A Benthic Carbon Budget for the Continental Slope off Cape Hatteras, N.C.

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ABSTRACT

The continental slope off Cape Hatteras, N.C. from approximately 36° 00'N to 35° 20'N is a region of relatively rapid sediment accumulation, organic matter deposition and subsequent remineralization. The measured fluxes are the highest reported for the slope off the eastern U.S. Sediment accumulation rates range from 40 to 140 cm ky^{-1}. Organic carbon deposition rates range from 3.5 to 7.4 moles C m^{-2} yr^{-1}. The areal coverage of this "depocenter" is probably controlled by interactions between physical oceanographic processes and the rugged topography of the seafloor.

The organic matter deposited on the seafloor is primarily marine in origin and a mix of old and fresh particles. 73-93% of the depositing detritus is rapidly oxidized near the sediment/water interface. The controls on subsurface remineralization appear to be a complex function of the relative amount of metabolizable carbon delivered to the seabed both now and in the distant past (≥500ybp) and the extent of seabed irrigation. The age of DIC and CH_4 produced within the seabed indicates that relatively young, reactive carbon is advected below the sediment surface and fuels subsurface remineralization. The stable isotopic composition of DIC produced within the seabed indicates the selective degradation of ^{13}C-enriched fractions of the organic matter. The metabolizable fraction has a carbon isotopic signature of ~-18‰, while the organic matter that survives degradation and is buried has a $\delta^{13}C$ closer to -20‰.

INTRODUCTION

The continental slope off Cape Hatteras has been proposed to be an area of enhanced carbon sequestration (Walsh *et al.* 1985). High animal densities are supported by elevated fluxes of organic material into the area (Rowe *et al.* 1988, Schaff *et al.* 1992, Blake and Grassle 1994). Rates of sediment accumulation and organic matter remineralization in the region off Cape Hatteras, N.C. are reportedly an order of magnitude higher (Blair *et al.* 1994 & 1996, DeMaster *et al.* 1994) than those reported for the slope further north in the Mid-Atlantic Bight (Biscaye and Anderson 1994, Anderson *et al.* 1994) where a portion (~11%, Walsh 1994) of the particles produced on the continental shelf is exported onto the adjacent slope via complex currents, largely associated with storms (Biscaye and Anderson 1994, Brunner and Biscaye 1997).

The unique physical oceanography of the region directly off Cape Hatteras, N.C. generates optimal conditions for the transport of particles to and subsequent deposition on the continental slope. The southward flowing Virginia Current and northward flowing Gulf Stream converge at the cape, focusing particulate transport into the region. Episodic upwelling and cold-core ring formation associated with the convergence cause localized areas of elevated production (Janowitz and Pietrafesa 1980, Csanady and Hamilton 1988, Flagg *et al.* 1998). Quiescent, near-bottom conditions facilitate deposition (Csanady *et al.*, 1988) of particles both exported from the adjacent shelf regions and produced over the slope. The bottom topography of steep canyons and gullies may further serve to funnel particles into the area (Biscaye and Anderson 1994, Suayah *et al.* In prep.). Mass wasting is an important process shaping the geomorphology of this region (Prior 1986, Mellor and Paull 1994).

Though there is considerable evidence to indicate that the slope offshore of Cape Hatteras

is a depocenter for sedimenting organic matter, there has not been a comprehensive benthic C budget prepared. To that end, this paper presents a benthic carbon budget for the continental slope directly off Cape Hatteras. In addition, the stable and radio-carbon isotopic compositions of remineralization products, as well as POC and animals, are used to characterize the metabolizable organic matter reaching the seabed. The data presented are used to refine our estimates of C preservation in slope sediments and evaluate the effects of non-steady state deposition on the early diagenesis of organic matter.

METHODS

Study area and sampling methods -- Sampling sites were part of the Department of Energy's Ocean Margin Program on the Cape Hatteras continental slope. Three transects were established along 36° 20'N, 35° 51'N and 35° 25'N between 400 and 1500m water depth (Table 1). An additional site was visited at 35° 23'N, 74° 48'W. This site has been described previously (Kelchner 1992, Schaff *et al.* 1992, Blair *et al.* 1994, DeMaster *et al.* 1994, Blair *et al.* 1996, Levin *et al.* 1997) and is referred to as Site III. Stations were occupied during three cruises aboard the *R/V Cape Hatteras* (September 1993), *R/V Seaward Johnson* (July 1996), and *R/V Edwin Link* (August 1996). The submersible, *R/V Johnson Sea-Link,* was used during the August 1996 cruise.

Sediment for ship board flux incubations was collected by submersible using a 15 x 15 x 20cm Ekman-style box corer fitted with a 14.5 cm-i.d. Lucite subcore. The round subcore was held in place by set screws. Sediments for dissolved inorganic carbon (DIC) production rate incubations were collected in 40cm long push cores using the submersible. Samples for porewater, particulate organic carbon (POC) analyses and ^{14}C chronologies were collected using

a 12cm x 12cm x 3m kasten corer during all three cruises.

We suspect that surface-deployed coring techniques introduced a sampling bias that was caused by seafloor topography. Cores that impacted the relatively flat tops of ridges were probably recovered more successfully than deployments that intersected steep slopes. Cores could be efficiently collected from all three geographies using the submersible.

Experimental and analytical methods -- Benthic DIC fluxes were measured both *in situ* and during shipboard incubations. All shipboard incubations were conducted in darkness at 4°C and atmospheric pressure. After recovery of the Ekman box corers, the Lucite subcores were removed and closed at the bottom. The overlying water was gently aerated for several hours to allow the core to equilibrate to atmospheric pressure and incubation temperature. The cores were sealed at the top prior to the start of the incubations. Cores were gently stirred and monitored for DIC and O_2 concentrations every 3-6 hours for 24 hours. DIC concentrations were determined on board ship by flow-injection analysis (Hall and Aller 1992). The precision of this technique is estimated to be ± 2%. O_2 concentrations were measured using a modified micro-Winkler technique (Strickland and Parsons 1972), which has a precision of ± 1%. Aliquots of overlying water from each sample were sealed in glass ampoules for isotope analysis of DIC at N.C.S.U. (see description below).

In situ diffusive fluxes were determined using a free-vehicle lander and submersible-emplaced chambers. The free-vehicle benthic chamber instrument (BECI) inserted a 30 x 30 cm titanium chamber, capped it and sampled the overlying water within the chamber every 2-3 hours (Jahnke and Christiansen 1989). Samples were drawn into spring-loaded syringes and gas tight

ampoules (for O_2 analyses). At the beginning of each incubation NaBr was injected into the overlying water to be used to estimate chamber volume. O_2, DIC, and nutrient concentrations were measured on samples recovered from the incubations. The smaller submersible-emplaced chamber operated in a similar fashion. The manually placed chamber allowed for control of placement adjacent to other experiments.

DIC production rates were determined using closed tube sediment incubations. Cut-off 60-ml plastic syringes were used to subcore the top 5 cm of push cores collected by submersible. The sediment plugs were then sealed in the syringes with a butyl rubber stopper. Four syringes were filled from each core. Stoppered syringes were placed in half gallon Mason jars (Ball ™). Then the jars were flushed with N_2 and capped in a glove bag. One sediment plug was immediately processed for porewater DIC concentration, and the remaining plugs were incubated at 4°C. Every 24 hours for three days, one incubation was ended and processed. DIC production rates (R) were calculated using the following equation:

$$R = (dC/dt)\ \phi_{\bar{x}}\, h$$

where,

dC/dt = change in concentration with time (μmoles cm_{pw}^{-3} hr^{-1})

$\phi_{\bar{x}}$ = average porosity for the 0-5cm interval (cm_{pw}^{3} cm_{sed}^{-3})

h = height of incubated plug (cm_{sed}).

Porewater profiles of DIC $\delta^{13}C$, $\Delta^{14}C$ and concentrations were determined on kasten cores. Sediment was subsampled using cut-off syringes. Porewater was separated by centrifuging the sediment in 30-ml Teflon centrifuge tubes at 7500 rpm (5000 *g*) for 15 min. DIC concentrations

of porewaters also were determined on board ship by flow-injection analysis (Hall and Aller 1992). Surplus porewater was sealed in glass ampoules for isotopic analyses. At N.C.S.U., the $\delta^{13}C$ of the DIC was determined on one milliliter aliquots of porewater. Samples were placed in 3ml bottles and sealed with crimped rubber stoppers (Wheaton). The samples were acidified and the resulting CO_2 was stripped with He and trapped cryogenically (Blair and Carter 1992). The $^{13}C/^{12}C$ ratio of the CO_2 was measured on a modified Finnigan MAT Delta E isotope ratio mass spectrometer (Hayes *et al.* 1977). The precision of the vacuum line concentration measurements was ± 5%. The precision of the carbon isotope measurements was ± 0.4‰. The isotopic signatures of the DIC samples were corrected for degassing during storage in the ampoules. Samples were assumed to have equilibrated with the headspace gas inside the containers. The corrected value ($\delta^{13}C_c$) was calculated using the following equation:

$$\delta^{13}C_c = (f \times \delta^{13}C_m) + (1 - f)\left(\frac{(\delta^{13}C_m + 1000)}{\alpha} - 1000\right)$$

where:

f = DIC concentration after storage/concentration before storage

$\delta^{13}C_m$ = isotopic signature measured after storage

α = fractionation factor for CO_2 - HCO_3^- equilibrium (Friedman and O'Neil 1977).

$\Delta^{14}C$-DIC measurements were made on porewater that was processed using a modified procedure of the stable isotope protocol. Sediment was quickly collected in cut-off syringes and

transferred to centrifuge tubes in a glove bag under N_2. After centrifugation, the porewater was placed in ampoules under N_2. At N.C.S.U. the samples were transferred to glass Wheaton bottles that had been previously flushed with He. The bottles were crimp-sealed, and the DIC was converted to CO_2 using the same method described above. The resultant gas was analyzed for its isotopic content by accelerator mass spectrometry at the Lawrence Livermore National Laboratory AMS Facility. The precision of the $\Delta^{14}C$ measurements was ± 7‰, which translates to an error of ± 10% on the age estimates.

