Organic matter preservation on the Pakistan continental margin as revealed by biomarker geochemistry

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Abstract

In order to assess whether the oxygen-minimum zone (OMZ) in the Arabian sea has an effect on the preservation and composition of organic matter in surface sediments we investigated samples from three different transects on the Pakistan continental margin across the OMZ. In addition to determining the total amount of organic carbon (TOC), we analyzed the extractable lipids by gas chromatography, combined gas chromatography/mass spectrometry, and compound-specific stable carbon isotope measurements. The extractable lipids are dominated by marine organic matter as indicated by the abundance of lipids typical of marine biota and by the bulk and molecular isotopic composition. Sediments from within the OMZ are enriched in organic carbon and in several extractable lipids (i.e. phytol, n-alcohols, total sterols, n-C35 alkane) relative to stations above and below this zone. Other lipid concentrations, such as those of total n-fatty acids and total n-alkanes fail to show any relation to the OMZ. Only a weak correlation of TOC with mineral surface area was found in sediments deposited within the OMZ. In contrast, sediments from outside the OMZ do not show any relationship between TOC and surface area. Among the extractable lipids, only the n-alkane concentration is highly correlated with surface area in sediments from the Hab and Makran transects. In sediments from outside the OMZ, the phytol and sterol concentrations are also weakly correlated with mineral surface area. The depositional environment of the Indus Fan offers the best conditions for an enhanced preservation of organic matter. The OMZ, together with the undisturbed sedimentation at moderate rates, seems to be mainly responsible for the high TOC values in this area. Overall, the type of organic matter and its lability toward oxic degradation, the mineral surface area, the mineral composition, and possibly the secondary productivity by (sedimentary) bacteria also appear to have an influence on organic matter accumulation and composition. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The possible causes of organic matter enrichment in marine sediments have already been a central issue of numerous organic geochemical investigations. Many of these studies revealed concentration maxima of organic carbon at intermediate water depths on continental slopes (e.g. Premuzic et al., 1982) where an oxygen-minimum zone (OMZ) in the water column impinges on the seafloor. This contributed to the widely accepted view that preservation of organic matter in marine sediments is chiefly controlled by low bottom-water oxygen levels (e.g. Schlanger and Jenkyns, 1976; Thiede and van Andel, 1977; Demaison and Moore, 1980; Paropkari et al., 1992, 1993; van der Weijden et al., 1999).

In contrast to this, other investigators collected evidence for organic matter enrichment by other factors such as upwelling-induced high primary productivity,
winnowing, sediment texture, grain size, and mineral surface area (Calvert, 1987; Pedersen and Calvert, 1990; Calvert and Pedersen, 1992; Calvert et al., 1995; Bergamaschi et al., 1997; Ganeshram et al., 1999). The role of adsorption of organic matter on mineral surfaces was emphasized in a number of studies (Keil et al., 1994a, b; Mayer, 1994). Ransom et al. (1998) pointed out that mineralogy and surface area of California margin sediments play a more important role in preservation than the oxygen level of bottom waters and the organic matter origin (marine or terrestrial), whereas Hulthé et al. (1998) suggested that oxygen does have an influence on organic matter degradation in continental margin sediments. Hartnett et al. (1998) pointed out that “the heart of the preservation controversy lies in the fact that no single factor seems to control preservation under all conditions”. The present organic geochemical investigation of three series of surface sediments from different transects across the OMZ on the Pakistan continental margin in the northeastern Arabian sea, collected during the SONNE-90 cruise in 1993, is a contribution to the ongoing discussion on the parameters affecting organic matter preservation. Besides determining bulk parameters like organic carbon content, stable carbon isotope composition of whole organic matter and mineral surface area, we have placed particular emphasis on possible effects of the OMZ on the composition and concentration of selected extractable lipids in the surface sediments.

2. Study area

The northern Arabian sea is characterized by strong seasonal variability of monsoonal upwelling (Slater and Kroopnick, 1984) and high primary productivity (Kabanova, 1968; Quasim, 1977, 1982) which, together with the supply of oxygen-depleted intermediate-depth water masses from the south (Swallow, 1984; Olson et al., 1993), favor the development of an exceptionally broad and stable mid-water OMZ. This OMZ (200–1100 m; down to 0.5 mg O2/l) for the purpose of this study was defined by laminated surficial sediments and the absence of benthic organisms (Fig. 1; von Rad et al., 1995). Recently, Schulz et al. (1996) demonstrated that the OMZ was persistently present during the last 6 kyeares.

3. Samples and analytical methods

3.1. Samples

During the SONNE-90 cruise in 1993, surface sediments in, and adjacent to, the OMZ on the Pakistan continental margin were collected, using box cores, on three different transects across the slope and at a distal reference site (Fig. 2). A preliminary description of sediment characteristics including the enrichment of organic carbon within and just below the OMZ was published by von Rad et al. (1995).

3.1.1. The Makran transect (Area A)

The area off the Makran coast south-west of Omara (Area A; Fig. 2) is an active continental margin slope with sedimentation rates between 2.5 and 3 mm/year over the last 90 kyear and a tendency of decreasing values with increasing water depth (Schulz and von Rad, 1997). The typical sediment in Area A is a hemipelagic carbonate- and quartz-rich silty clay with abundant chlorite. The annual surface productivity in this area (64.5°E/24.5°N) is estimated to be around 480 g C m²/year, with highest values in July during the SW monsoon, from a digitized productivity atlas (developed by Denis Dollfus, CEREGE Aix-en-Provence, France) based on satellite chlorophyll observations and a model of photosynthesis (Antoine et al., 1996). The mineral surface area of Area A sediments varies between 10.8 and 17 m²/g sediment and slightly increases with water depth (Keil and Cowie, 1999; Fig. 3).

