



# The influence of oxygen exposure time on the composition of macromolecular organic matter as revealed by surface sediments on the Murray Ridge (Arabian Sea)

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## Abstract

The Arabian Sea represents a prime example of an open ocean extended oxygen minimum zone (OMZ) with low oxygen concentrations (down to less than 2  $\mu\text{M}$ ) between 200 and 1000 m water depth. The OMZ impinges on the ocean floor, affecting organic matter (OM) mineralization. We investigated impact of oxygen depletion on the composition of macromolecular OM (MOM) along a transect through the OMZ on the slopes of the Murray Ridge. This sub-marine high in the northern Arabian Sea, with the top at approximately 500 m below sea surface (mbss), intersects the OMZ. We analyzed sediments deposited in the core of OMZ (suboxic conditions), directly below the OMZ (dysoxic conditions) and well below the OMZ (fully oxic conditions). The upper 18 cm of sediments from three stations recovered at different depths were studied. MOM was investigated by Rock Eval and flash pyrolysis techniques. The MOM was of a predominant marine origin and inferred from their pyrolysis products, most biomolecules (tetra-alkylpyrrole pigments, polysaccharides, proteins and their transformation products, and polyphenols including phlorotannins), showed a progressive relative degradation with increasing exposure to oxygen. Alkylbenzenes and, in particular, aliphatic macromolecules increased relatively. The observed differences in MOM composition between sediment deposited under various bottom water oxygen conditions (i.e. in terms of concentration and exposure time) was much larger than within sediment cores, implying that early diagenetic alteration of organic matter depends largely on bottom water oxygenation rather than subsequent anaerobic degradation within the sediments, even at longer time scales.

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## 1. INTRODUCTION

Oxygen minimum zones (OMZs) are well known for their essential role in global biogeochemical cycles (e.g. Codispoti et al., 2001). Together with the Eastern Tropical North Pacific, the Eastern South Pacific and the Bay of

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Bengal, the Arabian Sea is one of the four major oceanic tropical OMZs (Paulmier and Ruiz-Pino, 2008). The Arabian Sea covers about 1% of the World's ocean surface but it accounts for approximately 5% of global marine primary production (Cowie, 2005). Monsoon-driven upwelling leads to high productivity, whereas the OMZ causes limited organic matter (OM) decomposition within the water column, which results in relatively high organic carbon accumulation rates in Arabian Sea sediments (Lee et al., 1998). Consequently, these sediments represent a disproportionately large long-term carbon sink (Cowie, 2005).

The majority of OM leaving the productive surface waters is remineralized while settling through the water column (e.g. Berger et al., 1989). Still, subsequent processing in surface sediments results again in extensive degradation of OM after deposition (e.g. Middelburg, 1989). Consequently by far the largest part of OM produced in the photic zone of the ocean (i.e. 90–99%) is ultimately recycled back to inorganic carbon (Hedges and Keil, 1995). The mechanisms driving OM preservation in sediments have been subject of debate for several decades (Hedges, 1988; Hatcher and Spiker, 1988; Hedges and Keil, 1995; Derenne and Largeau, 2001; Vandenbroucke and Largeau, 2007; Zonneveld et al., 2010; Koho et al., 2013). The main factors considered include the molecular composition of the source organisms and their transformation products formed upon decay while passing through the water column, chemical and physical stabilization of OM by mineral surfaces and within aggregates, and the exposure to molecular oxygen (Hedges et al., 1999; Zonneveld et al., 2010; Koho et al., 2013). The latter factor is further influenced by bottom water and pore water oxygen concentrations and accumulation rates of the sediments (Hedges et al., 1999). However, there is no consensus about the role of oxygen in controlling OM preservation (Canfield, 1994; Calvert et al., 1995; Van der Weijden et al., 1999; Burdige, 2007). Many other factors also directly or indirectly affect OM preservation under oxygen-depleted conditions, under which electron donors such as nitrate, sulfate, iron and manganese oxides can be used by microorganisms to oxidize OM as well (e.g., Middelburg and Levin, 2009).

Apart from the quantity, the quality of the OM is affected by the extent (time, concentration) to which it has been exposed to oxygen. The composition of carbohydrates, lignin phenols and amino acids of surficial sediments in the Arabian Sea showed little cross-margin trend consistent with higher OM 'quality' (i.e., higher microbial degradability) within the OMZ (Cowie et al., 1999). In addition, based on the degradation index of hydrolysable amino acids, Vandewiele et al. (2009) concluded that all sedimentary OM across the OMZ has been extensively degraded, and under prolonged oxygen exposure even further degradation occurred compared to burial under oxygen depleted conditions. Sinninghe Damsté et al. (2002) showed that individual (extractable) organic biomarkers have different degradation rates when exposed to oxygen in Arabian Sea sediments, thereby leading to, for example, a significant relative enrichment of terrestrial biomarkers upon prolonged oxygen exposure. The major part of the

OM is, however, not extractable and is defined as macromolecular OM (MOM). Using solid-state  $^{13}\text{C}$  NMR Hedges et al. (2001) concluded that during transport through the water column (including that of the Arabian Sea) hardly any compositional differences took place even though 98–99% of the original particulate OM had been decomposed. Using oxidized and un-oxidized parts of Madeira abyssal plane turbidites, Hoefs et al. (1998) observed that isoprenoid compounds were less well preserved under oxic conditions while saturated aliphatic macromolecules were relatively enriched. While comprising the major constituents of marine biota, both polysaccharides and proteins represent much smaller fractions of sedimentary OM, whereas lignin is only important if terrestrial (i.e. higher plant-derived) OM is contributing substantially (e.g., Wakeham et al., 1997).

Part of the MOM is considered to be 'uncharacterizable', i.e. cannot be categorized as belonging to known biopolymers after transformations during diagenesis (Hedges et al., 2000). Solid state  $^{13}\text{C}$  NMR is one technique that is able to characterize all the carbons in insoluble MOM irrespective in which form it may exist. However, a drawback of  $^{13}\text{C}$  NMR is that in complex mixtures, such as MOM, the identification of individual molecules is difficult. Another technique that affords more insight into the overall MOM composition at the molecular level – independent of whether constituents are hydrolysable or not – is flash pyrolysis (Larter and Horsfield, 1993). Upon pyrolysis macromolecular compounds are thermally fragmented into volatile components that can be analyzed employing gas chromatography-mass spectrometry. Despite some limitations, this technique provides molecular fingerprints that allows for comparison of different samples of MOM.

Here we studied differences in the composition of MOM insoluble in organic solvents, often referred to as kerogen, as affected by differences in bottom water oxygen (BWO) concentrations overlying surface sediments (upper 20 cm) from the Arabian Sea. Assuming a similar composition of the OM produced within the photic zone overlying the Murray Ridge (cf. Schubert et al., 1998; Sinninghe Damsté et al., 2002), OM degradation within the water column and preservation of OM in the sediment is affected largely by exposure to oxygen. The rationale to argue that the organic matter flux is compositionally quite similar when sinking from the photosynthetic zone to the sea floor is that these stations are situated in the open ocean quite closely together. All stations are roughly 200 nautical miles off shore and hence rivers or other (local) influences on marine biomass composition are small. Although increasing BWO will increase microbial and faunal activity, which subsequently enlarge the bioturbation zones (Koho et al., 2013) and will impact OM degradation, all of these factors are governed by the differences in oxygenation, and, therefore, secondary with regard to BWO as well as oxygen exposure times. This makes the northern Arabian Sea a perfect natural laboratory to test the impact of oxygen-depleted bottom waters on sediment OM processing, and early diagenesis. Three different stations, representing the core of the OMZ, the dysoxic zone directly below the OMZ

and the oxic zone in the deeper part of the water column were examined to determine to which extent the various groups of OM constituents were susceptible towards oxic degradation.

## 2. MATERIALS AND METHODS

### 2.1. Sample area and collection

The Murray Ridge is a sub-marine mountain in the northern Arabian Sea with its top at approximately 500 m below sea surface (mbss) intersecting the OMZ. Annual high surface water productivity (between 200 and 400  $\text{gC m}^{-2} \text{yr}^{-1}$ ; [Kabanova, 1968](#); [Qasim, 1982](#); [Codispoti, 1991](#)) and moderate rates of thermocline ventilation ([You and Tomczak, 1993](#)), result in an intense OMZ between 150 and 1200 m ([Wyrтки, 1973](#); [Deuser et al., 1978](#); [Olson et al., 1993](#)). On geological timescales the intensity of Arabian Sea OMZ appears to fluctuate on orbital and sub-orbital timescales, minimum OMZ intensity coinciding with productivity low and high winter mixing during the climatic cooling in the North Atlantic ([Reichart et al., 1998](#)). Also seasonal changes occur between monsoon and winter. However, on the <10 ky time scale our study is dealing with the conditions in the Arabians Sea are quite similar ([Cowie and Levin, 2009](#)). Multicores were recovered from sediments during the PASOM cruise on the R/V Pelagia (6–25 January 2009) at ten different stations, which varied in water depth and thus in oxygen concentration of the bottom waters impinging on the slopes of the Murray Ridge ([Fig. 1](#)). Cores were sliced on board during the cruise immediately upon recovery.

