 2000). These lipids were first discovered in Black Sea sediments by de Leeuw et al. (1981). Commonly occurring long chain alkyl diols found in marine and lake environments are C_{28}-C_{32} 1,13-, 1,14- and 1,15-diols (Versteegh et al., 1997; Rampen et al., 2014a, b). Saturated and mono-unsaturated C_{28} and C_{30} 1,14-diols are produced by *Proboscia* diatoms (Sinninghe Damsté et al., 2003; Rampen et al., 2007) and saturated C_{28}, C_{30} and C_{32} 1,14-diols are synthesized by the marine Dictyochophyte *Apedinella radians* (Rampen et al., 2011). Mono-unsaturated long chain 1,14-alkyl diols have, up to now, only been found in *Proboscia* species, while C_{32} 1,14-diols have only been identified in *Apedinella*. Studies of the descending particle flux in the Arabian Sea confirmed the role of *Proboscia* diatoms as a source for long chain 1,14-alkyl diols in marine sediments, but the importance of *Apedinella* as a source remains uncertain (Rampen et al., 2008, 2011, 2014a). C_{28}-C_{32} long chain 1,13- and 1,15-alkyl diols have been identified in cultures of eustigmatophyte algae (Volkman et al., 1992, 1999; Gelin et al., 1997a; Méjanelle et al., 2003; Shimokwara et al., 2010; Rampen et al., 2014b). However, the role of eustigmatophyte algae as a source in the marine environment is still unclear since there are discrepancies in the long chain alkyl diol composition and distribution between cultures and marine settings (Volkman et al., 1992; Versteegh et al., 1997; Rampen et al., 2012, 2014b).

Different indices based on long chain alkyl diols have been proposed as indicators of upwelling and sea surface temperature (SST) (e.g. Versteegh et al., 1997, 2000; Rampen et al., 2008, 2012; Willmott et al., 2010). The Long chain Diol Index (LDI) is based on the correlation of the fractional abundance of long chain C_{28} 1,13-, C_{30} 1,13- and C_{30} 1,15-alkyl diols with SST (Rampen et al., 2012). Thus far, the LDI has been applied for reconstruction of

51   SST in the mid-latitude regions (Lopes dos Santos et al., 2013; Smith et al., 2013; Rodrigo-

52   Gámiz et al., 2014; Plancq et al., 2015). Upwelling indices are based on the relative

53   abundance of C_{28}-C_{30} 1,14-diols vs. 1,13-diols or C_{30} 1,15-diols (Rampen et al., 2008;

54   Willmott et al., 2010) and have been applied in several oceanic regions, including the Arabian

55   Sea (e.g. Rampen et al., 2008, 2014a; Pancost et al., 2009; Willmott et al., 2010; Lopes dos

56   Santos et al., 2012; Seki et al., 2012). C_{30} and C_{32} keto-ols also occur ubiquitously in marine

57   sediments (e.g., Jiang et al., 1994; Versteegh et al., 1997; Wakeham et al., 2002; Sinninghe

58   Damsté et al., 2003; Rampen et al., 2007; Bogus et al., 2012), and have been identified in a

59   cultured marine eustimatophyte, *Nannochloropsis gaditana,* although in lower amounts than

60   generally found in marine sediments (Méjanelle et al., 2003). Long chain keto-ols have been

61   inferred to be intermediate products of the oxidation of diols and the Diol Oxidation Index

62   (DOXI) has been proposed as an indicator for oxic degradation in the sedimentary record

63   (Ferreira et al., 2001; Versteegh et al., 2010; Bogus et al., 2012). However, the chain length

64   distributions and distributions of positional isomers for long chain alkyl diols and the

65   corresponding keto-ols differ (Versteegh et al., 1997), casting some doubts on the occurrence

66   of this oxidation process. Another suggestion for the origin of keto-ols is that they may be

67   produced by an as yet unknown biological source (Versteegh et al., 1997).

68   Like many other organic proxies, uncertainties remain in the application of long chain

69   alkyl diols as palaeoclimate reconstruction tools. Apart from the fact that the biological source

70   of 1,13- and 1,15-diols in the marine environment is still unknown, a variety of environmental

71   factors other than temperature (e.g. salinity, nutrient availability) could have an impact on

72   these proxies. Importantly, diagenesis can have a substantial effect on the abundance and

73   distributions of biomarker lipids (e.g. Arzayus and Canuel, 2004; Peters et al., 2005 and

74   references cited therein). One important factor affecting lipid distributions and preservation is

75   oxic degradation (e.g., Sun and Wakeham, 1994; Hoefs et al., 1998, 2002; Sinninghe Damsté

76   et al., 2002; Prahl et al., 2003; Rontani et al., 2009, 2013), particularly oxygen exposure time

77   (Hartnett et al., 1998; Hedges et al., 1999). For example, it has been shown that the $U^{K'}_{37}$-SST

78   proxy based on alkenones may be altered after long term exposure to oxygen (Hoefs et al.,

79   1998, 2002; Gong and Hollander, 1999; Prahl et al., 2003; Rontani et al., 2009, 2013). The

80   effect of degradation on long chain alkyl diol distributions, and the proxies based on these

81   components, is, however, still not clear (Ferreira et al., 2001; Versteegh et al., 2010; Bogus et

82   al., 2012).