3.1.2. The Hab transect (Area B)

The Hab transect south-west of Karachi (Area B; Fig. 2) has an extremely complicated slope morphology (Schulz et al., 1996). On the basis of varve counting and ²¹⁰Pb measurements, a sedimentation rate of 1.6 mm/year was determined (core 39 KG) and considered representative for the whole transect (von Rad et al., 1999; U. von Rad and H. Schulz, personal communication). The mass accumulation rates (MAR) for sediments from this transect range from 335 to 1000 g m²/year⁻¹ with higher values occurring within the OMZ (Suthoff et al., 2000). As in the Makran transect, the sediments are also characterized by hemipelagic carbonate-rich, silty clays with chlorite as an abundant clay mineral. The estimated primary productivity (about 435 g C m²/year at 65.5°E/24.5°N) is only slightly lower than in Area A. The surface area of the sediments increase with water depth from 5.4 to 17.6 m²/g (Keil and Cowie, 1999; Fig. 3).

3.1.3. Murray Ridge (Area C)

The Murray Ridge (Area C; Fig. 2) was selected as a pelagic reference site unaffected by downslope sediment transport, which is still located below the extended OMZ (Schulz et al., 1996). The estimated annual primary productivity in this area (64.5°E/23.5°N) is 375 g C m²/year. The reference sediment has a mineral surface area of 16.9 m²/g (Keil and Cowie, 1999).

3.1.4. The Indus transect (Area D)

The Indus slope (Area D; Fig. 2) is a broad and gently dipping passive continental margin which is significantly
less affected by sediment redeposition than Areas A and B (Schulz et al., 1996). Based on $^{210}$Pb measurements and varve counting, the sedimentation rate ranges from 0.6 to 1.1 mm/year (U. von Rad and H. Schulz, unpublished results; Crusius et al. 1996; Cowie et al., 1999). The hemipelagic carbonate-rich silty clays contain detrital carbonate fragments and quartz. The estimated primary productivity in this area ($66.5°E/23°N$) is about 375 gCm$^{-2}$/year, i.e. closer to that on the Murray Ridge than in Areas A and B. The mineral surface area of sediments from the Indus transect (13.8–20.7 m$^2$/g) are higher than in the other areas and do not show a systematic trend with water depth (Keil and Cowie, 1999; Fig. 3).

3.2. Methods

We analyzed 32 surface samples (upper 2 cm) from above, within, and below the OMZ for bulk parameters. Based on these results, 22 samples where selected for detailed studies of the molecular composition of the extractable organic matter.

After freeze-drying and grinding, the sediments were analyzed in duplicate or triplicate (when relative differences were larger than 5% after duplicate measurements) for total carbon content by combustion in a LECO-SC-444 instrument. Carbonate contents were determined in duplicate by acidification using a UIC-Coulometrics CM 5012 device. A detailed description of the system as well as a discussion of the accuracy and reproducibility of the method were provided by Engleman et al. (1985) and Jackson and Roof (1992). Total organic carbon (TOC) contents were calculated as the difference between total and inorganic carbon data.

Solvent extractions were performed for 48h in a Soxhlet apparatus with dichloromethane containing 1% methanol. After addition of internal standards (squalane, erucic acid, $5\alpha$-androstan-17-one) and removal of the hexane-insoluble fraction by the addition of a large excess of $n$-hexane (‘asphaltene’ precipitation), the
The hexane-soluble portion of the extract was separated by medium-pressure liquid chromatography (MPLC; Radke et al., 1980) into fractions of aliphatic hydrocarbons, aromatic hydrocarbons, and polar hetero-compounds (NSO fraction). Subsequently, carboxylic acids were separated from the NSO fraction on a column filled with KOH-impregnated silica gel (63–200 μm; a solution of 0.5 g KOH in 10 ml iso-propanol was added to 4 g silica gel). The nonacidic compounds were eluted with 120 ml dichloromethane. Following this, 120 ml of a solution of formic acid (2% in dichloromethane) transformed the potassium salts of the acids back to the original acids and eluted them from the column. For molecular analysis, the acids were methylated with diazomethane, and the nonacidic polar compounds were silylated with N-methyl-N-trimethylsilyl trifluoroacetamide (MSTFA).

Gas chromatography was performed on a Hewlett Packard 5890 Series II instrument equipped with a Gerstel KAS 3 temperature-programmed cold injection system and a fused silica capillary column (30 m length, inner diameter = 0.25 mm, coated with DB 5 (J&W), film thickness = 0.25 μm). Helium was used as the carrier gas, and the oven temperature was programmed from 60°C (1 min) to 305°C (50 min) at 3°C/min. The injector temperature was programmed from 60°C (5 s hold time) to 300°C (60 s hold time) at 8°C/s. GC/MS studies were performed under the temperature conditions given above with the same type of gas chromatograph interfaced directly to a Finnigan SSQ 710 B mass spectrometer operated at 70 eV.