For the present study, we choose three stations representing suboxic, dysoxic and oxygenated bottom water conditions. Multicores were selected accordingly from the OMZ core (885 mbss, 2.0  $\mu\text{M O}_2$ ) ('OMZ station'), in dysoxic waters below the OMZ (1306 mbss, 14.3  $\mu\text{M O}_2$ ) ('dysoxic station'), and from the oxic waters in the deeper part of the water column well below the OMZ (1791 mbss, 42.8  $\mu\text{M O}_2$ ) ('oxic station') ([Koho et al., 2013](#)). Samples from these cores at depth intervals 0–0.5 cm, 1.5–2 cm, 5–6 cm, 9–10 cm and 16–18 cm were selected for analysis, and were

stored at 4 °C until analysis. [Table 1](#) summarizes the main topographical and bulk chemical characteristics of the three stations selected.

### 2.2. Total organic carbon (TOC) analysis

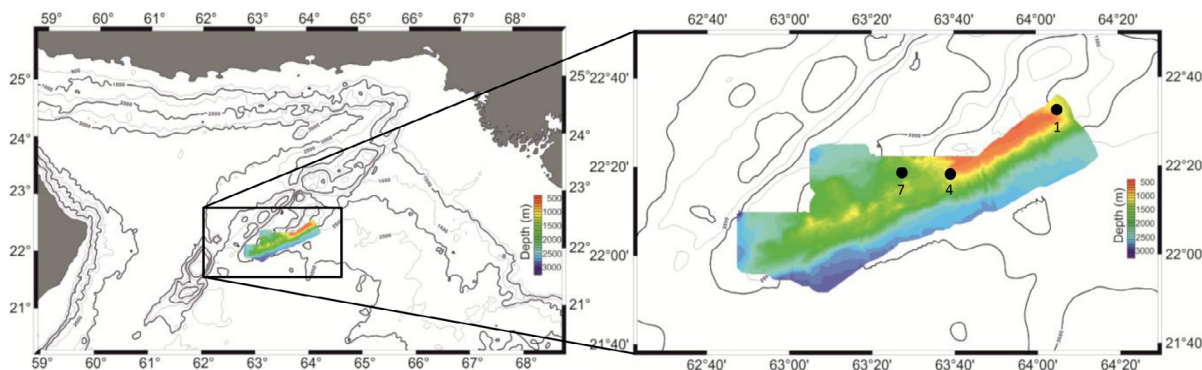
Prior to analysis, sediments were freeze-dried. Inorganic C was removed by shaking the sediments with 1 M HCl twice at room temperature for 4 and 12 h, respectively. The samples were then rinsed twice with demineralized water, centrifuged and decanted, freeze-dried and ground in an agate mortar. TOC was determined for all sediment samples with a Fisons Instruments CNS NA 1500 analyzer using methods previously described ([Kraal et al., 2012](#)). The relative error in the TOC analysis was <1%. Earlier tests showed that amount of TOC hydrolyzed by the HCl treatment is negligible ([Van Santvoort et al., 2002](#)).

### 2.3. Isolation of MOM

To isolate the MOM, 5–10 g of freeze-dried sediment were Soxhlet extracted with dichloromethane:methanol (9:1 (v/v)) for 24 h, after which the residues were air-dried. Next, the residues were treated with 1 M HCl for at least 4 h to remove carbonates. After that, water was added, and the samples were left standing over night. After centrifuging, the solution was decanted, and the container was filled up with water, shaken again for 1 h, centrifuged and decanted again. Subsequently, an excess of HF 40% was added and shaken for 2 h. Then the solution was diluted with water and left standing over one night after which the solution was decanted. An excess of HCl 30% was added and subsequently diluted with water. After decantation, the residues were rinsed three times with water reaching a neutral pH. Finally, the organic-rich residues obtained were freeze-dried.

### 2.4. Rock Eval pyrolysis

A Rock-Eval 6 apparatus (Vinci Technologies) ([Behar et al., 2001](#)) was used to characterize sediments and MOM isolated from these sediments, and in particular to



**Fig. 1.** Topographical map of the Arabian Sea of the Murray Ridge and the stations studied. 1: OMZ station, 4: dysoxic station, and 7: oxic station.

Table 1

Station positions, water depth, bottom water oxygen (BWO) content, sedimentation rates, median grain size, silt, total organic carbon (TOC) and total inorganic carbon (TIC) contents, bioturbation and O<sub>2</sub> penetration depths.

Station PASOM	Station name	Lat (N)	Lon (E)	Depth (mbss)	BWO (μM)	Sedimentation rate (cm/kyr)	Median (μm)	Silt (%)	TOC (%)	TIC (%)	Bioturbation depth (cm)	O <sub>2</sub> pen. depth (mm)
1	OMZ	22°32.9'	64°02.4'	885	2.1	13.4	35.4	70.4	6.6	6.3	2	0
4	Dysoxic	22°18.0'	63°36.0'	1306	13.8	3.8	29.6	71.4	2.7	7.2	3	3
7	Oxic	22°18.5'	63°24.5'	1791	45.2	4.5	16.6	92.2	1.1	6.5	6–7	10

determine the extent to which the organic-rich residues were pyrolysable. An amount of 5–80 mg was heated (N<sub>2</sub> atmosphere) for 3 min. at 300 °C, followed by a temperature ramp of 25 °C/min up to 650 °C. During the pyrolysis program, the mass of the released hydrocarbons ( $m_{\text{fid}}$ ) was determined with a flame ionization detector (FID) and the mass of the released CO ( $m_{\text{pyr-CO}}$ ) and CO<sub>2</sub> ( $m_{\text{pyr-CO}_2}$ ) by an infrared cell (Behar et al., 2001; Sanei et al., 2005). The pyrolysable organic C (PC) content is determined from these data, by correction for molecular weights:

$$\text{PC} = m_{\text{fid}} \cdot 0.83 + m_{\text{pyr-CO}} \cdot 12/28 + m_{\text{pyr-CO}_2} \cdot 12/44 \quad (1)$$

The value 0.83 is based the maximum amount of C present in organic matter and subsequently tested (Espitalié et al., 1987; Lafargue et al., 1998; Dahl et al., 2004). After the pyrolysis step, the residual organic C (RC) content was determined by oxidation (combustion) and the mass of the released CO ( $m_{\text{res-CO}}$ ) and CO<sub>2</sub> ( $m_{\text{res-CO}_2}$ ) was also measured with an infrared cell. The residual material refers to black carbon, soot, etc. Equivalent to Eq. (1) the RC is defined as:

$$\text{RC} = m_{\text{res-CO}} \cdot 12/28 + m_{\text{res-CO}_2} \cdot 12/44 \quad (2)$$

The sum of PC + RC yields the TOC content, from which the pyrolysable fraction can be calculated.

Two other parameters derived from Rock Eval pyrolysis are: (i)  $T_{\text{max}}$ , the temperature (in °C) at which maximal amount of hydrocarbon is released and (ii) the hydrogen index (HI, in mg HC/g TOC). HIs are primarily used as indicators of hydrogen richness and preservation state of OM, and thus of OM 'quality'. HI values between 200 and 400 indicates marine-derived OM, whereas terrestrial OM has an HI < 100 (Espitalié et al., 1984). Similarly, smaller HIs would point to a lower preservation state. A cross plot of HI and  $T_{\text{max}}$  provides the nature of organic matter in terms of kerogen types (I, II and III) (Tissot and Welte, 1984; Langford and Blanc-Valleron, 1990).

## 2.5. Pyrolysis-gas chromatography-mass spectrometry and thermally assisted hydrolysis and methylation (THM)

Pyrolysis was carried out on a Horizon Instruments Curie-Point pyrolyser. Samples (typically 1–2 mg) were pressed onto Ni/Fe Curie point wires and subsequently heated for 5 s at 600 °C. The pyrolysis unit was directly connected to a Carlo Erba GC8060 gas chromatograph and the products were separated by a fused silica column (Varian, 25 m, 0.32 mm i.d.) coated with CP-Sil5 (film thickness 0.40 μm). Helium was used as carrier gas. The

GC column was directly connected to the pyrolysis unit through a splitless injector set at 280 °C. The oven was initially kept at 40 °C for 1 min, next it was heated at a rate of 7 °C/min to 320 °C and maintained at that temperature for 15 min. The column was coupled to a Fisons MD800 mass spectrometer (mass range  $m/z$  45–650, ionization energy 70 eV, cycle time 0.7 s). Thermally assisted Hydrolysis and Methylation, i.e. pyrolysis in the presence of tetramethylammonium hydroxide (TMAH) was also employed to provide more insight in the composition of polar components. With THM, hydrolysable bonds are cleaved and the resulting carboxylic acid and hydroxyl groups are transformed *in situ* to the corresponding methyl esters and methyl ethers, respectively. Prior to THM, a droplet of a 25% solution of TMAH in water was added to the samples, which were subsequently dried under a 100 W halogen lamp. Analysis of the THM products by way of GC-MS was performed similar to the conditions used for conventional pyrolysis.