83   In this study we investigated the impact of oxic degradation on long chain alkyl diol

84   and long chain keto-ol (referred as diols and keto-ols hereafter) concentrations by analyzing

85   nine surface sediments from the Murray Ridge in the Arabian Sea. Previous studies have

86   shown that this submarine high in the northern Arabian Sea provides an excellent location to

87   study the effect of oxygen degradation on lipid distributions (Sinninghe Damsté et al., 2002;

88   Schouten et al., 2012; Lengger et al., 2012, 2014). The Murray Ridge protrudes into one of the

89   largest oxygen minimum zones (OMZ) presently found in the oceans, with molecular oxygen

90   (O_2) concentrations varying from minima of 0.1-1.0 μmol/L to maxima of ~22 μmol/L along

91   the OMZ (Olson et al., 1993; Paulmier and Ruiz-Pino, 2009). Below the OMZ, oxygen

92   concentrations substantially increase by up to ca. 80 μmol/L, providing a strong gradient in

93   bottom water oxygen concentrations. The set of surface sediments studied are in close lateral

94   proximity, and hence likely receive a similar flux of pelagic organic matter, but have

95   contrasting bottom water oxygen concentrations, thus allowing to constrain the effect of oxic

96   degradation on organic matter and biomarkers (cf. Sinninghe Damsté et al., 2002; Schouten et

97   al., 2012; Bogus et al., 2012; Lengger et al., 2012, 2014). Here, we have studied the effect of

98   the oxic degradation on concentrations of diols and related proxies (i.e. LDI, upwelling,

99   DOXI). We compared our results with those of alkenone concentrations and the $U^{K'}_{37}$ index.

100   Furthermore, we evaluated the possible origin of keto-ols as oxic transformation products of

101   diols.

102

103   **2. Material and methods**

104   *2.1. Sampling*

105   Surface sediments (0-0.5 cm sediment depth) were obtained in the Northern Arabian

106   Sea along a depth transect on the Murray Ridge during the PASOM cruise (64PE301) in

107   January 2009 with the *R/V Pelagia* (Fig. 1a; Koho et al., 2013; Lengger et al., 2014).

108   Sediments were stored in geochemical bags and frozen immediately at -80°C on board and

109   transported and subsequently stored at -20°C. A total of nine box cores were taken at different

110   water depths, ranging from 885 to 3010 m, with bottom water oxygen concentrations (BWO)

111   ranging from <3 to 77 µmol/L, i.e. three within the OMZ (P900, P1000, P1200), two in the

112   suboxic zone just below the OMZ (P1300, P1500) and four in the oxic zone well below the

113   OMZ (P1800, P2000, P2500, P3000) (Fig. 1b). Oxygen concentrations of the water column,

114   oxygen penetration depths, total organic carbon content and sedimentation rates have been

115   previously reported by Koho et al. (2013) and Lengger et al. (2014).

116

117   *2.2. Extraction*

118   Prior to analysis, surface sediments were freeze-dried and homogenized in an agate

119   mortar. After addition of pre-extracted diatomaceous earth, aliquots (1-2 g) of surface

120   sediments were extracted in an Accelerated Solvent Extractor 350 (ASE 350, DIONEX) using

121   a solvent mixture of 9:1 (v:v) dichloromethane (DCM) to methanol (MeOH) at 100 ºC and 7.6

122   x 10^6 Pa. The solvent was reduced by TurboVap LV Caliper. Extracts were dried over a

123   pipette column containing Na_2SO_4 and concentrated under a stream of N_2.

124   Two internal standards were added to the total lipid extracts (TLEs) prior to column

125   chromatography separation, i.e. 3.2 µg 10-nonadecanone for alkenone quantitation and 0.258

126   µg C_{22} 7,16-diol for quantitation of diols. Apolar, ketone and polar fractions were obtained by

127   column chromatography using a Pasteur pipette filled with Al_2O_3 (activated for 2 h at 150 ºC)

128   using respectively 9:1 (v:v) hexane:DCM, 1:1 (v:v) hexane:DCM, and 1:1 (v:v) MeOH:DCM

129   as the eluents.

