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Mineral associations and nutritional quality of organic matter in shelf and upper slope sediments off Cape Hatteras, USA: a case of unusually high loadings

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Abstract

Relationships among organic carbon (OC), enzymatically hydrolyzable amino acid (EHAA) concentrations and mineral surface area (SFA) were assessed for sediments from the shelf and slope region near Cape Hatteras, USA. Grain size, measured here as mineral-specific surface area, explained 55% of the variance in organic matter concentrations. Organic loadings, as ratios of organic carbon to surface area (OC:SFA), decrease with water column and core depth. OC:SFA ratios in this region are comparable to those found in areas with anoxic water columns, and are the highest reported for shelf-slope sediments underlying oxygenated water columns. With increasing water-column depth, organic matter becomes progressively incorporated into low-density ($<2.4 \text{ g cm}^{-3}$), organomineral aggregates, reflecting the increase in clay content in sediments with water-column depth. Organic coverage of mineral surfaces was determined by gas sorption methods; throughout the depth range minerals are essentially bare of organic coatings, in spite of high organic loadings. EHAA concentrations increase with water-column depth in a similar fashion as OC concentrations, and help to support intense heterotrophic communities at depth. Rapidly decreasing ratios of EHAA to total organic matter with water-column depth are consistent with previous inferences that largely refractory organic matter is exported from the shelf to the slope. Significant burial of EHAA downcore indicates protection of enzymatically hydrolyzable biopolymers with depth. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The slope of the US Atlantic margin has long been recognized as a depocenter for both fine-grained minerals and organic matter (Emery

and Uchupi, 1972), leading to hypotheses for the importance of such depocenters as sinks for shelf production of organic matter (Walsh et al., 1985). Various Department of Energy (DOE) oceanographic programs have sought to quantify the importance of this depocenter to budgets for energy production-derived waste products such as carbon and radionuclides.

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This component of the DOE Ocean Margins Program examines grain size control of labile and total organic matter concentrations in the Cape Hatteras region, building upon previous observations by Emery and Uchupi (1972) and Milliman (1994). We focus on the use of mineral specific surface area as a sensitive indicator of clay abundance, because of the importance of clays in organic matter accumulation (e.g., Premuzic et al., 1982; Ransom et al., 1998). Previously we have shown that differences in surface area-normalized organic matter contents can elucidate typologies among shelf environments in terms of organic carbon loading (Mayer, 1994a,b), as well as processes such as net oxidation of organic carbon in shelves of large deltas (Keil et al., 1997). We also have shown that the organic matter-clay association may be the result of organoclay aggregates with density $2.0\text{--}2.3\text{ g cm}^{-3}$ (Bock and Mayer, 2000), and so we examined their presence in this region.

Total organic matter is generally dominated by old and refractory material of little nutritional relevance to biota (DeMaster et al., 2002). The Cape Hatteras slope region is home to relatively dense populations of macrofauna and active bioturbation (Schaff et al., 1992), and the lability of the organic matter delivery has been subject to considerable discussion (Anderson et al., 1994). To better assess the spatial patterns of organic matter that is nutritionally available for such heterotrophic communities, we also examined digestively available proteinaceous material.

2. Methods and materials

Samples were collected from 1987 to 1997 at sites throughout the latitudinal range $35^{\circ}25'\text{--}37^{\circ}20'$, at water-column depths ranging from 21 to 2630 m (Fig. 1). Sediment collection was from both shipboard and submersible (Johnson Sea-Link) and utilized box, HAPS (Kannevorff and Nicolaisen, 1973), and Kasten corers or Shipek, Van Veen and Smith-McIntyre grabs. Most samples were frozen on board ship, and kept either frozen or freeze-dried until analysis, although a small number of samples were stored in a refrigerator for

2–3 months prior to freezing. Samples were always freeze-dried prior to analysis, to improve representative sub-sampling. Sand samples were sub-sampled using a riffle-type splitter.

A subset of samples were separated into fractions varying in density, using the approach described in Bock and Mayer (2000). For the present study we carried out separations at a density of 2.4 g cm^{-3} , slightly higher than our previous use of 2.3 g cm^{-3} , in order to increase the yield of organic matter associated with clays. Briefly, freeze-dried sediment was resuspended in a solution of sodium polytungstate ($\rho = 2.4\text{ g cm}^{-3}$), shaken on a vortex mixer, and then centrifuged. The low and high density phases were separated by pipetting off the floating material, and then washing both separates in 10:90 acetone:water (v/v) solutions. This wash solution promotes flocculation of the sediment but does not remove organic matter.

