



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



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ABSTRACT

Oxygen exposure has a large impact on lipid biomarker preservation in surface sediments and may affect the application of organic proxies used for reconstructing past environmental conditions. To determine its effect on long chain alkyl diol and keto-ol based proxies, the distributions of these lipids was studied in nine surface sediments from the Murray Ridge in the Arabian Sea obtained from varying water depths (900–3000 m) but in close lateral proximity and, therefore, likely receiving a similar particle flux. Due to substantial differences in bottom water oxygen concentration (<3–77 $\mu\text{mol/L}$) and sedimentation rate, substantial differences exist in the time the biomarker lipids are exposed to oxygen in the sediment. Long chain alkyl diol and keto-ol concentrations in the surface sediments (0–0.5 cm) decreased progressively with increasing oxygen exposure time, suggesting increased oxic degradation. The 1,15-keto-ol/diol ratio (DOXI) increased slightly with oxygen exposure time as diols had apparently slightly higher degradation rates than keto-ols. The ratio of 1,14- vs. 1,13- or 1,15-diols, used as upwelling proxies, did not show substantial changes. However, the C_{30} 1,15-diol exhibited a slightly higher degradation rate than C_{28} and C_{30} 1,13-diols, and thus the Long chain Diol Index (LDI), used as sea surface temperature proxy, showed a negative correlation with the maximum residence time in the oxic zone of the sediment, resulting in ca. 2–3.5 °C change, when translated to temperature. The U_{37}^K index did not show significant changes with increasing oxygen exposure. This suggests that oxic degradation may affect temperature reconstructions using the LDI in oxic settings and where oxygen concentrations have varied substantially over time.

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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}

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1,13-, C₃₀ 1,13- and C₃₀ 1,15-alkyl diols with SST (Rampen et al., 2012). Thus far, the LDI has been applied for reconstruction of SST in the mid-latitude regions (Lopes dos Santos et al., 2013; Smith et al., 2013; Rodrigo-Gámiz et al., 2014; Plancq et al., 2015). Upwelling indices are based on the relative abundance of C₂₈–C₃₀ 1,14-diols vs. 1,13-diols or C₃₀ 1,15-diols (Rampen et al., 2008; Willmott et al., 2010) and have been applied in several oceanic regions, including the Arabian Sea (e.g., Rampen et al., 2008, 2014a; Pancost et al., 2009; Willmott et al., 2010; Lopes dos Santos et al., 2012; Seki et al., 2012). C₃₀ and C₃₂ keto-ols also occur ubiquitously in marine sediments (e.g., Jiang et al., 1994; Versteegh et al., 1997; Wakeham et al., 2002; Sinninghe Damsté et al., 2003; Rampen et al., 2007; Bogus et al., 2012), and have been identified in a cultured marine eustimatophyte, *Nannochloropsis gaditana*, although in lower amounts than generally found in marine sediments (Méjanelle et al., 2003). Long chain keto-ols have been inferred to be intermediate products of the oxidation of diols and the Diol Oxidation Index (DOXI) has been proposed as an indicator for oxic degradation in the sedimentary record (Ferreira et al., 2001; Versteegh et al., 2010; Bogus et al., 2012). However, the chain length distributions and distributions of positional isomers for long chain alkyl diols and the corresponding keto-ols differ (Versteegh et al., 1997), casting some doubts on the occurrence of this oxidation process. Another suggestion for the origin of keto-ols is that they may be produced by an as yet unknown biological source (Versteegh et al., 1997).

Like many other organic proxies, uncertainties remain in the application of long chain alkyl diols as palaeoclimate reconstruction tools. Apart from the fact that the biological source of 1, 13- and 1,15-diols in the marine environment is still unknown, a variety of environmental factors other than temperature (e.g., salinity, nutrient availability) could have an impact on these proxies. Importantly, diagenesis can have a substantial effect on the abundance and distributions of biomarker lipids (e.g., Arzayus and Canuel, 2004; Peters et al., 2005 and references cited therein). One important factor affecting lipid distributions and preservation is oxic degradation (e.g., Sun and Wakeham, 1994; Hoefs et al., 1998, 2002; Sinninghe Damsté et al., 2002; Prahil et al., 2003; Rontani et al., 2009, 2013), particularly oxygen exposure time (Hartnett et al., 1998; Hedges et al., 1999). For example, it has been shown that the U₃₇^K-SST proxy based on alkenones may be altered after long term exposure to oxygen (Hoefs et al., 1998, 2002; Gong and Hollander, 1999; Prahil et al., 2003; Rontani et al., 2009, 2013). The effect of degradation on long chain alkyl diol distributions, and the proxies based on these components, is, however, still not clear (Ferreira et al., 2001; Versteegh et al., 2010; Bogus et al., 2012).