130

131   *2.2.1. GC analysis*

132   The ketone fractions were dried under N_2 and re-dissolved in an appropriate volume

133   (50-400 µl) of hexane. Analysis of the alkenones was performed in duplicate on an Hewlett

134   Packard 6890 Gas Chromatograph (GC) using a 50-m CP Sil-5 column (0.32-mm diameter,

135   film thickness of 0.12 µm), equipped with flame ionization detector and helium as the carrier

136   gas. The temperature of the oven was initially 70°C and increased with a rate of 20°C per min

137   to 200°C and subsequently with a rate of 3°C per min to 320°C, at which it was held for 25

138   min. Alkenone abundances were determined by integration of relevant peak areas and the

139   internal standard (10-nonadecanone).

140   The $U^{K'}_{37}$ index (Eq. 1) was calculated according to the equation by Prahl and

141   Wakeham (1987):

142

143    $$U^{K'}_{37} = \frac{[C_{37:2}]}{[C_{37:2}] + [C_{37:3}]}$$ (1)

144

145    $U^{K'}_{37}$ values were converted to SSTs using the global core top calibration of Müller et

146   al. (1998):

147

148    $$U^{K'}_{37} = 0.033 \times SST + 0.044$$ (2)

149

2.2.2. GC-MS analysis

The polar fractions were dried under N_2 and silylated by adding 15 µl N,O-

bis(trimethylsilyl)trifluoroacetamide (BSTFA) and pyridine and heating in an oven at 60°C

for 20 min. Diol and keto-ol distributions were analyzed in duplicate using a Thermo Finnigan

Trace Gas Chromatograph (GC) Ultra coupled to a Thermo Finnigan DSQ mass spectrometer

(MS). A 25-m CP Sil-5 fused silica capillary column was used (25 m x 0.32 mm; film

thickness = 0.12 µm) with helium as the carrier gas. The column was directly inserted into the

electron impact ion source of the DSQ quadrupole MS with an ionization energy of 70 eV.

Samples were dissolved in 30-500 µl ethyl acetate and injected at 70°C. The oven was

programmed to increase first at a rate of 20°C per min to 130°C, and then at a rate of 4°C per

min to the final temperature of 320°C (held 25 min). Various diols and the C_{22} 7,16-diol

standard were quantified using single ion monitoring (SIM) of *m/z* 299, 313, 327, 341, 369

and 187, respectively, and keto-ols were quantified using SIM of *m/z* 300, 314 and 328. A

correction factor for quantifying diol and keto-ol concentrations was applied as follows: the

mass fragments of the diols contributed on average 12.9% to the total ion counts, that of the

C_{22} 7,16-diol standard contributed on average 22% to the total ion counts and that of the keto-

ols contributed on average 9% to the total ion counts.

The Long chain Diol Index (LDI) was calculated and converted to SST following

Rampen et al. (2012):

$$LDI = \frac{[C_{30}1,15-diol]}{[C_{28}+C_{30}1,13-diol]+[C_{30}1,15-diol]} \tag{3}$$

$$LDI = 0.033 \times SST + 0.095 \tag{4}$$

174   The following two upwelling indices (Diol Index 1 and 2 referred as 1,15 upw and

175   1,13 upw, respectively, hereafter) were calculated according to Rampen et al. (2008) and

176   Willmott et al. (2010), respectively:

177

178    $$1,15 \; upw = \frac{[C_{28}+C_{30}\,1,14-diol]}{[C_{28}+C_{30}\,1,14-diol]+[C_{30}\,1,15-diol]}$$ (5)

179

180    $$1,13 \; upw = \frac{[C_{28}+C_{30}\,1,14-diol]}{[C_{28}+C_{30}\,1,14-diol]+[C_{28}+C_{30}\,1,13-diol]}$$ (6)

181

182   The Diol Oxidation Index (DOXI) was calculated according to Ferreira et al. (2001)

183   for diols and keto-ols with identical carbon chain-lengths and carbon position of the mid-

184   chain functional groups:

185

186    $$DOXI = \frac{[keto-ol]}{[keto-ol]+[diol]}$$ (7)

187

188   **3. Results**

189   *3.1. Bulk parameters*

190   The nine sampling stations along the Murray Ridge show an increase in bottom water

191   oxygen concentrations (from 3 to 77 µmol/L; Fig. 1b) and oxygen penetration depths, and a

192   decrease in sedimentation rates with increasing water depth (cf. Koho et al., 2013; Lengger et

193   al., 2014). Increasing oxygen penetration depth and decreasing sedimentation rate lead to an

194   increase in the maximum residence time the organic matter spends in the oxic zone (t_{OZ},

195   calculated from the oxygen penetration depth and the sediment accumulation rate; see

196   Lengger et al., 2014 for details). Concentrations of organic carbon (C_{org}) decreased

197   progressively with increasing water depth or increasing t_{OZ} (from 60 to 10 mg/g sediment dry

198   weight, referred as mg/g hereafter) (Fig. 2a) (data from Lengger et al., 2014). This indicates

199   that the surface sediments show an increasing degradation of organic matter as a result of the

200   increasing residence time in the oxic zone of the sediment (Lengger et al., 2012, 2014; Koho

201   et al., 2013).