Molecular isotope analyses were performed using the same type of gas chromatograph (fused silica capillary column; 30 m length, inner diameter = 0.25 mm, coated with Ultra 2 (HP), film thickness = 0.17 μm; temperature conditions as given above) attached to a Finnigan MAT 252 isotope ratio mass spectrometer via a combustion interface. This instrument was calibrated with a CO2 standard at the beginning and the end of each analysis and with compounds of known isotopic composition which were co-injected with each sample and served as internal isotopic standards. Isotopic ratios are expressed as δ13C values in per mil relative to the V-PDB standard.

4. Results

4.1. Composition of lipids

4.1.1. Gross molecular composition

The aliphatic hydrocarbon fractions of the surface samples are dominated by C17 and C43 n-alkanes in a...
carbon number range between with components containing more than 40 carbon atoms being present only in small amounts (Fig. 4; Schulte, 1997). The n-alkane distribution maximizes at n-C_{31} in eighteen of the analyzed samples, and at n-C_{35} in the other four samples which were all deposited within the OMZ. The long-chain homologs (C_{25}-C_{33}) show an odd-over-even carbon number predominance with a carbon preference index (CPI) between 1.3 and 4 (Schulte, 1997). Besides the n-fatty acids, branched-chain (iso and anteiso) isomers of the C_{15} and C_{17} acids were detected. Mono-unsaturated acids with 16 and 18 carbon atoms as well as a diunsaturated C_{18} acid were also present. The fatty acid distributions have a pronounced maximum in the short-chain compound range (at C_{16:1}, C_{16:0}, or C_{18:0}) and a second, lower maximum at C_{24:0} or C_{26:0} (Schulte, 1997). The even-carbon-numbered fatty acids are dominant in all samples.

Sterols were detected between C_{27} and C_{30} among which the C_{28} and C_{30} pseudohomologs dominate (Schulte, 1997). The most prominent sterol is dinosterol: 24-ethylcholesterol-5-en-3β-ol, its saturated counterpart, and cholesterol also occur in high abundance (Schulte, 1997; Fig. 5).

In the n-alcohol series ranging from 14 to 28, n-hexadecanol is the most abundant homolog. Furthermore, phytol, alkandiols, keto-ols, hopanoic acids and alcohols, and as well as C_{37} and C_{38} alkenones are significant constituents of the NSO fraction (Fig. 5; Schulte, 1997).

4.1.2. Isotopic composition of single compounds

Two samples, one from above and one from within the OMZ were investigated for the isotopic composition of n-alkanes. Most importantly, the isotopic composition of the n-C_{35} alkane significantly differs from those of the other long-chain n-alkanes (Schulte, 1997; Schulte et al., 1999). In the sample from above the OMZ, the n-C_{35} alkane has a δ^{13}C value of −26.2‰ compared with a mean δ^{13}C value of −28.1‰ (n = 8, S.D. = 1.21‰) for the other long-chain n-alkanes (C_{27}-C_{30}). In the sample from within the OMZ, the n-C_{35} alkane (−24.2‰) is isotopically even 4‰ heavier than, on average, the other long-chain n-alkanes (−28.06‰; n = 9, S.D. = 1.95‰) (Schulte et al., 1999). Chromatographic coelution of an unknown component with the n-C_{35} alkane can be excluded on the basis of GC/MS and GC-irm-MS analyses (Schulte, 1997).

For one sample from within the OMZ (12 KG, Table 1), the isotopic compositions of several fatty acids were determined. The δ^{13}C values vary between −24.6‰ and −28.4‰ with a mean value of −26.3‰ (n = 9, standard deviation = 1.17‰). The n-C_{24} and n-C_{26} acids have an isotopical composition that is 2‰ lighter than that of the other n-fatty acids (mean = −25.8‰, n = 7, standard deviation = 0.73‰; Schulte, 1997).

4.2. Organic matter abundance in relation to the OMZ

4.2.1. Total organic carbon (TOC)

In a plot versus water depth, the TOC data exhibit variations between 0.4 and 4 wt.% (Fig. 6). As was noted in previous studies (e.g. Paropkari et al., 1992; Calvert et al., 1995), there is a broad mid-slope organic carbon maximum, i.e. organic carbon values in surface sediments are higher on the continental slope within the present OMZ than above and well below (Table 1 and Fig. 6). On the Pakistan continental margin, this maximum is most pronounced for the Indus transect and less so in Areas A and B. These regional differences are in general agreement with the measurements of Paropkari et al. (1992). The shallow-water rise of the organic carbon content at the top of the OMZ is fairly sharp, whereas the carbon values decrease gradually with increasing water depth below the OMZ.

As can be seen from Fig. 6, the stable carbon isotope data of the total organic matter vary slightly between −20.8‰ and −19.2‰ (Cowie et al., 1999), i.e. the values are in the typical marine organic matter range of −20±2‰ (Hoefs, 1980). The δ^{13}C values of the sediments deposited within the OMZ are isotopically 0.5‰ lighter (mean: −20.5‰; n = 12; S.D. = 0.3‰) than those

Fig. 3. Mineral surface area of surface sediments versus water depth. The area shaded gray denotes the depth range of the OMZ. Letters indicate the transects A–D. MR corresponds to the sample from the Murray Ridge.
of the sediments deposited outside the OMZ (mean: -20.0%; \( n = 12; \) S.D. = 0.4%). No difference between the three transects was observed. The two samples from below 2500 m water depth show \( \delta^{13}C \) values that are slightly lighter than those of the other samples from below the OMZ (Fig. 6).