In this study we investigated the impact of oxic degradation on long chain alkyl diol and long chain keto-ol (referred to as diols and keto-ols hereafter) concentrations by analyzing nine surface sediments from the Murray Ridge in the Arabian Sea. Previous studies have shown that this submarine high in the northern Arabian Sea provides an excellent location to study the effect of oxygen degradation on lipid distributions (Sinninghe Damsté et al., 2002; Schouten et al., 2012; Lengger et al., 2012, 2014). The Murray Ridge protrudes into one of the largest oxygen minimum zones (OMZ) presently found in the oceans, with molecular oxygen (O₂) concentrations varying from minima of 0.1–1.0 μmol/L to maxima of ~22 μmol/L along the OMZ (Olson et al., 1993; Paulmier and Ruiz-Pino, 2009). Below the OMZ, oxygen concentrations substantially increase by up to ca. 80 μmol/L, providing a strong gradient in bottom water oxygen concentrations. The set of surface sediments studied are in close lateral proximity, and hence likely receive a similar flux of pelagic organic matter, but have contrasting bottom water oxygen concentrations, thus allowing to constrain the effect of oxic degradation on organic matter and

biomarkers (cf. Sinninghe Damsté et al., 2002; Schouten et al., 2012; Bogus et al., 2012; Lengger et al., 2012, 2014). Here, we have studied the effect of the oxic degradation on concentrations of diols and related proxies (i.e. LDI, upwelling, DOXI). We compared our results with those of alkenone concentrations and the U₃₇^K index. Furthermore, we evaluated the possible origin of keto-ols as oxic transformation products of diols.

2. Material and methods

2.1. Sampling

Surface sediments (0–0.5 cm sediment depth) were obtained in the Northern Arabian Sea along a depth transect on the Murray Ridge during the PASOM cruise (64PE301) in January 2009 with the *R/V Pelagia* (Fig. 1a; Koho et al., 2013; Lengger et al., 2014). Sediments were stored in geochemical bags and frozen immediately at –80 °C on board and transported and subsequently stored at –20 °C. A total of nine box cores were taken at different water depths, ranging from 885 to 3010 m, with bottom water oxygen concentrations (BWO) ranging from <3 to 77 μmol/L, i.e. three within the OMZ (P900, P1000, P1200), two in the suboxic zone just below the OMZ (P1300, P1500) and four in the oxic zone well below the OMZ (P1800, P2000, P2500, P3000) (Fig. 1b). Oxygen concentrations of the water column, oxygen penetration depths, total organic carbon content and sedimentation rates have been previously reported by Koho et al. (2013) and Lengger et al. (2014).

2.2. Extraction

Prior to analysis, surface sediments were freeze-dried and homogenized in an agate mortar. After addition of pre-extracted diatomaceous earth, aliquots (1–2 g) of surface sediments were extracted in an Accelerated Solvent Extractor 350 (ASE 350, DIONEX) using a solvent mixture of 9:1 (v:v) dichloromethane (DCM) to methanol (MeOH) at 100 °C and 7.6 × 10⁶ Pa. The solvent was reduced by TurboVap LV Caliper. Extracts were dried over a pipette column containing Na₂SO₄ and concentrated under a stream of N₂.

Two internal standards were added to the total lipid extracts (TLEs) prior to column chromatography separation, i.e. 3.2 μg 10-nonadecanone for alkenone quantitation and 0.258 μg C₂₂ 7,16-diol for quantitation of diols. Apolar, ketone and polar fractions were obtained by column chromatography using a Pasteur pipette filled with Al₂O₃ (activated for 2 h at 150 °C) using respectively 9:1 (v:v) hexane:DCM, 1:1 (v:v) hexane:DCM, and 1:1 (v:v) MeOH:DCM as the eluents.

2.2.1. GC analysis

The ketone fractions were dried under N₂ and re-dissolved in an appropriate volume (50–400 μl) of hexane. Analysis of the alkenones was performed in duplicate on an Hewlett Packard 6890 gas chromatograph (GC) using a 50 m CP Sil-5 column (0.32 mm diameter, film thickness of 0.12 μm), equipped with flame ionization detector and helium as the carrier gas. The temperature of the oven was initially 70 °C and increased with a rate of 20 °C per min to 200 °C and subsequently with a rate of 3 °C per min to 320 °C, at which it was held for 25 min. Alkenone abundances were determined by integration of relevant peak areas and the internal standard (10-nonadecanone).

The U₃₇^K index (Eq. 1) was calculated according to the equation by Prahil and Wakeham (1987):

