

Changes in organic matter–mineral interactions for marine sediments with varying oxygen exposure times

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Abstract

Density fractionation, X-ray photoelectron spectroscopy (XPS) and amino acid analyses were used to evaluate the physical form of preserved organic carbon (OC) in sediments from transects in the north east Pacific Ocean off the Mexican (Mazatlan) and Washington coasts. Low density (i.e. mineral-free) organic material dominated the OC in sediments with very short oxygen exposure times (OET <1 yr; total wt% OC 7.9–9.3, ~70% in $\rho < 1.9$ fractions). Quantities of low density OC decreased with increasing OET, suggesting that organic-rich debris was oxygen-sensitive. As OET increased from years to decades, OC was found predominately in the form of organic–mineral aggregates (58–77% of total OC was in the 1.9–2.2 ρ mesodensity fraction). Aggregated OC then decreased in abundance as a function of OET, suggesting that long-term oxygen exposure leads to destruction of organic–mineral aggregates. At OET values of centuries to millennia, the dominant forms of organic matter were OC sorbed to mineral surfaces (~50% of total) and OC locked within biogenic diatom frustules (~22% of total). These two physical forms of OC in marine sediments may provide the best long-term protection for OC.

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1. INTRODUCTION

More than 90% of organic carbon (OC) that reaches the ocean floor is degraded prior to burial in marine sediments (Hedges and Keil, 1995). How and why the remaining material is preserved is not well understood at present, but four main mechanisms have been proposed that afford OC protection from degradation. (1) Organic macromolecules can be recalcitrant to degradation depending on the prevailing depositional conditions (Keil et al., 1994a; Gelin et al., 1999; Nguyen et al., 2003). This class of protection would include OC that is stable only under reducing conditions, material referred to as oxygen-sensitive material (Hedges et al., 1999). (2) OC can be physically protected within biogenic minerals (Ingalls et al., 2003). (3) OC can be protected within organic–mineral aggregates (Tisdall

and Oades, 1982; Jastrow, 1996; Amézketa, 1999; Ransom et al., 1999; Balesdent et al., 2000; Bock and Mayer, 2000; Puget et al., 2000; Arnarson and Keil, 2001). (4) OC sorbed to particle surfaces may be protected from degradation (Sansone et al., 1987; Henrichs and Sugai, 1993; Keil et al., 1994b; Mayer, 1994; Arnarson and Keil, 2000; Ding and Henrichs, 2002; Arnarson and Keil, 2005).

The time organic matter is exposed to oxic conditions is another factor influencing the overall extent of OC degradation and preservation, and cumulative oxygen exposure has been hypothesized to override physical protection mechanisms at time scale of centuries to millennia (Hedges and Keil, 1995; Hartnett et al., 1998; Hedges et al., 1999; Keil et al., 2005). While the exact mechanisms for oxic degradation of OC in sediments remain poorly understood, ‘oxygen exposure time’ has been proposed as a proxy for the oxic degradation history of a sample (Keil et al., 1994a). Oxygen exposure time (OET) is calculated as the oxygen penetration depth into sediment pore waters divided by the sedimentation rate (Hedges and Keil, 1995). OET has been previously shown to be related to OC quantity and quality for sediments collected along the Washington

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margin (Hedges et al., 1999). The goal of this study is to use the X-ray photoelectron spectroscopy (XPS) and density fractionation approaches outlined in Arnarson and Keil (2001) in order to better understand the relationships between OC physical form and OET. Sediments from two continental margins with widely varying OETs (0–1000 yr) were evaluated and a budget was created to evaluate the importance of OC preservation mechanisms as a function of OET.

2. MATERIALS AND METHODS

2.1. Sampling sites

Samples were collected along two transects on the Pacific Ocean continental margins off the coasts of Mexico and Washington State, USA (Fig. 1 and Table 1). Mexican margin samples were collected during two cruises on R/V *New Horizon* in 1996 (stations M202–M208) (Lambourn and Devol, 1998) and 1999 (station M303; Van der Jagt et al., 2000). Washington margin samples were collected on R/V *Wecoma* in 1994 (stations W201–219; Lambourn et al.,

1996). Primary production is on the order of 200 (Longhurst et al., 1995) and $450 \text{ gC m}^{-2} \text{ yr}^{-1}$ (Perry et al., 1989) for the Mexican and Washington margins, respectively.

The Mexican margin has a prominent oxygen-deficient zone (ODZ), where water column denitrification occurs, between approximately 150 and 600 m (Hartnett et al., 1998; Ganeshram et al., 1999), with oxygen concentrations below the detection limit ($<5 \mu\text{M}$) over most of this range, as is characteristic of the eastern tropical North Pacific. Due to low bottom water oxygen concentration, OET off Mexico is as short as days within the ODZ (Table 1). Below the ODZ oxygen exposure increases to ~ 400 yr (Table 1). The ODZ coincides with OC concentrations in the sediments in the range of 4–10 wt% (Hartnett, 2003) and organic carbon to surface area (OC:SA) values of $>2 \text{ mg OC m}^{-2}$ (Table 1). The shelf station and the 2000 m station have OC:SA values of 1.1 and 1.5 mg OC m^{-2} , respectively (Table 1). The deep Mexican margin station has an OC:SA ratio of $0.28 \text{ mg OC m}^{-2}$ (Table 1). There is very little terrestrial input onto the Mexican continental margin (Ganeshram et al., 1999),

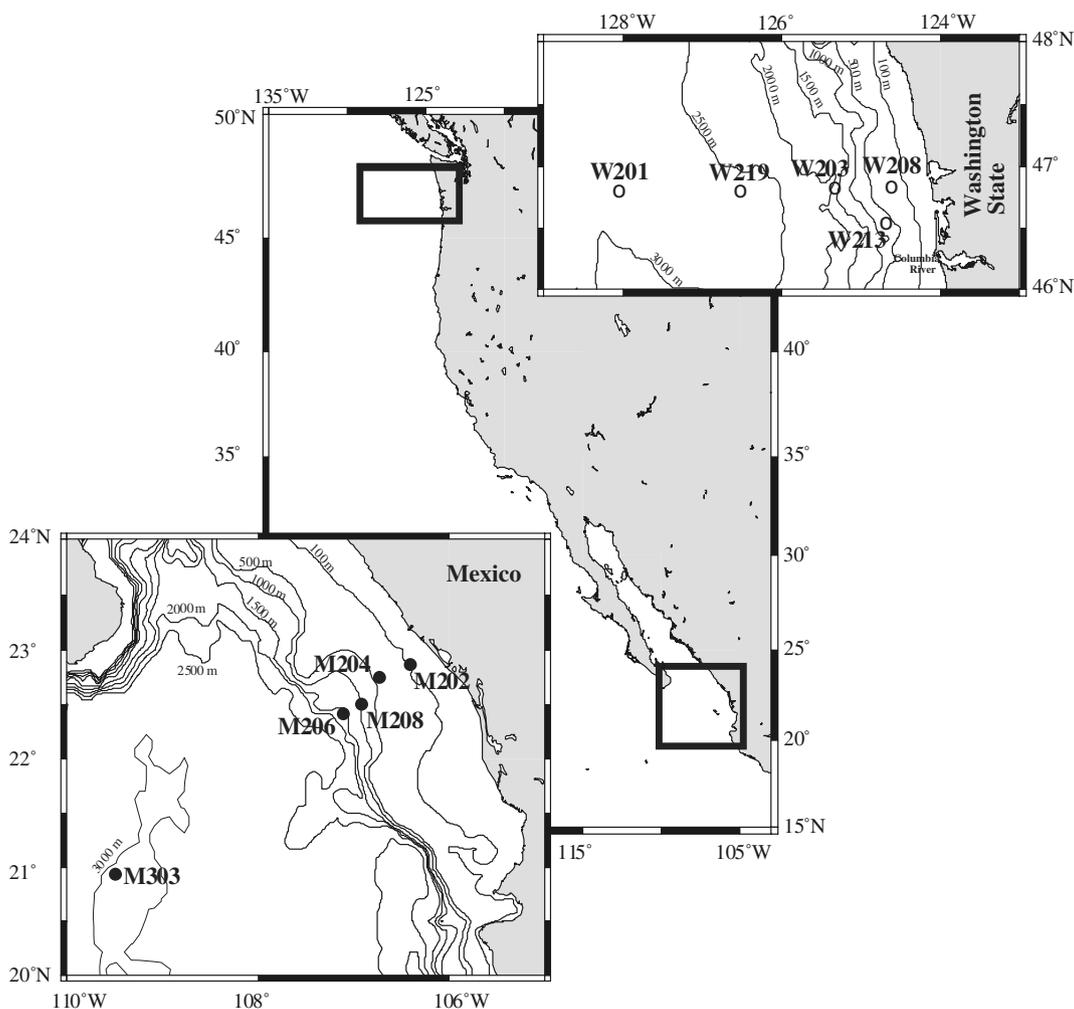


Fig. 1. Locations of sampling stations on the continental margins off Washington State and Mexico. Open symbols represent Washington margin samples and closed symbols represent Mexican margin samples.