202

203   *3.2. Diols and keto-ols*

204   The surface sediments contained a range of diols and keto-ols. Diols consisted of C_{28}-

205   C_{34} 1,13-, 1,14- and 1,15-isomers, dominated by the C_{30} 1,14-diol (Supplementary Table S1).

206   The keto-ols consisted of C_{30}-C_{34} homologues with the keto group at the 15 position

207   (Supplementary Table S1), and low abundance of the C_{30} 1,14-keto-ol (data not shown). The

208   concentrations of diols used for the LDI in the surface sediments decreased strongly with

209   water depth from 4.3, 0.14 and 0.11 µg/g to 0.15 and 0.01 µg/g for C_{30} 1,15-, and C_{30}-C_{28}

210   1,13-diols, respectively, with the largest decrease in the suboxic zone (Fig. 2c). The

211   concentration of the other abundant 1,15-diol, the C_{32} 1,15-diol, decreased with water depth

212   from 1.28 to 0.04 µg/g (Fig. 2b). The 1,14-diols shows a similar pattern as the 1,13 and 1,15-

213   diols, i.e. C_{28} and C_{30} 1,14-diols decreased from 4.5 and 4.1 µg/g, respectively, to ca. 0.2 µg/g

214   (Fig. 2b). The concentration of the mono-unsaturated C_{28} 1,14-diol decreased from 0.22 to

215   0.01 µg/g, while that of the mono-unsaturated C_{30} 1,14-diol decreased even more sharply from

216   2.90 up to 0.01 µg/g (Fig. 2b). Individual concentrations of C_{30}, C_{32} and C_{34} 1,15-keto-ols

217   ranged between 2.3-0.17, 3.3-0.29, and 0.46-0.03 µg/g, respectively, and also strongly

218   decreased with increasing water depth (Fig. 2e).

219   Calculation of the different indices based on the various diol isomers shows different

220   patterns. The LDI values ranged between 0.95 and 0.89, with a minimum value of 0.84 at

221   1970 m water depth, showing a distinct decrease with increasing water depth from the anoxic

222   to the oxic zone (Fig. 3a). The upwelling indices showed minor variations with 1,14- vs. 1,15-

223 diol upwelling index varying between 0.67 and 0.74 with a slight increase with water depth

224 (Fig. 3b), while the 1,14- vs. 1,13-diol upwelling index varied between 0.97 and 0.93 with a

225 slight decrease with increasing water depth (Fig. 3b). DOXI values varied between 0.24-0.37,

226 0.73-0.81, and 0.76-0.89 for the C_{30}, C_{32}, and C_{34} keto-ol/diol ratio based on 1,15 isomers,

227 respectively, with no distinct trends (Fig. 3c). The C_{28} 1,15-keto-ol was not detected and

228 therefore the C_{28} based DOXI value was 0.

229

230 *3.3. Alkenones*

231   The concentration of the individual C_{37} alkenones in surface sediments generally

232 decreased with increasing water depth (Supplementary Table S1), with concentrations

233 decreasing from 12.9 and 0.46 µg/g to 0.76 and 0.03 µg/g for the $C_{37:2}$ and $C_{37:3}$ alkenones,

234 respectively (Fig. 2f). Values for the $U^{K'}_{37}$ index varied between 0.97 and 0.95 with no

235 particular trend (Fig. 3a).

236

237 **4. Discussion**

238 *4.1. Impact of sedimentary oxic degradation on diol and alkenone concentrations*

239   In the surface sediments studied here, the 1,14-diols are more abundant than the 1,15-

240 diols and 1,13-diols (Fig. 2d), suggesting that *Proboscia* diatoms (Sinninghe Damsté et al.,

241 2003; Rampen et al., 2007) are an abundant source of diols in the Arabian Sea. This is in

242 agreement with previous studies in this area showing high abundances of these lipids with the

243 highest annual fluxes for the 1,14-diols compared to other diol isomers (Rampen et al., 2007,

244 2008). Wakeham et al. (2002) reported the dominance of C_{30} 1,15-diols over 1,13- and 1,15-

245 diols in descending particles trapped at shallow and middle depth (~500 and 1460 m,

246 respectively) in the Arabian Sea water column, which is consistent with the distribution

247 observed in this study. In general, all diols showed similar trends, i.e. a strong decrease in