$$U_{37}^K = \frac{[C_{37:2}]}{[C_{37:2}] + [C_{37:3}]} \quad (1)$$

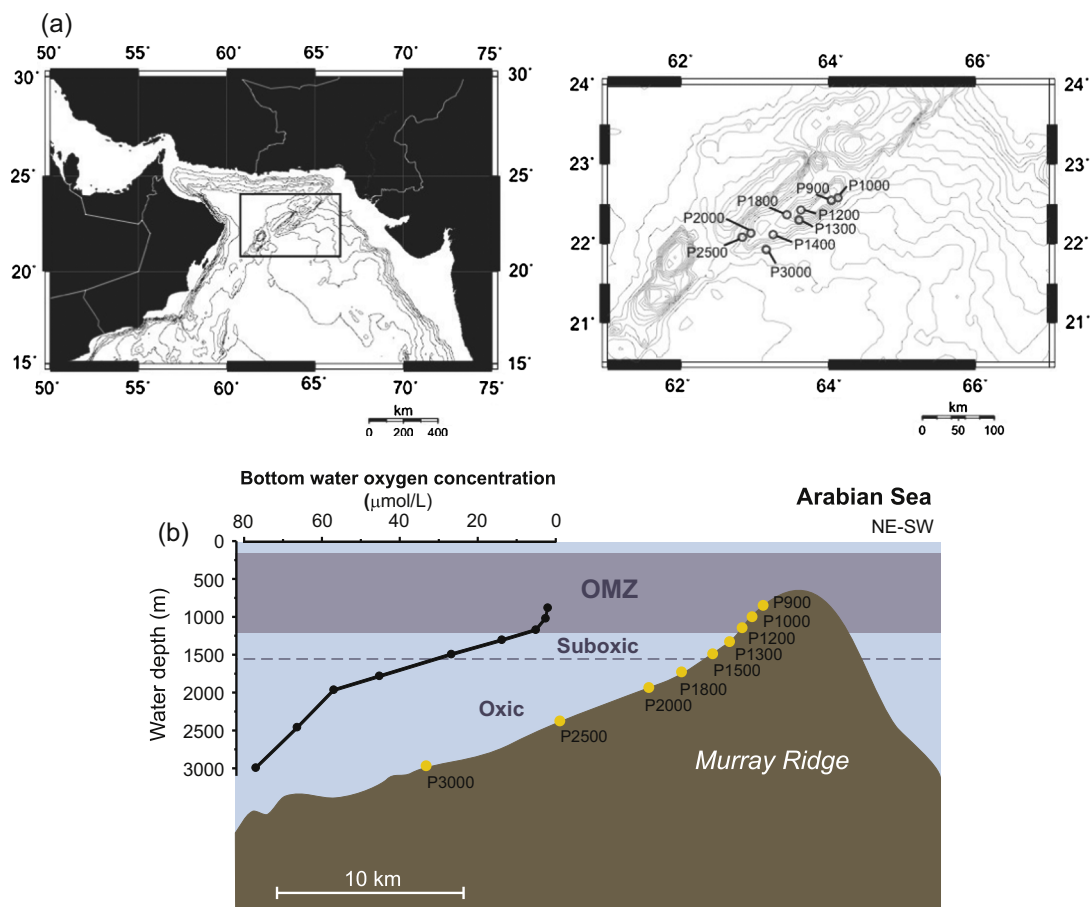


Fig. 1. (a) Location of the Murray Ridge in the North Arabian Sea with the surface sediments studied (from Lenggler et al., 2014). Bathymetric contour lines are at 100 m intervals. (b) Schematic illustration of the Murray Ridge with the sampling stations at different water depths. The blue area indicates 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. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

U_{37}^K values were converted to SSTs using the global core top calibration of Müller et al. (1998):

$$U_{37}^K = 0.033 \times \text{SST} + 0.044 \quad (2)$$

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 × 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):

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

$$\text{LDI} = 0.033 \times \text{SST} + 0.095 \quad (4)$$

The following two upwelling indices (Diol Index 1 and 2 referred as 1,15 upw and 1,13 upw, respectively, hereafter) were calculated according to Rampen et al. (2008) and Willmott et al. (2010), respectively:

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

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

The Diol Oxidation Index (DOXI) was calculated according to Ferreira et al. (2001) for diols and keto-ols with identical carbon chain-lengths and carbon position of the mid-chain functional groups:

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

3. Results

3.1. Bulk parameters

The nine sampling stations along the Murray Ridge show an increase in bottom water oxygen concentrations (from 3 to 77 $\mu\text{mol/L}$; Fig. 1b) and oxygen penetration depths, and a decrease in sedimentation rates with increasing water depth (cf. Koho et al., 2013; Lengger et al., 2014). Increasing oxygen penetration depth and decreasing sedimentation rate lead to an increase in the maximum residence time the organic matter spends in the oxic zone (t_{OZ} , calculated from the oxygen penetration depth and the sediment accumulation rate; see Lengger et al., 2014 for details). Concentrations of organic carbon (C_{org}) decreased progressively with increasing water depth or increasing t_{OZ} (from 60 to 10 mg/g sediment dry weight, referred as mg/g hereafter) (Fig. 2a) (data from Lengger et al., 2014). This indicates that the surface sediments show an increasing degradation of organic matter as a result of the increasing residence time in the oxic zone of the sediment (Lengger et al., 2012, 2014; Koho et al., 2013).

3.2. Diols and keto-ols

The surface sediments contained a range of diols and keto-ols. Diols consisted of C_{28} – C_{34} 1,13-, 1,14- and 1,15-isomers, dominated by the C_{30} 1,14-diol (Supplementary Table S1). The keto-ols consisted of C_{30} – C_{34} homologs with the keto group at the 15 position (Supplementary Table S1), and low abundance of the C_{30} 1,14-keto-ol (data not shown). The concentrations of diols used for the LDI in the surface sediments decreased strongly with water depth from 4.3, 0.14 and 0.11 $\mu\text{g/g}$ to 0.15 and 0.01 $\mu\text{g/g}$ for C_{30} 1,15-, and C_{30} – C_{28} 1,13-diols, respectively, with the largest decrease in the suboxic zone (Fig. 2c). The concentration of the other abundant 1,15-diol, the C_{32} 1,15-diol, decreased with water depth from 1.28 to 0.04 $\mu\text{g/g}$ (Fig. 2b). The 1,14-diols show a similar pattern as the 1,13 and 1,15-diols, i.e. C_{28} and C_{30} 1,14-diols decreased from 4.5 and 4.1 $\mu\text{g/g}$, respectively, to ca. 0.2 $\mu\text{g/g}$ (Fig. 2b). The concentration of the mono-unsaturated C_{28} 1,14-diol decreased from 0.22 to 0.01 $\mu\text{g/g}$, while that of the mono-unsaturated C_{30} 1,14-diol decreased even more sharply from 2.90 up to 0.01 $\mu\text{g/g}$ (Fig. 2b). Individual concentrations of C_{30} , C_{32} and C_{34} 1,15-keto-ols ranged between 2.3–0.17, 3.3–0.29, and 0.46–0.03 $\mu\text{g/g}$, respectively, and also strongly decreased with increasing water depth (Fig. 2e).