Organic carbon analyses were carried out on samples pretreated by HCl via vapor-phase transfer (Hedges and Stern, 1984), using a Perkin-Elmer 2400B CHN Analyzer. Sediments were analyzed for mineral surface area by N_2 sorption, after 350° oxidation overnight in a muffle furnace under an air atmosphere (Keil et al., 1997). Before gas-sorption analysis, all samples were outgassed, to remove adsorbed water, in a vacuum oven overnight at 150° . Gas sorption measurements were then conducted with a Quantachrome A-1 Autosorb or Monosorb, with the former used for mineral coverage assessments and surface area on coarse-grained samples and the latter used for surface area measurements on finer-grained samples. Excellent agreement is found for surface area values measured on the two instruments. Surface areas were determined using the BET equation (Brunauer et al., 1938). For a subset of samples, we analyzed the fractional coverage of mineral surfaces by organic matter, using the gas sorption approach described in Mayer (1999). This approach relies on the higher enthalpy of adsorption of N_2 on mineral surfaces than on organic surfaces, and has been calibrated using model adsorbate-adsorbant systems. For this analysis, sediments were measured for N_2 adsorption in both untreated and oxidized conditions, the latter

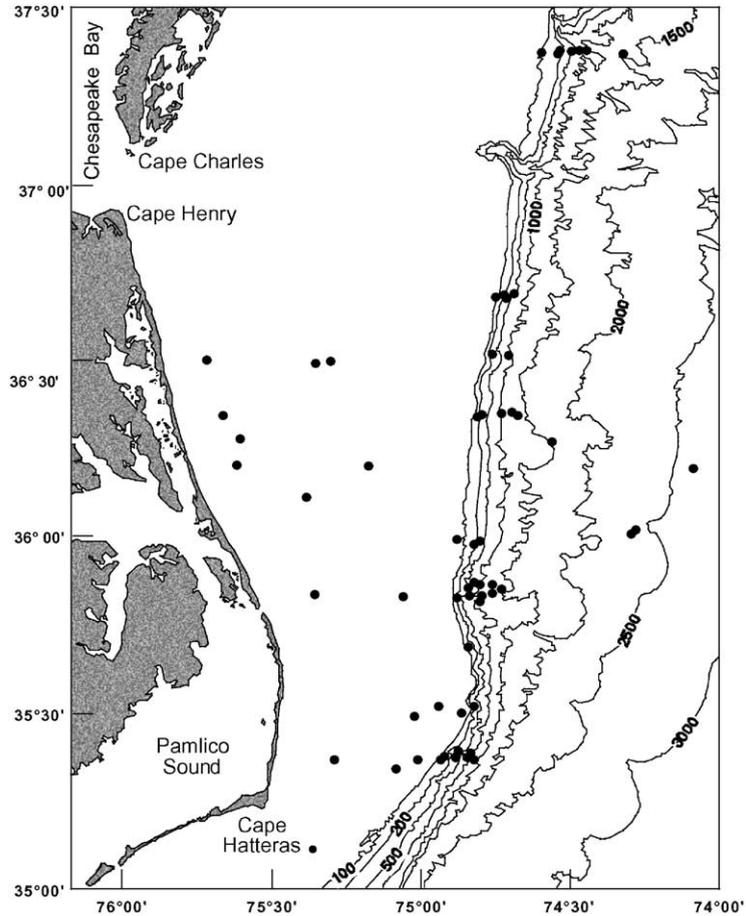


Fig. 1. Map of Hatteras region with sediment sampling locations.

to remove natural organic matter and assess the surface area and sorption energetics of the underlying mineral surfaces.

To measure the fraction of labile organic matter, we used the enzymatically hydrolyzable amino acids (EHAA) approach of Mayer et al. (1995). Briefly, freeze-dried sediments were incubated with a commercial protease preparation, the amino acids and peptides solubilized from the sediment were separated from the enzymes by trichloroacetic acid precipitation, and the supernatant subjected to strong acid hydrolysis followed by fluorometric detection of the ensuing monomeric amino acids using orthophthaldialdehyde (OPA).

3. Results and discussion

3.1. Total organic matter-grain size relationship

Both specific surface area and organic carbon concentrations generally increase with water-column depth in the study area (Figs. 2a and b). These two variables are highly correlated with one another, with 55% of the variance in organic carbon concentrations explained by the surface area parameter. The maxima in organic carbon concentrations in the 400–1200 m depth zone are thus primarily a grain size phenomenon, in which finer-grained mineral accumulation leads to higher total organic-matter concentrations.