Table 1
Location and general characteristics of sediment samples (letters before station numbers are M, Mexico and W, Washington State)

Station	Latitude (°N)	Longitude (°W)	Depth (m)	Distance offshore (km)	OET (yr)	OC ^b (wt%)	OC:SA ^b (mg OC m ⁻²)
M204	22° 41.78'	106° 32.00'	395	41	0.03	7.9	3.0
M208	22° 31.61'	106° 39.80'	1007	64	0.03	9.3	5.2
M202	22° 46.01'	106° 19.16'	103	22	1	2.6	1.1
W213	46° 29.88'	124° 43.75'	620	26.8	40	2.2	0.92
W208	46° 48.59'	124° 37.00'	132	22	45	1.5	1.3
M206	22° 25.16'	107° 00.33'	2048	98	73	4.3	1.5
W203	46° 47.22'	125° 22.81'	1994	52.5	74	2.5	0.78
W219	46° 45.02'	126° 29.93'	2153	98	210	1.4	0.35
M303	20° 55.25'	109° 25.08'	3032	393	380 ^a	1.5	0.28
W201	46° 45.08'	128° 00.09'	2682	158	1100	1.2	0.28

OET, oxygen exposure time, calculated as oxygen penetration depth divided by sedimentation rate. Except where noted otherwise, OET are calculated based on data for Mexico from Hartnett et al. (1998) and Hartnett (1998), and for Washington from Hedges et al. (1999). Stations are in order of increasing OET.

^a Sediment accumulation rate estimated as same as measured at station M207 (at 2955 m water depth; Hartnett, 1998) and using oxygen penetration depth from Van der Jagt et al. (2000).

^b OC and OC:SA are average values from the 10–20 cm interval of the cores. For full core values (0–30 cm) (see Hedges et al., 1999 and Hartnett, 1998).

and the sedimentary OC is predominantly of marine origin (Dickens et al., 2006).

The continental margin of Washington State is a more representative continental margin, with an oxygen minimum zone at a water depth at about 800 m (Hedges et al., 1999). Oxygen concentrations of the North Pacific waters impinging on the Washington margin do not go below 20 $\mu\text{mol O}_2$. OET increases off shore, ranging from ~40 to ~1000 yr (Table 1). Sedimentary OC concentration is <4 wt% throughout the Washington margin (Table 1; Hedges et al., 1999). The Washington shelf sample has a bulk OC:SA ratio of 1.3 mg OC m⁻² (Table 1). The two upper slope samples have OC:SA ratios of 0.92 and 0.78 mg OC m⁻², whereas the lower slope samples have OC:SA <0.5 mg OC m⁻² (Table 1). The Columbia River (Fig. 1) is a source of considerable amounts of terrestrial OC that are found in the sediments of Washington margin (Prah et al., 1994).

2.2. Sample collection and processing

Samples at all stations except M303 were collected by Soutar Box Core, which was sub-sampled using 10 cm diameter core tubes (for greater detail on sampling, see Lambourn et al., 1996; Lambourn and Devol, 1998). Sediment at station M303 was collected with a multi-corer and the samples were directly processed out of the multi-core barrels (Van der Jagt et al., 2000). All samples were sliced in a glove box under nitrogen gas. Porewater was separated from the bulk sediment by centrifugation at approximately 4000g. Sediment pellets were transported frozen back to the laboratory where they were freeze-dried prior to further processing and analyses.

Sediment slices chosen for this study were in the depth range 10–20 cm below the sediment surface. This is below the zones of oxygen penetration and active ²¹⁰Pb-based bioturbation at the sampling locations, but is near enough to the surface that comparisons of current oxygen penetration depths and sedimentation rates are likely still valid (e.g. Hedges et al., 1999). Samples were density fractionated into

five fractions (<1.6, 1.6–1.9, 1.9–2.2, 2.2–2.5 and >2.5 g cm⁻³) using the Na-metastatungstate, sonication and centrifugation approach described in Bock and Mayer (2000) and Arnarson and Keil (2001). Various data for bulk surface sediment samples (0–2 cm intervals) have been published previously (e.g. Hartnett et al., 1998; Hedges et al., 1999; Gélinas et al., 2001; Hartnett and Devol, 2003), but no data from the 10–20 cm intervals of the cores have previously been presented.

2.3. Analyses

Density fractions were analyzed for multiple properties: sample imaging (scanning electron microscope; SEM), bulk elemental content (CHN), mineral surface area (SA), surface characterization (XPS) and total hydrolysable amino acids (THAA). Microscopic analyses were performed at the University of Washington, Center for Nanotechnology using a Field Emission Electron Microscope (FEI Sirion XL 30). Bulk elemental content of organic carbon and total nitrogen were determined after vapor-phase acidification with a Carlo Erba model 1106 (Hedges and Stern, 1984). Mineral SA was determined by nitrogen adsorption using a five-point BET method (Lowell and Shields, 1991) on Micromeritics ASAP 2010 and Gemini surface area analyzers. Organic matter was removed from samples prior to SA analysis as described in Arnarson and Keil (2001). For seven low density isolates (<1.6 and 1.6–1.9 ρ , excepting M204, M206, M208), there was not enough mineral material to allow direct SA analyses. Because there is a linear relationship between mineral mass and measured SA in the bulk samples and isolates for which SA was directly measured ($n = 53$), SA for the seven remaining low density isolates was extrapolated. Extrapolated values were used to calculate OC:SA ratios, and were used as a visual guide, but were not used for subsequent calculations or statistical treatments.

XPS surface characterizations were done at the University of Washington, Surface Analysis Recharge Center, with

Surface Science Instruments (SSI) S- and M-probes as described in Arnarson and Keil (2001). Analyses were made in duplicate with an average spot size of $\sim 200 \mu\text{m}$ and a theoretical average scanning depth into the sample matrix of $\sim 20 \text{ nm}$. The measured atom percent of each detected element was multiplied by its molecular weight and then carbon weight percentages were calculated. We assume that hydrogen has a negligible contribution on a weight basis (hydrogen is the only element that the XPS cannot see; the detection limits for most other elements are ~ 1 atom percent; Arnarson and Keil, 2001).

Amino acid analyses were conducted following the protocol of Cowie and Hedges (1992). The amino acid degradation index (DI) was calculated as described by Dauwe and Middelburg (1998) and Dauwe et al. (1999). The index calculated here does not include the non-protein amino acids, which we interpret separately (e.g. Dauwe et al., 1999). OET was calculated as the total time sediment samples were to exposed to oxygen prior to burial beneath the ^{210}Pb mixing zone, including settling times through the water column for samples with extremely short OET (see Hartnett et al., 1998; Gélinas et al., 2001; Van Mooy et al., 2002). Statistical manipulation of data was done according to Miller and Miller (1984), using the Analysis ToolPak of Microsoft Excel, 2000 and SPSS 13.0 for Windows. Supplemental analyses not presented here, but available in Arnarson (2004) include TEM-EDS (elemental diffraction analysis) analyses and mineralogical estimates based on EDS and XPS elemental compositions.

3. RESULTS

3.1. Recovery efficiency

Recovery efficiencies after density fractionation averaged 84% for mass, organic carbon, total nitrogen and surface area. Analysis of variance (ANOVA) indicated that the values were not significantly different between the four parameters when compared with the variation between stations ($P = 0.24$). Raw data and statistical analyses for all samples are available in Arnarson (2004).