Identification of the compounds was carried out by their mass spectra using a NIST library or by interpretation of the spectra, by their retention times and/or by comparison with literature data. Quantification was performed by peak integration using two main fragment ions of each compound (see Supplementary Table 1). Of the peak areas relative contributions of each compound and groups of compounds were calculated using the correction factors reported by Menzel et al. (2005). For the polysaccharide-derived compounds a correction factor of 2.5 was applied assuming a similar MS response as alkylthiophenes used by Menzel et al. (2005). Relative preservation of compound classes ( $x$ ) for the dysoxic and oxic stations relative to the OMZ station were calculated as follows:

$$\begin{aligned} &\text{Preservation efficiency}(x) \\ &= [\text{RA}(x) \cdot \text{organic carbon accumulation rate}(\text{station } y)] \\ & \quad / [\text{RA}(x) \cdot \text{organic carbon accumulation rate} \\ & \quad (\text{OMZ station})] \cdot 100\% \end{aligned} \quad (3)$$

where  $\text{RA}(x)$  = relative abundance of compound class  $x$ , and  $y$  the dysoxic or oxic station. Organic carbon accumulation rates were taken from Koho et al. (2013): 0.41 (OMZ station), 0.11 (dysoxic station) and 0.05 g C/cm<sup>2</sup> kyr (oxic station), respectively.

This approach does not imply absolute preservation, but rather normalizes preservation to a common denominator, assuming that this represents conditions with optimal preservation.



### 3. RESULTS

#### 3.1. Total organic carbon, selection of sediments

The average TOC content as a function of overlying BWO concentration of all ten stations recovered during the PASOM cruise ranged from 6.6% within the OMZ to 0.76% well below the OMZ at 3000 mbss (Fig. 2a).

The downcore profile of the TOC content for the three stations selected showed that, apart from the sediment interval at 2 cm, that contained the smallest TOC concentration, the OMZ station displayed an increase in TOC content with increasing sediment depth (Fig. 2b). For the dysoxic station the TOC content was rather constant, while the oxic station had somewhat higher TOC concentrations at the sediment-water interval than the intervals at 2 cm and deeper.

#### 3.2. Rock Eval pyrolysis

Rock Eval pyrolysis was applied to the sediments obtained after organic solvent extraction and to isolated,

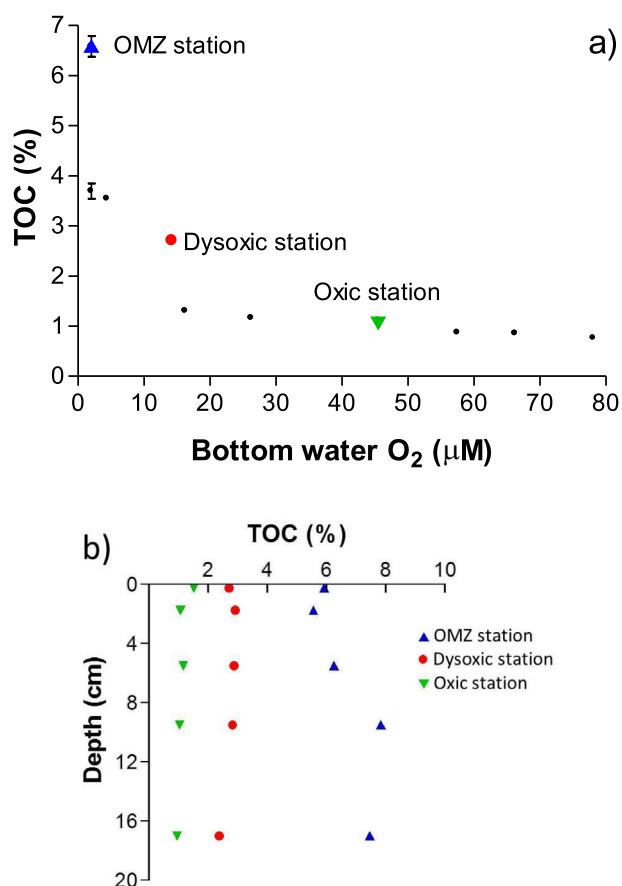


Fig. 2. (a) Average TOC contents of surface sediments sampled along the Murray Ridge in the Arabian Sea as a function of BWO concentration. (b) Downcore profiles of the TOC content of the sediments sampled at 885 (OMZ station), 1306 (dysoxic station) and 1791 mmbs (oxic station).

demineralized MOM to characterize the MOM at a bulk level. On average, the relative amounts of pyrolysable TOC compared to the total TOC in sediments ranged from 37.9% (OMZ station) to 32.8% (dysoxic station) and 26.2% (oxic station). The hydrogen index (HI) increased clearly with increasing TOC content ( $R^2 = 0.60$ ) (Fig. 3). HIs are primarily used as measures of OM hydrogen richness and preservation state, and thus of OM ‘quality’ (cf. Cowie et al., 1999).

By contrast, after HF-HCl treatment, no dependence of HI on TOC content was evident; the HI was more or less constant at around 350 mg HC/g TOC (Fig. 3). On average, 39.3% (SD 1.9%) of all isolated MOM was pyrolysable, ranging from 40.0% (OMZ station) to 39.7% (dysoxic station) and 38.1% (oxic station). The average HI for each station ranged from 365 mg HC/g TOC (OMZ station) to 355 mg HC/g TOC (dysoxic station) and 327 mg HC/g TOC (oxic station). From the HI- $T_{max}$  plot (not shown) the so-called kerogen type can be deduced and, not surprisingly, all our samples were of type II, which is generally of marine origin (Tissot and Welte, 1984; Langford and Blanc-Valleron, 1990). In addition, the declining HI when going from the OMZ to the dysoxic and oxic stations suggests a lower preservation state of the latter. For the (organic solvent extracted) sediments the organic matter shows a somewhat wider range, and can be classified as kerogen type II/III.

#### 3.3. Flash pyrolysis

To characterize the isolated MOM at a molecular level, flash pyrolysis in combination with gas chromatography-mass spectrometry was employed. The pyrolysates of the MOM isolated from the three stations were dominated by aromatic moieties (alkylbenzenes, furans, pyranes, alkylpyrroles, alkylpyridines, alkylindoles, diketodipyrrole, diketopiperazines, alkylphenols, tocopherol), anhydrosugars, and a homologous series of *n*-alkenes/*n*-alkanes along with some isoprenoids (prist-1-ene and phytadienes) (Supplementary Figs. S1–3 and supplementary Table 1).

Alkylbenzenes represented prominent pyrolysis products of the isolated MOM and included benzene, toluene, C<sub>2</sub>-, C<sub>3</sub>- and C<sub>4</sub>-benzenes. The alkyl substituents were limited to methyl and ethyl groups only. The C<sub>4</sub>-benzenes were dominated by 1,2,3,4-tetramethylbenzene. In addition, small traces of C<sub>5</sub>-benzenes such as 1-ethyl-2,3,6-trimethylbenzene were identified.

The pyrolysates also contained prominent peaks of phenol and methylphenols. Dimethyl- and ethylphenols were also observed albeit in much smaller abundance, while traces of catechol were found for the OMZ station only. Upon THM 1,2,3-, 1,2,4- and 1,3,5-trimethoxybenzenes were identified in the isolated MOM. In all sediment intervals studied from the OMZ station 1,3,5-trimethoxybenzene (and 2,4,6-trimethoxytoluene) were relatively abundant, while for the other stations they were hardly (dysoxic) or not present (oxic), in contrast to 1,2,3- and 1,2,4-trimethoxybenzenes (Fig. 4).