248 concentration with increasing water depth and thus increasing oxygen content in the bottom

249 and pore waters of the sediment and increasing residence time in the oxic part of the sediment

250 (Figs. 2b-c). This suggests that all diols are affected by oxic degradation, in agreement with

251 earlier studies (e.g., Hoefs et al., 2002; Sinninghe Damsté et al., 2002). Indeed, 1,13-, 1,14-

252 and 1,15-diol concentrations revealed a significant negative correlation with t_{OZ} (e.g. Figs. 4b-

253 c, f). However, the slopes of the equations describing these linear correlations differ between

254 the various diols, with some diols (e.g. the C_{30} 1,13-diol) having a smaller slope than other

255 diols, suggesting lower degradation rates. Different degradation rates have been described for

256 different lipid biomarker classes and even between structurally similar biomarker lipids such

257 as di- and tri-unsaturated alkenones (e.g., Hoefs et al., 1998, 2002; Gong and Hollander, 1999;

258 Sinninghe Damsté et al., 2002; Versteegh et al., 2010).

259 To compare the extent of oxic degradation for the different diols, we calculated the

260 relative preservation efficiency (RPE; in %). This was calculated by taking the average of the

261 concentrations of a specific diol in the three surface sediments with the highest t_{OZ} (i.e.

262 stations P2000, P2500, and P3000 from the oxic zone below the OMZ; Fig. 1b) and compare

263 this with that in the shallowest surface sediment with the lowest t_{OZ}, i.e. from within the OMZ

264 (i.e. station P900 within the core of the OMZ; Fig. 1b) (Fig. 5a). This shows that increased

265 oxygen exposure time leads to the degradation of 89-96% of the diols. Values of the RPE

266 show differences between positional isomers, i.e. the 1,13-diols show the best preservation ($\sim$

267 11 %), followed by 1,14-diols ($\sim$ 6 %) and finally 1,15-diols ($\sim$ 4 %) but is independent of

268 chain length of the diols (Fig. 5a).

269 The difference in the extent of degradation of the various diols could be related to the

270 different biological sources of diols, i.e. 1,14-diols are mainly synthesized by *Proboscia*

271 diatoms (Sinninghe Damsté et al., 2003; Rampen et al., 2007), while 1,15- and 1,13-diols are

272 produced by eustigmatophyte algae (Volkman et al., 1992, 1999). However, we observed a

273 rather large difference in RPE for 1,15- and 1,13-diols, which in principle are presumed to be

274 derived from the same biological source (Rampen et al., 2012). Structurally, there seems no

275 reason for such a significant difference in RPE. This may imply a different physical protection

276 of the diol isomers, e.g. adsorbed to different ballast minerals (Hedges et al., 2001; Armstrong

277 et al., 2002), which would also imply different sources for these diols. Alternatively, the

278 different degradation rates may indicate that diols do not only occur as free-lipids but also in a

279 bound form (Gelin et al., 1997a; Grossi et al., 2001; Shimokwara et al., 2010; Rampen et al.,

280 2014a), which may cause a release of diols by hydrolysis during early diagenesis. If, for

281 example, 1,13-diols are more abundant in a bound form than in the free form, then the release

282 of these bound diols during diagenesis could lead to an apparent higher RPE for 1,13-diols.

283   Alkenone concentrations also dropped substantially with increasing water depth and

284 t_{OZ} (Figs. 2f, 4h-i), indicating that they are affected by oxic degradation as well. They showed

285 similar values for RPE, i.e. 10-12 % (Fig. 5b) as the 1,13-diols (~ 11 %), but higher than those

286 for 1,14- and 1,15-diols. There is a slight difference in RPE for both alkenones, i.e. 12 % for

287 $C_{37:3}$ and 10.6 % for $C_{37:2}$ (Fig. 5b), but this is mainly caused by the sediment of station P900

288 (at 885 m water depth), which seems somewhat anomalous with respect to the concentration

289 of the $C_{37:3}$ alkenone. If the alkenone concentrations in the sediment of station P1000 (at 1013

290 m water depth, still within the OMZ, Fig. 1b) are used, then RPEs of both alkenones are

291 relatively similar, in agreement with previous observations in this region (Sinninghe Damsté

292 et al., 2002).

293

294 *4.2. Impact of oxic degradation on paleoenvironmental proxies*

295   Because the 1,13-diols are slightly better preserved (Fig. 5a) than 1,15-diols, the LDI

296 decreases from 0.94 to 0.85 with increasing water depth (Fig. 3a). Moreover, a linear negative

297 correlation of LDI with t_{OZ} is observed ($R^2 = 0.86$; Fig. 4a), suggesting that the LDI is

298   affected by oxic degradation. Low abundances of biomarkers may lead to analytical biases as

299   has been observed with the $U^{K'}_{37}$ (Villanueva and Grimalt, 1997). However, a dilution test

300   (data not shown) showed that the changes in LDI values are not because of analytical artifacts

301   due to the low amounts of diols present in the oxidized sediments. When translated to SST,

302   the LDI variations correspond to a change from 25.5 to 24 ºC, with a minimum of 23 ºC at ca.