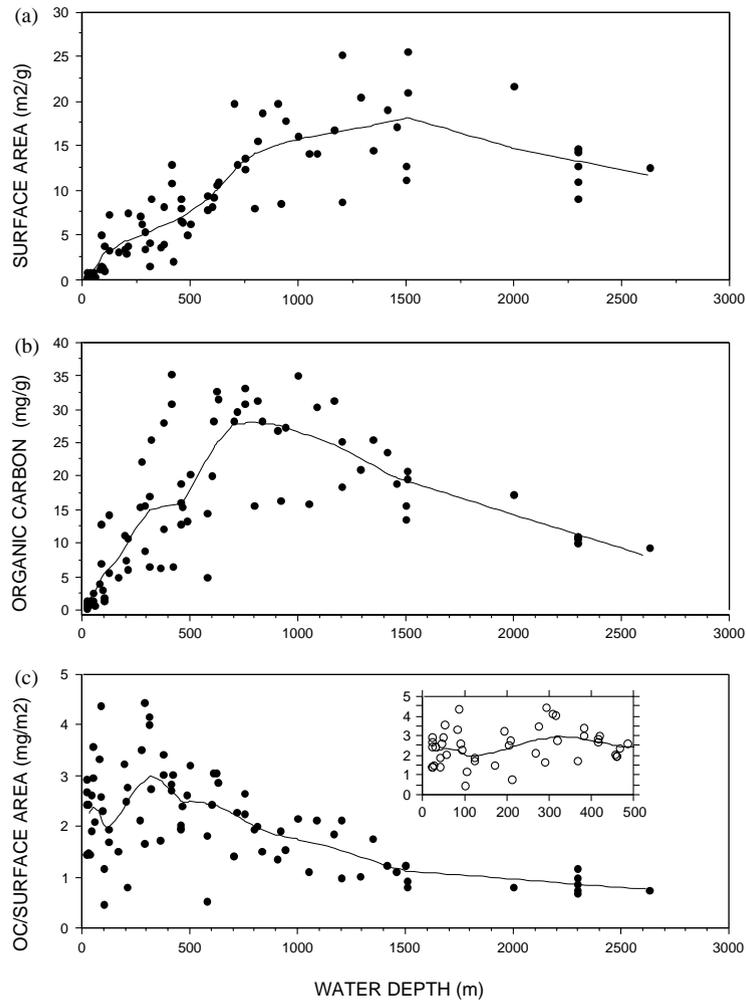


Fig. 2. Sediment surface area (a), organic carbon concentration (b), and their ratio (OC:SFA, c) for samples from the sediment–water interface, plotted vs. water depth. Lines in each plot represent locally weighted regressions (LOWESS, tension = 25). Depth maxima of organic carbon and surface area are offset, with the latter peaking in deeper water. An inset in 2c expands the shelf break data to illustrate the low values at 99–212 m.

Locally weighted regressions (LOWESS) of the data, however, show an offset between the maxima for organic carbon concentrations and surface area values. Surface area shows maximum values at greater water-column depths of about 1200–1500 m, while OC shows a broad maximum at about 500–1000 m. Thus, there is some other control besides grain size on organic matter concentrations. Taking the ratio of these two parameters (Fig. 2c) allows normalization of this

grain size control. This organic carbon:surface area ratio (OC:SFA) shows a highly significant inverse correlation ($p < 0.001$) with water-column depth, with generally high values of 1–4.5 mg OC m^{-2} in shallow waters that fall with water-column depth to stabilize at values of 0.6–1 mg OC m^{-2} at depths > 1400 m. This normalization thus provides a parameter that reflects the expected drop in organic-matter loadings with depth that might be predicted from the drop in

organic-matter delivery with depth (Suess, 1980). This drop with water-column depth is not due simply to the covarying drop in surface area values, as plots that group narrow ranges of surface area values over extended depth ranges show the same depth trend.

In spite of a general decrease with water-column depth, the highest OC:SFA values found in this study are in the 50–325 m depth range. These elevated values may reflect enhanced organic matter inputs from relatively high, springtime primary production at the shelf break (Lohrenz et al., 2002). However, within this depth range several samples taken just below shelf break depths—at 99–212 m—appear to have lower OC:SFA ratios than samples taken at immediately shallower and deeper stations (Fig. 2c, inset). A possible explanation for these low values is discussed below.