One series of heterocyclic pyrolysis products from all stations included 2-furaldehyde, 5-methyl-2-furaldehyde

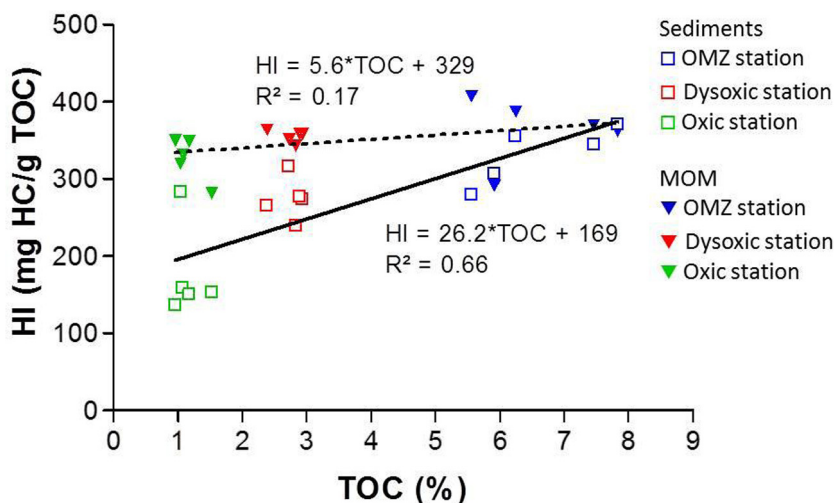


Fig. 3. Hydrogen index (HI) of the sediments after organic solvent extraction and of the MOM isolates as a function of the sedimentary TOC content.

and levoglucosenone. Apart from these major products traces of other oxygen containing heterocyclic pyrolysis products were found for 2-methyl-3-hydroxy-(4H)-pyran-4-one and 5-methyl-4-hydroxy-5,6-dihydro-(2H)-pyran-2-one.

Alkylpyrroles comprised the main group of N-containing heterocyclic compounds detected in the pyrolysates of the Arabian Sea sedimentary MOM. All alkyl substituents of these alkylpyrroles consisted either of a methyl or an ethyl group. Alkylpyridines were a second group of N-compounds identified, but in a smaller relative abundance than the alkylpyrroles. Although observed in relatively small amounts, indole, 3-methylindole, diketopyrrole and diketopiperazines were distinctly identifiable in all pyrolysates using characteristic fragment ions.

*n*-Alkenes/*n*-alkanes ranged from C<sub>9</sub> to maximal C<sub>25</sub>, and their abundances were rather similar until C<sub>19</sub> or C<sub>20</sub>, after which their abundance decreased. In addition to the compounds identified, all chromatograms of the pyrolysates exhibited ‘humps’, which represent unresolved complex mixtures.

### 3.4. Compositional trends

Fig. 5 displays the relative quantities of the eight major groups of pyrolysis products (*n*-alkenes/*n*-alkanes, prist-1-ene, phytadienes, alkylbenzenes, alkylphenols, polysaccharides, alkylpyrroles, and other N-compounds) and reveals differences in MOM composition between the three stations as well as with increasing sediment depth for each station. Polysaccharides refer to oxygen bearing heterocyclic compounds, which will be further discussed in Section 4.2.

With increasing oxygen exposure, the relative abundance of the summed *n*-alkenes/*n*-alkanes increased from 24% (OMZ station) and 25% (dysoxic station) to 40% (oxic station), suggesting that their source molecules have greater resistance against oxic degradation compared to other MOM constituents. Prist-1-ene and phytadienes decreased

relatively under oxic conditions, from 5.3% to 1.6% and from 2.2% to <0.5%, respectively. Polysaccharide-derived compounds comprised the second most abundant group of pyrolysis products at the OMZ station (20%), but decreased under dysoxic (13%) and oxic conditions (8%). Alkylbenzenes (benzene, toluene, styrene, C<sub>2</sub>-, C<sub>3</sub>- and C<sub>4</sub>-benzenes) represented the third largest group of pyrolysis products at the OMZ station (19%). Their relative abundance increased substantially at the oxic station (27%). Alkylphenols increased relatively from OMZ station (17%) to dysoxic station (19%) and oxic station (20%). The alkylpyrroles were relatively highest at the dysoxic station (13%), and were lower at the OMZ station (10%) and much lower at the oxic station (2%). Similarly, the other N-containing pyrolysis products (alkylpyridines, indoles and others) were much lower in relative abundance at the oxic surface sediment (0.3%) as compared to the OMZ and dysoxic stations (both 1.4%).

With sediment depth, *n*-alkenes/*n*-alkanes varied between 20% and 24% at the OMZ station without any depth trend, while at the dysoxic station their relative abundance was higher in the 5–18 cm range (28–32%) than in the upper part of the sediment (25% between 0 and 2 cm). At the oxic station the *n*-alkenes/*n*-alkanes remained fairly constant at 39–40%. Alkylpyrroles increased with sediment depth under OMZ conditions (from 10% to 20%), remained fairly constant at the dysoxic station (around 12–15%) and decreased under oxic conditions (from 5% to less than 2%). Other compound classes were relatively constant or showed invariable but small changes.

### 3.5. Oxic preservation efficiency

Fig. 6 plots the relative abundances of the various groups of pyrolysis products as functions of the TOC content, and thus inversely to increasing oxygen exposure time. The alkylpyrroles (Fig. 6g) and phytadienes (Fig. 6c) are relatively most abundant when the TOC content is high.

Also the relative abundance of prist-1-ene (Fig. 6b) exhibited a strong positive correlation with the TOC content. Polysaccharide pyrolysis products (Fig. 6f) and other N-compounds (Fig. 6h) differed mainly between the OMZ and dysoxic station (at smaller TOC concentrations), while at higher TOC concentrations their relative abundances remained almost similar to that of the dysoxic TOC contents. The opposite trend was found for *n*-alkenes/*n*-alkanes (Fig. 6a) and, to a lesser extent, alkylphenols (Fig. 6e) that were relatively enriched when the TOC content was low. The relative abundance of alkylbenzenes did not depend on the TOC content (Fig. 6d).

The HI index of all MOM isolated were within a relatively close range, and as the relative amounts of MOM that generated pyrolysis products were also similar across all stations and independent of sediment depth, the preservation efficiency, defined as the flux of the various pyrolysis groups per sediment core could be estimated. These efficiencies were based on the relative amount of each pyrolysis group and the organic carbon accumulation rates (cf. [Sinninghe Damsté et al., 2002](#)) and were calculated relative to the composition of the OMZ surface sediment (formula (3); Fig. 7a). As expected and following the trend in the accumulation rate of TOC, the relative preservation efficiency of all groups of pyrolysis products was much smaller than 100% under dysoxic and oxic conditions. For the dysoxic station the preservation efficiencies varied from 27.2% to 13.1% in decreasing order: alkylpyrroles > alkylbenzenes > alkylphenols > *n*-alkenes/*n*-alkanes > other N compounds > phytadienes > polysaccharides > prist-1-ene. For the oxic surface sediment the preservation efficiency was, in general, even lower than for the dysoxic station from 27.6% to 2.9% in the following order: *n*-alkenes/*n*-alkanes (actually slightly increased compared to dysoxic station) > alkylbenzenes > alkylphenols > other N compounds > polysaccharides > alkylpyrroles > prist-1-ene > phytadienes.

Although the composition of the MOM pyrolysates changed with depth, this change is rather small as compared with differences between sampling stations (Fig. 5). Therefore, to compare the preservation efficiencies on a longer time scale, average values were calculated by using the flash pyrolysate composition averaged over the five sediment slices studied (Fig. 7b). By doing this we do not obtain only better weighed estimates but also an indication of the differences over several thousands of years that span the top 18 cm of the cores (1340 y for OMZ, 4700 y for dysoxic, and 4000 y for the oxic station). Generally, the trends observed were similar to those for the surface sediments, although relative differences in preservation efficiency between dysoxic and oxic stations resembled each other more than for the surface sediments only. For the dysoxic station preservation decreased from 24.5% to 13.4% in the order: *n*-alkenes/*n*-alkanes > other N-compounds > alkylphenols > alkylbenzenes > polysaccharides > phytadienes > alkylpyrroles > prist-1-ene. At the oxic station the relative preservation decreased from 20.3% to 2.0% in the order: *n*-alkenes/*n*-alkanes > alkylphenols > alkylbenzenes > other N-compounds > polysaccharides > prist-1-ene > alkylpyrroles > phytadienes.

## 4. DISCUSSION

### 4.1. Organic carbon content vs. oxygen concentrations

As aforementioned, due to their close proximity within the Arabian Sea we consider the phytoplankton composition responsible for the primary production and predominant source of the sedimentary OM identical for all stations (cf. [Schubert et al., 1998](#); [Sinninghe Damsté et al., 2002](#)). Hence, differences in OM content and composition are interpreted to be due primarily to degradation during both travelling through the water column and subsequent deposition and burial in the sediment. These differences are further affected by anaerobic degradation in both the OMZ and anoxic part of the sediment, and oxygen mediated decomposition in the photic zone, the water column below the OMZ and in the upper part of the sediment in which oxygen has penetrated. For the OMZ station, oxygen penetration within the sediments is almost non-existent, for the dysoxic station the oxygen penetration depth is 3 mm, while for the oxic station it is 10 mm ([Caulle et al., 2014](#)). Based on the linear sedimentation rates the (sedimentary) oxygen exposure times are ~0 (OMZ station), 70 (dysoxic station) and 150 y (oxic station).