Calculation of the different indices based on the various diol isomers shows different patterns. The LDI values ranged between 0.95 and 0.89, with a minimum value of 0.84 at 1970 m water depth, showing a distinct decrease with increasing water depth from the anoxic to the oxic zone (Fig. 3a). The upwelling indices showed minor variations with 1,14- vs. 1,15-diol upwelling index varying between 0.67 and 0.74 with a slight increase with water depth (Fig. 3b), while the 1,14- vs. 1,13-diol upwelling index varied between 0.97 and 0.93 with a slight decrease with increasing water depth (Fig. 3b). DOXI values varied between 0.24–0.37, 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, respectively, with no distinct trends (Fig. 3c). The C_{28} 1,15-keto-ol was not detected and therefore the C_{28} based DOXI value was 0.

3.3. Alkenones

The concentration of the individual C_{37} alkenones in surface sediments generally decreased with increasing water depth (Supplementary Table S1), with concentrations decreasing from 12.9 and 0.46 $\mu\text{g/g}$ to 0.76 and 0.03 $\mu\text{g/g}$ for the $C_{37:2}$ and $C_{37:3}$

alkenones, respectively (Fig. 2f). Values for the U_{37}^K index varied between 0.97 and 0.95 with no particular trend (Fig. 3a).

4. Discussion

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

In the surface sediments studied here, the 1,14-diols are more abundant than the 1,15-diols and 1,13-diols (Fig. 2d), suggesting that *Proboscia* diatoms (Sinninghe Damsté et al., 2003; Rampen et al., 2007) are an abundant source of diols in the Arabian Sea. This is in agreement with previous studies in this area showing high abundances of these lipids with the highest annual fluxes for the 1,14-diols compared to other diol isomers (Rampen et al., 2007, 2008). Wakeham et al. (2002) reported the dominance of C_{30} 1,15-diols over 1,13- and 1,15-diols in descending particles trapped at shallow and middle depth (~ 500 and 1460 m, respectively) in the Arabian Sea water column, which is consistent with the distribution observed in this study. In general, all diols showed similar trends, i.e. a strong decrease in concentration with increasing water depth and thus increasing oxygen content in the bottom and pore waters of the sediment and increasing residence time in the oxic part of the sediment (Fig. 2b–c). This suggests that all diols are affected by oxic degradation, in agreement with earlier studies (e.g., Hoefs et al., 2002; Sinninghe Damsté et al., 2002). Indeed, 1,13-, 1,14- and 1,15-diol concentrations revealed a significant negative correlation with t_{OZ} (e.g. Fig. 4b, c, and f). However, the slopes of the equations describing these linear correlations differ between the various diols, with some diols (e.g. the C_{30} 1,13-diol) having a smaller slope than other diols, suggesting lower degradation rates. Different degradation rates have been described for different lipid biomarker classes and even between structurally similar biomarker lipids such as di- and tri-unsaturated alkenones (e.g., Hoefs et al., 1998, 2002; Gong and Hollander, 1999; Sinninghe Damsté et al., 2002; Versteegh et al., 2010).

To compare the extent of oxic degradation for the different diols, we calculated the relative preservation efficiency (RPE; in %). This was calculated by taking the average of the concentrations of a specific diol in the three surface sediments with the highest t_{OZ} (i.e. stations P2000, P2500, and P3000 from the oxic zone below the OMZ; Fig. 1b) and compare this with that in the shallowest surface sediment with the lowest t_{OZ} , i.e. from within the OMZ (i.e. station P900 within the core of the OMZ; Fig. 1b) (Fig. 5a). This shows that increased oxygen exposure time leads to the degradation of 89–96% of the diols. Values of the RPE show differences between positional isomers, i.e. the 1,13-diols show the best preservation ($\sim 11\%$), followed by 1,14-diols ($\sim 6\%$) and finally 1,15-diols ($\sim 4\%$) but is independent of chain length of the diols (Fig. 5a).

The difference in the extent of degradation of the various diols could be related to the different biological sources of diols, i.e. 1,14-diols are mainly synthesized by *Proboscia* diatoms (Sinninghe Damsté et al., 2003; Rampen et al., 2007), while 1,15- and 1,13-diols are produced by eustigmatophyte algae (Volkman et al., 1992, 1999). However, we observed a rather large difference in RPE for 1,15- and 1,13-diols, which in principle are presumed to be derived from the same biological source (Rampen et al., 2012). Structurally, there seems no reason for such a significant difference in RPE. This may imply a different physical protection of the diol isomers, e.g. adsorbed to different ballast minerals (Hedges et al., 2001; Armstrong et al., 2002), which would also imply different sources for these diols. Alternatively, the different degradation rates may indicate that diols do not only occur as free-lipids but also in a bound form (Gelin et al., 1997a; Grossi et al., 2001; Shimokwara et al., 2010; Rampen et al., 2014a), which may cause