4.2.2. Compound group concentrations

We analyzed a suite of biomarkers characteristic of marine and terrigenous organic matter to investigate whether or not the low bottom-water oxygen concentrations within the OMZ have an influence on the preservation of these compounds. Because these compounds belong to different chemical compound classes, they should have different sensitivities toward degradation during early diagenesis.

The \( C_{16}-C_{42} \) \( n \)-alkane concentrations vary between 31 and 184 \( \mu g/g \) TOC, with the exception of sample 164 KG, which has an \( n \)-alkane concentration of 385 \( \mu g/g \) TOC (Fig. 7). The extremely high \( n \)-alkane concentration in this latter sediment may be related to the sampling location south of the Indus Canyon. Other than the rest of the samples from Area D, the sediment represented by 164 KG may have accumulated organic matter supplied by the Indus River and deflected south by the prevalent surface ocean current (Rao and Rao, 1995). \( n \)-Alkane concentrations in sediments from Areas A and B increase with water depth (\( r^2 = 0.93 \) and \( r^2 = 0.94 \), respectively), whereas the \( n \)-alkane concentrations in Area D sediments are less significantly correlated with the water depth (Fig. 7; \( r^2 = 0.61 \); sample 164 KG south of the Indus Canyon not included).

The concentrations of \( n \)-fatty acids in the surface sediments from the four sampling areas vary between 460 and 2940 \( \mu g/g \) TOC and exhibit nearly the same average values within and outside the OMZ (991 \( \mu g/g \) TOC within OMZ, \( n = 12 \), and 884 \( \mu g/g \) TOC outside OMZ, \( n = 9 \); Fig. 7). However, there are differences among the transects studied. In the sediments from the Indus transect, the fatty acid concentrations are almost invariable over the entire range of water depth (164 KG excluded). By contrast, the sediments from the Makran transect show a strong decrease in fatty acid concentration between 200 and 1000 m water depth, and those from the Hab transect have slightly elevated concentrations within the depth range of the OMZ (Fig. 7).

\( n \)-Alcohols (\( C_{12}-C_{28} \)) were detected in concentrations between 90 \( \mu g/g \) TOC for the reference sample (MR)
and 2420 μg/g TOC for sample 164 KG (Fig. 8). Without taking into account sample 164 KG, the concentrations of the n-alcohols in sediments deposited within the OMZ on average are 1.6 times higher (430 μg/g TOC, n=10; Fig. 8) than outside the OMZ (273 μg/g TOC, n=10; Fig. 8). We note that three samples from within the OMZ have comparatively low concentrations of n-alcohols.

The concentrations of total sterols (C27–C30) vary between 83 and 2070 μg/g (Fig. 8). The mean concentration in samples deposited outside the OMZ is 415 μg/g TOC (n=10), whereas the samples from within the OMZ have a mean concentration (1020 μg/g TOC, n=11) almost 2.5 times higher with highest values being attributed to samples from Areas A and B. Sediments from Area D, with the exception of sample 164 KG, fail to show elevated sterol concentrations within the OMZ.

4.2.3. Specific biomarkers

The major source of phytol is chlorophyll a and released from it by hydrolysis already in the water column (Baker and Louda, 1983). Due to the highly reactive allylic hydrogen atoms, phytol is rapidly degraded by oxidation (Rontani et al., 1990). The phytol concentrations in the surface sediments from the Pakistan margin vary between 1.5 and 126 μg/g TOC with the highest concentrations occurring within the OMZ (up to six times higher than above and below; Fig. 9), especially in sediments from the Hab transect (B). The phytol concentration in several sediments within the OMZ on the Makran (A) and Indus transects (D) are also significantly higher than the average value of samples from outside the OMZ.

Dinosterol, a specific marker for dinoflagellates (e.g. Boon et al., 1979; Nichols et al., 1984; Robinson et al., 1984) which were abundant organisms in plankton tows from the overlying surface waters in the study areas (von Rad et al., 1999), was detected in a concentration range from 14 to 320 μg/g TOC. Concentrations of dinosterol are two times higher in sediments from within the OMZ (mean: 165 μg/g TOC, n=10) than in sediments deposited outside the OMZ (mean: 85 μg/g TOC, n=10; Fig. 9). The higher abundance of dinosterol...
within the OMZ is most pronounced in sediments from Areas A and B. By contrast, Area D sediments do not show a remarkable variation of dinosterol concentration as a function of water depth.

Because the stable carbon isotopic compositions of the C_{24} and C_{26} fatty acid di/C_{12}er from those of the other fatty acids, they may have a distinct origin. Sediments from within the OMZ have a 1.6 times higher concentration of C_{24} plus C_{26} fatty acids (mean: 130 mg/g TOC, n = 11; Fig. 9) than sediments which were deposited outside the OMZ (mean: 80 mg/g TOC, n = 11; Fig. 9). The maxima of C_{24} and C_{26} fatty acid concentrations cover the water depth range of the OMZ, with no obvious differences between the transects.