The TOC values observed here are similar to those reported by [Van der Weijden et al. \(1999\)](#) on NIOP cores collected close to our sites and exhibit clear differences between the three stations and hence with respect to oxygen exposure times. According to [Sinninghe Damsté et al. \(2002\)](#) the dominant factor determining OM preservation is aerobic degradation in the sediment of these cores. [Koho et al. \(2013\)](#) determined that, while oxygen penetration was absent, the bioturbation depth at the OMZ station was 2 cm, and therefore, anaerobic degradation may have taken place down to 2 cm deep leading to the TOC decrease observed by e.g. macrofaunal-sized shelled foraminiferan biomass ([Pozzato et al., 2013](#)). The downcore decline in TOC at the oxic station may likely be due to prolonged (oxic) degradation within the sediment at this station as the oxygen penetration was 10 mm deep here along with around 8 cm of bioturbation that enhances particle manipulation by macrofauna and may also increase oxygen exposure times, which together promote microbial OM degradation ([Koho et al., 2013](#)). These more pronounced differences for the oxic station may reflect not only longer oxygen exposure times, but also the comparatively longer periods of anaerobic degradation for the same depth intervals at the other stations: the linear sedimentation rate at the OMZ station is on average 1.7 times higher than that of the oxic station ([Koho et al., 2013](#)). In addition, the dysoxic and oxic stations are impacted by bioturbation down to 8 cm depth, with red-brownish surfaces overlying a more greyish sediment for the oxic station, which indicates a shallow oxidation front ([Koho et al., 2013](#)). Such bioturbation may cause renewed oxygen supply to the anaerobic zone thereby affecting overall oxygen exposure times and certainly influencing aerobic and anaerobic conditions to which OM is exposed within the sediment ([Hedges et al., 1999](#)). Bioturbation also causes alterations between oxic

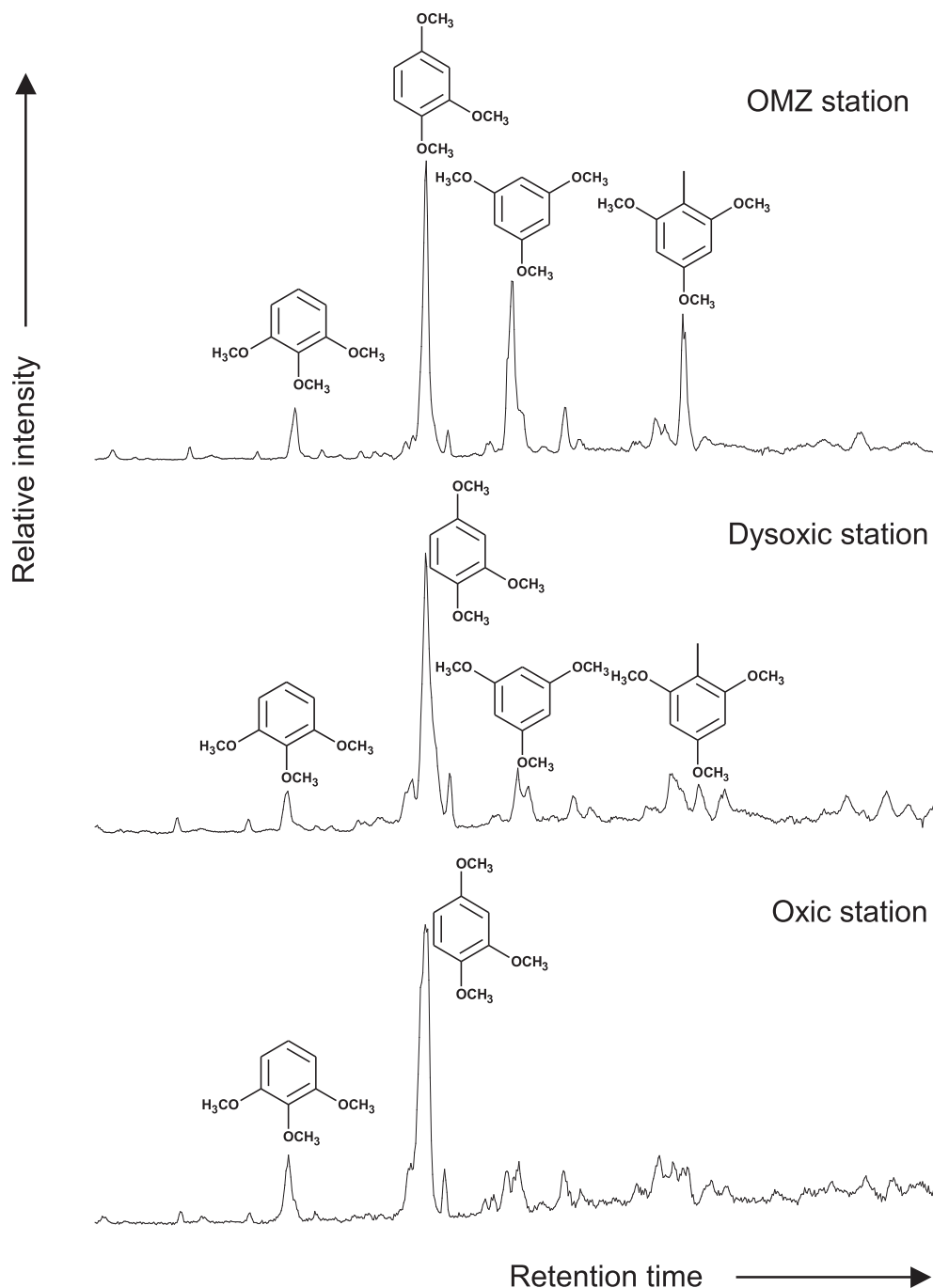


Fig. 4. Partial mass chromatograms ( $m/z$  168 + 182) revealing the relative abundance of the (alkyl)trimethoxybenzenes upon THM of MOM from the 0–0.5 cm sediment intervals from the OMZ, dysoxic and oxic stations.

and anoxic conditions, and such redox oscillations may affect OM preservation and diagenesis (Aller, 1994). Despite these complications our sample suite clearly allows the interpretation of oxygen exposure time on MOM.

#### 4.2. Assignment of flash pyrolysis products

##### 4.2.1. *n*-Alkenes/*n*-alkanes

*n*-Alkenes/*n*-alkanes are often considered to be derived from non-hydrolysable aliphatic biopolymers that represent

small amounts of living biomass and function as protective barriers in, for example, algae (Tegelaar et al., 1989; Versteegh and Blokker, 2004). In case of marine biota, particularly algae, such biopolymers are collectively termed algaenans, and consist of highly linear, sometimes unsaturated, aliphatic cross-linked polymers (De Leeuw et al., 2006). Alternatively, *n*-alkenes/*n*-alkanes may be pyrolysis products of macromolecules produced by an abiotic mechanism called oxidative polymerization of unsaturated fatty acids (Versteegh et al., 2004; De Leeuw et al., 2006).