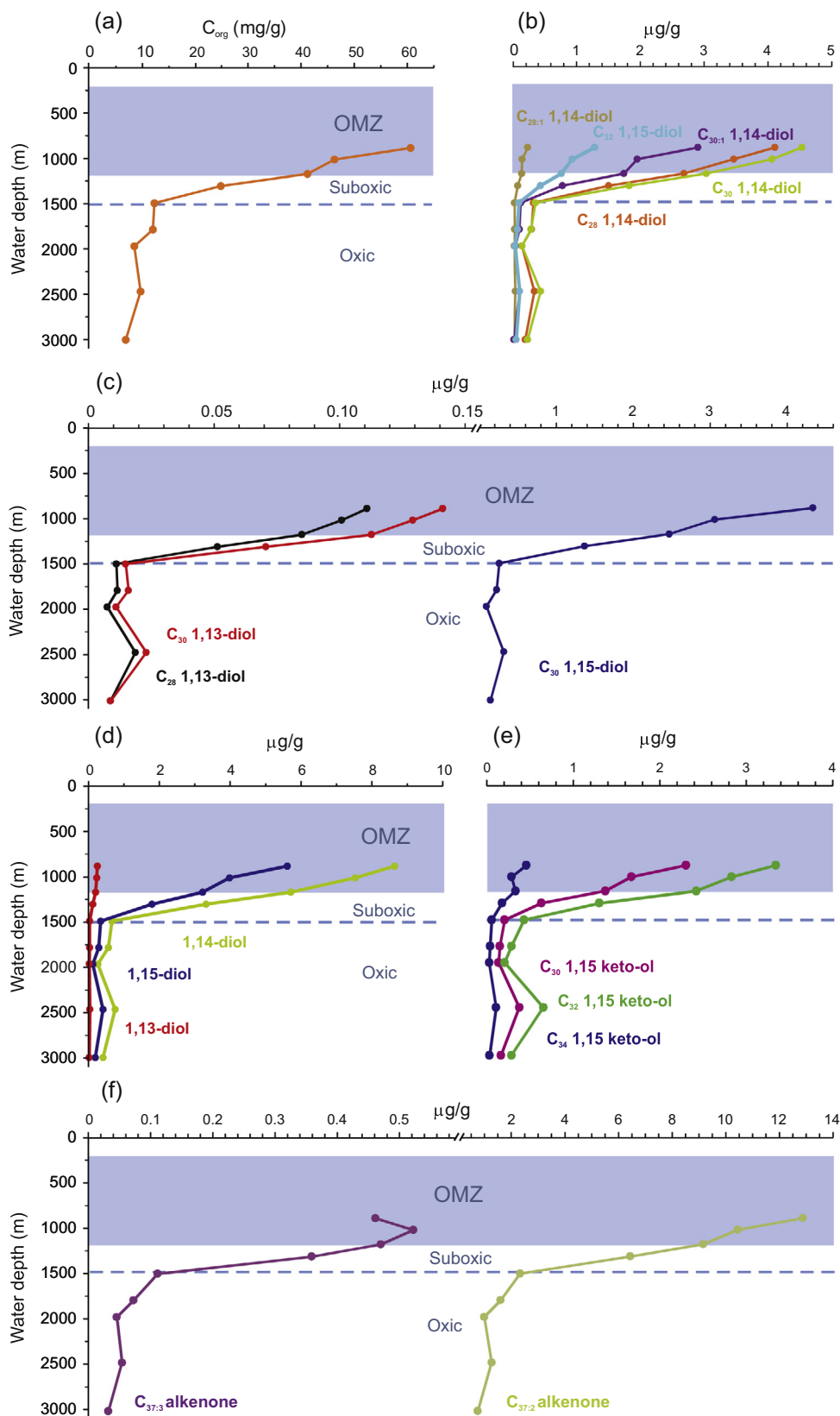


Fig. 2. Profiles of different parameters in the surface sediments (0.5 cm) from the Murray Ridge plotted with water depth. (a) organic carbon content (mg/g), (b) diol concentrations ($\mu\text{g/g}$), (c) LDI-diol concentrations ($\mu\text{g/g}$), (d) summed 1,15-, 1,14- and 1,13-diol concentrations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

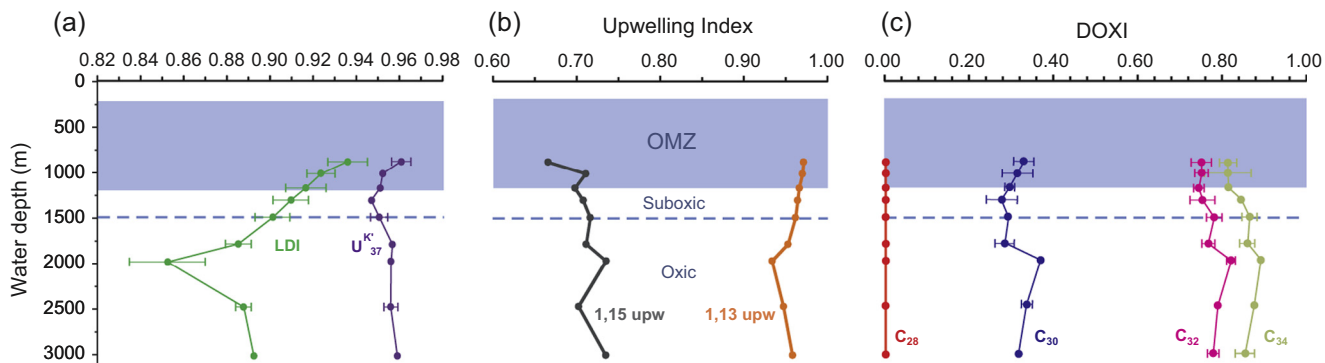


Fig. 3. Indices determined in the surface sediments (0.5 cm) from the Murray Ridge. (a) U_{37}^K and LDI indices, (b) Upwelling indices (1,15 upw = 1,14-diols over 1,14- + 1,15-diols, cf. Rampen et al., 2008; and 1,13 upw = 1,14-diols over 1,14- + 1,13-diols, cf. Willmott et al., 2010), and (c) DOXI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