3.2. SEM

SEM images showed small amounts of identifiable organic matter such as woody debris in the lowest density isolates (<1.6 and $1.6\text{--}1.9 \rho$; Fig. 2). Visually, the three lightest fractions (<1.6 , $1.6\text{--}1.9$ and $1.9\text{--}2.2 \rho$) nearly exclusively contained aggregated organic matter–mineral complexes ('aggregates'). Conversely, the higher density isolates ($2.2\text{--}2.5$ and $>2.5 \rho$) contained mostly individual mineral grains without much aggregation (Fig. 2). We define aggregates as clumps of mineral and organic matter that survive the density fractionation processes (Bock and Mayer, 2000; Arnarson and Keil, 2001; Baisden et al., 2001; Arnarson and Keil, 2005). Arnarson and Keil (2005) suggested that these aggregates were not created during the density fractionation process because we did not observe aggregate formation in controlled mixtures of plankton and minerals. Each sample was visually

scanned using SEM and a qualitative estimate of the extent of aggregation was made (Table 2). In general, there was a decrease in aggregation from light to heavy fractions and from short to long OET (Table 2). However, there were also differences in aggregation for the two transects; Mexican margin sediments contain no recognizable woody debris and have more aggregated

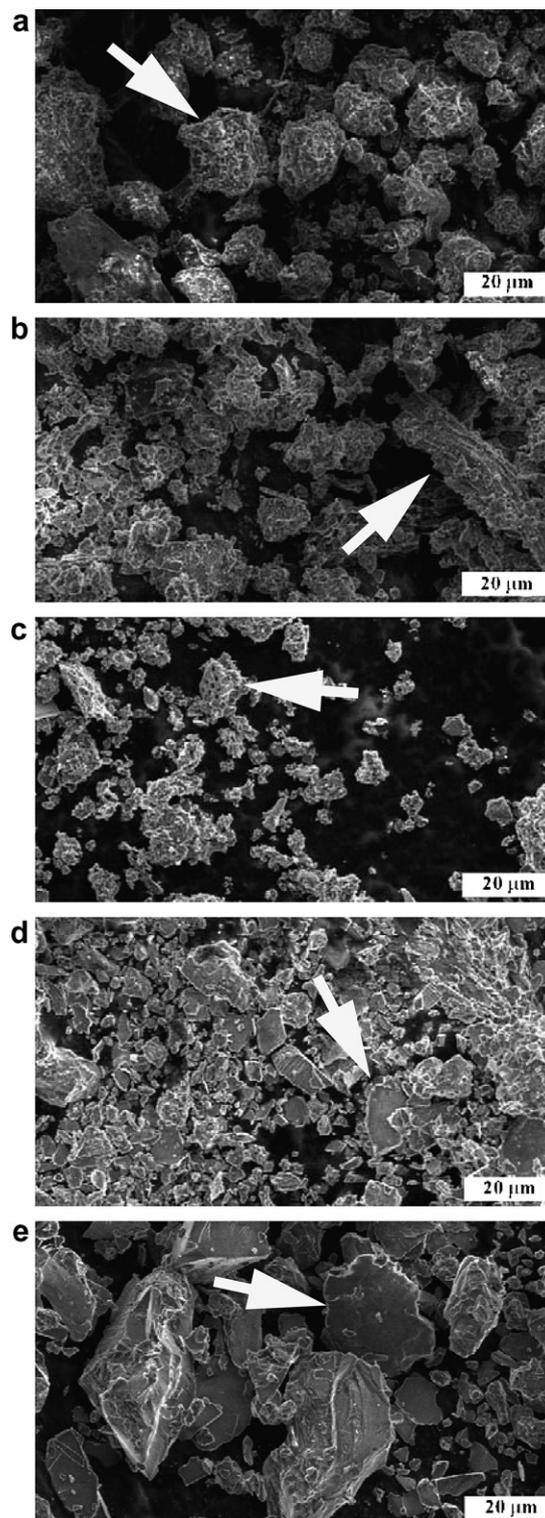


Table 2
Qualitative description of extent of aggregation based on visual evaluation of SEM images for density fractions (g cm^{-3})

Station	<1.6	1.6-1.9	1.9-2.2	2.2-2.5	>2.5p
M204	████████	████████	████████	████	██
M208	████████	████████	████████	████	██
M202	████████	████████	████████	████	██
W213	████████	████████	████	████	
W208	████████	████████	████	████	
M206	████████	████████	████████	████	██
W203	████████	████████	████	████	
W219	████████	████████	████	████	
M303	████████	██	██		
W201	████████	██	██		

Stations are in order of increasing OET. Four blocks indicate that almost all particles are aggregated; three indicate a visible presence of unaggregated particles; two blocks indicate an approximately even mixture of aggregated and unaggregated particles; one block indicates a minor contribution by aggregates; and no blocks signify no apparent aggregates.

material in the higher density isolates compared to the Washington margin.

Biogenic mineral debris, e.g. diatom frustules, was concentrated in the intermediate density interval ($1.9\text{--}2.2 \text{ g cm}^{-3}$) although some was also found in the lighter fractions. The amount of diatom frustules relative to lithogenic mineral grains in the intermediate density interval increased with distance from shore. The $2.2\text{--}2.5 \rho$ isolates from the two stations furthest off Washington were visually dominated by diatom frustules. Despite being important visual constituents of the $1.9\text{--}2.2 \rho$ isolate, biogenic debris was in general only a minor constituent of the total mineral material in the samples (see Section 4).

3.3. Distribution of mass, SA and OC

The OC (Fig. 3) and total mass (not shown) content of each density isolate varied with OET. More than half of OC in samples with short OET (M204 and M208; OET <1 yr) was contained in the lightest two density fractions (Fig. 3). Most OC in samples of intermediate OET



Fig. 2. Representative SEM images. (a) $<1.6 \text{ g cm}^{-3}$ density fraction for station M206, arrow denotes one of several aggregates visible in this fraction. (b) $1.6\text{--}1.9 \text{ g cm}^{-3}$ density fraction for station M202, arrow denotes aggregate containing woody debris. (c) $1.9\text{--}2.2 \text{ g cm}^{-3}$ density fraction for station M204, arrow denotes small aggregate containing visible diatomaceous debris. (d) $2.2\text{--}2.5 \text{ g cm}^{-3}$ density fraction for station W208, arrow denotes clean face of a mineral grain without substantial aggregation. (e) $>2.5 \text{ g cm}^{-3}$ density fraction for station W201, arrow denotes clean face of a mineral that is not aggregated. The widths of white scale bars correspond to $20 \mu\text{m}$.

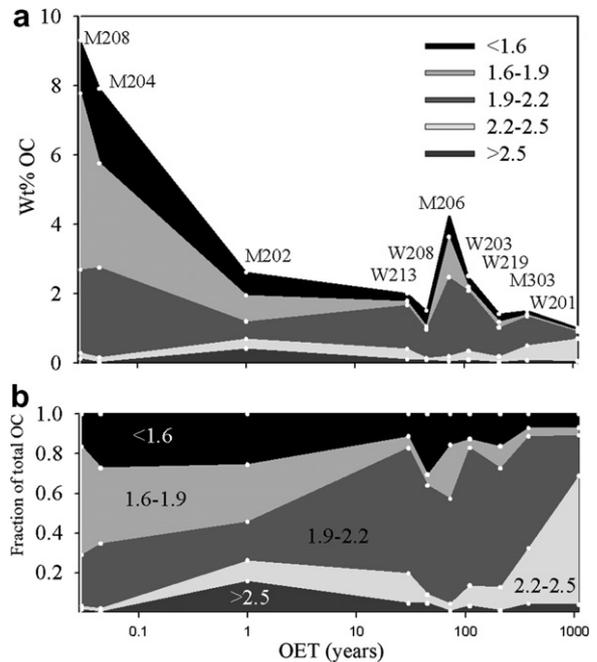


Fig. 3. (a) Cumulative organic carbon content at each station as a function of OET. (b) fraction of organic carbon found in each density isolate. Station order as in Table 1.

(M202, W213, W208, M206, W203, W219 and M303; OET between 1–380 yr) was in the intermediate density intervals of $1.9\text{--}2.2 \rho$, and the sample with the longest OET (W201; OET ~ 1100 yr) contained most of its OC in the $2.2\text{--}2.5 \text{ g cm}^{-3}$ isolate (Fig. 3).

3.4. Elemental concentrations

Regardless of which density isolate contained the most OC on a proportional basis (Fig. 3), there was remarkable agreement on the quantity of the OC within each isolate, regardless of station location or OET (Fig. 4). Concentrations of OC and TN in each density fraction decreased with increasing density (Fig. 4). Differences in OC, TN and atomic C:N ratios between density fractions were found to be highly significant by ANOVA ($P \ll 0.01$), while in each density fraction differences between stations were not ($P > 0.05$). While any given density fraction was not significantly different from counterparts at other stations, there was a statistically significant difference in the lightest two fractions between the *transects* (two-tailed *t*-test, $P < 0.01$), with elevated C:N values in the low density Washington margin samples (Fig. 4), consistent with the presence of woody debris found in SEM images.