Branched-chain fatty acids are more common in bacteria than in other organisms (Volkman et al., 1980; Parkes and Taylor, 1983), and so they are useful indicators of bacterial contributions to sediments. The sum of C_{15} and C_{17} branched fatty acids versus water depth is shown in Fig. 10. Sediments within the OMZ are richer in branched-chain fatty acids by a factor of up to nearly 3 (maximum about 260 µg/g TOC) relative to sediments which were deposited above or below the OMZ (mean: 110 µg/g TOC, n = 11).

The C_{35} n-alkane is enriched within the water depth range of the OMZ in all transects (up to more than 15 µg/g TOC) by a factor of about 2 on average relative to the sediments deposited outside the OMZ (mean: 6 µg/g TOC) (Fig. 10). The molecular carbon isotopic composition of this component is significantly more positive than those of the other long-chain n-alkanes pointing to a distinct origin of the C_{35} homolog (Schulte, 1997; Schulte et al., 1999). In contrast to the C_{35} n-alkane, the C_{31} n-alkane which is typically derived from higher plants (e.g. Eglinton and Hamilton, 1967; Rieley et al., 1991; Meyers and Ishiwatari, 1993) is not enriched within the OMZ. The concentration, normalized to TOC, increases with increasing water depth in Areas A and B similar to those of the C_{27} and C_{29} n-alkanes. In the Indus transect, such an increase was not observed (Fig. 10).

4.3. Organic matter abundance in relation to mineral surface area

It was suggested that organic matter settling through the water column and in surface sediments may be protected against oxidation and microbial degradation by sorption on mineral surfaces (Keil et al., 1994a; Mayer, 1994; Hedges and Keil, 1995, Bergamashi et al., 1997). For this reason, we compared published data on mineral surface area for the surface sediments on the Pakistan continental margin (Keil and Cowie, 1999) with organic geochemical data generated in this study.

4.3.1. Total organic carbon (TOC)

The TOC contents of the investigated samples do not show an overall significant correlation with mineral surface area (Fig. 11). However, within the OMZ, the organic carbon content with a correlation coefficient of $r^2=0.49$ may indicate an organic load on minerals of about 2.2 mg C/m².

4.3.2. Extractable lipids

A strong correlation between n-alkane concentration and mineral surface area was observed for sediments from Areas A and B ($r^2=0.83$ and 0.84, respectively; Fig. 11). The concentrations of the other extractable lipids analyzed do not show any relationship with the surface area, except for phytol and sterol concentrations of sediments deposited outside the OMZ (Fig. 11) exhibiting a weak to good correlation.
5. Discussion

5.1. Information on the origin of organic matter based on straight-chain lipid distributions and the carbon isotopic composition of individual components

The occurrence of long-chain \( n \)-alkanes with an odd-over-even carbon number predominance in marine sediments is commonly interpreted as a contribution from higher land plants (e.g. Eglinton and Hamilton, 1967; Rieley et al., 1991; Meyers and Ishiwatari, 1993). Very long chain \( n \)-alkanes (>C\textsubscript{35}) with no carbon number preference were detected in a surface sediment from the western Arabian Sea (Oman upwelling; Eglinton et al., 1997), and they do occur in a number of other marine sediments (Volkman, private communication 1998). However, the origin of these very long-chain \( n \)-alkanes is still unknown.

The stable carbon isotope ratio of higher-plant \( n \)-alkanes is lower by about 5–10\% than the bulk plant tissue (Collister et al., 1994; Lichtfouse et al., 1994). A similar difference (7 − 9\%) between \( n \)-alkanes and total biomass was detected in a surface sediment from the western Arabian Sea (Oman upwelling; Eglinton et al., 1997), and they do occur in a number of other marine sediments (Volkman, private communication 1998). However, the origin of these very long-chain \( n \)-alkanes is still unknown.

The stable carbon isotope ratio of higher-plant \( n \)-alkanes is lower by about 5–10\% than the bulk plant tissue (Collister et al., 1994; Lichtfouse et al., 1994). A similar difference (7 − 9\%) between \( n \)-alkanes and total biomass was reported for a cyanobacterium (Sakata et al., 1997). Nothing has been reported so far about the isotopic depletion of \( n \)-alkanes in marine organism, but assuming the same difference in marine organism as in other plants (about 7.5\%), \( n \)-alkanes deriving from \( C_3 \), \( C_4 \) land plants and from marine organism should have \( \delta^{13}C \) values of −35.5\%, −19.5\%, and −27.5\%, respectively. The carbon isotope ratios measured for the \( n \)-alkanes from the Pakistan margin sediments (C\textsubscript{27}–C\textsubscript{39} mean: −28.1\%; \( n = 9 \), S.T.D. = 2.0\%) would be closest to those of marine organism, but these values could also result from a mixed origin of the \( n \)-alkanes from \( C_3 \) and \( C_4 \) plants or a mixture from all three sources. Thus, the origin of the \( n \)-alkanes cannot be unambiguously determined on the basis of their isotopic composition alone.