Porewater profiles of CH_4 concentrations, $\delta^{13}C$, and $\Delta^{14}C$ were determined on kasten cores. Sediment targeted for CH_4 concentration analyses was subsampled using 3-ml cut-off syringes. The sediment was then extruded into 50-ml serum vials (Wheaton) containing 1 ml of 3M NaOH and sealed with rubber stoppers. CH_4 concentrations were determined by gas chromatography on a Shimadzu Mini-2 GC using a molecular sieve 5A column (Alltech) and flame ionization detector. Analytical precision was ± 6%. Based on previous observations, sample to sample variability could have been an order of magnitude greater due to the gaseous losses of CH_4 during core retrieval and sampling.

Sediment targeted for CH_4 isotopic analyses was collected in 60-ml cut-off syringes and extruded into one pint Mason jars that had been flushed with N_2 and contained 20 ml DI water. Samples were stored frozen. At N.C.S.U. the thawed samples were shaken vigorously for five minutes. Headspace gas was removed from the jar using a can piercing sampler (Alltech). The methane was converted to CO_2 by passing it through a 790°C furnace packed with CuO (Matthews and Hayes 1978). The resultant CO_2 was either analyzed for its $^{13}C/^{12}C$ or $^{14}C/^{12}C$ content as described above. Precision of the $\delta^{13}C$ measurement was 0.3‰. The relative standard

deviation on the $\Delta^{14}C$ measurement was ± 6%.

Particulate organic carbon data-- Particulate organic carbon ^{14}C ages, sediment porosities and dry bulk densities were determined at N.C.S.U. POC ^{14}C ages were determined following the procedures described in Harden *et al.* (1992) and DeMaster *et al.* (1994). POC concentrations and $\delta^{13}C$ on sediment from all stations except Site III were generated at U.N.C.-Chapel Hill using a Carlo-Erba 1500 Elemental Analyzer. Small aliquots of sediment were weighed into aluminum boats. Vapor Phase acidification with HCl was used to remove carbonates prior to analyses (Hedges and Stern 1984). Precision on the concentration analyses was 3%.

Particulate organic carbon concentrations and isotopic compositions of sediments from Site III were determined at N.C.S.U. Sediments were dried and then acidified with 4N HCl. Sediments were redried and ground to a fine powder. Subsequently, several milligrams were combusted in a Carlo Erba 1108 CHNS analyzer (Blair and Carter 1992). The resultant CO_2 was cryogenically collected and analyzed for its $^{13}C/^{12}C$ content as described above.

Grain size determinations -- Sediment from Site III (kasten core 142, CH93) was analyzed for its carbonate-free grain size distributions downcore. Approximately 5g of dry sediment from each depth interval were acidified with 4N HCl to remove all carbonates. The sample was rinsed repeatedly with DI water until the pH reached 4. Then the sediment was sonicated for 2 minutes and rinsed through nested 63 and 25 μm sieves. The mud fraction that passed through the sieves was collected in a 1L graduated cylinder for separation of mud and clay particles at 8 phi (4 μm). Five mls of a 250g L^{-1} solution of sodium metaphosphate were added to each cylinder, the

volume brought to 1L and allowed to equilibrate overnight. Subsequently, the samples were stirred for one minute and 20mls were removed (≤ 4 phi). After 1hr 59min at 19°C, 20mls were removed from a depth of 10cm (≤ 8 phi). All of the grain-size samples were oven dried and weighed.

Calculation of budget terms -- Mass balance equations were used to model C fluxes within slope sediments. This method required the assumption that the system has been at steady state in terms of sediment accumulation and organic matter input over the last 5,000 y. Stations were considered to violate this assumption if the change in the ^{14}C age of POC downcore was not linear (least square fit, $r^2 \leq 0.6$). All budget terms (*i.e.* fluxes and rates) were converted to the common units of moles C m^{-2} yr^{-1} to facilitate additional calculations and comparisons.

Organic carbon deposition rates (J_{tot}) were estimated for four stations on the North Carolina slope by summing the flux of remineralization products (J_{diff}) leaving the seabed with the total burial flux (J_{bur}) of remineralization products in porewaters and of particulate organic matter escaping remineralization:

$$J_{tot} = J_{diff} + \Sigma J_{bur}.$$

Error of J_{tot} was estimated by taking the square root of the sum of the squares of the standard deviations associated with the diffusive flux and POC burial terms. Porewater burial terms were not included in the propagation of error because multiple measures were not made, and the size of the terms was an insignificant portion of the total.

The diffusive flux (J_{diff}, μmoles C cm^{-2} hr^{-1}) of DIC out of sediment contained in flux chambers was estimated using the following relationship:

$$J_{diff} = H \frac{dC}{dt}$$

where,

H = height of headspace in the flux chamber (cm)

dC/dt = linear concentration gradient with time (μmoles cm^{-3} hr^{-1}).

Availability of flux measurements restricted the number of stations at which budget calculations could be made. Flux measurements were largely made on the August 1996 cruise when the July kasten coring stations were revisited with the submersible. As a result, fluxes were pooled with porewater and POC measurements made at the same coordinates on different dates. The water depth of collection given for each station is the depth from which the kasten core was collected. The water depths of flux measurements at a given site vary as much as 50m due to the rugged topography of the seafloor.

Burial rates for dissolved species were determined using the following relationship:

$$J_{bur} = \phi_z \, \omega \, C_z$$

where,

ϕ_z = sediment porosity at depth, z (cm^3_{pw} cm^{-3}_{sed})

ω = sediment accumulation rate (cm_{sed} ky^{-1})

C_z = concentration of DIC or CH_4 at depth (mM).

Burial terms would ideally be calculated at depth where concentrations become asymptotic.

However, in most cores, concentrations of dissolved species never reached that point. As a result, burial depth was defined as the deepest interval sampled for all carbon pools.

Burial rates for the POC fraction were calculated as follows:

$$J_{bur} = \omega \rho_{DB} C_Z$$

where,

ρ_{DB} = sediment dry bulk density at depth ($g_{dry\ sed}\ cm^{-3}_{wet\ sed}$)

C_z = concentration of POC at the burial depth (moles C $g^{-1}_{dry\ sed}$).

RESULTS AND DISCUSSION

Overview of site-specific carbon budgets

Complete carbon budgets (*i.e.* containing estimates of organic carbon accumulation rate, benthic DIC fluxes, and CH_4 + DIC porewater burial rates) could be constructed for four of the twelve study stations. Organic carbon deposition rates at the four sites were estimated to be 3.6 to 7.7 moles C m^{-2} yr^{-1} (Table 2). The carbon that is deposited in these locations appears to be marine in origin based on the $\delta^{13}C$ composition (~-21‰) and C/N weight percent ratio (~8) of the organic matter that accumulates. The ^{14}C ages of organic material at the sediment surface ranges from 500 (upslope, 400m) to 2500 ybp (downslope, 1000m). Some portion of the particles sedimenting in this region of the slope are derived from higher latitude regions and may be heavily weathered. This is inferred from previous examinations of the clay mineralogy at Site III which revealed an abundance of chlorite, a high-latitude weathering product proposed to have originated in the Chesapeake Bay area (Kelchner 1992).

Some fraction of the POC reaching the seafloor is considerably younger and more labile

than the POC that accumulates in the seabed. ^{14}C dating of benthic infauna collected in the study area gives modern ages and requires incorporation of nuclear bomb-tagged ^{14}C into body tissues (DeMaster *et al.* 1998, Blair *et al.* Submitted). Visual observations during submersible dives reveal a steady rain of marine snow and the occurrence of green phytodetritus near the bottom in these locations. Viable diatoms and measurable Chl *a* within the slope sediments also indicate the delivery of recently fixed carbon to the slope seafloor (Cahoon *et al.* 1994). Although at some locations the surface POC-^{14}C ages are offset from the material that is accumulating below the surface (e.g. Site III, Fig. 1 & 2), the relatively old ages (≥500ybp) measured in most surface sediments and the high flux of DIC out of the seabed (Table 2) suggest that most young carbon deposited is quickly remineralized.

Diffusive loss of carbon from slope sediments is not limited to DIC. Fluxes of dissolved organic carbon (DOC) have been measured at one of the carbon budget sites, Station N740, on the 36°20'N transect (Alperin *et al.* Submitted.). The flux of DOC out of the sediment was estimated at 0.028 moles C m^{-2} yr^{-1}. This loss is approximately 1% of the remineralization flux and is well within the level of error in the DIC flux measurements. For this reason, DOC flux out of the sediment was not included in carbon budget calculations.

Also not included in the budget was the loss of organic carbon through predation by demersal and pelagic species. Infauna biomass (>300μm) is by far most abundant at Site III, averaging 54.5 ± 14.4 g wet wt. m^{-2} (Schaff *et al.* 1992). Infauna is generally half as abundant at nearby slope sites (Blake and Grassle 1994). As a high end estimate, consider the following calculated loss of carbon due to predation. If we assume that the infauna were 40% water and 15 dry wt. % OC

(based on slope infauna analyzed at N.C.S.U.), then infauna biomass accounts for 0.4 moles C m^{-2}. If all of this biomass were removed by predation annually, the loss is $\leq 10\%$ of the carbon deposited on the seafloor and well within the error of the largest budget term, diffusive flux.

Approaching the predation issue from the consumer end of the trophic chain provides an additional estimate of the potential loss. Reported maximum fish densities at mid-slope depths (400-1000m) are 1-1.3 individuals m^{-2} (Hecker 1994). Most fishes in this environment weigh between 2 and 10g wet weight (Sulak and Ross 1996). Using an average respiration rate reported for deep-sea fishes of 0.3 moles O_2 $g^{-1}_{wet\ wt.}$ yr^{-1} (Smith 1978, Smith and Laver 1981), an average fish weight of 5g, and the above densities, the respiration demand from demersal fishes at mid-slope depths is 1.5 -1.9 moles O_2 m^{-2} yr^{-1}. If each mole of O_2 consumed by the fish oxidizes one mole of C, then the fishes must consume 1.5 - 1.9 moles C m^{-2} yr^{-1} to create this metabolic demand. If the entire C demand is met by predation on benthic infauna, then the loss is equivalent to 25 - 50% of the diffusive fluxes recorded in this environment (Table 2). Without more accurate estimates of predation rates for this environment, this term cannot be assessed more directly.