Use of OC:SFA ratios in this study yields somewhat different interpretations of organic matter loadings than the use of residuals from regional regressions employed by Milliman (1994). In his study, positive residuals from regressions between nitrogen concentrations and percent silt-clay implied maximum organic loadings at water-column depths of ca. 1000 m. Our data are certainly consistent with a maximum in weight-normalized, organic matter concentrations at this depth (Fig. 2b), but the normalization for grain size provided by OC:SFA ratios implies that the loadings, *per fine-grained component of the sediment*, are highest at much shallower depths. We suggest that the maximum residuals at 1000 m observed by Milliman (1994) results from the higher absolute concentrations of OC in finer-grained sediments of this depth zone, so that the accompanying variance is also greater. The differences in interpretation are subtle but important, because the generally decreasing OC:SFA ratios with water-column depth that we observe here are consistent with higher input of fresh organic matter at shallower depths, and are corroborated by a similar, water depth-dependent decrease in CO₂ production in the sediments (R.C. Aller, pers. comm.), rather than a 1000 m maximum as might be inferred from the high standing stocks.

Within our study area there was no discernible latitudinal pattern of OC:SFA ratios. Values of 2–3 mg OC m⁻² at upper slope depths were common throughout the area, and appeared to be bounded to the north just north of 37°20', based on values of 1.2–1.4 mg OC m⁻² reported for 37°34' (cores END 187-2 and 187-3 in Mayer, 1994b). No southern boundary was determined in this study.

Cores of 30–250 cm penetration show significant loss—averaging 38%—of OC:SFA ratios with depth (Fig. 3). There was no relation between the extent of loss and water-column depth. Significant correlation ($p < 0.01$) between the OC:SFA ratios at the sediment–water interface vs. those at core-bottom depth indicates that the former provides excellent predictive value for spatial patterns of OC:SFA ratios that are buried in this region, at least to the 30–250 cm depths sampled here. These variable downcore OC:SFA ratios contrast with our previous results in the Gulf of Maine and other areas, where different OC:SFA ratios at the sediment–water interface all decayed downcore to similar values of ca. 0.5–1.1 mg OC m⁻² (termed the “monolayer-equivalent” level, Mayer, 1994a).

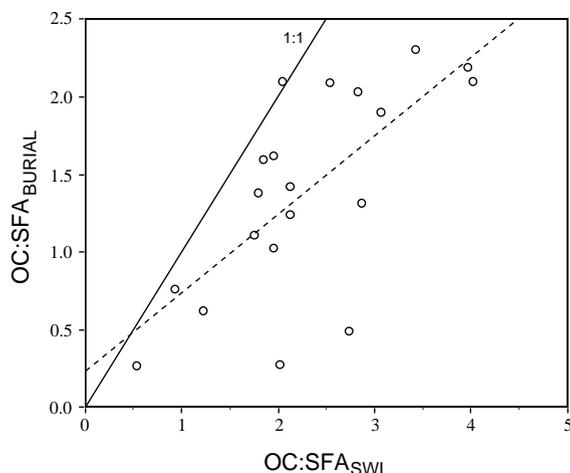


Fig. 3. Ratio of organic carbon to sediment surface area (OC:SFA, as mg OC m⁻²) in samples from the sediment water interface (OC:SFA_{SWI}, x-axis) vs. those buried at depths ranging from 30 to 250 cm (OC:SFA_{BURIAL}, y-axis). Virtually all cores show some loss, with average loss of 38%. The 1:1 line indicates no loss. Linear regression of the data in this plot yields the dashed line, $OC:SFA_{DEPTH} = 0.51 OC:SFA_{SURFACE} + 0.24$, $r^2 = 0.489$.

Relatively few of the sediments in the Hatteras region reach this 0.5–1.1 mg OC m⁻² loading, where decay is likely to slow down considerably, though they may reach this level with further burial.

Some cores show changes in their specific surface area values with core depth, implying nonsteady state deposition and consistent with occasionally erratic ¹⁴C dates of the organic matter (DeMaster et al., 2002). Downcore changes in grain size can complicate quantitative interpretations of carbon loss based on weight-normalized concentrations, but downcore decreases in the OC:SFA ratios provide confidence that downcore losses in organic carbon (Thomas et al., 2002) are due to metabolism and not simply to grain size changes.