3.5. XPS

Ratios of carbon detected at particle surfaces by XPS and the bulk OC measured by CHN were close to one ($0.6\text{--}1.2$) in the two light fractions (Fig. 5). With increasing density there was an increase in the concentration of OC at particle surfaces (e.g. visible using XPS) relative to the bulk

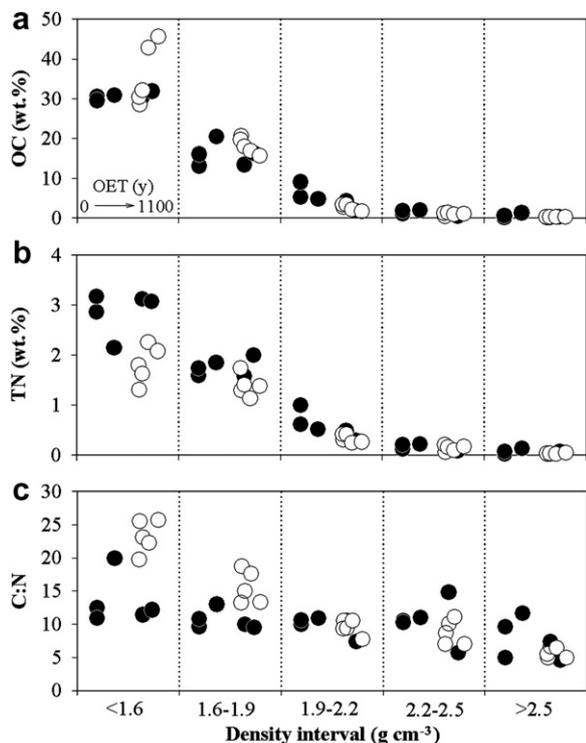


Fig. 4. Weight percentages of (a) organic carbon, (b) total nitrogen and (c) atomic C:N ratio for density fractions as a function of OET. Closed circles, Mexico; open circles, Washington. Within each density interval, the data are separated by OET with short OET on the left and long OET on the right.

OC (ANOVA, $P \ll 0.01$; Fig. 5). In a given density fraction, there were no significant variation in surface to bulk ratios of OC between stations (ANOVA, $P = 0.2$). XPS analyses of other Si, Al, Fe and Mg were used to help estimate the contribution of quartz, opal and clay minerals to the sediment samples (data not shown, but see Arnarson and Keil (2001) for examples and Arnarson (2004) for analytical details).

3.6. OC:SA

OC:SA ratios ranged between 0.15 and 21 mg OC m^{-2} (Fig. 5). For the four density isolates $>1.9 \text{ g cm}^{-3}$, there were statistically significant trends with lower OC:SA ratios being associated both with increased density of the isolates and longer OET (ANOVA, $P < 0.01$; Fig. 5). Samples investigated in this study have a wide range in bulk (unfractionated) sedimentary OC:SA ratios (0.28–5.2 mg OC m^{-2} ; Table 1). As expected, samples off Mexico affected by the ODZ (OET $\ll 1$ yr; M204 and M208) have elevated OC:SA values (Table 1). Stations on the deep slopes with OET >200 yr all had bulk OC:SA less than 0.5 mg OC m^{-2} (Table 1). Only stations on the upper slope of the Washington margin with intermediate OET (1–200 yr) have OC:SA values within the ‘typical’ range (Table 1). The shelf stations at both margins and the 2000 m Mexican margin station (M206, which is below the ODZ) all have bulk OC:SA values that are slightly elevated above the ‘typical’ range

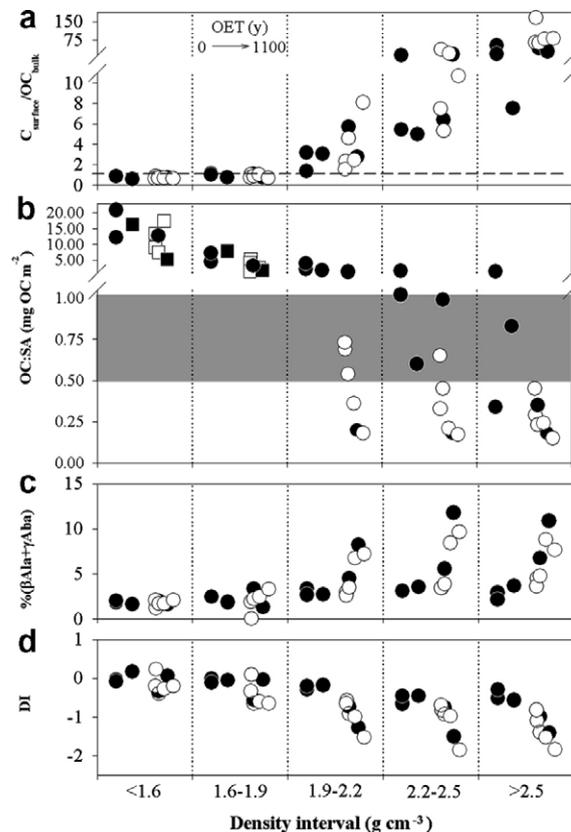


Fig. 5. Influence of both OET and density interval on measured parameters. (a) OET dependence within density fractions of the ratio of surface carbon concentration (measured by XPS; wt%) and bulk organic carbon concentration (measured by elemental analyzer). (b) Organic carbon to surface area ratios (OC:SA). Square symbols represent OC:SA ratios that were calculated based on estimated SA values (see text for details). (c) Sum of mol% non-protein amino acids (β -alanine and γ -aminobutyric acid) and (d), amino acid degradation index (DI; Dauwe et al., 1999). Closed circles, Mexico; open circles, Washington.

($\sim 1 \text{ mg OC m}^{-2}$). At least one other exception to the OC:SA range at intermediate OET has been noted previously in the literature (Mayer et al., 2002), which was thought to be due to export of mineral associated, refractory minerals from the shelf to the slope. The three samples with intermediate OET and elevated bulk OC:SA ratios in the present study (M202, W208 and M206) have OC:SA values of 0.85–1.0 mg OC m^{-2} , i.e. within the ‘typical’ OC:SA range, if the OC and SA contained in the lightest isolate ($<1.6 \text{ g cm}^{-3}$) is subtracted out. OC:SA values of mineral associated OC in ODZ samples M204 and M208 remain elevated (1.7 and 3.0 mg OC m^{-2}) even after subtracting contributions by low density material. Fractionation into multiple density intervals reveals a continuum of OC:SA values for each sediment sample, and that few density fractions are within the ‘typical’ bulk range of OC:SA (shaded area of Fig. 5). Sample locations that have bulk OC:SA ratios within the range typically observed for coastal sediments (0.7–1.1 mg OC m^{-2} ; Table 1) include components that have OC:SA values that are either above or below that bulk average (Fig. 5).

3.7. Amino acids

Amino acids comprise, on average, 9.3 ± 3.2 and $30.4 \pm 9.1\%$ of the total OC and ON, respectively. There is no significant variation in OC-normalized amino acid yield as a function of density or OET for the Mexican margin samples. For the Washington margin samples, the $<1.6 \rho$ isolate contains a minimum contribution (4% and 21%) from amino acids to the total OC or TN (consistent with the visual observations of abundant woody debris in those isolates) and the maximum contribution is in the 1.6–1.9 and 1.9–2.2 ρ isolates (12% and 40% of OC and TN; $P < 0.01$, ANOVA). Also, within the $>1.9 \rho$ density isolates from the Washington margin, the contribution of amino acids to the total OC (but not to total TN) decreased as a function of OET ($P < 0.01$, ANOVA). Thus, while each density isolate has a characteristic amino acid concentration (and composition—described next), there is a subtle secondary imprint related to OET. The relative contribution of non-protein amino acids to the total amino acid pool increased significantly both with increasing density and longer OET ($P \ll 0.01$, ANOVA; Fig. 5). In a similar fashion, the amino acid degradation index (DI) decreased significantly (i.e. became ‘more degraded’) both with increasing density and longer OET ($P \ll 0.01$, ANOVA; Fig. 5). The two lightest density fractions stayed relatively ‘fresh’ throughout the OET range, so changes in degradation indicators occurred predominately in the three heavier fractions.