The CPI of higher plant \( n \)-alkanes ranges from 3 to 40.3 (McCaffrey et al., 1991 and references therein; Collister et al., 1994), whereas CPI values of bacterial and phytoplankton \( n \)-alkanes generally are closer to unity (McCaffrey et al., 1991). Accordingly, the CPI values between 1.3 and 4 of the Pakistan margin samples point to a mainly marine origin of \( n \)-alkanes in the sediments, which is in agreement with the molecular carbon isotope data. Zegouagh et al. (1998) interpreted \( n \)-alkane CPI values of 1.4–2.7 in arctic surface sediments as a marine signal, and a marine origin was also suggested for \( n \)-alkanes showing a CPI of 3–4 in Peruvian surface sediments (McCaffrey et al., 1991). The absence of an unresolved complex mixture in the sediment extracts (Fig. 4) and the relatively low concentrations of \( n \)-alkanes make a petrogenic origin of the \( n \)-alkanes in the studied samples unlikely, except for possibly a minor
portion as indicated by traces of saturated steranes and hopanes in the extracts (Schulte, 1997).

Short-chain fatty acids (C\textsubscript{12}–C\textsubscript{18}) are commonly produced by marine micro-organisms (Schnitzer and Kahn, 1978; Sargent and Whittle, 1981), whereas long-chain fatty acids mainly derive from higher land plants (Matsuda and Koyama, 1977). For the Pakistan margin sediments, this interpretation is supported by the isotopic composition of the fatty acids with heavier \( \delta^{13}C \) values for the short-chain members and lighter values for the C\textsubscript{24} and C\textsubscript{26} acids (Schulte, 1997). Because lipids in general are depleted in \( ^{13}C \) relative to the total biomass by around 4\% (Monson and Hayes, 1982; Hayes, 1993) and since C\textsubscript{3} land plants commonly have a \( \delta^{13}C \) value of \(-28\%\) (Bird et al., 1995), one would expect a \( \delta^{13}C \) value of around \(-32\%\) for a C\textsubscript{3} plant-derived lipid. Therefore, the C\textsubscript{24} and C\textsubscript{26} acids may not be exclusively contributed by C\textsubscript{3} land plants, but also include an isotopically heavier C\textsubscript{4} land plants and/or marine component (\(-12\%\) and \(-20\%\), respectively; Smith and Epstein, 1971; Hoefs, 1980).

Despite the vicinity to the Indus river, the proportion of terrestrial organic matter is conspicuously small in the sediments studied. This terrigenous contribution to the sediments is most clearly reflected by long-chain \( n \)-alcohols (\( >C_{20} \)) believed to derive from higher land plants (Eglinton and Hamilton, 1967; Kolattukudy, 1976). The biomarker evidence of a predominance of the marine organic matter, however, is consistent with the \( \delta^{13}C \) values of bulk organic matter (Cowie et al., 1999) and microscopical observations indicating that in the study area OM is mainly (75–95\%) amorphous with only a small fraction of terrigenous organoclasts (von Rad et al., 1995; Litte et al., 1997; Lückge et al., 1999).

5.2. Factors influencing the accumulation of organic matter

5.2.1. Bottom water oxygen concentration

The TOC profile across the OMZ on the Pakistan margin shows a mid-slope maximum roughly coincident with the extension of the OMZ (Fig. 2). This result is in good agreement with those of previous studies (Paropkari et al., 1992; Calvert et al., 1995; Cowie et al., 1999). As an exception to this general picture, the organic carbon contents of two samples directly beneath the OMZ on the Indus transect were found to be high. von Rad et al. (1995), on the basis of their Parasound data, suggested that surface sediment, originally deposited within the OMZ on the Indus transect were found to be high. von Rad et al. (1995), on the basis of their Parasound data, suggested that surface sediment, originally deposited within the OMZ, had been displaced down-slope by slumping. This idea, however, is not compatible with the excess \(^{210}Pb\) profiles which, rather, indicate continuous in-situ sedimentation below the OMZ (Cowie et al.,
Thus, although the organic carbon maximum in the surface sediments appears to be related to the present position of the OMZ, not all of the organic carbon accumulation pattern can be readily explained by water-column oxygen concentrations. The more complex organic carbon patterns in the Hab and Makran transects, compared to the Indus transect, may be related to the tectonic activity in those active margin areas, which is also reflected in common turbidities found in deeper core sections from the same areas.

Among the individual lipids and lipid groups in the sediment extracts, the C_{35} \text{n-alkane}, the sum of the C_{24} and C_{26} \text{n-fatty acids}, phytol, the \text{n-alcohols}, and dinosterol have elevated concentrations relative to total organic carbon within the present depth range of the OMZ. This suggests that the oxygen content of the overlying water column may be an important factor controlling the accumulation of these components. For dinocysts, considered labile under normal marine conditions, it was recently demonstrated that anoxic conditions controlled their preservation in Mediterranean Sea sediments (Combrourieu-Nebout et al., 1998). Because dinosterol is a common constituent of dinoflagellates (Robinson et al., 1984), the relative extent of preservation of this biomarker may well be controlled by the water-column redox conditions.

Recent studies also demonstrated slower degradation of some sterols under anaerobic conditions (Teece et al., 1994; Sun and Wakeham, 1998). This slower degradation rate may be invoked for the concentration maximum of the sum of sterols and of dinosterol within the OMZ of Areas A and B. On the other hand, elevated sterol concentrations do not extend over the whole depth range of the OMZ, and in Area D there is no enrichment of sterols at all within the OMZ. This also holds true for the other extractable lipids studied in some detail (phytol, branched-chain C_{15} and C_{17} fatty acids, \text{n-alcohols}) which are enriched within the OMZ, but not over the entire depth range, and which also show differences between the three transects. Thus, although oxygen depletion in the water column may have a favorable influence on biogenic lipids in marine sediments, this parameter alone does not appear to be sufficient.