Data from other slope environments provide context in which to interpret the patterns found in this study. Many shelf and slope environments show organic carbon loading at ca. 0.5–1.2 mg OC m⁻² (Fig. 4); examples shown here emphasize shelf and slope sediments from the coasts of California, Washington, the NE USA, and the North Sea. Many other shelf environment samples also show this loading (Mayer, 1994a). Several slope environments show levels below this loading,

such as off the Mississippi delta (unpub. data, not shown), the Laptev Sea, and the Nigerian coast. Interestingly, both the Washington and Nigerian slopes show anomalously low OC:SFA ratios at the shelf-break, similar to the shelf-break minima found in this study.

Several environments show loadings well above this level, including slopes off Peru, the Arabian peninsula, and California. All of these areas of high loading are characterized by very low oxygen contents in the overlying water, which has stimulated suggestions that absence of bottom-water oxygen is critical to building OC:SFA ratios higher than 1.5 mg OC m⁻² (Keil and Cowie, 1999). The Hatteras upper slope does exhibit oxygen minima (Sulak and Ross, 1994), but only down to concentrations of >4 mg l⁻¹. Thus the sediments of the Hatteras slope region, with a moderately well-oxygenated water-column, exhibit many similar, and even higher, OC:SFA ratios as those areas with severe oxygen deficits in the overlying water column. The high organic matter supply, apparently due to convergence and off-shore export of shelf waters from north and south (Walsh, 1994), are apparently sufficient to create such high loadings, at least for surficial sediments. Similarly high OC:SFA ratios are found in

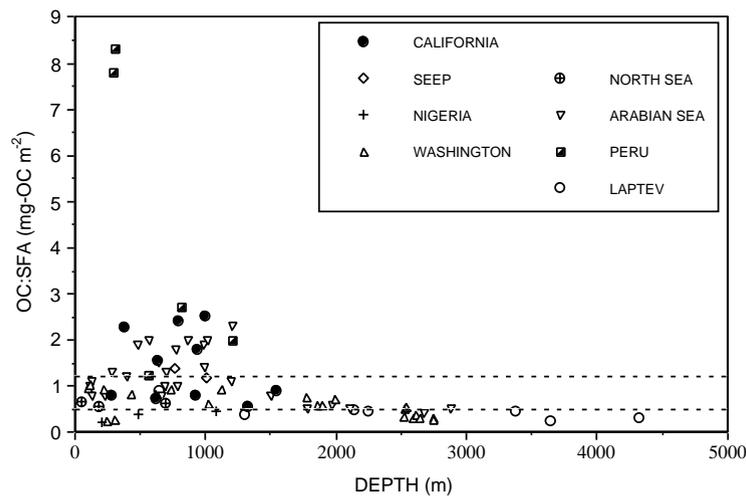


Fig. 4. Ratio of organic carbon to sediment surface area (OC:SFA, as mg OC m⁻²) in samples from various shelf and slope areas, plotted vs. water depth. Data are from Mayer (1994b); Hedges et al. (1999); Bergamaschi et al. (1997); Keil and Cowie (1999). Peru samples courtesy of L. Levin and Laptev Sea samples courtesy of K. Lochte. Horizontal, dashed lines represent bounds of "monolayer-equivalent" loading.

estuarine situations with high productivity (e.g., Long Island Sound, coast of Maine: Mayer, 1994a).

3.2. Density separations

Sediments were separated in heavy liquids to assess the potential incorporation of organic matter into organoclay aggregates. We previously showed that organic matter in fractions of density $2.0\text{--}2.3\text{ g cm}^{-3}$ from a coastal sediment were dominated by aggregates consisting of organic matter and very fine-grained clay minerals in close association (Bock and Mayer, 2000). Organomineral associations achieve these lower densities most easily with clay minerals, which have very little mass per surface area. Our use of the 2.4 g cm^{-3} density cutoff also provided low-density separates with higher specific surface area values than the whole sediments, implying an enrichment of clay-rich materials. However, the surface area values were not as high as in our previous study and therefore the clay enrichments were presumably not so pronounced. Greater percentages of organic carbon were found in the low-density separates than were found for total sediment mass (Fig. 5), consistent with a preferential association of organic matter with this clay-rich subset of the mineral fraction.