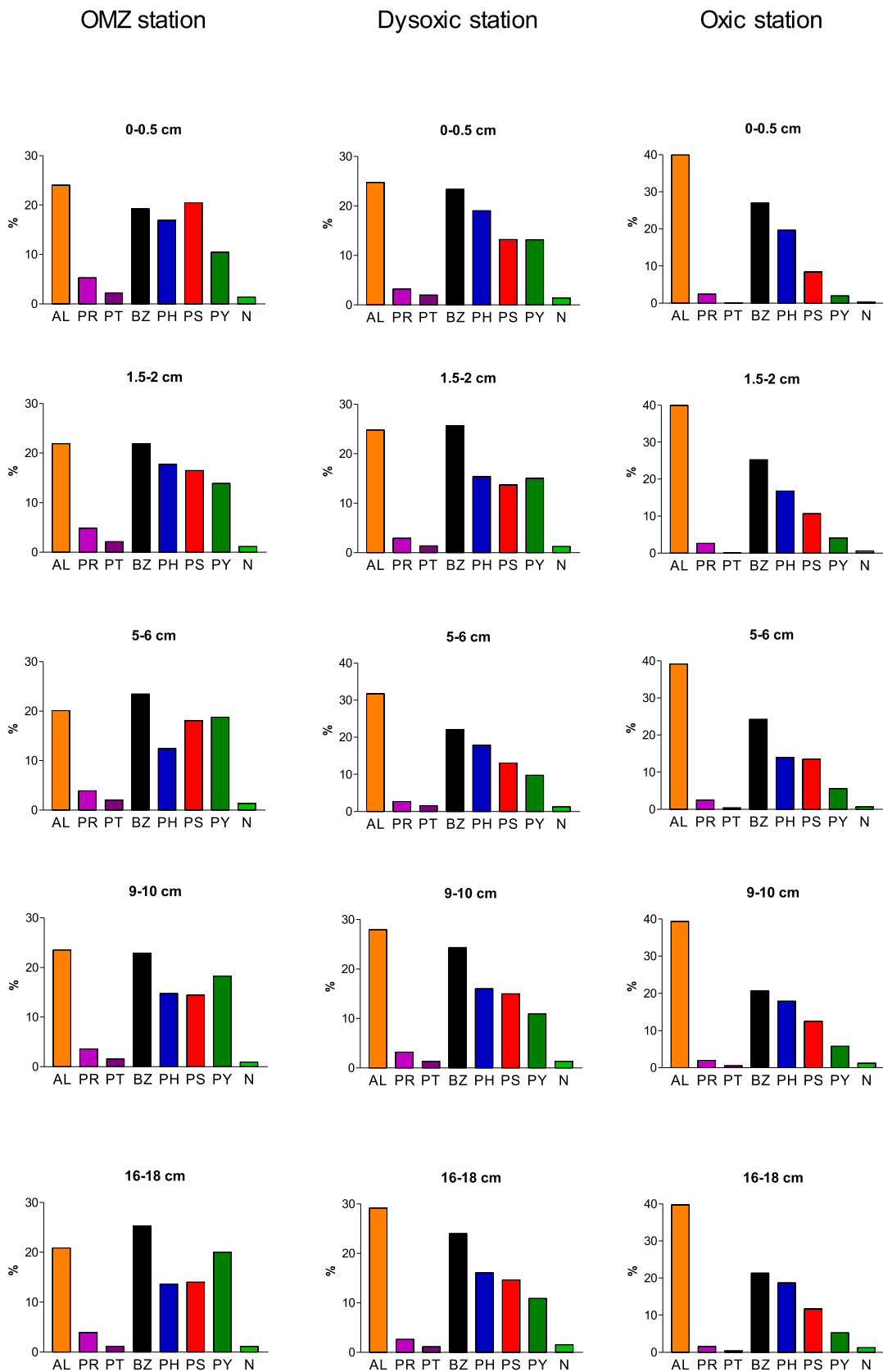


Fig. 5. Relative abundances of the eight main groups of identified pyrolysis products of MOM from sediment cores of the OMZ, dysoxic and oxic stations at 885, 1306 and 1791 mmbs. Key: AL = alkenes/alkanes, PR = prist-1-ene, PT = phytadienes, BZ = alkylbenzenes, PH = alkylphenols, PS = polysaccharides, PY = alkylpyrroles, and N = other N-compounds.

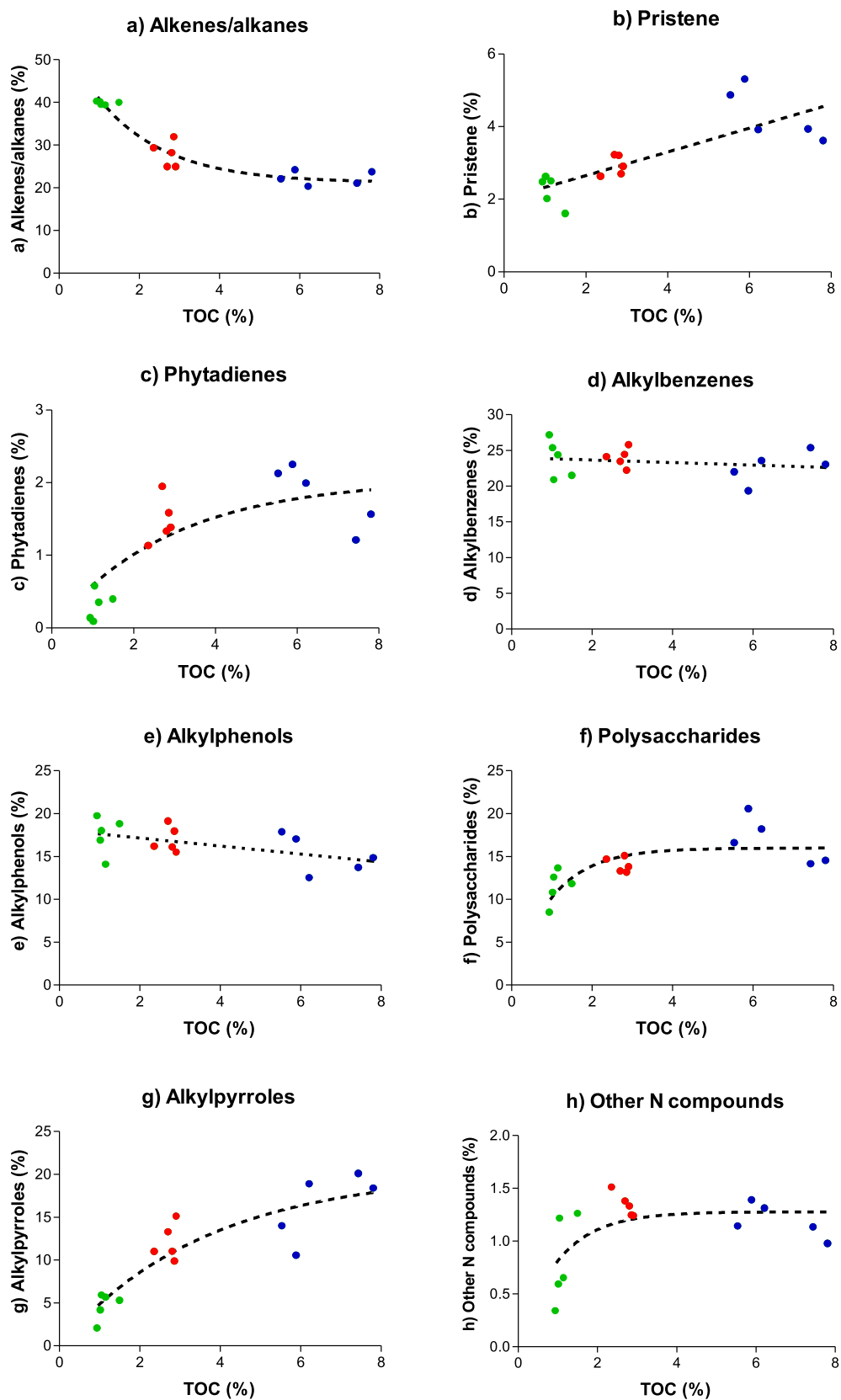


Fig. 6. Relative abundance of groups of pyrolysis products (a) alkenes/alkanes, (b) prist-1-ene, (c) phytadienes, (d) alkylbenzenes, (e) alkylphenols, (f) polysaccharides, (g) alkylpyrroles, and (h) other N-compounds) of MOM from three cores of the Murray Ridge plotted vs. TOC content of the sediment. Dashed lines indicate best fitted trends. Blue = OMZ station, red = dysoxic station and green is oxic station. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

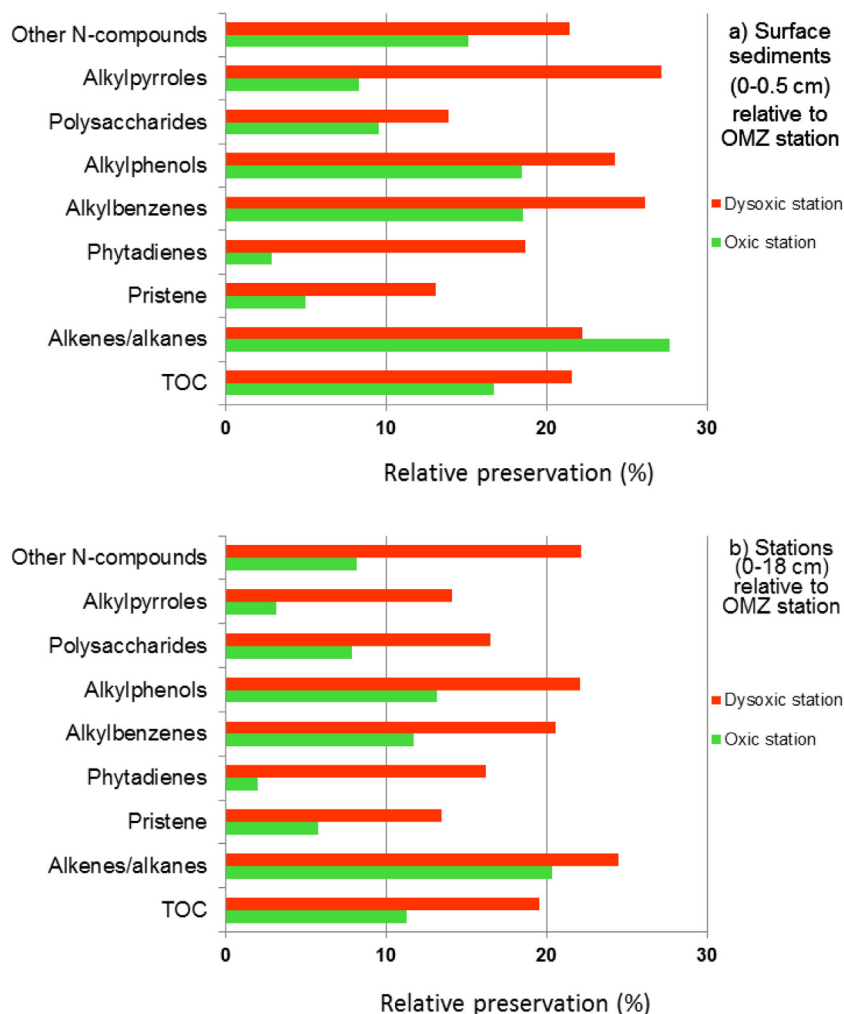


Fig. 7. Relative preservation of TOC and groups of pyrolysis products at (a) the 0–0.5 cm intervals of the three stations relative to that of the OMZ station, (b) averaged over 0–18 cm intervals relative to that of the OMZ station.