4. DISCUSSION

What is the nature of the relationship between OC and mineral matrices in marine sediments, and does the relationship change as a function of oxygen exposure time? A general scenario relating OC, mineral matrices and OET is that organic matter–mineral interactions are predominately established in the benthic boundary layer (Thomsen et al., 2002), where settling OC interacts with lithogenic mineral material resulting in aggregates of low density (high OC content). Diagenesis removes OC and results in aggregates of greater density. Changes in OC ‘quality’ (defined in this manuscript using amino acids) are dependent on diagenesis and are likely to be mechanistically independent of density unless there are mineral-specific OC interactions such as those observed between amino acids and clays in river systems (Aufdenkampe et al., 2001). However, aggregate density and OC quality are correlated by the fact that changes in both are the result of diagenesis. Over time, as fresh OC is continually added to a sediment, the sediment will accumulate OC along a continuum of differing quantity, quality and density, with the ‘freshest’ material in the lightest fractions and the ‘most degraded’ in the densest fractions. This trend gets ‘smeared’ when high density fractions (containing remnant survivor OC from prior diagenesis) contribute to the creation of new lower density aggregates. If this general hypothesis for how OC and mineral interact is correct, then the density distribution of OC within a bulk sediment will be controlled by the relative extent of OC preservation and degradation that have occurred. It might be expected that sediments containing

large amounts of OC will have undergone relatively little diagenesis and most of the OC should be in low density aggregates with a ‘fresh’ quality. Conversely, sediments that have experienced extensive diagenesis ought to have their OC relatively enriched in the high density fractions.

Bock and Mayer (2000) showed that along continental margins, where the majority of OC is buried (Hedges and Keil, 1995), most OC is found in the ‘mesodensity’ fraction (2.0–2.3 ρ). We then showed that mesodensity aggregates can slow oxic diagenesis (Arnarson and Keil, 2005). Along the Mexican margin, where there is extensive OC preservation (Hartnett et al., 1998), OC is predominately in the lighter 1.6–1.9 ρ fraction (Arnarson and Keil, 2001). Our 10-station sample set here spans the margin to the rise, encompasses OET values from $\ll 1$ to >1000 yr, and allows for the first time the evaluation of how OC is distributed along a density continuum as a function of diagenesis and OET. We indeed observe a shift in the physical relationship between OC and mineral that is accompanied by changes in OC quality estimated using amino acid analyses. At OET $\ll 1$ yr, the majority of OC in sediments occurs as distinct material isolated in the low density fractions (stations M204 and 202). As much as 70% of the OC is in $<1.9 \text{ g cm}^{-3}$ density fractions, comparable amounts to that observed by Pichevin et al. (2004) and Dickens et al. (2006) for other sediments underlying low oxygen waters. However, for the majority of our samples (Fig. 3; $n = 7$ of 10 excepting the oxygen minimum samples M204, M202 and the woody-rich W208), the OC is intimately associated with mineral materials, and this tight association remains even when sediments are subjected to intensive density fractionation procedures that include sonication to disaggregate loosely coupled materials. On average, $79 \pm 8\%$ of the OC in our samples is found in $>1.9 \text{ g cm}^{-3}$ density fractions (Fig. 3). Other investigators have similarly found that generally $>70\%$ of organic carbon is tightly associated with mineral grains (Ertel and Hedges, 1985; Mayer et al., 1993; Keil et al., 1994c; Bock and Mayer, 2000; Dickens et al., 2006). At the station with long OET (Fig. 3; >1100 yr, W201) 68% of the OC is found in the two most dense fractions (2.2–2.5, $>2.5 \rho$) and is associated with non-aggregated minerals. To the best of our knowledge, a hemipelagic sediment sample of this type has not previously been evaluated for its OC–mineral interrelationships in context with more typical coastal sediments.

The shift in organic–mineral relationships and in OC ‘quality’ along the density continuum and as a function of OET can be used to differentiate between protective processes (e.g. mineral interactions, biomineral protection, etc.; Nguyen and Harvey, 2001; Arnarson and Keil, 2005) and destructive processes (e.g. OET). For example, OC is present in low density isolates in all samples regardless of OET, implying that factors creating stable low density aggregates (e.g. organic shielding, selective preservation; Nguyen and Harvey, 2001) may be important in all conditions. However, the quantities of low density material change with OET, as does the amino acid signature of the material, suggesting that OET leads to loss of material protected in this way. High density material is also found in all samples, and with increasing OET it becomes a more

quantitatively important portion of the total OC (Figs. 5 and 3). Overall, we interpret this as evidence that several potential preservation mechanisms are at work within marine sediments, and that as a function of OET certain mechanisms become less important and others assume a more predominant role. Thus, we suggest that as a function of diagenesis and OET, the OC that resists degradation is ‘moved’ along a continuum where it is progressively degraded and progressively more associated with mineral grains. At short OET and during the early stages of diagenesis, most OC is predominately low density organic debris (Fig. 3). At intermediate OET values such as those found in many continental margin sediments, OC–mineral aggregates dominate (Figs. 2 and 3) and the amino acids in the OC are ‘more degraded’. At long OET typical of hemipelagic sediments, aggregates are not found in abundance, the OC that remains is associated with individual mineral grains (Figs. 2 and 3), and has the most degraded amino acid signature.

4.1. Changes in OC–mineral interactions with density and OET

XPS is a surface-specific technique, and as such, the amount of OC measured by XPS can be compared with the amount measured by elemental analysis (CHN), giving information on whether OC in the sample is concentrated at sample surfaces or is within thicker materials (Yuan et al., 1998; Arnarson and Keil, 2001). The two lightest density fractions have surface:bulk OC ratios ≤ 1 (Fig. 5). Thus, even though these fractions in most cases have minimal amounts of mineral mass, the few mineral grains there are ‘seen’ by XPS in higher proportions than in the bulk analysis, and they can be conceptualized as being ‘glued’ to the outside of organic particles resulting in a surface to bulk ratio less than one (Arnarson and Keil, 2001). These low density fractions dominate the OC content of samples with very short OET and become progressively less important with increasing OET. The contribution by low density OC to the total OC is correlated ($r^2 = 0.91$, $n = 4$, $p < 0.05$) with the amount of oxygen-sensitive, non-protein alkyl-carbon in samples from identical ($n = 2$) or ‘nearby’ (within 50 m of water depth along same transect, $n = 2$) sampling locations (Gélinas et al., 2001), which supports the argument that the majority of the OC in the light fractions is recalcitrant under reducing conditions but can be remineralized as OET increases.

Surface:bulk OC ratios are >1 for the intermediate density isolates (1.9–2.2 and 2.2–2.5; Fig. 5). This is interpreted as an indication that OC is concentrated in the outer portions of aggregates in these density fractions. With the two intermediate density isolates, the surface:bulk OC ratio increases with increasing OET (ANOVA $P \ll 0.01$) and the OC:SA ratio decreases (ANOVA $P \ll 0.01$; Fig. 5). Visually we observe fewer aggregates and more distinct non-aggregated minerals (Table 2). Therefore, the intermediate density fraction has much of its OC in aggregates when OET is short, and grades toward having most of the OC sorbed to particle surfaces in samples with long OET.

The $>2.5 \rho$ isolates, which contained primarily only individual mineral grains as observed by SEM (Fig. 2 and Table 2)

have very high surface:bulk OC ratios >50 . Similar to the intermediate density fractions, OC:SA ratios in the $>2.5 \rho$ isolates significantly decreased as a function of OET (ANOVA $P < 0.01$; Fig. 5). The statistically significant increase in surface to bulk ratios with increasing density is in agreement with the qualitative analysis of SEM images (Table 2), and is thus further evidence that heavier fractions have their carbon content highly concentrated on particle surfaces and presumably bound there by sorption.