Of the carbon that survives near-surface degradation and is advected below the interface, only a small amount (1 - 7%) is remineralized within the upper 2-3m of seabed (Table 2). The age of the organic matter that is remineralized below the sediment surface at Stations S480, M620a and S818 is significantly younger than the POC buried (1σ). Both the age of the DIC and CH_4 buried is offset from POC ages downcore (Fig. 3), again suggesting at least two pools of organic carbon, one younger and more reactive and another older and more recalcitrant. At one station, M415, both the CH_4 and the DIC at depth are older than the POC (Fig.3). Either the

fraction of the organic matter that is degraded at this station is old, or older DIC and CH_4 are diffusing up from deeper in the sediment.

Slope-wide variability in budget terms

POC burial -- Variations in POC burial rates across the slope result from differences in sediment accumulation rates and weight percent OC. Sediment accumulation rates across the entire study region vary by a factor of less than four, ranging from 37 to 140 cm ky^{-1} (DeMaster *et al.* 1998). On average, the rates are highest on the two southern transects and peak at water depths between 400 and 900m.

Conversely, mean sediment organic carbon content decreases to the south, averaging 2.6% (dry wt.) on the northernmost two transects and 1.5% on the southernmost transect and at Site III. The shift in organic carbon content may be the result of at least two processes. First, dilution from increased amounts of large sand-size particles could reduce the weight percent organic carbon in southern locations. Kelchner (1992) reports similar POC distributions for the region and used grain-size analyses to attribute lower levels in the area between 35°00' and 35°30' to an increase in the relative amount of silt and sand size particles. The bulk of those particles were planktonic foraminifera. Second, increased loading on fine particles sedimenting in northern regions could cause the relatively elevated percentages. We have no gauge of the occurrence or magnitude of the second process.

Depth distributions for POC concentrations, its $\delta^{13}C$ and ^{14}C age for the budget stations are displayed in Fig. 1. They are typical of distributions found at other stations. Isotopic shifts in the upper 1m are associated with an enrichment in the ^{13}C content of the POC at Stations S818 and

Site III (Fig. 1). Though a diagenetic isotope effect cannot be ruled out *a priori*, the shifts in $\delta^{13}C$ in these and other cores are most likely the result of source variations.

For example, at Station M811 (Fig. 2), downcore POC concentration changes are irregular, large (3-4%), and associated with a depletion in ^{13}C content as compared to the other stations. These downcore shifts are associated with an offset in the ^{14}C ages of the POC (Fig. 2), suggesting that deposition at Station M811 has been non-steady state in the recent past. POC buried as shallow as 100cm was produced before the Holocene, while POC ages in the upper 50cm of the seabed range from 1000 to 9000 ybp. The $\delta^{13}C$ and weight percent of the POC suggest at least three, and perhaps four, changes in the source of organic matter. Given the high accumulation rates for adjacent sites (72-115 cm ky^{-1}), it seems unlikely that an extended hiatus in deposition has caused the observed profiles. It is more likely that some mass-wasting event affected the sediment column in the past. Steady state accumulation may have resumed recently. The organic matter accumulating over the upper 20cm or so resembles that accumulated at other stations on this transect (wt % OC = 2.5, $\delta^{13}C$ = -20.9). Similar discontinuities in POC ages and $\delta^{13}C$ are found at M620a, S480, S818 and Site III, suggesting non-steady state deposition (Figs. 1 & 2).

At Site III subsurface ^{14}C ages are consistently ~2000ybp between 50 and 150cm depth (Fig. 1) suggesting very rapid deposition. The vertical subsurface ^{14}C age profile at Site III requires cautious interpretation of accumulation rates. If sediment accumulation has been steadily rapid and the young offset at the surface of the core represents recent delivery of fresh detritus, the budget terms reported in Table 2 could be an order of magnitude higher. Conversely, if rapid accumulation of sediment occurred long ago(> 500), and deposition has been

slower since then, the estimated burial rates in Table 2 may be too rapid relative to current rates.

A previous report of accumulation at the site supported the first scenario – rapid, steady state accumulation (DeMaster *et al.* 1994). A kasten core recovered from 1150m of water at 35° 24'N had a nearly vertical ^{14}C depth profile. The ^{14}C ages of the POC became somewhat younger downcore, but averaged an age of 2400ybp with no young offset at the sediment surface. Calculation of an accumulation rate from a vertical ^{14}C profile was impossible, so ^{210}Pb profiles from the region between 35°20' and 35°38'N were used to estimate the unusually high sediment accumulation rate of ~1 cm yr^{-1} (DeMaster *et al.* 1994)

While rapid, recent accumulation in the region cannot be ruled out, it seems likely that the ^{210}Pb profiles were affected by bioturbation to the bottom of the short cores (15-30cm). Biological mixing of the sediment would make the ^{210}Pb profiles more vertical and increase the apparent accumulation rate (Benninger *et al.* 1979, Cochran and Aller 1979, Nittrouer *et al.* 1979). Porewater profiles from the region (Fig. 4) clearly show bioirrigation of the seabed to depths of 40cm and deeper. It follows that biological transport of particles could also occur to these depths. X-ray images and biological mixing parameters for sediment in the region show rapid bioturbation to 20cm that overshadows accumulation and strata formation (Diaz *et al.* 1994).

Additional evidence now available also supports the second scenario – non-steady state accumulation potentially including a mass-wasting event. First, ^{234}Th inventories do not suggest that recent deposition (last 100 days) at Site III has been any more rapid than at Station S818 where ^{14}C accumulation rates are considerably slower (Table 2). ^{210}Pb inventories also vary little throughout the region, suggesting that delivery of organic particles over the last one hundred

years has been similar at Site III and other locations slightly north of it (DeMaster *et al.* 1994, Suayah *et al.* In prep.).

Second, discontinuities occur in POC ^{14}C age, grain size distributions, weight percent C, and POC $\delta^{13}C$ at 60-65cm deep in the sediment. The organic carbon age at the sediment surface is 1000y younger than organic carbon deeper in the core. Carbonate-free grain size distributions shift from 70% sand and 30% silt + clay to a 50:50 mix. Weight percent carbonate is 8% over the upper 60cm. In the 60-65cm interval, the same interval where the other discontinuities occur, the carbonate concentration drops to 6%. Below that depth, the percentage is highest (10%). Finally, the wt. % OC shifts from 1.6 to 1.4%, and the POC $\delta^{13}C$ shifts from -21 to -20‰ (Fig.1).

Similar isotopic shifts in both ^{14}C ages and POC $\delta^{13}C$ can be found in sediments at stations in close proximity to Site III (S480, S818, and M620b; Figs. 1 & 2). The calculation of accumulation rates at non-steady state sites is tenuous; however, rates calculated above the transitions in the ^{14}C-age profiles can be used to constrain the timing of the changes. Dividing the depth of the transition by accumulation rate yields similar dates of 550 and 540 years ago at Site III and Station S480, respectively. The transitions at Stations M620a and S818 appear to have occurred 1,200 and 2,700 years ago.

Benthic fluxes -- Benthic fluxes were not only variable from one station to another, but also variable at each study site. The standard deviation of fluxes were nearly as large as the mean flux at any given station. Fluxes at four sites (Stations N740, M620, S818, and Site III) were replicated four to nine times using *in situ* and shipboard techniques (Table 3). The large variances were due mainly to submersible-emplaced *in situ* fluxes (August 1996) that were 2-3

times higher than fluxes obtained by shipboard incubations during the same cruise and lander deployments during the cruise in 1993. The range of values may reflect the patchiness of benthic communities in this dynamic environment (Blake and Hilbig 1994, Rhoads and Hecker 1994). The submersible-deployed chambers were specifically placed on high-accumulation rate plateaus where other experiments had to be deployed. These flat areas were not the normal topography, thus, it is unlikely that surface-deployed landers would sample these locations.

Additional experimental artifacts associated with the flux measurements cannot be ruled out. Porewater profiles suggest that irrigation represents a major transport mechanism. Other studies have provided evidence for irrigation at Site III (Blair *et al.* 1994, 1996, Submitted). However, irrigation did not appear to be an important mechanism for water exchange in any of the chambers. Br^- tracer concentrations in chamber headspaces did not change significantly during lander and submersible-placed chamber incubations. Shipboard incubations chambers were sealed, preventing water exchange. If irrigation were inhibited, then the measured fluxes may have been too low. Because we had no gauge of the source of the variability, we chose to include all of the data when computing average fluxes for the sites used in the budget.

Across the entire study area, individual measurements of benthic fluxes of DIC out of the sediment ranged from 0.8 to 13.2 moles C m^{-2} yr^{-1}. Fluxes of O_2 into the sediment ranged from 0.7 to 9.9 moles O_2 m^{-2} yr^{-1}. The magnitude of the fluxes was not clearly correlated with sediment accumulation rate or weight percent organic carbon. For example, Station S818 had the highest DIC flux of the budget stations and the lowest accumulation rate and weight percent organic carbon.

Sediment accumulation rates and weight percent organic carbon contents are not

necessarily good proxies for assessing the delivery of reactive carbon. Organic-poor particles may dilute more reactive material, creating high delivery rates and low weight percent carbon. Conversely, high weight percent organic carbon does not insure high concentrations of labile organic matter. Non-steady state conditions may also restrict correlations between long-term accumulation rates and fluxes that are more responsive to short-termed variations in the delivery of organic material.