Considering that  $C_{18:1}$  fatty acids are normally the most abundant unsaturated ones in biota, the decline in abundance of the *n*-alkenes/*n*-alkanes pyrolysis products after  $C_{19}/C_{20}$  would suggest that such a mechanism is a possible pathway in the formation of aliphatic macromolecules in the sediments studied here.

#### 4.2.2. *Prist-1-ene and phytadienes*

A relatively small group of pyrolysis products comprised prist-1-ene and phytadienes. The latter are considered to be derived from pigments such as chlorophyll (Van de Meent et al., 1980). Prist-1-ene has been attributed to tocopherol (Goossens et al., 1984) and the identification of tocopherol itself in the MOM pyrolysates confirms this possible origin. However, Ishiwatari et al. (1991) suggested prist-1-ene can be formed upon pyrolysis of chlorophyll as well, in particular with increasing thermal alteration under natural conditions such as diagenesis. As the sediments in the present study are thermally immature the relative contribution of chlorophyll to prist-1-ene generation will be negligible.

#### 4.2.3. *Alkylbenzenes*

The alkylbenzenes comprised very prominent pyrolysis products of the isolated MOMs. Of these components, 1,2,3,4-tetramethylbenzene is often associated with macromolecularly-bound carotenoids including isorenieratene (Hartgers et al., 1994; Hoefs et al., 1998). However, in view of the relatively small abundance of 1-ethyl-2,3,6-trimethylbenzene in our pyrolysates such components are not very likely, which is in line with lack of anoxygenic photosynthesis at the surface waters of the Arabian Sea (Farrenkopf et al., 1997). Furthermore, Hoefs et al. (1995) concluded that green sulfur bacteria were not the source of 1,2,3,4-tetramethylbenzene in pyrolysates of Arabian Sea sediments. Based on isotopic data they found that 1,2,3,4-tetramethylbenzene could originate from algae, such as *Chlorococcum* sp., *Ulva fenestrata*, *Nereocystis luetkeana* and *Emiliania huxleyii*. The  $C_2$ - and  $C_3$ -benzenes, in particular 1,3- and 1,4-dimethylbenzenes and 1,2,3-trimethylbenzene have been attributed to non-aromatic carotenoids that underwent aromatization

followed by loss of methyl groups upon transformation (Hartgers et al., 1994). Toluene and styrene have been found as pyrolysis products of the amino acid phenylalanine-containing proteins (e.g., Chiavari and Galletti, 1992).

#### 4.2.4. Alkylphenols

Alkylphenols have various possible pyrolytic origins, such as lignin, proteins and transformed proteins (in particular tyrosine derivatives), and tannins (Galletti and Reeves, 1992; Van Heemst et al., 1999). The latter authors also postulate that particularly phenol and methylphenols derive from macromolecules that are formed by cross-linking of protein units (tyrosine) producing non-amide bonds on hydrolysis of polysaccharide/protein material in the water column.

As catechol is the main pyrolysis product of condensed tannins, whereas phenol and methylphenols are only minor products (Galletti and Reeves, 1992), the high abundance of phenol and methylphenols as compared to catechol (for the sediment within the OMZ core) rules out tannins as their main source. Moreover, the virtual absence of catechol from the pyrolysates of the sediments buried under more oxygenated conditions implies that phenol and methylphenols are likely to be largely derived from proteins and products from proteins and polysaccharides (Van Heemst et al., 1999). However, polyphenols occurring in marine biota other than brown algae (e.g., green and red algae (Van Alstyne and Paul, 1990)) cannot be completely excluded as contributors to OM.

As terrestrial MOM does hardly or not contribute to the sedimentary MOM of the Arabian Sea in the area of the Murray Ridge, lignin can be excluded as a major source of these phenols (cf. Cowie et al., 1999, 2014). This lack of lignin is supported by THM: no unambiguous lignin-derived methoxybenzenes were found. Instead compounds that are indicative of other polyphenols, such as tannins were recognized albeit in relatively small abundances. For example, 1,2,3-, 1,2,4- and 1,3,5-trimethoxybenzenes were identified in chromatograms upon THM of the isolated MOMs. In all sediment intervals studied from the OMZ station 1,3,5-trimethoxybenzene (and 2,4,6-trimethoxytoluene) were relatively abundant, while for the other stations they were hardly (dysoxic) or not present (oxic), in contrast to 1,2,3- and 1,2,4-trimethoxybenzenes (Fig. 4). 1,3,5-Trimethoxybenzene is a common THM product of phloroglucinol, which represents the A ring of condensed tannins (Nierop et al., 2005) and the building blocks of phlorotannins such as found in algae (Ragan, 1984). While 1,2,4-trimethoxybenzene can be derived from both polysaccharides (Fabbri and Helleur, 1999) and condensed tannins, the 1,2,3-trimethoxybenzene is likely a tannin or more generally polyphenol-related product.

#### 4.2.5. Furans and anhydrosugars (polysaccharide-derived products)

Oxygen-bearing heterocyclic aromatic pyrolysis, in particular 2-furaldehyde and 5-methyl-2-furaldehyde are typically derived from polysaccharides (e.g. Van der Kaaden et al., 1983). Another abundant characteristic

polysaccharide-derived product comprised levoglucosenone, which is an acid-catalyzed dehydration product of levoglucosan (Van der Kaaden et al., 1983). In turn, levoglucosan is generally the most abundant pyrolysis product of glucose-containing polysaccharides, such as cellulose (Pouwels et al., 1989). Levoglucosan, however, was detected in trace amounts only in our pyrolysates, which is most likely due to a major conversion to levoglucosenone caused by relicts of the acid pre-treatment during the MOM isolation from the sediments.

#### 4.2.6. Alkylpyrroles and other N-containing compounds

Alkylpyrroles comprised the main group of N-containing compounds detected in the pyrolysates of the Arabian Sea MOM. All alkyl units of these alkylpyrroles consisted either of a methyl or an ethyl group. Pyrrole and 2- and 3-methylpyrroles have been associated with proteins (Tsuge and Matsubaru, 1995) or chitin (Stankiewicz et al., 1996) as identified in pyrolysates of algae (Van Heemst et al., 1996) and organic linings of foraminifera (Ní Fhlaithearta et al., 2013). However, the di-, tri- and tetra-alkylpyrroles (C<sub>3</sub>-C<sub>5</sub>), are likely mainly derived from tetrapyrrole pigments such as chlorophyll (Sinninghe Damsté et al., 1992). The presence of phytadienes in all pyrolysates, whose relative abundance decreased similarly as the C<sub>3</sub>-C<sub>5</sub>-pyrroles from the OMZ station to oxic station, confirms the latter as a likely origin of the alkylpyrroles.

The alkylpyridines detected included pyridine, 3-methylpyridine and 3-ethylpyridine. The origin of alkylpyridines in pyrolysates is not well known. They have been found in chitin pyrolysates, such as from shrimp (Stankiewicz et al., 1996), and thus the alkylpyridines may be relicts of chitin-derived moieties. In addition, pyridine was also found as pyrolysis product from peptidoglycan, the cell wall component of bacteria (Snyder et al., 2004; Dworzanski et al., 2005).

Indole, 3-methylindole, diketodipyrrole and diketopiperazines are derived from the amino acids tryptophan (indoles), hydroxyproline (diketodipyrrole) and dimers of proline and a second amino acid including glycine, lysine and proline (Tsuge and Matsubara, 1985; Chiavari and Galletti, 1992; Stankiewicz et al., 1996; Moldoveanu, 1998), and confirm the presence of proteinaceous material in all sediments and intervals analyzed.