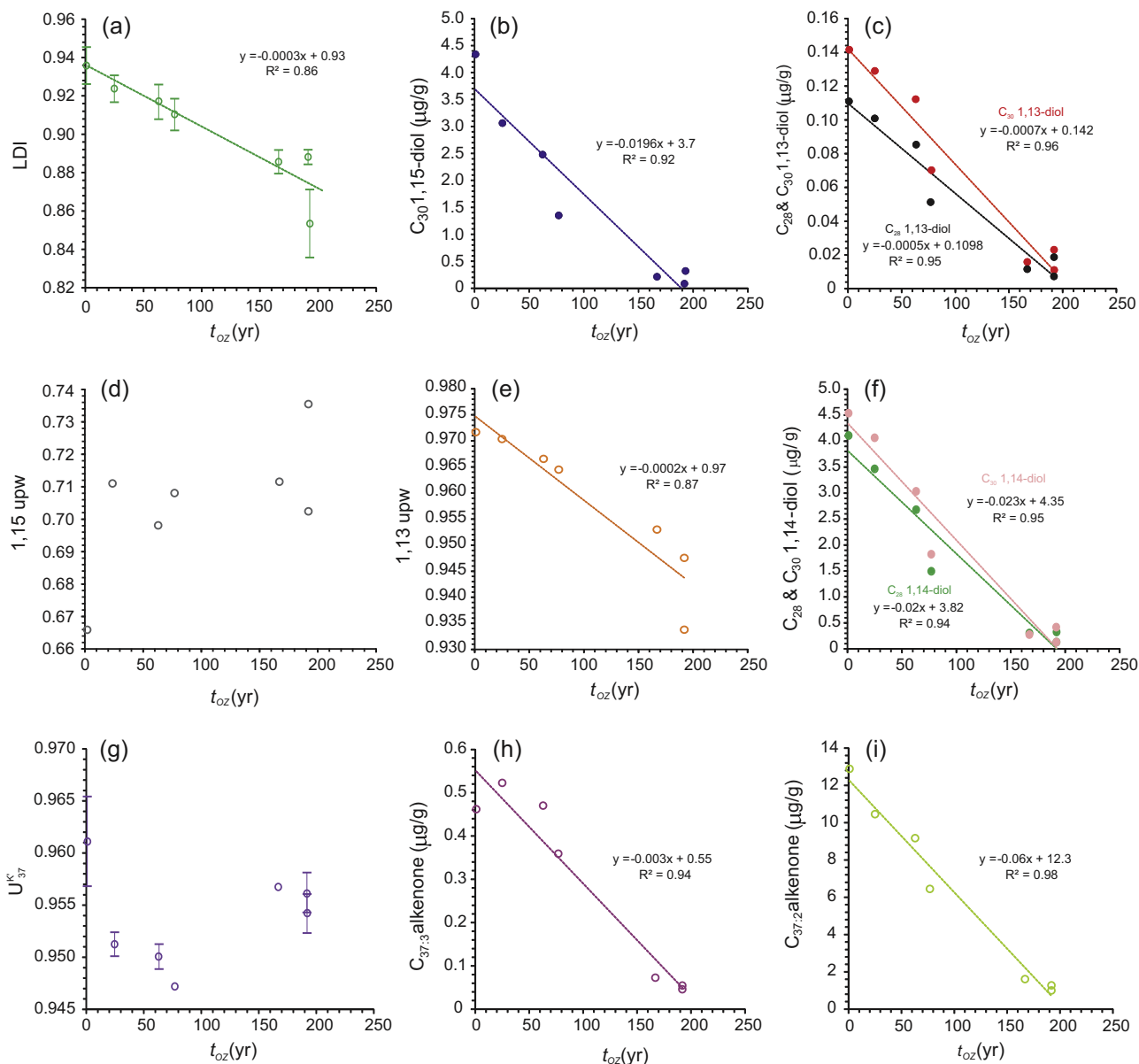


Fig. 4. Cross-plots of the residence time in the oxic zone of the sediment (t_{oz}) expressed in years (yr) with (a) LDI, (b) C_{30} 1,15-diol concentration ($\mu\text{g/g}$), (c) C_{28} – C_{30} 1,13-diol concentrations ($\mu\text{g/g}$), (d) 1,15 upw, (e) 1,13 upw, (f) C_{28} – C_{30} 1,14-diol concentrations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