These separates that show sedimentary organic matter and minerals are progressively incorpo-

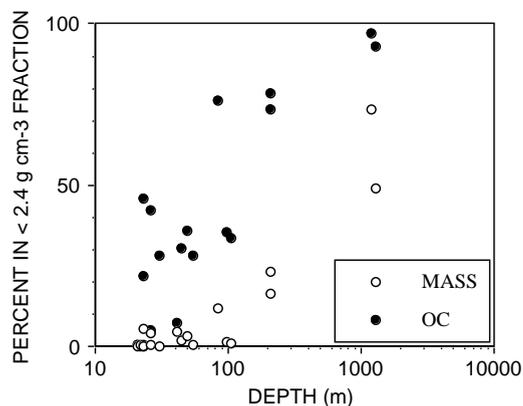


Fig. 5. Fraction of mass and organic carbon (OC) found in separates of density $<2.4\text{ g cm}^{-3}$, plotted vs. water depth. Note that the water depth axis is logarithmic, in order to better present the data, and thus different than other figures.

rated into low-density fractions with increasing water-column depth (Fig. 5). This trend is opposite to that to be expected if fresh organic matter on the shelf were primarily in discrete organic particles—either live or recently dead. Organic matter in shelf sediments is largely associated with larger mineral grains, and is increasingly associated with fine clay grains as depth increases. Alternatively, the organic matter at shelf depths is also associated with clays but the resultant organoclay aggregates are in turn attached to larger mineral grains. In either case, the sediment on the shelf is poor in resuspendable organic material, both in terms of finer-grained and lower density materials, with both characteristics enriching progressively downslope. This trend is consistent with a winnowing of organoclay aggregates off of the shelf.

3.3. Organic matter coatings on mineral grains

We examined the coverage of mineral surfaces by organic matter using the gas sorption energetics approach described in Mayer (1999). This analysis provides a measure of the C constant in the BET equation, which is related to the enthalpy of adsorption of gas on surfaces. From the enthalpies of oxidized and unoxidized sub-samples can be calculated the fractional coverage of organic matter on the mineral surfaces, with the assumptions that organic matter shows a low enthalpy of N_2 gas adsorption while uncoated mineral surfaces show high enthalpies. The fractional coverages are generated using a simple mixing model of organic and mineral endmembers.

The C constants of the unoxidized sub-samples (i.e. with organic matter) showed little variation along the depth gradient (Fig. 6), with the exception of several samples at shelf-break depths. The fractional coverages calculated for samples over the entire depth range, with OC:SFA ratios ranging from 0.33 to 4.4, were all $<10\%$. Mineral surfaces are therefore essentially uncoated with organic matter, in spite of the high organic matter loadings. This finding is thus consistent with the data for other marine sediments reported in Mayer (1999).

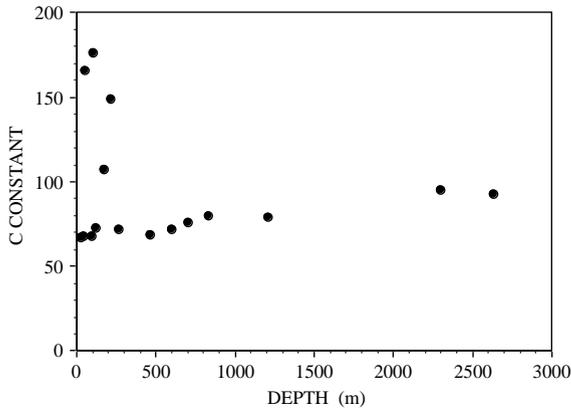


Fig. 6. C constants of unoxidized samples vs. water depth.

Those samples with anomalously low OC:SFA values from the shelf break area (water-column depths of 50–212 m, Fig. 2c inset) that were analyzed by this approach also showed anomalously high C constants of N₂ adsorption, for both unoxidized and oxidized (350° overnight). These high C constants imply the presence of micropores (pores of <2 nm diameter). The cause of these anomalously high values was not determined in this study. However, in a recent work we found similarly high adsorption enthalpies in a series of sub-surface soil samples, which correlated positively with iron and aluminum sesquioxide concentrations (Mayer and Xing, 2001). We did not analyze these sediments for such oxide phases, but we suggest that iron or manganese coatings may be present. Examination under a dissecting microscope did not show extensive staining of mineral grains. If such phases were present, then the minimum in OC:SFA ratios at these water-column depths may not be due to changes in the ratio of organic matter to clay, but instead result from surface area values elevated by other oxide phases.