The concentrations of the sum of \text{n-alkanes}, the sum of \text{n-fatty acids}, and of the C_{31} \text{n-alkane} fail to show any relationship with oxygen content in the overlying water column on the Pakistan margin. It was demonstrated in incubation experiments that the \text{n-alkane} concentration in sediments is not affected by different redox conditions (Teece et al., 1994). The chemical inertness of saturated alkanes may explain these observations, but it is less
easy to conceive that this should also hold for the fatty acids.

5.2.2. Mineral surface area

A positive correlation between TOC content and mineral surface area has previously been observed in several studies of marine sediments and was invoked to emphasize that organic matter can be protected against mineralization, and thus be preserved, by sorption on mineral surfaces (Keil et al., 1994a,b; Mayer, 1994; Bergamaschi et al., 1997). In the Pakistan margin samples of this study, there was no general significant correlation between TOC and mineral surface area. Only for sediments deposited within the OMZ, a weak positive correlation was observed ($r^2 = 0.49$; Fig. 11), which suggests that part of the organic matter within the OMZ is associated with mineral surfaces at a relatively high level of loading (2.2 mg C/m$^2$). Similarly high loadings were determined in size fractions of a Peru Margin sediment (Bergamaschi et al., 1997), but with a much higher correlation coefficient between TOC and surface area. It should be noted, however, that the highest TOC contents on the Pakistan margin occur in Area D in sediments that also have the highest surface areas among the samples studied (Figs. 3 and 6). Our results are in conflict with those of Ransom et al. (1998) and van der Weijden et al. (1999) who reported a positive correlation between organic matter content and mineral surface area for continental margin sediments from outside the OMZ and no correlation between TOC and surface area for sediments deposited within the OMZ.

Among the investigated biomarker concentrations, only those of the $n$-alkanes in Area A and B samples show a significant positive correlation with mineral surface area (Fig. 11). This is in disagreement with the results of Jeng and Chen (1995), who did not detect any grain-size effect (which is indistinguishable from the effects caused by surface area; Jeng and Chen, 1995 and references therein) for the concentration of $n$-alkanes in sediments of northeastern Taiwan. By contrast, the lack of correlation between $n$-alkane concentrations and mineral surface area in Area D sediments (Fig. 11) is consistent with the results of Jeng and Chen (1995).

Phytol and the sum of sterols also are correlated with mineral surface area, but in contrast to $n$-alkanes this is true only for sediments from outside the OMZ. This is in accordance with the results of Jeng and Cheng (1995) who reported a pronounced grain-size effect for phytol and sterols in sediments off northeastern Taiwan. The investigation of the Pakistan margin sediments also corroborates the observation of Jeng and Cheng (1995) that $n$-alcohols do not correlate with mineral surface area.
area. Apparently, the simple presence of a hydroxyl group is not sufficient to explain the association of lipids with mineral surfaces.

Mineral composition may also play a role on the extent of lipid adsorption. As was pointed out by Ransom et al. (1998), organic matter appears to be preferentially sequestered in smectite-rich sediments compared to those whose clay fractions are dominated by chlorite. The relatively high abundance of chlorite in the investigated Pakistan margin sediments (particularly Areas A and B) may explain the weak correlation between organic matter content and mineral surface area.

5.2.3. Type (origin) of organic matter

Relative to marine organic matter, continentally derived organic matter commonly includes a higher proportion of biologically resistant organic compounds and a fraction already strongly degraded by soil microbes (e.g. de Leeuw and Largeau, 1993; Bergamaschi et al., 1997). Furthermore, there is evidence that terrigenous organic matter generally suffers biological degradation at a lower rate than marine organic matter (Huc, 1988; Littke and Sachsenhofer 1994) which leads to a better preservation of this material.

The isotopic composition of the C\textsubscript{24} and C\textsubscript{26} fatty acids suggests that they are at least partly of terrestrial origin. This may account for the pronounced enrichment of these compounds in sediments deposited within the OMZ in all investigated areas (Fig. 8). Canuel and Martens (1996) demonstrated that the terrigenous C\textsubscript{24} acid is degraded more slowly in coastal sediments than marine-derived short-chain fatty acids (e.g. C\textsubscript{14} and C\textsubscript{16:1}). The C\textsubscript{24}/C\textsubscript{16} fatty acid ratio was employed to determine the relative contribution of fatty acids from terrestrial and marine sources (Leenheer et al., 1984; LeBlanc et al., 1989). On the Pakistan margin, this ratio in general is higher in sediments deposited within the OMZ (Table 1) possibly indicating a higher proportion of terrigenous fatty acids in sediments within the OMZ, although the non-terrigenous contribution (isotopic evidence) to the same acid may have varied as well. As can be seen by the n-alkane concentrations, which do not relate to the OMZ, a terrestrial origin per se does not lead to a higher accumulation rate within the OMZ.

A better preservation of terrigenous organic matter within the OMZ, however, is suggested by the lighter ("more terrestrial") $\delta^{13}$C values of the total organic matter in the corresponding sediments. A redox potential related difference in organic matter preservation, with heavier values above and below the OMZ, reflecting preferential remineralization of $^{12}$C compounds, would be an alternative explanation (Cowie et al., 1999).