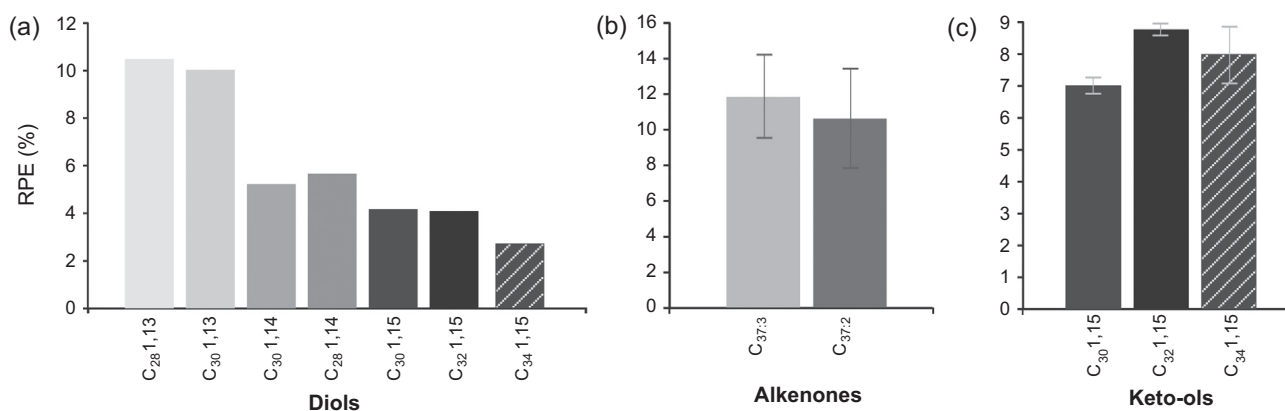


Fig. 5. Bars plot of relative preservation efficiency (RPE) (i.e. relative amount in oxic sediment versus anoxic sediment, in %) of (a) diols, (b) individual C₃₇ alkenones, and (c) keto-ols. Error bars represent duplicate analysis.

a release of diols by hydrolysis during early diagenesis. If, for example, 1,13-diols are more abundant in a bound form than in the free form, then the release of these bound diols during diagenesis could lead to an apparent higher RPE for 1,13-diols.

Alkenone concentrations also dropped substantially with increasing water depth and t_{OZ} (Figs. 2f, 4h and i), indicating that they are affected by oxic degradation as well. They showed similar values for RPE, i.e. 10–12% (Fig. 5b) as the 1,13-diols (~11%), but higher than those for 1,14- and 1,15-diols. There is a slight difference in RPE for both alkenones, i.e. 12% for C_{37:3} and 10.6% for C_{37:2} (Fig. 5b), but this is mainly caused by the sediment of station P900 (at 885 m water depth), which seems somewhat anomalous with respect to the concentration of the C_{37:3} alkenone. If the alkenone concentrations in the sediment of station P1000 (at 1013 m water depth, still within the OMZ, Fig. 1b) are used, then RPEs of both alkenones are relatively similar, in agreement with previous observations in this region (Sinninghe Damsté et al., 2002).

4.2. Impact of oxic degradation on paleoenvironmental proxies

Because the 1,13-diols are slightly better preserved (Fig. 5a) than 1,15-diols, the LDI decreases from 0.94 to 0.85 with increasing water depth (Fig. 3a). Moreover, a linear negative correlation of LDI with t_{OZ} is observed ($R^2 = 0.86$; Fig. 4a), suggesting that the LDI is affected by oxic degradation. Low abundances of biomarkers may lead to analytical biases as has been observed with the U₃₇^K (Villanueva and Grimalt, 1997). However, a dilution test (data not shown) showed that the changes in LDI values are not because of analytical artifacts due to the low amounts of diols present in the oxidized sediments. When translated to SST, the LDI variations correspond to a change from 25.5 to 24 °C, with a minimum of 23 °C at ca. 2000 m water depth in the oxic zone. This change of ca. 1.5–2.5 °C is similar to, or even exceeds if we consider the somewhat anomalous data point at ca. 2000 m water depth, the calibration error of this proxy (2 °C; Rampen et al., 2012), suggesting that this SST proxy can be affected by oxic degradation.

For comparison, we also analyzed the established SST proxy based on alkenones, the U₃₇^K index. A previous study of alkenones in sediments from the Murray Ridge in the Arabian Sea documented no significant degradation effect (Sinninghe Damsté et al., 2002). Indeed, U₃₇^K values showed, with the exception of the shallowest sediment, no significant variation with increasing water depth (Fig. 3a) and thus with increasing residence time in the oxic zone of the sediment (Fig. 4g). The mean U₃₇^K value of 0.96 corresponds to 27.6 °C when translated to SST (Fig. 3a). This U₃₇^K-estimated SSTs are in good agreement with present annual mean SST in the Arabian Sea (ca. 27 °C, World Ocean Atlas 09 database; Locarnini et al., 2010).

Another paleotemperature proxy, the TEX₈₆, was previously measured in the same set of surface sediments as studied here and showed differences in derived SST with increasing water depth and t_{OZ} , corresponding to higher values of up to 3 °C (Lengger et al., 2014). Although several hypotheses were put forward, the reasons for this change in TEX₈₆ were not clear.

The upwelling indices based on diols showed contrasting patterns compared to each other as a result of the different degradation rates of 1,14-diols vs. 1,15- and 1,13-diols (Fig. 2b–c). The upwelling index based on 1,14- vs. 1,15-diols (Rampen et al., 2008), did not correlate with t_{OZ} (Fig. 4d), but an apparent correlation is observed for the upwelling index based on 1,14- vs. 1,13-diols (Willmott et al., 2010) (Fig. 4e). Indeed, the latter index displays a small, but significant, decreasing trend with increasing water depth (Fig. 3b). However, these changes (<0.05 units) are relatively small compared to changes documented in Arabian Sea sediment trap records (>0.05 units; Rampen et al., 2007) and in globally distributed surface sediments (Rampen et al., 2014a).

Thus, among the diol based proxies tested in this study the LDI seems to be most affected by preferential oxic degradation in the Arabian Sea. These results indicate that this effect has to be taken into consideration, especially when paleotemperature reconstructions are performed in sediments where bottom water oxygen concentrations or oxygen penetration depths have varied substantially over time.