Benthic fluxes of DIC as measured in the flux chambers can be affected not only by the rate of organic matter oxidation, but also by seabed irrigation and carbonate dissolution (Aller 1982a). Aerobic oxidation of organic matter, $S^{=}$, Fe^{+2} and Mn^{+2} can decrease alkalinity and cause carbonate dissolution to release an equivalent amount of DIC in carbonate-rich sediments (Emerson *et al.* 1982). In other words, the expected DIC/O_2 flux ratio would be 2 if a stoichiometric quantity of carbonate were dissolved. In general, the flux of DIC out of the sediment was balanced by the flux of O_2 into the sediment (Table 3). The ratio of DIC/O_2 fluxes at the budget stations were 0.7 - 1.1, indistinguishable from an ideal ratio of 0.9-1.0 based on the complete oxidation of organic matter according to the Redfield ratio without dissolution (Emerson *et al.* 1980).

The sediments in the study region are well above the $CaCO_3$ lysocline and have carbonate concentrations of 10-25 wt. %. As a result, porewaters may be super-saturated with respect to $CO_3^{=}$. Acid production from remineralization reactions could titrate alkalinity without causing significant carbonate dissolution. The flux ratio of total alkalinity to O_2 was approximately 1.7 because of the NO_3^{-} and PO_4^{-3} coincidently released during remineralization.

The DIC production incubations provided a measure of the rate at which organic matter can be degraded near the sediment surface. Rates at the budget stations were 4.7 (n = 1), 2.6 ± 0.5 (n = 2), and 3.1 ± 0.01 moles C m^{-2} yr^{-1} (n = 2) at Stations N740, M620, and S818, respectively. The DIC production rate from one other site on the 35°51'N transect at 543 m water depth was 3.2 moles C m^{-2} yr^{-1}. These production rates indicate that 50 - 100% of organic remineralization in these sediments potentially occurs in the upper 5cm.

Porewater burial terms -- Porewater profiles of dissolved species also were variable across the slope region (Fig. 3). Nearly vertical profiles of low DIC concentrations and high $\delta^{13}C$ indicate irrigation of overlying waters to depths of ~40cm in most cores. Deeper irrigation, as deep as 100cm in many locations, is implicated by $SO_4^{=}$ concentration profiles (Alperin *et al.* Submitted) and the occurrence of burrows to >100cm (visual observations). Two cores from Stations S818 and S1200 show no signs of irrigation.

Comparatively low DIC concentrations (5-25mM) at depth in sediments along the 36°20'N transect could be the result of irrigation or carbonate precipitation. Relatively high DIC production rates for surface sediment at Station N740 on this transect (Table 3) suggests that the low concentrations downcore may be either the result of oxidation localized in the upper 5cm of sediment or some loss mechanism downcore. Alperin *et al.* (Submitted) report Ca^{++} concentrations that drop downcore indicating carbonate precipitation in sediment near the 36° 20'N transect. Irrigation likely controls porewater concentrations at Stations N501 and N1027, because DIC concentrations at these stations are nearly constant downcore and only slightly higher than that of overlying water (Fig. 4). Given the high degree of patchiness over small

spatial scales on the slope, this evidence can hardly be considered conclusive. Without ancillary data such as DIC $\delta^{13}C$, the potential mechanisms are difficult to resolve.

Below the biologically irrigated zone, the ratio of $SO_4^=$ consumed to the amount of DIC accumulating is approximately 2 at most locations indicating that the source of accumulating DIC is primarily $SO_4^=$ reduction (Emerson *et al.* 1980, $SO_4^=$ data from Alperin *et al.* Submitted). Plotting the concentration of DIC against its isotopic composition further helps to resolve the sources of porewater DIC (Fig. 5). An isotope mass balance (see discussion below) indicates that the organic material being degraded has an isotopic signature of ~-18‰. The ideal mixing curve shown in Fig. 5 represents the addition of -18‰ DIC to overlying seawater assumed to contain 2mM DIC with a $\delta^{13}C$ of 0‰. Deviations from the ideal curve indicate that processes other than the accumulation of organic material-derived DIC are affecting DIC concentrations and isotopic compositions.

Data from only two stations, S818 and S1200, (Fig. 5, Station S818 not shown)fall along the ideal mixing curve. Porewater profiles of DIC and $SO_4^=$ concentration at both Stations S818 and S1200 do not show signs of irrigation. In fact, the concave-down appearance of the profiles strongly suggests that DIC is diffusing up with little or no precipitation or advective loss (Reeburgh 1976, Martens and Berner 1977). As discussed in the preceding section, sediment low in organic carbon is accumulating slowly at these stations. Diffusive fluxes at Station S818 are high, indicating rapid oxidation of OC at the sediment/water interface. Subsurface degradation rates are apparently low, based on the lack of accumulating DIC and CH_4 (Table 2).

At Stations M415, M620a, S480 and Site III methanogenesis drives DIC $\delta^{13}C$ values more positive as $^{12}CO_2$ is preferentially reduced to methane at depths 1.5-2.5m deep in the sediment

(Fig. 4 & 5). DIC concentrations reach 50-60mM at these stations and can be explained by the complete reduction of 25-30mM $SO_4^=$ prior to methanogenesis as the porewater was buried.

The four stations with relatively shallow methane production all have current sediment accumulation rates over 100 cm ky^{-1}, comparatively high for this region. Stations M415, M620, and S480 all accumulate organic carbon at rates on the order of 2.0 $\pm$ 0.1 moles C m^{-2} yr^{-1}, and begin to produce methane somewhere between 150 and 200cm. Site III accumulates OC at a rate of 0.6 $\pm$ 0.4 moles C m^{-2} yr^{-1} and has the shallowest methanogenic zone. Station M1170 accumulates OC twice as quickly (1.2 moles C m^{-2} yr^{-1}) as Site III (based on the conservative accumulation rate estimate), yet methane is not produced within the top 2m of sediment.

Methane production typically occurs at depths below where $SO_4^=$ concentrations become <1mM (Claypool and Kaplan 1974, Martens and Berner 1974). Accumulation rate and irrigation are thought to control the thickness of the $SO_4^=$ reduction zone (Reeburgh and Heggie 1977, Berner 1978, Reeburgh 1980, Blair in press). Accumulation rate clearly covaries with sulfate gradients over wide ranges of accumulation rates (Berner 1978); however, non-steady state accumulation and irrigation obscure the relationship on the North Carolina slope.

Present-day OC depositional environment is not an accurate predictor of shallow methane production in this region. Of the methanogenic cores, only station M415 has had steady state accumulation over the length of the core. Deposition at the other three methanogenic stations, M620a, S480 and Site III, apparently has not been steady state, and may have been very rapid in the past. The quality, composition and accumulation rate of the organic matter 500+ years ago may be the factor controlling methane accumulation.

In addition, advection of $SO_4^=$-rich overlying water to depth during irrigation may expand

the $SO_4^=$ reducing zone, pushing the methanogenic zone deeper in locations where rapid accumulation should support shallower production (Reeburgh and Heggie 1977, Reeburgh 1980). Again, evidence for deep irrigation comes from porewater profiles and animal distributions. Deep burrowing crustaceans, tube building anemones and deep dwelling polychaetes are abundant in these areas and most likely responsible (Schaff *et al.* 1992, Blake and Hilbig 1994, Hecker 1994). This deep irrigation may be spatially patchy and temporally variable.

Associated with the methanogenic zone at these stations is an overlying zone of anaerobic methane oxidation that contributes to the DIC pool. Little if any methane was lost diffusively out the sediment water interface, because methane concentrations in surface sediments were approximately equal to those of the overlying water. The concave-up appearance of the methane profiles implies that CH_4 is consumed as it diffuses upward (Fig. 4). Methane oxidation rates are estimated to be 0.05 - 0.09 moles C m^{-2} yr^{-1} based on the porewater methane gradients. DIC $\delta^{13}C$ values from intervals where methane oxidation occurs are offset from the ideal mixing curve due to the addition of ^{13}C-depleted DIC (Fig.5).

In addition to the stations where the methanogenic zones were sampled, sediments collected at Stations M620a and M1170 have CH_4 profiles indicative of the oxidation of CH_4 diffusing up from depth (Fig. 4). CH_4 concentrations are low, and the profiles are concave-up in shape (Martens and Berner 1974). Sediments collected at Station M620b clearly became methanogenic at depths of ~1.5m, therefore evidence of methane oxidation in the shorter core (1m) collected at M620a is not surprising.

The lack of methane production, coupled with low concentrations of ^{13}C-depleted DIC, suggests *in situ* carbonate precipitation at Station M811 (Fig. 5). Calcite precipitation is

generally inhibited in marine sediments by $Mg^{=}$, DOC and dissolved sulfide (Garrels and Christ 1965, Berner 1975, Berner *et al.* 1978, Morse and Mackenzie 1990). However, given the extremely old age of the sediment at this station with the probable low $S^{=}$ and DOC concentrations (Alperin *et al.* Submitted), enough time may have elapsed for carbonate to precipitate. Pressure changes during core retrieval may cause additional precipitation, although the contribution is expected to be small (Murray *et al.* 1980).

Isotope mass balance

A complete carbon isotope mass balance can be constructed for Station M620, further characterizing the carbon isotopic composition of the metabolizable fraction (Table 4). The $\delta^{13}C$ of the labile organic matter was estimated using three approaches to minimize potential biases and uncertainties that might be associated with any single methodology. The three approaches were based on the measured $\delta^{13}C$ of the: 1) DIC fluxes, 2) benthic fauna, and 3) burial flux of DIC and CH_4.

The magnitude and isotopic composition of the total benthic and the diffusive DIC fluxes were measured and calculated using two separate techniques. First, the isotopic composition of DIC in the overlying water was measured during three of the ship-board flux core incubations at Station M620b. The ratio of the change in concentrations of $DI^{13}C/DI^{12}C$ with time (R_{flux}) was determined by the following relationship:

$$R_{flux} = \frac{(^{13}D_s)\ \frac{d^{13}C}{dt}}{(^{12}D_s)\ \frac{d^{12}C}{dt}}$$

where:

C = concentration of $DI^{13}C$ or $DI^{12}C$

t = time

D_s = diffusivity (assumed $^{13}D/^{12}D = 1.0$, Boehme *et al.* 1996).