### 4.3. Organic matter compositional changes upon oxygen exposure

The measured range of HI values suggests a general predominance of marine-derived OM (HIs ca. 200–400) over terrestrial OM (HI < 100) (Espalié et al., 1985). The clear increase of HI with increasing TOC content contradicts with the slightly negative HI-TOC correlation observed in sediments on the continental slope of the eastern Arabian Sea (Calvert et al., 1995). Although predominantly marine derived, the OM source in this shore-affected site was possibly more heterogeneous, leading to a poorer HI-TOC correlation. This is confirmed by the much wider range in HI index (42–890 mgHC/gTOC; Calvert et al., 1995) compared to the range reported here (136–372 mgHC/gTOC).



Although Rock Eval pyrolysis and flash pyrolysis are two different techniques, the nearly identical yields of Rock Eval pyrolysable fractions (all between 38% and 40%) implies that the relative amount of isolated MOM that becomes pyrolyzed upon flash pyrolysis when using similar amounts is almost identical across the three stations and can be evaluated not only qualitatively but also quantitatively with each other.

#### 4.3.1. Surface sediments

The sedimentation rates of 13.4 cm/kyr (OMZ station), 3.8 cm/kyr (dysoxic station) and 4.5 cm/kyr (oxic station) (Koho et al., 2013) differed substantially. Given these differences in sedimentation rate, only the surface sediments can be directly compared with regard to OM input and subsequent degradation as they are of similar age. With increasing oxygen exposure, the relative abundance of the summed *n*-alkenes/*n*-alkanes increased, suggesting that their source molecules have greater resistance against oxic degradation compared to other molecules (Fig. 5). Alkylbenzenes also increased relatively upon increasing oxygen exposure, implying a relative resistance against oxic degradation of their precursors. By contrast, oxygen-bearing heterocyclic pyrolysis products decreased, in line with the idea that their precursors, polysaccharides, are rapidly degradable components (De Leeuw and Largeau, 1993; Emerson and Hedges, 2008).

The contrasting trends of N-containing compounds and alkylphenols upon oxygen exposure implies that ‘unaltered’ proteins decreased, while ‘transformed’ ones increased relatively upon oxic conditions. Based on THM, tannins and related compounds were clearly affected by oxygen exposure: at the OMZ station they were clearly present, whereas at the dysoxic station only traces were observed and they were absent in the pyrolysate of the MOM from the oxic station. The decrease of phytadienes under more oxic conditions is in line with the decrease of alkylpyrroles, in particularly the C<sub>3</sub>-C<sub>5</sub> ones as both are related to pigments which degrade rapidly under oxic conditions (e.g. Furlong and Carpenter, 1988). Similarly, the decrease of prist-1-ene coincided with the decline of tocopherols (Supplementary files S1–3), suggesting that prist-1-ene was mainly derived from tocopherols.

#### 4.3.2. Downcore sediments

In contrast to the differences between the surface sediments of the three stations, the differences in composition with sediment depth were fairly small, and more often the differences varied over depth rather than there were steady increases or decreases with depth. Although organic matter flux and composition might also vary over time this should have affected all three cores studied down core similarly. For example, with sediment depth, *n*-alkenes/*n*-alkanes varied between 20% and 24% at the OMZ station without any depth trend, while at the dysoxic station their relative abundance was higher in the 5–18 cm range (28–32%) than in the upper part of the sediment (25% between 0 cm and 2 cm). At the oxic station the *n*-alkenes/*n*-alkanes remained fairly constant within the range of 39–40%. Apparently the formation and preservation of their source molecules over time

seems hardly affected by the conditions under which the MOM was buried as compared to sinking through the water column. In addition, bioturbation may have homogenized changes over time, leading to the relatively invariant trends observed.

The relative amounts of the tetra-alkyl pyrroles differed mostly between the OMZ and the other stations: within the OMZ sediment core tetra-alkyl pyrrole units showed a progressive relative increase with sediment depth (from 10% to 20%), implying that with short oxygen exposure times the microbial community was not able to decompose them. The tetra-alkyl pyrrole pigments are subjected to a sequence of diagenetic reactions under anoxic conditions as summarized by Killops and Killops (2005, and references cited therein). Subsequently they may have formed complexes with metal cations, such as VO that decrease their solubility in organic solvents after which they became part of the MOM fraction. However, if they occurred in complexes with metals they would not generate alkylpyrroles upon pyrolysis (Sinninghe Damsté et al., 1992). Therefore, tetra-alkyl pyrroles may either have lost their metals over time and became covalently bound to the macromolecular fraction, which could shield them from further decay. (MacKenzie et al., 1980; Premović et al., 1996; Killops and Killops, 2005).

Both the polysaccharide-derived compounds and the alkylphenols decreased with increasing sediment depth at the OMZ station, while they varied for the other stations. The relative abundance of prist-1-ene and, in particular, phytadienes decreased with increasing depth at the OMZ station, which coincides again with the decrease of the alkylpyrroles that have the same source (pigments) as the phytadienes. Analogously, the relative abundance of prist-1-ene coincided again as well with the increased relative abundance of tocopherol, the most likely precursor of prist-1-ene, in sediments with a high TOC content (Supplementary files S1–3).

#### 4.4. Implications for organic matter preservation

Overall, Fig. 5 shows that the impact of MOM diagenesis within the sediments is relatively small compared to that taking place within the water column and at the sediment-water interface, with the resulting composition reflecting to a large extent the exposure of MOM to oxygen. The relative enrichment of *n*-alkenes/*n*-alkanes when the TOC content was low (Fig. 6), coinciding with the higher oxygen exposure times, indicates that these products may indeed be derived from aliphatic geopolymers formed through polymerization or selectively preserved algaenans (Versteegh et al., 2004). In particular the small differences in preservation efficiency between dysoxic and oxic stations suggest their conspicuous resistance against oxic degradation.

Assigning the pyrolysis products to bio- and geo(macro)molecules, the overall composition of the MOM comprises from the Arabian Sea (1) polysaccharides (as indicated by furans, pyrans and anhydrosugars), (2) intact and altered proteins (indicated by part of the N-compounds, toluene, styrene and part of the alkylphenols), (3) tyrosine based non-amide bound macromolecules

produced upon hydrolysis of polysaccharides and proteins (alkylphenols), (4) algaenan and/or geopolymerized lipids (reflected by *n*-alkenes/*n*-alkanes), (5) pigment-derived tetra-alkyl pyrroles (indicated by C<sub>2</sub>-C<sub>5</sub>-pyrroles), (6) carotenoids (particularly the C<sub>2</sub>-C<sub>4</sub>-benzenes), (7) chlorophyll, other pigments and tocopherol (prist-1-ene and phytadienes), and (8) tannins and other polyphenols (based on trimethoxybenzenes upon THM). The preservation efficiency as a function of oxygen exposure times of the various bio- and geopolymers increase from pigments including tetra-alkyl pyrrole moieties and tocopherol; tannins < polysaccharides ≤ proteins and their combination products with polysaccharides ≈ carotenoids < algaenans and/or aliphatic geopolymers.

Alkylpyrroles have been identified in pyrolysates of Pliocene Mediterranean sapropels but not in those of their over- and underlying homogenous intervals (Menzel et al., 2005), while Payeur et al. (2011) also found this difference between sapropels (alkylpyrroles present) and surrounding marls (alkylpyrroles absent). Our Arabian Sea study reveals that their presence is highly influenced by BWO concentrations upon deposition, and, thus, most probably oxygen exposure times. As such, the relative abundance of alkylpyrroles in pyrolysates can thus be considered as a tentative proxy for oxygen exposure time.

Hedges et al. (2001) found evidence of non-selective degradation of sinking OM particles through the water column and attributed this to binding to mineral particles. Once deposited at the seafloor and buried in sediments such organo-mineral associations would likely continue to exist and, consequently, OM degradation would be expected to remain more or less non-selective. Our results indicate, however, that MOM in the top of the sediment (0–0.5 cm interval) clearly undergoes selective degradation/preservation as compared to the MOM when passing the water column.

## 5. CONCLUSION

The MOM buried in the sediments of the Murray Ridge in the Arabian Sea is clearly affected by BWO concentration and, consequently, oxygen exposure times, and, to a far lesser extent, subsequent diagenesis within the sediments. Most pronounced differences were seen for the pigments which accumulated with sediment depth buried under low, dysoxic conditions, while their abundance decreased with sediment depth underlying higher BWO concentrations. Thus, the presence of macromolecularly-bound tetrapyrrole pigments in marine sediments is highly affected by the redox conditions prior to burial within the anaerobic zone of the sediment. The aliphatic bio- and geopolymers accumulated in the oxic station whereas the remaining other compounds were less preserved upon burial under higher BWO concentrations. The large differences in MOM composition as a consequence of oxygen exposure implies that the occurrence of low oxygen conditions (such as in sediment within the OMZ) have significant consequences for short-term, but hence also long-term preservation of sedimentary MOM in marine sediments.

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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.gca.2017.02.032>.

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