As a third hypothesis, the supply of isotopically light organic matter by chemoautotrophic bacteria in oxygen-depleted water was suggested to explain the lighter $\delta^{13}$C values within the OMZ (Cowie et al., 1999). A specific in
situ supply of organic matter by organism living within the OMZ might also explain the enrichment of the C35 n-alkane in sediments from within the OMZ, reflecting a secondary productivity signal (Schulte et al., 1999). The isotopic composition of this compound is significantly different from that of the other n-alkanes pointing to another, yet unknown source. The higher concentrations of the bacterial branched fatty acids within the OMZ point to significant bacterial activity and support the suggestion of secondary productivity within the OMZ. This interpretation would be consistent with the results of Lee (1992) who suggested that the production of new organic matter by bacteria in sediments may be a way of preserving carbon in anoxic sediments (regardless of O2).

5.2.4. Reactivity toward oxic degradation

As mentioned above, phytol, the n-alcohols, and the sterols all have higher organic-carbon-normalized concentrations within the OMZ (Figs. 8 and 9). Chemically, all these compounds are alcohols, but the reactivity toward oxidation of their hydroxyl groups decreases in the order allylic > secondary > primary (March, 1992). Apparently, the relative degree of preservation under the oxygen-depleted conditions of the OMZ increases parallel to the reactivity of the hydroxyl group under oxic conditions (phytol > sterols > n-alcohols).

The relationship between preservation and reactivity can also be demonstrated by differences in the preservation of sterols with different degrees of unsaturation. In the Pakistan margin sediments, the concentration of the sum of sterols with two double bonds is three times higher within the OMZ (mean concentration: 170 μg/g TOC; n = 11; Schulte, 1997) than outside the OMZ (mean concentration: 55 μg/g TOC; n = 9, Schulte, 1997). By comparison, the saturated and monounsaturated sterols are only enriched by factors of 2.5 and 2.3 within the OMZ (Schulte, 1997). This relationship between preservation and the number of double bonds underlines the influence of the sensitivity to oxidation of a lipid molecule on its preservation under suboxic conditions. This is in accordance with the conclusions of Sun and Wakeham (1998) who recently demonstrated that cholesterol is more rapidly degraded under oxic than under anoxic conditions and that under anoxic conditions it is degraded faster than C26–C29 dienols. All these interpretations on specific compounds are consistent with the statement of Hulthe et al. (1998) who suggested that the effect of oxygen on the degradation of organic matter depends on its lability.

Fig. 11. TOC, n-alkanes (C17–C43), phytol, and sum of sterols (C27–C30, cf. Fig. 5; Schulte, 1997) versus mineral surface area (Keil and Cowie, 1999). Letters correspond to study areas. Letters in open circles indicate samples from within the OMZ. The regression lines were calculated for sediments within the OMZ (TOC) and outside the OMZ (phytol, sterols) only.
On the other hand, the lack of enrichment of sterols in sediments within the OMZ in the Indus transect (Area D) cannot be explained by reactivity alone. The mineral composition may be responsible for the higher enrichment of sterols (and alcohols in general) in Areas A and B, where the sediments are dominated by chlorite with strong adsorptive properties. In contrast, sediments of Area D are dominated by detrital carbonates.

5.2.5. Sedimentation rate and primary productivity
Sedimentation rate and primary productivity are recognized as important factors controlling the quantity of OM buried in marine sediments (cf. Rullkötter, 1999, for an overview). The three transects on the Pakistan margin differ in primary productivity and sedimentation rate. Highest TOC values were observed within the OMZ of the Indus transect where primary productivity and sedimentation rate are lowest, whereas lower TOC values occur in areas with higher primary productivity and sedimentation rate (Areas A and B; Fig. 6). This disagrees with the empirical relationship between TOC content of sediments and primary productivity and sedimentation rate observed by Müller and Suess (1979). On the basis of mean values of primary productivity and sedimentation rate (sedimentation rate may, however, vary across the margin), the accumulation of organic matter in the studied sediments apparently cannot be explained simply by differences in primary productivity and sedimentation rate.

6. Conclusions
The composition of extractable lipids and the bulk stable carbon isotope data of organic matter in sediments from the Pakistan continental margin indicate that despite the vicinity of the Indus River the organic matter is mainly derived from marine sources. This organic geochemical evidence is in good agreement with the results of organic petrographic analyses (Littke et al. 1997; Lücke et al., 1999).

Supported by a biological marker approach we could demonstrate that accumulation of organic matter in marine sediments underlying an extended OMZ is a complex process involving several different mechanisms. Apparently, the OMZ plays a significant role in the accumulation and preservation of organic matter as indicated by a pronounced TOC maximum and the enrichment of single compounds within the OMZ in all investigated areas.

However, the low oxygen concentrations of the bottom waters underlying the OMZ are not an exclusive factor explaining all organic matter properties and their variations on the Pakistan continental margin. The type (origin) of certain organic matter constituents and their (related) lability toward oxic degradation, the mineral surface area, the mineral composition, and possibly the secondary productivity by (sedimentary) bacteria also appear to have an influence on the accumulation and composition of organic matter in this area and in some cases to explain discrepancies with published observations for other continental margin settings.

Apparently, the depositional environment of the Indus Fan (Area D) offers the best conditions for enhanced preservation of organic matter. The OMZ together with the undisturbed sedimentation (slope morphology) at moderate sedimentation rates seems to be responsible for the high TOC values in this area.

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