The $\delta^{13}C$ of the DIC flux out of the sediment was then calculated by inserting R_{flux} into the following equation:

$$\delta^{13}C_{flux} = (1 + (\frac{R_{flux}}{R_{std}})) \ 10^3.$$

where R_{std} is the $^{13}C/^{12}C$ ratio of the standard and equals 0.0112372. The measured benthic flux was 5.7 ± 4.0 moles C m^{-2} yr^{-1} and had a $\delta^{13}C$ of -17.1 ± 1.3‰.

In addition, the apparent diffusive flux supported by porewater concentrations in one tube core was calculated as above with R_{flux} defined by the gradient of ^{12}C and ^{13}C across the sediment/water interface. The magnitude of the supported flux was calculated using (Li and Gregory 1974, Ullman and Aller 1982):

$$J_{diff} = \Phi_o^3 (D_o \frac{\partial C}{\partial z})$$

where:

Φ_o = porosity at the surface (0.82 $cm^3_{pw}/cm^3_{wet\ sed}$)

$\partial C/\partial z$ = linear concentration gradient across the interface

D_o = free solution diffusivity of HCO_3^- (0.0224 cm^2 yr^{-1}).

The concentration gradient supports a diffusive flux of 5.4 moles C m^{-2} yr^{-1} with a $\delta^{13}C$ of

-18.9‰.

Several factors other than the production of DIC via organic carbon oxidation may influence both the magnitude and isotopic composition of the flux. First, carbonate dissolution could shift the isotopic signature of the benthic flux. This mechanism would be exacerbated by acid produced during remineralization of OC and the oxidation of solid phase sulfides and by irrigation (Aller 1978 & 1982b, McNichol *et al.* 1991, Green *et al.* 1992). Assuming that there is no fractionation associated with the oxidative degradation of -21.3‰ POC and assuming an addition of carbonate with a $\delta^{13}C$ of 1-2‰, an average range for shells and forams (McNichol *et al.* 1991, Berger and Killingley 1977), mass balance indicates that 18-20% of the diffusive flux would have to be from carbonate dissolution to shift the signal from -21.3 to -17.1‰. As mentioned previously, dissolution does not likely occur to a large degree at this station because the DIC/O_2 flux ratio was 1.1.

Second, there could be an isotope effect associated with chemosynthesis along burrow linings. The presence of bioturbating organisms enhances bacterial activities, including chemoautotrophic oxidation of NH_4^+ and Fe-sulfides (Aller and Yingst 1978, 1985, Kristensen *et al.* 1985). Porewater DIC would be fractionated during autotrophic consumption of CO_2 as a direct result of the isotope effect associated with ribulose 1,5 bisphosphate carboxylase (Schidlowski *et al.* 1983, Roeske and O'Leary 1984, Ruby *et al.* 1987). As mentioned above, high rates of sulfide and metal oxidation would drive carbonate dissolution as alkalinity is reduced during CO_2 consumption and metal oxidation, further enriching porewaters in ^{13}C. The additional fractionation from biosynthetic reactions could enrich the flux and reduce the amount of aerobic metabolism required to explain the signal. We cannot constrain the importance of this

potential mechanism.

Third, the ^{13}C-enrichment of DIC in deep-sea sediments has been argued to occur as a result of a steep pH gradient at the sediment water interface (Sayles and Curry 1988, Archer *et al.* 1989). If the DIC flux is sufficiently low, the HCO_3^- gradient is reversed, ^{13}C-enriched bicarbonate diffuses into the sediment, and ^{13}C-depleted CO_2 diffuses out. This cannot be the explanation for the ^{13}C-enrichment on the North Carolina slope, because the DIC flux out is not ^{13}C-depleted, as would be predicted from the deep-sea model. In all likelihood, the presumed deep-sea process is not operative in coastal sediments in general. In near-shore sediments DIC fluxes are greater, and the net direction of bicarbonate diffusion is out of the seabed as demonstrated at Cape Lookout Bight, N.C. (Boehme *et al.* 1996).

Finally, the ^{13}C-enriched benthic flux could be created by the selective degradation of a specific fraction of the POC, either organic matter from a specific source where a variety of sources are represented (Anderson 1994, Blair *et al.* 1994, Harvey 1994) or specific compound classes (McNichol *et al.* 1991). The enrichment most likely results from biodegradation of fresh marine carbon and burial of a mix of reworked marine and terrestrial material (Blair *et al.* 1994, DeMaster *et al.* 1994). Lipid markers for both marine and terrestrial material are found in these sediments (Harvey 1994). Terrestrial material typically is characterized by more ^{13}C-depleted isotopic signatures (-25 to -27‰) than marine material (-19 to -22‰, Anderson and Arthur 1984). Presumably any terrestrial material deposited at mid-slope depths is refractory, while the marine material could be either fresh or reworked.

Animals from colected from the areas have isotopic compositions that differ only slightly in $\delta^{13}C$ but drastically in $\Delta^{14}C$. Metazoans from stations N740 and M620 had average isotopic

compositions of -20.3 ± 1.4 (n=14) and -18.6 ± 1.5‰ (n=9). The $\delta^{13}C$ of annelids at Site III is -19.0 ± 0.2 ‰ (n=30, Levin *et al.* In press). Generally, the isotopic signatures of consumers are similar to that of their food, but because the animals are at least one trophic level removed from the bulk organic matter in the sediment, they are often ~1‰ enriched in ^{13}C than their diet (DeNiro and Epstein 1978, Rau *et al.* 1983, and many others). The animal's $\delta^{13}C$ values therefore suggest that the diet of the animals could be anywhere from -18 to -20‰. However, the ^{14}C ages of animals recovered from the region are modern indicating a selective diet of a young, reactive fraction (DeMaster *et al.* 1998, Blair *et al.* Submitted).

The $\delta^{13}C$ of the organic matter deposited on the seafloor can be calculated using the following relationship:

$$\delta J_{tot} = \frac{\Sigma\ [(\delta J_i)(J_i)]}{\Sigma\ (J_i)}$$

where J_i = the diffusive and burial fluxes of DIC, CH_4 and POC (Boehme *et al.* 1996). Because the magnitude of the benthic DIC flux term dominates J_{tot}, its $\delta^{13}C$ basically determines the δJ_{tot} of -17.8‰ (Table 4). Removing the POC burial term and simply examining the diffusive and burial fluxes of DIC and CH_4 gives a remineralization flux (J_{rem}) of 5.8 moles C m^{-2} yr^{-1} with a $\delta^{13}C$ of -17.1‰ (Table 4). Additionally, the burial flux of remineralization products (DIC + CH_4) is 0.051 moles C m^{-2} yr^{-1} with an associated $\delta^{13}C$ of -17.4‰. Burial fluxes at five stations; Stations M415, M620, S480, S818 and Site III; have an average $\delta^{13}C$ of -17.6 ± 1.7‰. The isotopically heavy porewater burial flux is probably not caused by carbonate dissolution. Alkalinity changes associated with $SO_4^=$ reduction and methanogenesis are generally associated

with carbonate precipitation, not dissolution (Pisciotto and Mahoney 1981, Gautier 1982).

In summary, most if not all of the DIC flux is directly related to organic matter oxidation. The similarity of the $\delta^{13}C$ values of the buried remineralization products with the $\delta^{13}C$ values of the diffusive DIC flux and the animals supports the conclusion that the metabolizable fraction of the organic matter has an isotopic composition ($\delta^{13}C$) of $-18 \pm 1‰$. Comparison of this value to the isotopic composition of the bulk POC fraction suggests that certain organic carbon fractions are preferentially oxidized. These fractions are apparently marine in origin. The ^{14}C ages of animals, DIC and CH_4 further indicate that this fraction is also younger than the bulk POC (Figure 3 and DeMaster *et al.* 1998).

Location of Cape Hatteras "Depocenter"

During the 1970's and 1980's the U.S. Department of Energy conducted the Shelf Edge Exchange Program (SEEP) experiment in two phases. SEEP-I examined the production and fate of organic particles in the northern Middle Atlantic Bight. SEEP-II focused on the southern end of the Mid-Atlantic Bight. This project has focused on the slope region off Cape Hatteras, N.C., a region immediately adjacent to the SEEP-II research area. Each program produced carbon budgets for the continental slope within its latitudinal range (Table 5) with the purpose of determining how much shelf production is deposited and sequestered within slope sediments. Methods for determining sediment accumulation and diffusive fluxes were similar in all three studies; however, deposition rates from the SEEP studies were determined from sediment trap data. The SEEP-II trap data were validated with the same calculations used in this study to estimate deposition rates, so comparisons between studies should be valid.

Comparisons of the three budgets reveal clear latitudinal trends in sediment accumulation rates, diffusive fluxes, and therefore, deposition rates (Tables 2 & 5). More carbon is deposited in the rapidly accumulating sediments of the southern slope region off Cape Hatteras. This deposition in turn supports higher DIC diffusive fluxes. Interestingly, burial efficiencies do not vary significantly with latitude, and appear to be slightly lower to the south. Many factors may control burial efficiencies, including the relative mix of labile and recalcitrant source material deposited and the residence time of particles in the bioactive zone. The material that is deposited on the slopes of all three of the regions appears to be largely marine and a mix of old and fresh particles (Anderson *et al.* 1994, DeMaster *et al.* 1998). In addition, burial efficiency calculations will be biased in environments such as this because deposition has been non-steady state. Consequently, DIC flux measurements and estimated POC burial rates diverge as a result of the mismatched timescales each represents.

There are apparent trends within the budgets from this study that further constrain the region of elevated deposition and remineralization, in addition to the latitudinal trends from New England to Cape Hatteras. The fluxes and C budget at stations on the northernmost transect (36° 20') are quite similar to those described for the Mid-Atlantic Bight (Anderson *et al.* 1994, Tables 2 & 5). However, diffusive fluxes, POC burial rates and OC deposition rates nearly double on the 35° 51'N transect and are elevated as far south as Site III at 35° 23'N. Accumulation and remineralization rates are lower further south at 34° 15'N (Site II, Schaff *et al.* 1992, DeMaster *et al.* 1994, Blair *et al.* 1994) placing a rough southern limit on the location of the Cape Hatteras depocenter.