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

Keto-ols have been described as oxic transformation products of diols (e.g. Jiang et al., 1994; Ferreira et al., 2001; Versteegh et al., 1997, 2010). Keto-ol concentrations in an unoxidised sapropel layer in the eastern Mediterranean were lower than at the base of the oxidized sapropel (Ferreira et al., 2001), suggesting that keto-ols are formed by oxidation of diols. Based on these observations, the DOXI was proposed as a potential indicator for paleo-oxicity in the water column (Ferreira et al., 2001). In the Arabian Sea surface sediments, one might expect higher abundances of keto-ols relative to diols in sediments with a higher exposure time to oxygen. The C₃₀–C₃₄ 1,15-keto-ol concentrations showed a strong decrease with increasing water depth, similar to that of the diols (Fig. 2e), and remained always lower than the corresponding 1,15-diols (Fig. 2c–e). However, the C₃₀–C₃₄ keto-ols were apparently slightly better preserved than the corresponding diols, i.e. the RPE of the 1,15-keto-ols (~8%) is slightly higher than that of the 1,15-diols (~4%) (Fig. 5c). Indeed, the C₃₀, C₃₂ and C₃₄ 1,15 DOXI ratios are slightly higher in the oxic zone compared to the anoxic zone but the differences are relatively minor (Fig. 3c). This

is in contrast with results of a similar study along the OMZ transect on the Pakistan continental margin, which showed a much stronger increase of the C_{30} 1,15 DOXI ratio with increasing oxygen concentrations (Bogus et al., 2012). The reason for the reduced DOXI values increase in the Arabian Sea sediments might be the much lower bottom water oxygen concentrations (45–77 $\mu\text{mol/L}$) and oxygen penetration depths (6–19 mm; Lengger et al., 2014) vs. those at the Pakistan margin (220 $\mu\text{mol/L}$ and 25 mm, respectively; Bogus et al., 2012). Indeed, Bogus et al. (2012) observed a much smaller increase in DOXI values in sediments with bottom water oxygen concentrations and oxygen penetration depths comparable to the Arabian Sea sediments studied here. This suggests that DOXI values only substantially increase after a long-term exposure to high oxygen concentrations.

Interestingly, the keto-ols are already observed in sediments from within the OMZ. This may suggest that they were already formed in the upper part of the oxic water column overlying the OMZ. This is supported by sediment trap material collected in and below the OMZ of the Arabian Sea, which contained both C_{30} 1,15-keto-ols and saturated and mono-unsaturated C_{30} 1,14-keto-ols (Rampen et al., 2007). However, a previous study of biomarkers in sedimenting particles in and below the OMZ in the Arabian Sea documented that the degree of degradation of biomarkers in the water column is insignificant relative to that in the surface sediment (Wakeham et al., 2002) due to relatively short oxygen exposure time during sinking of the particles. Therefore, it is not expected that keto-ols are formed solely by oxic transformation in the water column during the vertical transport to the sea floor.

Another possibility is that keto-ols are synthesized by the algae themselves, i.e. eustigmatophytes or as yet unknown algae (Versteegh et al., 1997; Méjanelle et al., 2003). Méjanelle et al. (2003) identified C_{28} – C_{36} diols and C_{30} – C_{32} keto-ols with the C_{32} keto-ol slightly dominating over the other homologs in a marine eustigmatophyte, *Nannochloropsis gaditana*. In addition, only the 1,15-isomer was observed for the C_{32} keto-ol, while 1,13-isomer together with the 1,15-isomer in minor amounts were observed for the C_{30} keto-ol (Méjanelle et al., 2003). In the Arabian Sea surface sediments we identified C_{30} to C_{34} keto-ols with a predominance of 1,15- over 1,13-isomers, while 1,14-isomers were below detection limit (data not shown). Similar to what has been observed in *Nannochloropsis gaditana*, the C_{32} 1,15 keto-ol was in slightly highest abundance (Fig. 2e). Nevertheless, keto-ols and diols are within the same order of magnitude in marine sediments whereas a marked disproportion is observed in the algal cultures. Further evidence for a biological imprint on the distribution of keto-ols comes from the observation that DOXI values differ substantially between carbon chain lengths (Fig. 3c), suggesting some initial biological control for either diols or keto-ols, possibly eustigmatophytes and/or yet additional unidentified algae, and the contribution, at least to some extent, to the sediment.

5. Conclusions

In order to determine the effect of oxic degradation on diols and keto-ols, we analyzed nine surface sediments in the Arabian Sea deposited under contrasting bottom water oxygen concentrations. In general, the concentrations of all diols showed a strong decrease with increasing oxygen concentration and increasing residence time in oxic zone of the sediment. A higher degradation rate was found for 1,15-diols, followed by 1,14-diols and 1,13-diols. The LDI showed a decrease from 0.95 to 0.88 with increasing water depth, corresponding to ca. 2–3.5 °C when translated to SST. For comparison with an established SST proxy, we have also analyzed alkenone concentrations and the U_{37}^K index, obtaining that individ-

ual alkenones were affected by oxic degradation as well, but no significant changes are observed in the U_{37}^K index. Therefore, care has to be taken when the LDI is applied as SST proxy in sediments underlying OMZs or where bottom water oxygen concentrations have varied substantially over time. In contrast, upwelling indices based on the ratios of 1,14-diols versus 1,13- or 1,15-diols showed relatively small changes, indicating that these proxies are not substantially affected by variations in bottom water oxygen conditions. C_{30} – C_{34} keto-ol concentrations are apparently slightly less degraded with increasing oxygen exposure time compared to diols and DOXI values show a small increase between the anoxic to the oxic zone. Possibly, longer exposure times to oxygen are needed in order to substantially increase DOXI values.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.orggeochem.2016.07.003>.

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