4.2. Changes in OC composition with density and OET

As OC moves along the continuum from relatively abundant fresh material in low density fractions to relic surviving OC in more dense isolates, it passes through the series of discrete density fractions that we isolated. The interrelationship between these density fractions and OET is complex. On the one hand and as discussed previously, the continuum from high amounts of OC in low density material to low amounts in the high density material occurs in all samples regardless of the location the sample was obtained from (margin, slope, rise). Each density fraction has a general OC character (concentration, amino acid content and composition, etc.) that is different from the other density fractions regardless of where the bulk material was isolated from (e.g. Figs. 4a and 5b). This type of general trend has been reported for bulk samples from the Washington

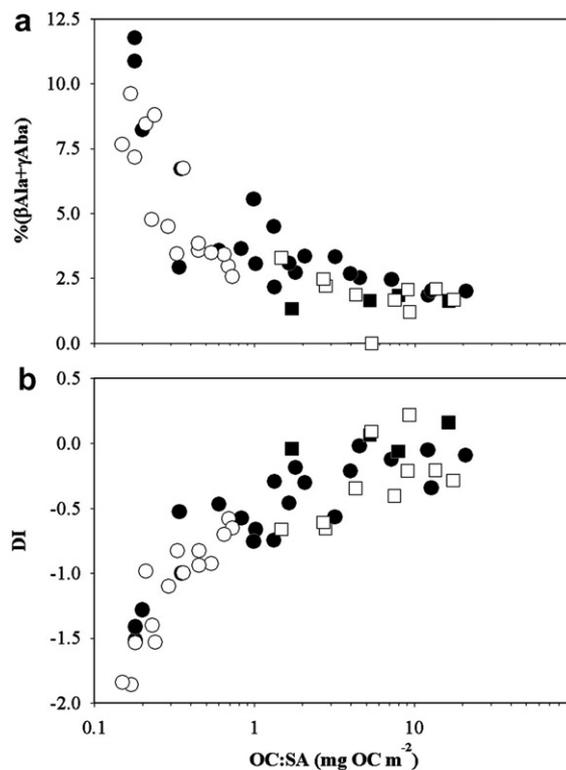


Fig. 6. Indices of degradation; (a) sum of mol% non-protein amino acids, and (b) amino acid degradation index, plotted against OC:SA on a \log_{10} scale. Closed circles, Mexico; open circles, Washington. Square symbols represent OC:SA ratios that were calculated based on estimated SA values (as in Fig. 5).

coast (Hedges et al., 1999) and for hydrodynamically isolated components of Washington margin sediments (Keil et al., 1994c; Keil et al., 1998).

On the other hand, the amino acid composition within specific density fractions also changes as a function of OET. That is, as OET increases the degradation state of the OC in a density fraction becomes 'more degraded'. The atomic C:N ratios (Fig. 4c), amino acid compositions and degradation indices (Fig. 5c and d) and the OC:SA ratio (Fig. 5b) are all significantly correlated with OET within a given density fraction ($P \ll 0.01$). These parameters are also correlated with each other, as is perhaps best illustrated by the relationship between amino acid compositions and OC:SA (Fig. 6). This allows delineation of the importance of oxygen exposure on OC quality. As OC:SA decreases within a density fraction and as a function of OET (e.g. Fig. 5b–d), OC compositions should change if the factor leading to changes in OC:SA are also leaving an imprint upon the remaining OC that was not degraded. The strong curvilinear relationship between OC:SA and both non-protein amino acid yield and amino acid DI (Fig. 6) thus indicates that diagenesis as a function of OET is not simply and unilaterally removing OC from certain density intervals, but relative to what was there before it is also altering the composition of the material that remains.

Thus, the relative proportions of OC (Fig. 2b) along the density continuum can be viewed as a general indicator of protective mechanism, and how degraded the OC is within a certain density interval (Fig. 5) may reflect the influence of degradative attack (OET) on the various protective mechanisms.

4.3. A budget for potential preservation mechanisms

We constructed a budget that proportions organic matter into different physical classes, and presumed preservation mechanisms, as a function of OET (Fig. 7). Data

were grouped into three OET regimes; very short OET indicative of ODZ situations M204 and M208, intermediate OET values of 40–400 yr that are typical of most continental margin sediments, and long OET > 1000 yr typical of stations that are deep and distal from shore (e.g. W201).

The sum of the quantity of OC in the two light isolates is referred to as organic debris and is taken as an estimate of the OC preserved in sediment due to some inherent resistance to degradation under the conditions (e.g. OET) of the depositional site (Hedges et al., 1999; Nguyen et al., 2003). Alternatively, the distinct OC that is present could simply be younger, not-yet-degraded material recently bioturbated downward to the 10–20 cm material that we sub-sampled. Bioturbation of younger material into our samples might be occurring at oxygenated macrofauna-rich sites, but ^{210}Pb -based mixing depths only reach 5 cm even at the deepest site off Washington (Keil et al., 2005), suggesting that this mixing is slow. Additionally, the excessive presence of distinct debris in the short OET samples from the non-bioturbated oxygen minimum zone off the Mexican (Levin, 2003) and Nambian (Pichevin et al., 2004) margins argues for preservation under local conditions rather than substantial mixing in of younger material. The amount of OC in the two light fractions decreases with increasing OET (Fig. 2), indicating that the distinct debris is at least partially oxygen-sensitive (also see Hedges et al., 1999). Despite becoming quantitatively and proportionally less abundant, the amino acids in this material exhibit minimal degradation regardless of OET (Figs. 5 and 6).

Intermediate density fractions contain OC that is aggregated, sorbed, or present within biogenic matrices. These physical relationships correspond to potential preservation mechanisms, where aggregated OC is preserved through mineral protection and retardation of diffusive fluxes (Baldock and Skjemstad, 2000; Arnarson and Keil, 2005), sorbed OC is preserved through irreversible reactions with the surfaces (Henrichs, 1995), and the OC in biogenic minerals is protected by the mineral sheath (Ingalls et al., 2003).

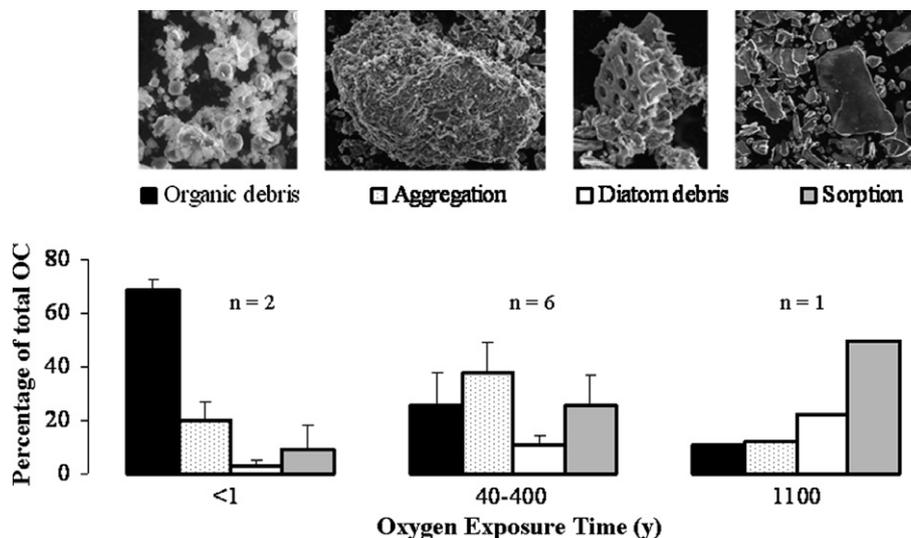


Fig. 7. Calculated distribution of preservation mechanisms as a function of OET.

The XPS and elemental data can be used to probe these possibilities. To estimate the amount of OC in the $>1.9 \text{ g cm}^{-3}$ isolates that is sorbed to mineral surfaces, we calculated the fraction of the total OC (determined by bulk elemental analysis) that was detected in the surface-specific XPS analysis. This was done by extrapolating the OC measured within an average XPS spot (200 μm diameter by 20 nm depth) to the total measured surface area and then dividing by the measured bulk organic carbon content. Calculated values range from $<1\%$ in some 1.9–2.2 ρ fractions to 90–120% for the $>2.5 \rho$ fractions. The calculated values for the $>1.9 \text{ g cm}^{-3}$ isolates were then weight-normalized to the total weight percent OC of the bulk fractions to determine the proportion of total OC in a sample that was sorbed to mineral surfaces. The remaining OC was split up between being protected by biogenic minerals or aggregates.