Not only are DIC and O_2 diffusive fluxes, deposition, sediment accumulation and POC

burial rates the highest reported for the western Atlantic, they are also higher than those reported for slope sediments off Washington and central California (Table 5). In fact, the sediment accumulation rates reported here are similar to those reported for the highly productive area off the coast of Peru. The carbon content of sediments on the Peru slope (2-3%) and the resultant POC burial rates are similar to those reported here for the 35° 51'N transect (Muller and Suess 1979, Walsh *et al.* 1985).

Although the POC burial rates and diffusive fluxes reported for the slope off Cape Hatteras are comparatively high for slope environments, they are lower than those reported for rapidly accumulating shelf environments such as Skan Bay, Alaska, Cape Lookout Bight (CLB), and the Amazon shelf. Reported organic carbon deposition rates for these locations are 1-2 orders of magnitude higher and support diffusive DIC fluxes of 15-40 moles C m^{-2} yr^{-1} (Alperin *et al.* 1992, Martens *et al.* 1992, and Aller *et al.* 1996).

Present-day depocenters are largely identified as upwelling regions and areas undergoing eutrophication (Walsh *et al.* 1985). The area of elevated deposition described here is apparently defined by the convergence of the Virginia Current and the Gulf Stream. Oscillations in the position of the zone over hundreds or thousands of years may have caused episodic changes in the rate of delivery and composition of organic matter delivered to the seabed, in turn creating offsets in the organic carbon $\Delta^{14}C$ and $\delta^{13}C$ records. Future investigations should examine other convergence zones that may also function as depocenters, such as the slope off eastern Japan.

CONCLUSIONS

1. The continental slope off Cape Hatteras, N.C. from approximately 36° 00'N to 35° 20'N

is a region of relatively high sediment accumulation, organic matter deposition and subsequent remineralization. The rates reported are the highest reported for the slope off of the eastern U.S. The areal coverage of this "depocenter" is probably controlled by interactions between physical oceanographic processes and the rugged topography of the seafloor.

2. Most of the organic matter deposited on the seafloor is marine in origin and reactive. Seabed preservation efficiencies range from 7 to 27%. The age of DIC and CH_4 produced within the seabed, as well as the age of infauna, indicate that relatively young, reactive carbon is advected below the sediment surface and fuels subsurface remineralization.

3. Non-steady state deposition of organic material affects subsurface remineralization. Some methane production may be the result of more rapid deposition in the past. In addition, present-day deep irrigation extends the zone of $SO_4^=$ reduction, increasing the depth of biogenic methanogenesis.

4. The stable isotopic composition of DIC is produced within the seabed by the selective degradation of a fraction of the organic matter. This metabolizable apparently has a carbon isotopic signature of -17 to -19‰, while the organic matter that survives degradation and is buried has a $\delta^{13}C$ closer to -20‰. Carbonate dissolution does not extensively affect the isotopic signature of the DIC subsequently fluxing out of and being buried in the seabed.

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Table 1. Locations of sampling stations.

Transect	Station	Depth (m)
36° 20'	N501	501
	N740	740
	N1027	1027
35° 51'	M415	415
	M620	620
	M811	811
	M1170	1170
35° 25'	S295	295
	S480	480
	S818	818
	S1200	1200
35° 23'	Site III	850

Table 2. Carbon budgets for four continental slope sites off Cape Hatteras, NC. Reported depths are for kasten core deployments at each site. Units are moles C m^{-2} yr^{-1} ± S.D., unless otherwise noted. Data for DIC fluxes and production rates are pooled from sub deployments at the same coordinates. Water depths recorded during sub core collection deviate as much as 50m from depths recorded during Kasten core collection. N.d. means no data collected.

Station **Transect** **Water Depth (m)**	**N740** **36° 20'** **740**	**M620** **35° 51'** **620**	**S818** **35° 25'** **818**	**Site III** **35° 23'** **850**
^{14}C Accumulation Rate (cm ky^{-1})†	84 ± 5	115 ± 4	37 ± 4	108 ± 57
Weight % Organic Carbon	2.5 ± 0.2*	2.7 ± 0.3*	1.4 ± 0.2*	1.4 ± 0.1
Dry Bulk Density (g sed cm^{-3})	0.40	0.68	1.07	0.43
Burial Depth for Calculations (cm)	225	175	185	125
^{234}Th inventory (dpm cm^{-2})	2.9 ± 0.5 (n = 4)	9.9 (n = 1)	30.6 ± 9.5 (n = 2)	28.4 ± 7.9++ (n = 5)
Minimum C_{org} Deposition Rate	3.6 ± 3.3	7.7 ± 4.0	7.2 ± 3.7	4.3 ± 1.1
DIC Diffusive Flux	2.9 ± 2.8 (n = 9)	5.7 ± 4.0 (n = 6)	6.7 ± 3.7 (n = 4)	3.7 ± 1.0 (n = 4)
Porewater Burial: DIC	0.01	0.05	0.004	0.04
CH_4	n.d.	1.0×10^{-3}	2.0×10^{-6}	2.0×10^{-3}
POC Burial	0.7 ± 0.04	2.0 ± 0.1	0.5 ± 0.06	0.6 ± 0.35
Preservation Efficiency (%)‡	20 ± 22	27 ± 14	7 ± 3	14 ± 9

* From Martens *et al.* (In prep.)

++ From Fornes (1996)

† Values are the slope ± standard error of a line fit by least squares to ^{14}C ages and depth.

‡ $$\textit{Preservation Efficiency} = \frac{\textit{POC Burial Rate}}{\textit{Deposition Rate}} \times 100$$

Table 3. Diffusive fluxes and DIC production rates at four sites on the Cape Hatteras continental slope.

Station **Transect**	**N740** **36°20' N**	**M620** **35°51' N**	**S818** **35°25' N**	**Site III** **35°23' N**
DIC Flux (moles C m^{-2} yr^{-1})	2.9 ± 2.8 (n = 9)	5.7 ± 4.0 (n = 6)	6.7 ± 3.7 (n = 4)	3.7 ± 1.0 (n = 4)
O_2 Flux (moles O_2 m^{-2} yr^{-1})	3.9 ± 1.8 (n = 8)	5.3 ± 2.9 (n = 6)	5.8 ± 3.8 (n = 4)	3.8 ±0.7 (n = 4)
DIC Production (moles C m^{-2} yr^{-1})	4.7 (n = 1)	2.6 ± 0.5 (n = 2)	3.1 ± 0.01 (n = 2)	
DIC/O_2 Flux Ratio	0.7	1.1	1.1	1.0

Table 4. Carbon isotope mass balance for Station M620 on the 35° 51'N transect.

	J (moles m^{-2} yr^{-1})	**$\delta^{13}C$** (‰)
DIC		
Diffusive	5.7 ± 4.0	-17.1 ± 1.3
Buried	0.05	-16.0
CH_4		
Buried	0.001	-86.2
J_{rem}	5.8	-17.1
POC		
Buried	1.6	-20.9
J_{tot}	**7.4**	**-17.8**

Table 5. Carbon budgets for other slope sediments. Units are moles C m^{-2} yr^{-1} unless otherwise noted. N.r. means not reported. Compiled from: Müller and Suess 1979, Henrichs and Farrington 1984, Walsh *et al.* 1985, Walsh *et al.* 1988, Rowe *et al.* 1988, Anderson *et al.* 1988, Archer and Devol 1992, Reimers *et al.* 1992, and Anderson *et al.* 1994.

Budget Term	Slope off Cape Cod (SEEP-I)	Mid-Atlantic Bight (SEEP-II)	Washington Slope	Central California Slope	Peru
ω-- cm ky^{-1}	10-20	30 - 60	n.r.	1.3 - 77	66 - 140
g_{sed} cm^{-2} yr^{-1}	0.02	0.02 - 0.05	0.02 - 0.05	n.r.	n.r.
Wt. % OC	1	1 - 3	2.7	0.7 - 4.3	2-3
OC Deposition Rate	1 - 2	2	3	0.4 - 1	
C Equivalent O_2 Flux*	0.2 - 0.4	1.5 - 2.1	0.8	0.05 - 0.5	
POC Burial	0.1 - 0.2	0.5 - 1.0	1.1	0.02 - 0.3	3
Burial Efficiency (%)	20	25 -50	35	5 - 30	12

* DIC fluxes out of the sediment were not actually measured, instead the authors estimated the DIC flux from measured O_2 fluxes.