3.4. Labile organic matter

EHAA concentrations show qualitatively similar spatial patterns as OC, increasing with water-column depth onto the upper-slope and thereafter decreasing with further depth (Fig. 7a). The two distributions differ primarily in higher relative values for EHAA on the shelf, compared

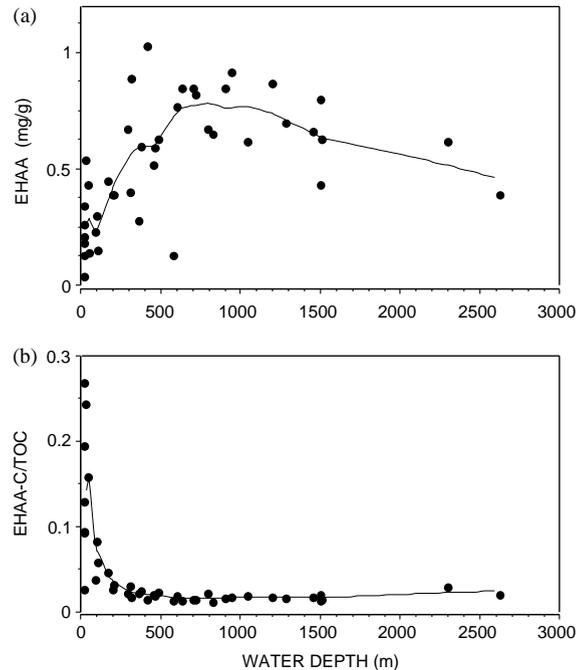


Fig. 7. Sediment–water interface concentrations of enzymatically hydrolyzable amino acids (EHAA; a) and the ratio of EHAA-carbon to total organic carbon (EHAA-C:TOC; b), each vs. water depth. Lines represent locally weighted regressions (LOWESS, tension=25). Samples that had been stored for 2–3 months in the refrigerator were excluded from this plot.

to organic carbon. The upper slope maximum in EHAA is reflected in macrofaunal biomass peaks at similar depths (Aller et al., 2002). EHAA concentrations were a little less dependent on grain size than were those of total organic carbon, with surface area values explaining 37% of the variance. Nevertheless, the correlation between these two variables was highly significant ($p < 0.001$).

The relatively elevated values of EHAA on the shelf lead to decreasing nutritional quality of the sedimentary organic matter, expressed as the ratio of EHAA-carbon to total organic carbon—with increasing water-column depth (Fig. 7b). The EHAA-C:OC ratios are generally high on the shelf, up to 25%, with the exception of one site south of Cape Hatteras. Such high values are indicative of a dominance of very labile organic matter. These ratios fall off with depth very quickly, to values generally <5% at depths greater

than about 100 m. The EHAA-C:OC ratios from this area are consistent, in both magnitude and depth dependence, as those found by Dauwe et al. (1999) for a transect of samples from sandy, shallow, western North Sea sites to a muddy 270 m site in the Skagerrak. The North Sea transect represents a situation analogous to that of Cape Hatteras; its shallow sandy area represents a source of planktonic production whose detritus migrates eastward to deeper water and finer-grained sediments. Accompanying a drop in EHAA-C:OC ratio, Dauwe et al. (1999) also found a drop in the kinetics with which EHAA were enzymatically hydrolyzed from the sediment, further implying a decrease in lability of the EHAA. We did not measure these kinetic aspects here, but a similar drop in lability would imply changes in both quality and quantity of the nutritionally available organic matter.

Bacon et al. (1994) suggested that mostly degraded OM is exported from the shelf due to holding times and consequent reworking in shelf sediments, an idea corroborated by the ^{14}C data of Anderson et al. (1994). The high EHAA-C:OC ratios in shelf sediments that we sampled may not represent the same ratio as the shelf material that is exported. The lower EHAA-C:OC ratios of sediments downslope from the shelf sediments may indicate that the exported material is of lower quality, in the sense of being diluted by old, refractory organic matter. However, the higher absolute EHAA concentrations, normalized to sediment weight, on the slope combined with the intense macrofaunal biomass downslope (Aller et al., 2002) and their ^{14}C content (DeMaster et al., 2002) indicate that significant quantities of labile food are received at these depths. The most likely source is export from the shelf, though offshore production cannot be excluded with our data. The decreasing EHAA-C:OC ratios with water-column depth are thus consistent with winnowing of refractory organic material from the shelf as suggested by Bacon et al. (1994) and Anderson et al. (1994). However, this trend also may result from import of higher quality organic matter, from shelf or offshore, with rapid degradation upon arrival, resulting in a depth trend that reflects dilution by the increasing concentrations of

older organic matter with depth controlled by decreasing grain size.

