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Doctoral Dissertation

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Abstract

Organic carbon input, degradation and preservation in continental margin sediments: an assessment of the role of a strong oxygen deficient zone

by Hilairy Ellen Hartnett

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Rates of organic carbon input, oxidation and burial in marine sediments were studied with the goal of assessing the role of an oxygen deficient water column in the preservation of organic matter. Factors influencing these rates were investigated in two locations: the Washington state and NW Mexican continental margins. The Mexican continental margin is in contact with the oxygen deficient zone of the eastern tropical North Pacific. Carbon budgets for the Washington and Mexican margins indicated a larger percentage of the surface export flux reached the sediments and a greater fraction of the material arrived at the seafloor escaped degradation to be buried permanently. The attenuation in the carbon oxidation rate with water column depth for the Mexican margin was less than is typical of other margin regions. Empirical attenuation coefficients derived from a power function relation were 0.931 and 0.439 for the Washington and Mexican margins, respectively. Multi-G type models suggested that organic matter degraded in Mexican sediments was less reactive than that in Washington sediments. Sediment slurry and whole-core incubations were conducted to assess the effects of mixing and oxygen exposure on the rate and extent of carbon degradation. Sediments from the Mexican oxygen-deficient zone were less susceptible to degradation than sediments from the oxic Mexican shelf and the Washington margin under all incubation

conditions, suggesting that the organic matter in the oxygen-deficient zone may be intrinsically less reactive. The isotopic fractionation of oxygen and nitrogen during respiration was measured on both margins. The apparent respiration fractionation factor, α , for oxygen under conditions of carbon-limited degradation was 0.992. It was hypothesized that long oxygen exposure times, respiration under isotopically fractionating conditions and organic carbon:mineral surface-area ratios less than 1.0 are each related to the extent of degradation and imply low carbon burial efficiencies. High carbon burial efficiencies (and low carbon oxidation efficiencies) were found in oxygen-deficient zone sediments which had short oxygen exposure times, little or no fractionation of oxygen and nitrogen and carbon:surface-area ratios >3.0 .

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DEDICATION

The author wishes to dedicate this dissertation to the memory of my grandfather, Joseph Henry Twist. He would have been proud to know that, like him, I had become a scientist.

CHAPTER 1: INTRODUCTION

ORGANIC CARBON PRESERVATION IN MARGIN SEDIMENTS

Organic carbon exists on this planet in forms that range from shales to sharks, bacteria to blue whales, humics to humans. Organic carbon is the basis for all life on earth and the pool sizes and time scales through which it cycles range from micrograms to megatons and milliseconds to millions of years. The global organic carbon (OC) cycle is balanced between the very large pool of carbon in sedimentary rocks ($15,000 \times 10^{18}$ g C, Hedges, 1992) with extremely slow turnover times and the smaller, but extremely dynamic pools of carbon on land and in the ocean. Primary production in the surface ocean produces a flux of approximately 50 Gt OC yr^{-1} ($1 \text{ Gt} = 10^{15} \text{ g}$) to the deep ocean. This flux is recycled so efficiently that less than 0.1 Gt yr^{-1} reaches the sediments; therefore, a relatively tiny flux feeds the enormous pool of organic carbon in sedimentary rock. The 'bottleneck' in the carbon cycle, where organic matter is buried, is potentially the best place to investigate relationships between how and why carbon is degraded and how and why carbon is preserved. The processes that degrade and preserve carbon establish links between the carbon cycle and the oxygen cycle as well as the cycles of other biogeochemically relevant elements: nitrogen, phosphorus, sulfur, iron, and manganese (Bernier, 1982; Canfield, 1993; Holland, 1978; Ingall et al., 1993). This balance between organic carbon preservation and supply of oxygen to the atmosphere is fundamental to contemporary life on Earth because it maintains the concentrations of oxygen in our atmosphere. The task remains, however, to illuminate the links between the rapid and virtually complete decomposition of organic carbon in the waters of the ocean and the preservation of the tiny residual fraction of that same carbon in the essentially non-reactive pool of sedimentary organic carbon (Hedges, 1992).

Over 90% of all organic carbon burial presently occurs in continental margin sediments (Hedges and Keil, 1995; Premuzic et al., 1982; Romankevich, 1984), making the continental margins geochemically important as one of the long term sinks in the global carbon cycle. In spite of numerous studies demonstrating empirical relationships between organic carbon burial and such factors as primary productivity (Calvert and Pederson, 1992; Pedersen and Calvert, 1990), organic carbon rain rate (Jahnke, 1990), sedimentation rate (Betts and Holland, 1991; Müller and Suess, 1979; Stein, 1990), organic carbon degradation rate (Emerson, 1985b), bottom-water oxygen concentration (Demaison and Moore, 1980; Paropkari et al., 1992), and oxygen exposure time (Hartnett et al., 1998; Hedges et al., in press), the mechanisms directly controlling sedimentary organic carbon preservation remain unclear.