303   2000 m water depth in the oxic zone. This change of ca. 1.5-2.5 ºC is similar to, or even

304   exceeds if we consider the somewhat anomalous data point at ca. 2000 m water depth, the

305   calibration error of this proxy (2 °C; Rampen et al., 2012), suggesting that this SST proxy can

306   be affected by oxic degradation.

307   For comparison, we also analyzed the established SST proxy based on alkenones, the

308   $U^{K'}_{37}$ index. A previous study of alkenones in sediments from the Murray Ridge in the

309   Arabian Sea documented no significant degradation effect (Sinninghe Damsté et al., 2002).

310   Indeed, $U^{K'}_{37}$ values showed, with the exception of the shallowest sediment, no significant

311   variation with increasing water depth (Fig. 3a) and thus with increasing residence time in the

312   oxic zone of the sediment (Fig. 4g). The mean $U^{K'}_{37}$ value of 0.96 corresponds to 27.6 ºC

313   when translated to SST (Fig. 3a). This $U^{K'}_{37}$-estimated SSTs are in good agreement with

314   present annual mean SST in the Arabian Sea (ca. 27 ºC, World Ocean Atlas 09 database;

315   Locarnini et al., 2010). Another paleotemperature proxy, the TEX_{86}, was previously measured

316   in the same set of surface sediments as studied here and showed differences in derived SST

317   with increasing water depth and t_{OZ}, corresponding to higher values of up to 3 ºC (Lengger et

318   al., 2014). Although several hypotheses were put forward, the reasons for this change in

319   TEX_{86} were not clear.

320   The upwelling indices based on diols showed contrasting patterns compared to each

321   other as a result of the different degradation rates of 1,14-diols vs. 1,15- and 1,13-diols (Figs.

322   2b-c). The upwelling index based on 1,14- vs. 1,15-diols (Rampen et al., 2008), did not

323   correlate with t_{OZ} (Fig. 4d), but an apparent correlation is observed for the upwelling index

324   based on 1,14- vs. 1,13-diols (Willmott et al., 2010) (Fig. 4e). Indeed, the latter index displays

325   a small, but significant, decreasing trend with increasing water depth (Fig. 3b). However,

326   these changes (< 0.05 units) are relatively small compared to changes documented in Arabian

327   Sea sediment trap records (> 0.05 units; Rampen et al., 2007) and in globally distributed

328   surface sediments (Rampen et al., 2014a).

329   Thus, among the diol based proxies tested in this study the LDI seems to be most

330   affected by preferential oxic degradation in the Arabian Sea. These results indicate that this

331   effect has to be taken into consideration, especially when paleotemperature reconstructions

332   are performed in sediments where bottom water oxygen concentrations or oxygen penetration

333   depths have varied substantially over time.

334

335   *4.3. Keto-ols: intermediate products or biologically sourced?*

336   Keto-ols have been described as oxic transformation products of diols (e.g. Jiang et al.,

337   1994; Ferreira et al., 2001; Versteegh et al., 1997, 2010). Keto-ol concentrations in an

338   unoxidised sapropel layer in the eastern Mediterranean were lower than at the base of the

339   oxidized sapropel (Ferreira et al., 2001), suggesting that keto-ols are formed by oxidation of

340   diols. Based on these observations, the DOXI was proposed as a potential indicator for

341   paleoxicity in the water column (Ferreira et al., 2001). In the Arabian Sea surface sediments,

342   one might expect higher abundances of keto-ols relative to diols in sediments with a higher

343   exposure time to oxygen. The C_{30}-C_{34} 1,15-keto-ol concentrations showed a strong decrease

344   with increasing water depth, similar to that of the diols (Fig. 2e), and remained always lower

345   than the corresponding 1,15-diols (Figs. 2c-e). However, the C_{30}-C_{34} keto-ols were apparently

346   slightly better preserved than the corresponding diols, i.e. the RPE of the 1,15-keto-ols (~ 8%)

347   is slightly higher than that of the 1,15-diols (~ 4 %) (Fig. 5c). Indeed, the C_{30}, C_{32} and C_{34}

348   1,15 DOXI ratios are slightly higher in the oxic zone compared to the anoxic zone but the

349   differences are relatively minor (Fig. 3c). This is in contrast with results of a similar study

350   along the OMZ transect on the Pakistan continental margin, which showed a much stronger