Figure Legends

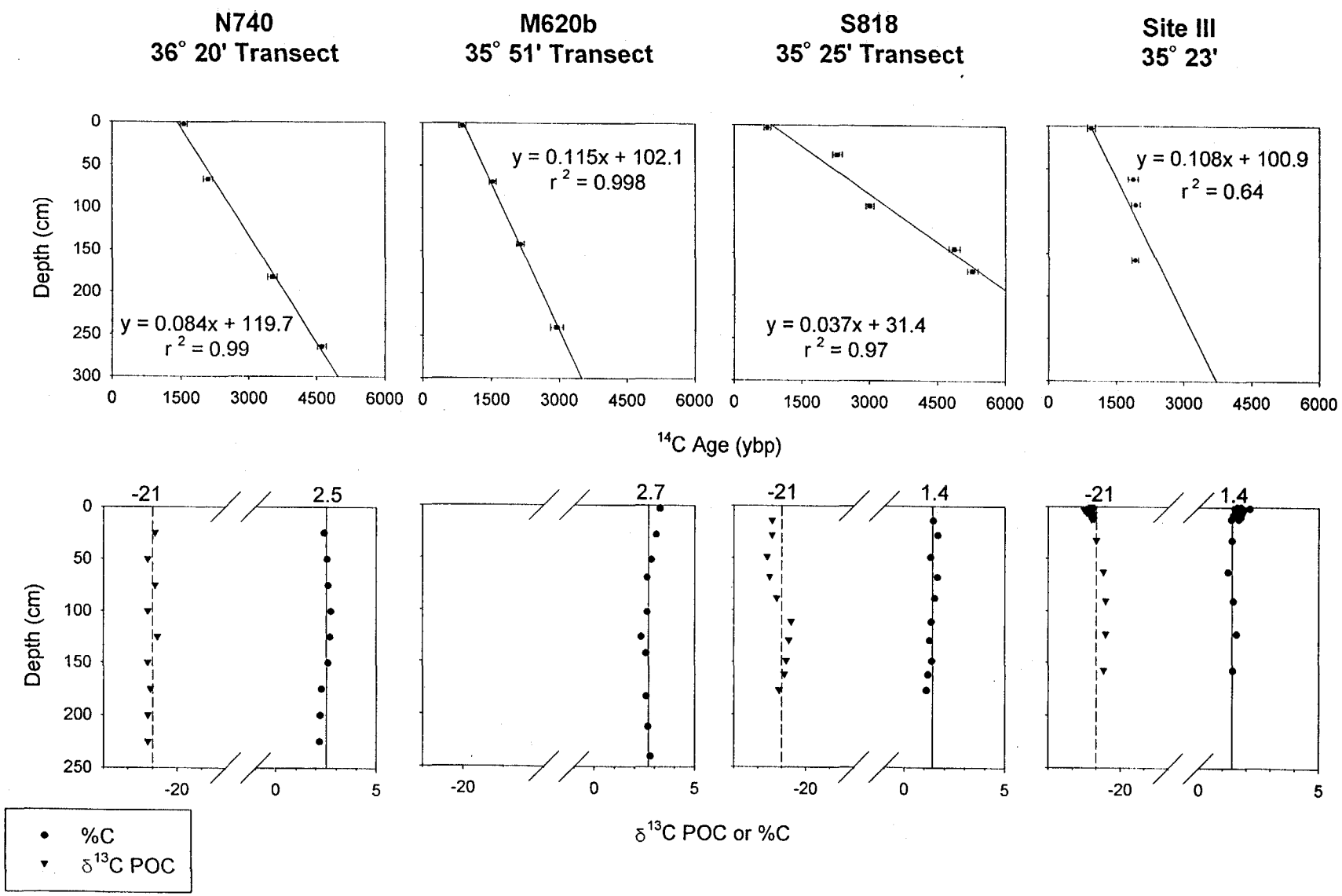
Fig. 1. POC ^{14}C ages, wt. % OC, and $\delta^{13}C$ POC for the four budget stations. The regressions between POC ^{14}C ages and depth used to generate sediment accumulation rates are shown in the upper panels.

Fig. 2. POC ^{14}C ages, wt. % OC, and $\delta^{13}C$ POC for non-steady state stations.

Fig. 3. ^{14}C ages of POC, DIC and CH_4 from kasten cores collected at four locations on the N.C. continental slope.

Fig. 4. Porewater profiles of $\delta^{13}C$ DIC and DIC and CH_4 concentrations in slope sediments. Actual CH_4 concentrations are 100x higher than shown in the (*) plots.

Fig. 5. The concentration versus $\delta^{13}C$ value of porewater DIC. Solid and broken lines represent the mixing curve for the addition of DIC with a $\delta^{13}C$ of -18 ± 1‰ to bottom water (2 mM, 0‰).


N740
36° 20' Transect
M620b
35° 51' Transect
S818
35° 25' Transect
Site III
35° 23'
Depth (cm)
y = 0.084x + 119.7
r 2 = 0.99
y = 0.115x + 102.1
r 2 = 0.998
y = 0.037x + 31.4
r 2 = 0.97
y = 0.108x + 100.9
r 2 = 0.64
14C Age (ybp)
-21
2.5
2.7
1.4
δ13C POC or %C
%C
δ13C POC

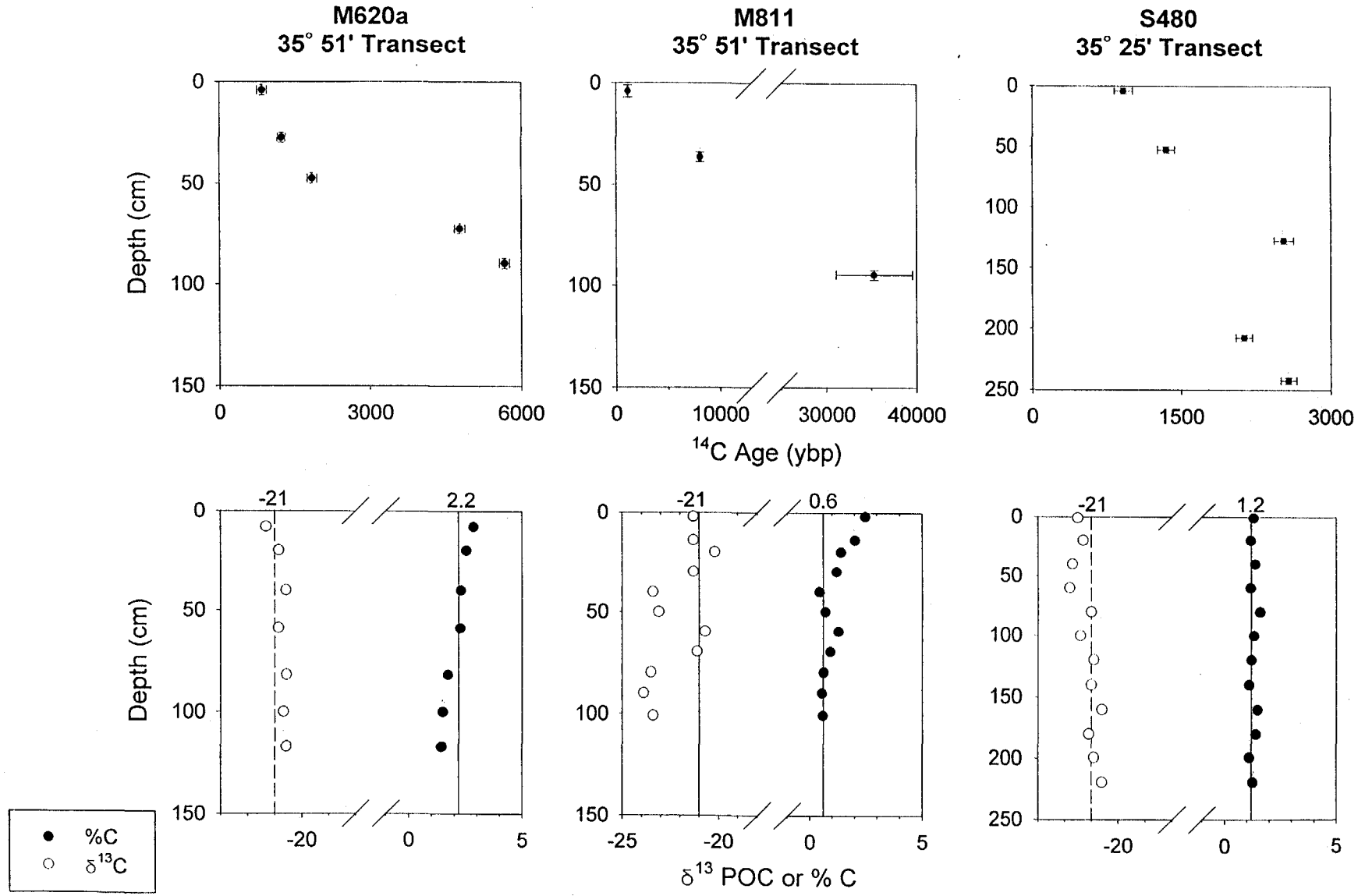

M620a
35° 51' Transect
M811
35° 51' Transect
S480
35° 25' Transect
Depth (cm)
0
50
100
150
200
250
0
3000
6000
10000
30000
40000
1500
^{14}C Age (ybp)
-21
2.2
0.6
1.2
-25
-20
5
δ^{13} POC or % C
%C
δ^{13}C