OXYGEN AND ORGANIC CARBON PRESERVATION

One of the long-standing debates in the geochemical community has been the precise nature of the role oxygen plays in the preservation of organic carbon. It was determined very early on in the history of oceanography that sediments with the highest organic carbon contents were often found in association with high surface water productivity or with low bottom-water oxygen concentrations (Fleming and Revelle, 1939; Trask, 1939). The first reported correlation between the concentration of bottom-water oxygen and the carbon content of the sediments was that of Richards and Redfield (1954). It has since been shown that some of the highest sedimentary organic carbon contents are found in association with the three permanent oxygen deficient zones in the ocean: the Arabian sea (Paropkari et al., 1992; Pedersen et al., 1992), the Peru upwelling zone in the eastern tropical south Pacific (Demaison and Moore, 1980; Henrichs and Farrington, 1984) and the eastern tropical north Pacific off the coast of central America (Hartnett et al., 1998). High sedimentary organic carbon is also found in more localized low-O₂ regions: the Black Sea, Cariaco Trench, Santa Monica Basin, and numerous small, permanently or seasonally anoxic embayments (most notably the fjords of Scandinavia and the Pacific Northwest of N. America). Taken as a group these regions

encompass a broad range in location, depth, proximity to shore, sedimentation rate, productivity, and organic carbon input rate. They also share a common feature very low bottom-water oxygen concentrations.

In addition to the classical mechanisms for carbon preservation mentioned earlier, recently it has been suggested that the oxygen control on organic carbon preservation may work in concert with a variety of other mechanisms. These include adsorption to mineral surfaces and redox oscillation between oxic and anoxic conditions. Organic carbon is associated mineral grains in proportion to particle size. Organic matter protection via surface adsorption may operate by sterically excluding microorganisms and/or their enzymes from the micropores where the organic matter is concentrated (Keil et al., 1994b; Keil et al., 1994c; 1994a; Mayer, 1994b). Surface adsorption may also involve some chemical interaction which renders the organic matter less reactive. Redox oscillation has also been proposed as a mechanism for more efficient degradation of organic matter (Aller, 1994) in which exposure to oxygen is most effective when it alternates with sub-oxic conditions.

GOALS AND STRUCTURE OF THIS WORK

To understand what controls the preservation of organic carbon in sediments it is critical to determine what factors control the rates and extents of organic carbon degradation in sediments. To this end, I have endeavored to evaluate the degradation of organic carbon in continental margin sediments from three investigative perspectives. The majority of my work has been based on samples collected during four major cruises, two each to the eastern tropical and eastern temperate north Pacific. The eastern tropical north Pacific is one of the three permanent oceanic oxygen deficient zones, while the eastern temperate north Pacific is a typical western continental margin. I have utilized *in situ* measurements, controlled laboratory incubation experiments and stable isotope measurements to address the rate and extent of carbon degradation under different redox conditions and over various time scales. These studies were then evaluated in terms of

carbon burial efficiency and oxygen exposure time to assess preservation of organic matter in marine sediments.

Chapter two is an investigation of carbon oxidation rates in continental margin sediments. The total carbon oxidation rate was determined from the measured oxidation rates by individual electron acceptors (O_2 , NO_3^- , and SO_4^{2-}); the relative importance of the different electron acceptors was evaluated for the two margins. The carbon oxidation rate was related to carbon input rate, and the attenuation of the carbon oxidation (or input) rate with depth was determined for each margin. The Mexican margin carbon oxidation rates did not attenuate as rapidly with depth as rates for the Washington margin did, such that a much greater percentage of the organic matter produced in the surface ocean reaches the Mexican sediments. I hypothesized that the lower attenuation was a result of reduced organic matter decomposition in the oxygen deficient zone. In addition, the benthic fluxes and total carbon oxidation rates were used to calculate nutrient regeneration ratios; these ratios revealed non-Redfield regeneration of carbon, nitrogen and phosphorous. The differences between the C:N regeneration ratios on the two margins provide evidence that no oxidation of NH_4^+ occurred in the anoxic Mexican sediments. Carbon budgets for each margin indicated that a greater percentage of the export flux from the surface ocean reached the Mexican margin sediments and that a larger fraction of the material that reached the seafloor escaped oxidation to be permanently buried.

In the third chapter, I present results from a series of sediment incubation experiments to determine the effects of oxygen exposure and physical mixing on organic carbon degradation using sediments from the same continental margins sites where I had previously examined organic carbon oxidation rates. A combination of well-mixed slurry experiments and whole-core incubations, each under oxic and anoxic incubation conditions, indicated that organic matter reactivity was potentially as important as oxygen exposure and/or physical mixing in such short-term incubations. Very high rates of organic matter degradation were observed in the incubation experiments, but little or no effect in the rates could be attributed to the oxic versus anoxic treatment. The pattern of

apparent organic matter reactivity corresponded instead to the broad distribution in organic carbon content on the two margins.