351   increase of the C_{30} 1,15 DOXI ratio with increasing oxygen concentrations (Bogus et al.,

352   2012). The reason for the reduced DOXI values increase in the Arabian Sea sediments might

353   be the much lower bottom water oxygen concentrations (45-77 μmol/L) and oxygen

354   penetration depths (6-19 mm; Lengger et al., 2014) versus those at the Pakistan margin (220

355   μmol/L and 25 mm, respectively; Bogus et al., 2012). Indeed, Bogus et al. (2012) observed a

356   much smaller increase in DOXI values in sediments with bottom water oxygen concentrations

357   and oxygen penetration depths comparable to the Arabian Sea sediments studied here. This

358   suggests that DOXI values only substantially increase after a long-term exposure to high

359   oxygen concentrations.

360   Interestingly, the keto-ols are already observed in sediments from within the OMZ.

361   This may suggest that they were already formed in the upper part of the oxic water column

362   overlying the OMZ. This is supported by sediment trap material collected in and below the

363   OMZ of the Arabian Sea, which contained both C_{30} 1,15-keto-ols and saturated and mono-

364   unsaturated C_{30} 1,14-keto-ols (Rampen et al., 2007). However, a previous study of biomarkers

365   in sedimenting particles in and below the OMZ in the Arabian Sea documented that the degree

366   of degradation of biomarkers in the water column is insignificant relative to that in the surface

367   sediment (Wakeham et al., 2002) due to relatively short oxygen exposure time during sinking

368   of the particles. Therefore, it is not expected that keto-ols are formed solely by oxic

369   transformation in the water column during the vertical transport to the sea floor.

370   Another possibility is that keto-ols are synthesized by the algae themselves, i.e.

371   eustigmatophytes or as yet unknown algae (Versteegh et al., 1997; Méjanelle et al., 2003).

372   Méjanelle et al. (2003) identified C_{28}-C_{36} diols and C_{30}-C_{32} keto-ols with the C_{32} keto-ol

373   slightly dominating over the other homologues in a marine eustigmatophyte, *Nannochloropsis*

374   *gaditana*. In addition, only the 1,15-isomer was observed for the C_{32} keto-ol, while 1,13-

375   isomer together with the 1,15-isomer in minor amounts were observed for the C_{30} keto-ol

376   (Méjanelle et al., 2003). In the Arabian Sea surface sediments we identified C_{30} to C_{34} keto-

377   ols with a predominance of 1,15- over 1,13-isomers, while 1,14-isomers were below detection

378   limit (data not shown). Similar to what has been observed in *Nannochloropsis gaditana*, the

379   C_{32} 1,15 keto-ol was in slightly highest abundance (Fig. 2e). Nevertheless, keto-ols and diols

380   are within the same order of magnitude in marine sediments whereas a marked disproportion

381   is observed in the algal cultures. Further evidence for a biological imprint on the distribution

382   of keto-ols comes from the observation that DOXI values differ substantially between carbon

383   chain lengths (Fig. 3c), suggesting some initial biological control for either diols or keto-ols,

384   possibly eustigmatophytes and/or yet additional unidentified algae, and the contribution, at

385   least to some extent, to the sediment.

386

387   **5. Conclusions**

388   In order to determine the effect of oxic degradation on diols and keto-ols, we analyzed

389   nine surface sediments in the Arabian Sea deposited under contrasting bottom water oxygen

390   concentrations. In general, the concentrations of all diols showed a strong decrease with

391   increasing oxygen concentration and increasing residence time in oxic zone of the sediment.

392   A higher degradation rate was found for 1,15-diols, followed by 1,14-diols and 1,13-diols.

393   The LDI showed a decrease from 0.95 to 0.88 with increasing water depth, corresponding to

394   ca. 2-3.5 ºC when translated to SST. For comparison with an established SST proxy, we have

395   also analyzed alkenone concentrations and the $U^{K'}_{37}$ index, obtaining that individual alkenones

396   were affected by oxic degradation as well, but no significant changes are observed in the $U^{K'}_{37}$

397   index. Therefore, care has to be taken when the LDI is applied as SST proxy in sediments

398 underlying OMZs or where bottom water oxygen concentrations have varied substantially

399 over time. In contrast, upwelling indices based on the ratios of 1,14-diols versus 1,13- or 1,15-

400 diols showed relatively small changes, indicating that these proxies are not substantially

401 affected by variations in bottom water oxygen conditions. C_{30}-C_{34} keto-ol concentrations are

402 apparently slightly less degraded with increasing oxygen exposure time compared to diols and

403 DOXI values show a small increase between the anoxic to the oxic zone. Possibly, longer

404 exposure times to oxygen are needed in order to substantially increase DOXI values.