Fig 3

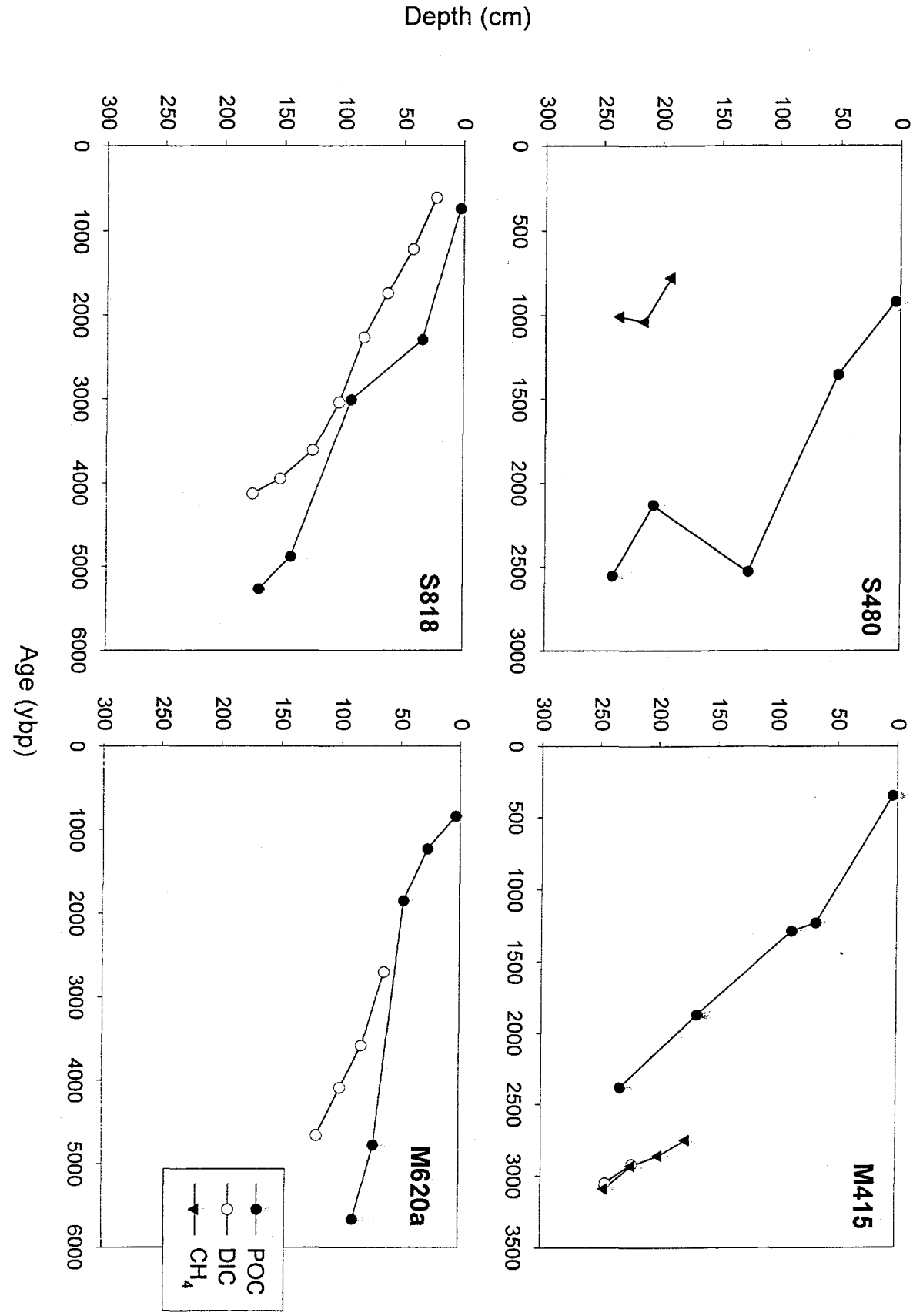


Fig. 4

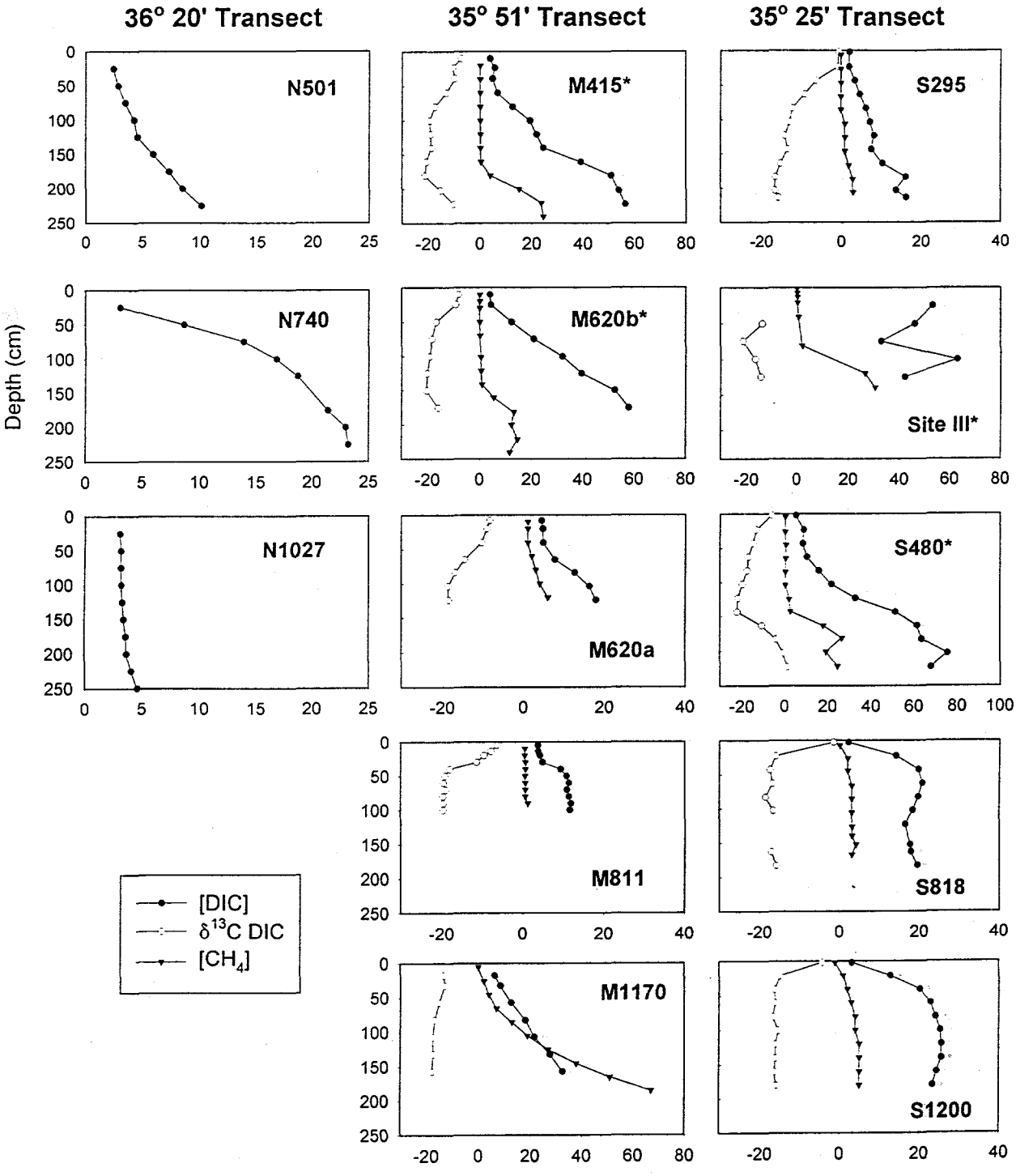
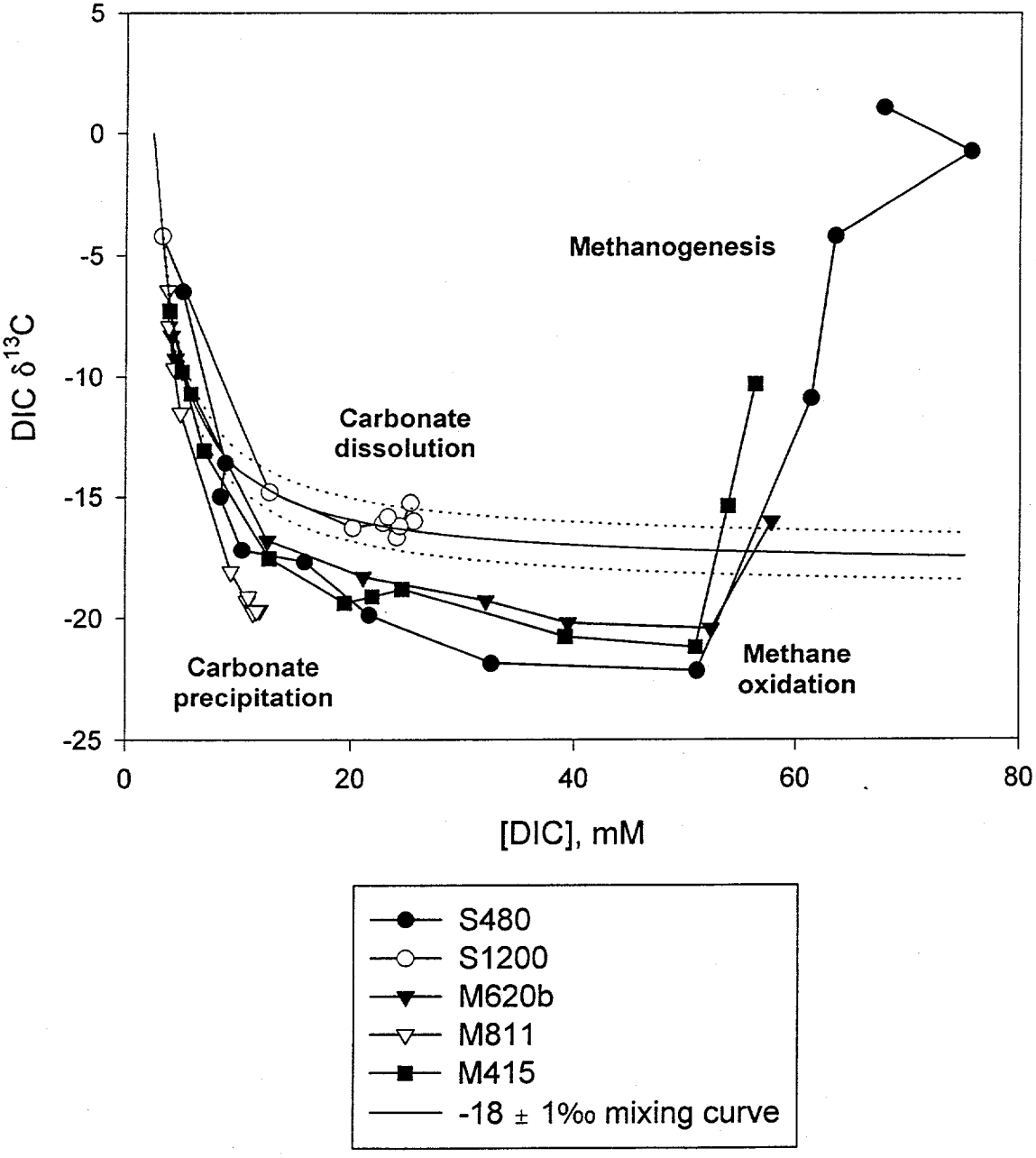

36° 20' Transect
35° 51' Transect
35° 25' Transect
Depth (cm)
N501
M415*
S295
N740
M620b*
Site III*
N1027
M620a
S480*
M811
S818
M1170
S1200
[DIC]
δ13C DIC
[CH4]
δ13C DIC, [CH4] µM, or [DIC] mM
* [CH4] µM x 10-2

Fig 5


5
0
-5
-10
-15
-20
-25
DIC δ13C
0
20
40
60
80
[DIC], mM
Methanogenesis
Carbonate dissolution
Carbonate precipitation
Methane oxidation
S480
S1200
M620b
M811
M415
-18 ± 1‰ mixing curve