A rough estimate of the amount of OC protected by diatom frustules can also be made using the XPS data. Because visually recognizable biogenic debris is strongly concentrated in the intermediate density fraction (1.9–2.2 ρ), it is assumed that preservation of OC associated with diatom frustules is only quantitatively important in this fraction. The XPS-detected elements Si and Al are used to quantify the opaline-Si and clay-Si content (Yuan et al., 1998; Arnarson and Keil, 2005). Using a pure clay end-member with the Si:Al ratio of 2.2 (Ganeshram et al., 1999) and zero Al in opal, the excess atom% Si above the Si:Al ratio of 2.2 identifies the opaline-derived Si in the samples. This calculation assumes that there is no quartz in the intermediate density fraction, which if present would be tallied as opal. Both Keil et al. (1994c) and Ganeshram et al. (1999) show quartz is predominately found in coarse size-fractions, and thus is not likely to be associated with enough organic material to become light enough to contribute significantly to the intermediate density fraction. In order to convert from Si to OC, the fraction of Si that is opal is multiplied by the OC in the intermediate density fraction after subtracting the OC that is in aggregates. The estimate of OC protected by association with diatom frustules is a minimum estimate of biogenic-protected OC because some of the material that is accounted for as being protected by organic–mineral aggregates could be protected by diatom frustules incorporated into aggregates. However, the true value for biogenic protection cannot be much higher than estimated here because (a) using SEM we visually quantified few diatom frustules at any sites except the ones with long OET, (b) the Si:Al ratio is only statistically higher than an average of 2.2 in the intermediate density fraction and (c) the amount of OC in the intermediate density fraction decreases with increasing OET, totaling only $\sim 20\%$ of total OC in the long OET station W201.

Finally, the amount of OC protected by aggregation is calculated as the remainder after subtracting contributions by all other mechanisms. In the intermediate density fractions it is the dominant form of OC. The results of the budgets are shown in Fig. 7. At short OET organic debris dominates, but it decreases in importance as OET increases. This oxygen-sensitive material may persist due to recalcitrance or encapsulation of some components within an

organic matrix such as organic–organic aggregates (Nguyen et al., 2003). OC protected in mineral aggregates reaches a maximum at medium OET (Bock and Mayer, 2000) then decreases as OET extends to millennia. Protection within diatom frustules (Ingalls et al., 2003) and sorption (Arnarson and Keil, 2005) both increase with increasing OET, with sorption dominating over diatom frustules at all stations. Thus, these two mechanisms appear to afford the longest lasting protection to OC in marine sediments. Extensive degradation and low OC:SA at locations where OC is mostly protected within diatom frustules or by sorption may indicate that these organic materials are remnants of extensively degraded OC. Sorbed OC may, for example, be leftover material that was previously protected in organic–mineral aggregates. It is also possible that the sorbed material is enriched in old refractory OC derived from continental weathering (Blair et al., 2003; Dickens et al., 2004, 2006).

The observed distribution of physical forms and presumed preservation mechanisms is consistent with and can help explain some observations previously made in the literature. Organic–mineral aggregates may play an important role in the loss of terrestrial OC from deltaic sediments where large amounts of terrestrial OC are degraded that might have been expected to be recalcitrant because of extensive previous exposure to microbes in soils and rivers (Hedges et al., 1997). The increase in ionic strength from riverine to marine environment may result in destabilization of terrestrial organic–mineral aggregates, subsequent disaggregation and microbial access to the previously aggregate-protected terrestrial OC. Thus, aggregate-protected OC ($\sim 40\%$ at 620 m off Washington) may account for the material that has been found to be labile once extracted from the mineral matrix (33 + 12% at 650 m off Washington; Keil et al., 1994b); the extraction conditions employed may have been severe enough to disrupt aggregates and release the OC within to microbial degradation.

In summary, distinct organic debris is the dominant physical form of organic matter present in the short OET environments that are thought to be modern sites that will eventually lead to petroleum generation. This is consistent with the body of literature on selective preservation of recalcitrant macromolecules under low oxygen conditions (Gélinas et al., 2001, and references therein). Aggregated, sorbed and biomineral-protected OC are the dominant forms for organic material at OET values of decades. This is the typical situation for continental margin sediments where the majority of OC is buried. Within this typical margin environment, as OET increases the importance of aggregation processes decreases. At the long OET values (centuries to millennia) typical of the deep sea, the dominant physical forms of OC are for the material to be sorbed or contained within a biomineral matrix. Given the large changes in OC content and physical form as a function of OET, with organic contents varying by a factor of 10 and OC physical form changing from mineral-free to mineral-protected materials, it appears that small changes in OET can dramatically alter OC burial and physical form in marine sediments.

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REFERENCES

- Amézketa E. (1999) Soil aggregate stability: a review. *J. Sustain. Agric.* **14**, 83–151.
- Arnarson T. S. (2004) Organic–mineral interactions in marine sediments, Ph.D. thesis, University of Washington.
- Arnarson T. S., and Keil R. G. (2000) Mechanisms of pore water organic matter adsorption to montmorillonite. *Mar. Chem.* **71**, 309–320.
- Arnarson T. S., and Keil R. G. (2001) Organic–mineral interactions in marine sediments studied using density fractionation and X-ray photoelectron spectroscopy. *Org. Geochem.* **32**, 1401–1415.
- Arnarson T. S., and Keil R. G. (2005) Influence of organic–mineral aggregates on microbial degradation of the dinoflagellate *Scrippsiella trochoidea*. *Geochim. Cosmochim. Acta* **69**, 2111–2117.
- Aufdenkampe A. K., Hedges J. I., Richey J. E., Krusche A. V., and Llerena C. A. (2001) Sorptive fractionation of dissolved organic nitrogen and amino acids onto fine sediments within the Amazon Basin. *Limnol. Oceanogr.* **46**, 1926–1935.
- Baisden W. T., Amundson R., Cook A. C., and Brenner D. L. (2001) Turnover and storage of C and N in five density fractions from California and annual grassland surface soils. *Global Biogeochem. Cycles* **16**(4), 1–2. Art. No. 1117.
- Baldock J. A., and Skjemstad J. O. (2000) Role of soil matrix and minerals in protecting natural organic materials against biological attack. *Org. Geochem.* **31**, 697–710.
- Balesdent J., Chenu C., and Balabane M. (2000) Relationship of soil organic matter dynamics to physical protection and tillage. *Soil Till. Res.* **53**, 215–230.
- Blair N. E., Leithold E. L., Ford S. T., Peeler K. A., Holmes J. C., and Perkey D. W. (2003) The persistence of memory: the fate of ancient sedimentary organic carbon in a modern sedimentary system. *Geochim. Cosmochim. Acta* **67**, 63–73.
- Bock M. J., and Mayer L. M. (2000) Mesodensity organo-clay associations in a near-shore sediment. *Mar. Geol.* **163**, 65–75.
- Cowie G. L., and Hedges J. I. (1992) Improved amino acid quantification in environmental samples: charge-matched recovery standards and reduced analysis time. *Mar. Chem.* **37**, 223–238.
- Dauwe B., and Middelburg J. J. (1998) Amino acids and hexosamines as indicators of organic matter degradation state in North Sea sediments. *Limnol. Oceanogr.* **43**, 782–798.
- Dauwe B., Middelburg J. J., Herman P. M. J., and Heip C. H. R. (1999) Linking diagenetic alteration of amino acids and bulk organic matter reactivity. *Limnol. Oceanogr.* **44**, 1809–1814.
- Dickens A. F., Baldock J. A., Smernik R. J., Wakeham S. G., Arnarson T. S., Gélinais Y., and Hedges J. I. (2006) Solid-state ¹³C NMR analysis of size and density fractions of marine sediments: insight into organic carbon sources and preservation mechanisms. *Geochim. Cosmochim. Acta* **70**, 666–686.
- Dickens A. F., Gélinais Y., and Hedges J. I. (2004) Separation of combustion and rock sources of graphitic black carbon in sediments. *Mar. Chem.* **92**, 215–223.
- Ding X., and Henrichs S. M. (2002) Adsorption and desorption of proteins and polyamino acids by clay minerals and marine sediments. *Mar. Chem.* **77**, 225–237.
- Ertel J. R., and Hedges J. I. (1985) Sources of sedimentary humic substances: vascular plant debris. *Geochim. Cosmochim. Acta* **49**, 2097–2107.
- Ganeshram R. S., Calvert S. E., Pedersen T. F., and Cowie G. L. (1999) Factors controlling the burial of organic carbon in laminated and bioturbated sediments off NW Mexico: implications for hydrocarbon preservation. *Geochim. Cosmochim. Acta* **63**, 1723–1734.
- Gelin F., Volkman J. K., Largeau C., Derenne S., Sinnighe Damsté J. S., and de Leeuw J. W. (1999) Distribution of aliphatic, nonhydrolyzable biopolymers in marine microalgae. *Org. Geochem.* **30**, 147–159.
- Gélinais Y., Baldock J. A., and Hedges J. I. (2001) Organic carbon composition of marine sediments: effect of oxygen exposure on oil generation potential. *Science* **294**, 145–148.
- Hartnett H. E. (1998) Organic carbon input, degradation and preservation in continental margin sediments: an assessment of the role of a strong oxygen deficient zone, Ph.D. thesis, University of Washington.
- Hartnett H. E. (2003) Role of a strong oxygen-deficient zone in the preservation and degradation of organic matter: a carbon budget for the continental margin of northwest Mexico and Washington State. *Geochim. Cosmochim. Acta* **67**, 247–264.
- Hartnett H. E., and Devol A. H. (2003) Role of a strong oxygen-deficient zone in the preservation and degradation of organic matter: a carbon budget for the continental margins of northwest Mexico and Washington State. *Geochim. Cosmochim. Acta* **67**, 247–264.
- Hartnett H. E., Keil R. G., Hedges J. I., and Devol A. H. (1998) Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. *Nature* **391**, 572–574.
- Hedges J. I., Hu F. S., Devol A. H., Hartnett H. E., Tsamakis E., and Keil R. G. (1999) Sedimentary organic matter preservation: a test for selective degradation under oxic conditions. *Am. J. Sci.* **299**, 529–555.
- Hedges J. I., and Keil R. G. (1995) Sedimentary organic matter preservation: an assessment and speculative synthesis. *Mar. Chem.* **49**, 81–115.
- Hedges J. I., Keil R. G., and Benner R. (1997) What happens to terrestrial organic matter in the ocean? *Org. Geochem.* **27**(5/6), 195–212.
- Hedges J. I., and Stern J. H. (1984) Carbon and nitrogen determinations of carbonate containing solids. *Limnol. Oceanogr.* **29**, 657–663.
- Henrichs S. M. (1995) Sedimentary organic matter preservation: an assessment and speculative synthesis—a comment. *Mar. Chem.* **49**, 127–136.
- Henrichs S. M., and Sugai S. F. (1993) Adsorption of amino acids and glucose by sediments of Resurrection Bay, Alaska, USA: functional group effects. *Geochim. Cosmochim. Acta* **57**, 823–835.
- Ingalls A. E., Lee C., Wakeham S. G., and Hedges J. I. (2003) The role of biominerals in the sinking flux and preservation of amino acids in the Southern Ocean along 170°W. *Deep-Sea Res. II* **50**, 713–738.
- Jastrow J. D. (1996) Soil aggregate formation and the accrual of particulate and mineral-associated organic matter. *Soil Biol. Biochem.* **28**, 665–676.