405

406   *Data from this publication are archived in the data centre "Pangaea"*

407 *(www.Pangaea.de).*

408

423

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577

Figure Captions

Fig. 1. (a) Location of the Murray Ridge in the North Arabian Sea with the surface sediments studied (from Lengger et al, 2014). Bathymetric contour lines are at 100 m intervals. (b) Schematic illustration of the Murray Ridge with the sampling stations at different water depths. The blue area indicates the OMZ and the dashed blue line the suboxic area just below the OMZ (oxygen concentrations $>15 < 27$ µmol/L). The bottom water oxygen concentration (BWO, µmol/L) profile from Koho et al. (2013) is drawn.

Fig. 2. Profiles of different parameters in the surface sediments (0.5 cm) from the Murray Ridge plotted with water depth. (a) organic carbon content (mg/g), (b) diol concentrations (µg/g), (c) LDI-diol concentrations (µg/g), (d) summed 1,15-, 1,14- and 1,13-diol concentrations (µg/g), (e) C_{30}-C_{34} 1,15 keto-ol concentrations (µg/g), and (f) individual C_{37} alkenone concentrations (µg/g).

Fig. 3. Indices determined in the surface sediments (0.5 cm) from the Murray Ridge. (a) $U^{K'}_{37}$ and LDI indices, (b) Upwelling indices (1,15 upw = 1,14-diols over 1,14- + 1,15-diols, cf. Rampen et al., 2008; and 1,13 upw = 1,14-diols over 1,14- + 1,13-diols, cf. Willmott et al., 2010), and (c) DOXI indices based on 1,15-diols and 1,15-keto-ols (Ferreira et al., 2001). Error bars represent duplicate analysis.

Fig. 4. Cross-plots of the residence time in the oxic zone of the sediment (t_{OZ}) expressed in years (yr) with (a) LDI, (b) C_{30} 1,15-diol concentration (µg/g), (c) C_{28}-C_{30} 1,13-diol concentrations (µg/g), (d) 1,15 upw, (e) 1,13 upw, (f) C_{28}-C_{30} 1,14-diol concentrations (µg/g), (g) $U^{K'}_{37}$, (h) $C_{37:3}$ alkenone concentration (µg/g), (i) $C_{37:2}$ alkenone concentration (µg/g). Error bars represent duplicate analysis.

Fig. 5. Bars plot of relative preservation efficiency (RPE) (i.e. relative amount in oxic sediment versus anoxic sediment, in %) of (a) diols, (b) individual C_{37} alkenones, and (c) keto-ols. Error bars represent duplicate analysis.

a)

b) Bottom water oxygen concentration
(μmol/L)

Arabian Sea
NE-SW

OMZ

Suboxic

Oxic

Murray Ridge

Water depth (m)

P900
P1000
P1200
P1300
P1500
P1800
P2000
P2500
P3000

10 km

a) C_{org} (mg/g)

b) μg/g

$C_{28:1}$ 1,14-diol
C_{32} 1,15-diol
$C_{30:1}$ 1,14-diol
C_{30} 1,14-diol
C_{28} 1,14-diol

OMZ
Suboxic
Oxic

c) μg/g

C_{30} 1,13-diol
C_{28} 1,13-diol
C_{30} 1,15-diol

d) μg/g

1,14-diol
1,15-diol
1,13-diol

e) μg/g

C_{30} 1,15 keto-ol
C_{32} 1,15 keto-ol
C_{34} 1,15 keto-ol

f) μg/g

$C_{37:3}$ alkenone
$C_{37:2}$ alkenone

Water depth (m)

a)

0.82 0.84 0.86 0.88 0.90 0.92 0.94 0.96 0.98

LDI $U^{K'}_{37}$

b) Upwelling Index

0.60   0.70   0.80   0.90   1.00

OMZ

Suboxic

Oxic

1,15 upw   1,13 upw

c) DOXI

0.00   0.20   0.40   0.60   0.80   1.00

C_{28} C_{30} C_{32} C_{34}

Water depth (m)

a) $y = -0.0003x + 0.93$
$R^2 = 0.86$

b) $y = -0.0196x + 3.7$
$R^2 = 0.92$

c) C_{30} 1,13-diol
$y = -0.0007x + 0.142$
$R^2 = 0.96$

C_{28} 1,13-diol
$y = -0.0005x + 0.1098$
$R^2 = 0.95$

e) $y = -0.0002x + 0.97$
$R^2 = 0.87$

f) C_{30} 1,14-diol
$y = -0.023x + 4.35$
$R^2 = 0.95$

C_{28} 1,14-diol
$y = -0.02x + 3.82$
$R^2 = 0.94$

h) $y = -0.003x + 0.55$
$R^2 = 0.94$

i) $y = -0.06x + 12.3$
$R^2 = 0.98$