Downcore losses in EHAA were greater in cores having the highest EHAA concentration at the sediment–water interface (Fig. 8). EHAA concentrations showed greater relative downcore drops than OC concentrations in the same cores, as should be the case for labile organic matter and consistent with our previous work on protein diagenesis (Mayer and Rice, 1992). However, because EHAA rarely accounts for more than a few percent of the total organic carbon, downcore EHAA losses never accounted for more than a few percent of the downcore loss of total carbon. Thus, the EHAA analysis detects only a small fraction of the degradable organic matter. The strong downcore EHAA losses, along with the low EHAA-C:OC ratios at the sediment–water interface, attest to the short lifetime of labile organic matter in Mid-Atlantic slope sediments inferred by Anderson et al. (1994).

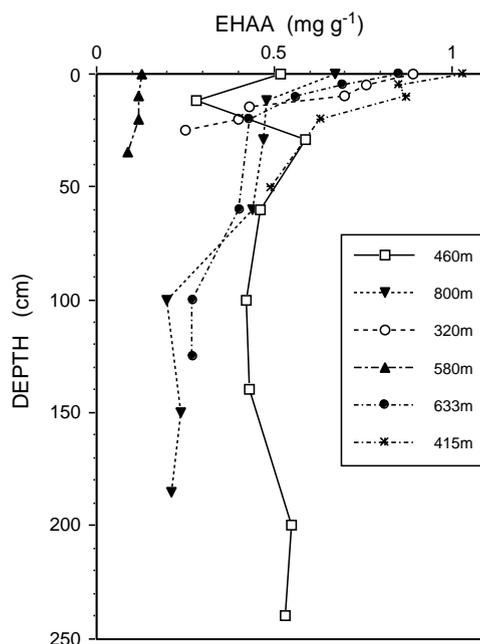


Fig. 8. Downcore profiles of enzymatically hydrolyzable amino acids (EHAA) in cores from various water depths. Key to cores (all taken in 1996; see Thomas et al., 2002): 460 m (Stn. S3, Kasten core), 800 m (Stn. S6, Kasten core), 320 m (Stn. S11, Box core), 580 m (Stn. S2, Kasten core), 633 m (Stn. S14, Kasten core), 415 m (Stn. S15, Box core).

The downcore stabilization of EHAA concentrations at values of 0.1–0.5 mg g⁻¹ may lead to a grain size dependence of this protected fraction and partially explain the increase in standing stocks of EHAA with water-column depth (Fig. 7). These stabilized values range from significant to major fractions of the EHAA concentrations at the sediment water interface. It is not clear why the conditions of this analytical method allow access of hydrolytic enzymes to proteinaceous materials that are apparently only very slightly available to the resident biota, as evidenced by nearly constant concentrations for burial periods on the order of centuries. For some reason these biopolymers are protected against enzyme attack.

4. Conclusions

The data presented here show that organic matter burial patterns in the shelf and slope region of Cape Hatteras are indeed explained largely by grain size, as proposed by Emery and Uchupi (1972). Increases in OC and EHAA concentrations with increasing depth are due to significant to major contributions of relatively refractory components whose content is controlled by clay abundance. The depocenter function of the upper slope is strongly influenced by the grain size distribution and hence the delivery of clays to the various parts of the slope. However, the OC:SFA ratios are anomalously high for slopes with oxygenated water columns. Grain size correlations, particle separations and microscopy indicate that sedimentary organic matter is in general associated with very fine clays (Mayer, 1994a, b; Keil et al., 1994; Ransom et al., 1997; Bock and Mayer, 2000). Total accumulations of organic carbon in ocean-margin sediment are thus often limited by supply of fine-grained clays and this limitation is expressed as consistent OC:SFA ratios of 0.5–1 mg OC m⁻² (formerly called the “monolayer-equivalent” level; Mayer, 1994a). Nevertheless, the supply of organic matter is sufficiently high in this region to allow accumulation at levels higher than those predicted from clay control that are exhibited in all other shelf and

slope environments with oxygenated water-columns studied to date. The standing stock measures used here do not allow direct inference of rates such as organic matter supply or degradation, though the decreasing EHAA:OC ratios and OC:SFA ratios with water-column depth are consistent with a similar depth-dependence of fresh organic matter supply. The offsets between the water-column depth dependence of grain size (i.e. surface area) and of OC and EHAA, which reduce the explanatory power of grain size for the other two parameters, are due to the depth-dependent supply of organic matter. These trends can be explained by a shallow-water winnowing of organic matter containing both labile and refractory organic material, perhaps in the form of organoclay aggregates, which are transported to greater water-column depths while decreasing in lability and organic matter:clay mineral ratio. Use of normalizations, such as OC:SFA ratios, allows these standing stock measures to more accurately reflect flux-dependent processes such as sediment metabolism than use of weight-normalized concentrations of organic matter.

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