- Keil R. G., Dickens A. F., Arnarson T. S., Nunn B. L., and Devol A. H. (2005) What is the oxygen exposure time of laterally-transported organic matter along the Washington margin? *Mar. Chem.* **92**, 157–165.
- Keil R. G., Hu F. S., Tsamakis E. C., and Hedges J. I. (1994a) Pollen in marine sediments as an indicator of oxidation of organic matter. *Nature* **369**, 639–641.
- Keil R. G., Montluçon D. B., Prahl F. G., and Hedges J. I. (1994b) Sorptive preservation of labile organic matter in marine sediments. *Nature* **370**, 549–551.
- Keil R. G., Tsamakis E., Fuh C. B., Giddings J. C., and Hedges J. I. (1994c) Mineralogical and textural controls on the organic composition of coastal marine sediments: hydrodynamic separation using SPLITT-fractionation. *Geochim. Cosmochim. Acta* **58**, 879–893.
- Keil R. G., Tsamakis E., Giddings J. C., and Hedges J. I. (1998) Biochemical distributions among size-classes of modern marine sediments. *Geochim. Cosmochim. Acta* **62**, 1347–1364.
- Lambourn L. D., and Devol A. H. (1998) Porewater data from the Mexican shelf and slope: Cruise TTAN2 of the R/V New Horizon. In *Special Report No. 114*, University of Washington School of Oceanography, p. 21.
- Lambourn L. D., Hartnett H. E., and Devol A. H. (1996) Porewater data from the Washington shelf and slope: Cruise WE9407B of the R/V Wecoma. In *Special Report No. 113*, University of Washington School of Oceanography, p. 32.
- Levin L. A. (2003) Oxygen minimum zone benthos: Adaptation and community response to hypoxia. In *Oceanography and Marine Biology: An Annual Review*, vol. 41 (eds. R. N. Gibson and R. J. A. Atkinson). Taylor & Francis.
- Longhurst A., Sathendranath S., Platt T., and Caverhill C. (1995) An estimate of global primary production in the ocean from satellite radiometer data. *J. Plankton Res.* **17**, 1245–1271.
- Lowell S., and Shields J. E. (1991) *Powder Surface Area and Porosity*. Chapman & Hall.
- Mayer L., Benninger L., Bock M., DeMaster D., Roberts Q., and Martens C. (2002) Mineral associations and nutritional quality of organic matter in shelf and upper slope sediments off Cape Hatteras, USA: a case of unusually high loadings. *Deep-Sea Res. II* **49**, 4587–4597.
- Mayer L. M. (1994) Surface area control of organic carbon accumulation in continental shelf sediments. *Geochim. Cosmochim. Acta* **58**, 1271–1284.
- Mayer L. M., Jumars P. A., Taghon G. L., Macko S. A., and Trumbore S. (1993) Low-density particles as potential nitrogenous foods for benthos. *J. Marine Res.* **51**, 373–389.
- Miller J. C., and Miller J. N. (1984) *Statistics for Analytical Chemistry*. Ellis Horwood Ltd.
- Nguyen R. T., and Harvey H. R. (2001) Preservation of protein in marine systems: hydrophobic and other noncovalent associations as major stabilizing forces. *Geochim. Cosmochim. Acta* **65**, 1467–1480.
- Nguyen R. T., Harvey H. R., Zang X., van Heemst J. D. H., Hetényi M., and Hatcher P. G. (2003) Preservation of algaenan and proteinaceous material during the oxic decay of *Botryococcus braunii* as revealed by pyrolysis-gas chromatography/mass spectrometry and ¹³C NMR spectroscopy. *Org. Geochem.* **34**, 483–497.
- Perry M. J., Bolger J. C., and English D. C. (1989) Primary production in Washington coastal waters. In *Coastal oceanography of Washington and Oregon* (eds. M. L. Landry and B. M. Hickey). Elsevier.
- Prahl F. G., Ertel J. R., Goñi M. A., Sparrow M. A., and Eversmeyer B. (1994) Terrestrial organic carbon contributions to sediments on the Washington margin. *Geochim. Cosmochim. Acta* **58**, 3035–3048.
- Puget P., Chenu C., and Balesdent J. (2000) Dynamics of soil organic matter associated with particle-size fractions of water-stable aggregates. *Eur. J. Soil Sci.* **51**, 595–605.
- Ransom B., Bennett R. H., Baerwald R., Hulbert M. H., and Burkett P.-J. (1999) In situ conditions and interactions between microbes and minerals in fine-grained marine sediments: a TEM perspective. *Am. Mineral.* **84**, 183–192.
- Sansone F. J., Andrews C. C., and Okamoto M. Y. (1987) Adsorption of short-chain organic acids onto nearshore marine sediments. *Geochim. Cosmochim. Acta* **51**, 1889–1896.
- Pichevin L., Bertrand P., Boussafir M., and Disnar J.-R. (2004) Organic matter accumulation and preservational controls in a deep sea modern environment: an example from Nambian slope sediments. *Org. Geochem.* **35**, 543–559.
- Thomsen L., vanWeering T., and Gust G. (2002) Processes in the benthic boundary layer at the Iberian continental margin and their implication for carbon mineralization. *Prog. Oceanogr.* **52**, 315–329.
- Tisdall J. M., and Oades J. M. (1982) Organic matter and water-stable aggregates in soils. *J. Soil Sci.* **33**, 141–163.
- Van der Jagt G. M., Devol A. H., and Keil R. G. (2000) Interstitial porewater and water column data from the Mexican shelf and slope: Cruise Rhumba '99 of the R/V New Horizon. In *Special Report no. 116*. University of Washington, School of Oceanography.
- Van Mooy B., Keil R. G., and Devol A. H. (2002) Enhanced flux of POC in oxygen deficient waters: impact of suboxia on early diagenesis of bulk OC and amino acids. *Geochim. Cosmochim. Acta* **66**, 457–465.
- Yuan G., Soma M., Seyama H., Theng B. K. G., Lavkulich L. M., and Takamatsu T. (1998) Assessing the surface composition of soil particles from some Podzolic soils by X-ray photoelectron spectroscopy. *Geoderma* **86**, 169–181.

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