Chapter four presents an investigation of the potential for using the microbial fractionation of the stable isotopes of oxygen and nitrogen during respiration as an indicator of the relative degree of substrate or oxidant limitation on organic matter degradation. Experimental results indicated that oxygen isotopes were fractionated by approximately 8‰ under carbon-limited conditions, as evidenced by changes in the isotopic composition of the dissolved oxygen in the overlying water. This represents a significant fractionation, not observed during respiration under oxidant-limited conditions. Observed changes in the ^{15}N isotopic composition of NO_3^- , NH_4^+ , and N_2 during *in situ* and laboratory experiments suggested that sedimentary processes can effect the isotopic composition of overlying waters and that many combinations of processes were possible. Comparison of the results to a similar study from a shallow, estuarine environment led to a scenario in which, depending on the combination of nitrification and denitrification rates, sediments can serve as a net sink for either heavy or light nitrate.

The overarching goal of this thesis was to relate these degradation studies to the patterns and distributions of organic carbon preservation in continental margin sediments. In the final chapter I have interpreted my studies of carbon oxidation rates, the roles of oxygen and mixing in organic matter degradation and the stable isotope signature of sedimentary processes during organic matter decomposition in the context of the burial and preservation of organic carbon. I have also re-assessed the role of the Mexican margin oxygen deficient zone in the transfer of organic matter to the sediments using a multi-G (*sensu* Berner) type model and suggested that the organic matter reaching the sediments off Mexico is less reactive than that off Washington. The relationships between the controls on carbon oxidation in sediments and between regions of oxidant-limited and carbon-limited organic matter degradation are used to provide a more detailed mechanism for the preservation of organic matter in marine sediments.

CHAPTER 2: CARBON INPUT AND OXIDATION ON THE CONTINENTAL MARGINS OF NORTHWESTERN MEXICO AND WASHINGTON STATE: THE INFLUENCE OF THE OXYGEN DEFICIENT ZONE

INTRODUCTION

Continental margin sediments are ultimately the sink for >90% of the organic matter buried in the world's oceans (Hedges and Keil, 1995; Romankevich, 1984; Walsh, 1991). The high organic matter content of the sediments adjacent to the continents results from a combination of higher primary production rates over continental margins and rapid export of that production to sediments on shelves (Eppley and Peterson, 1979), and slopes (Walsh, 1991; Walsh et al., 1985). In addition to being regions of high carbon burial, continental margins are also sites of intense benthic recycling of organic matter and, as such, are a significant and dynamic component of the global budgets for organic carbon and nitrogen (Bender et al., 1989; Berelson et al., 1996; Christensen et al., 1987; Devol and Christensen, 1993; Jahnke, 1990; Jahnke et al., 1990; Reimers et al., 1992).

The oxidation of carbon in margin sediments proceeds at rates that are much higher than those in deep-sea sediments and despite being regions of high burial, the majority of the organic matter reaching the sediments is efficiently remineralized. However, little consensus has been reached, as to the factors that control the balance between carbon degradation and preservation in sediments. The role of oxygen in particular, because it is the primary electron acceptor for organic matter degradation, has been especially controversial (Calvert et al., 1992; Canfield, 1994; Hartnett et al., 1998; Hedges et al., 1997; Henrichs and Reeburgh, 1987; Lee, 1992; Paropkari et al., 1992; Pedersen et al., 1992). Despite the debate over the role of O₂ in organic matter preservation and degradation, only a few studies of carbon input and oxidation have specifically compared the input and degradation of organic carbon under normal and low

oxygen conditions in oceanic environments (Henrichs and Farrington, 1984; Paropkari et al., 1992; Pedersen et al., 1992).

Continental margins are relatively shallow regions compared to the deep sea (generally < 3000 m, Pickard and Emery, 1982) and therefore may be more sensitive to the input of carbon from the surface ocean. The degree of attenuation in the carbon flux from the surface ocean is the primary factor controlling the amount of carbon reaching the sediments (Betzer et al., 1984; Martin et al., 1987; Suess, 1980). In this chapter I will present the results of an investigation of carbon oxidation in sediments and carbon input on the Washington and Mexican continental margins. Specifically I will address the role played by the oxygen-deficient zone (ODZ) of the Mexican margin in the oxidation of sedimentary organic matter by different metabolic pathways and the impact of the oxygen-deficient zone on the flux of carbon to the sediments. A carbon budget will be constructed which allows the efficiency of burial and oxidation on the two margins to be compared.

EXPERIMENTAL METHODS

STUDY AREAS

Samples were collected during three cruises (Figure 2.1 and Table 2.1) of the R/V New Horizon (spring, 1990, designated NH90; fall, 1993, NH93; and fall, 1996, NH96) to the continental margin of Northwestern Mexico and one cruise on the R/V Wecoma (summer, 1994, WE94) to the Washington State continental margin. The Mexican margin is distinguished by the presence of the strong oxygen-deficient zone of the eastern tropical North Pacific which impinges on the shelf and slope between depths of ~100 and 1000 m (for a general description of the regional oceanography *see* Roden, 1964). Water-column oxygen concentrations (Figure 2.2) between depths of 150 and 800 m were below the detection limit (<5 μM) for the standard oxygen titration method (Broenkow and Cline, 1969; Carpenter, 1964). The water column in this region has very

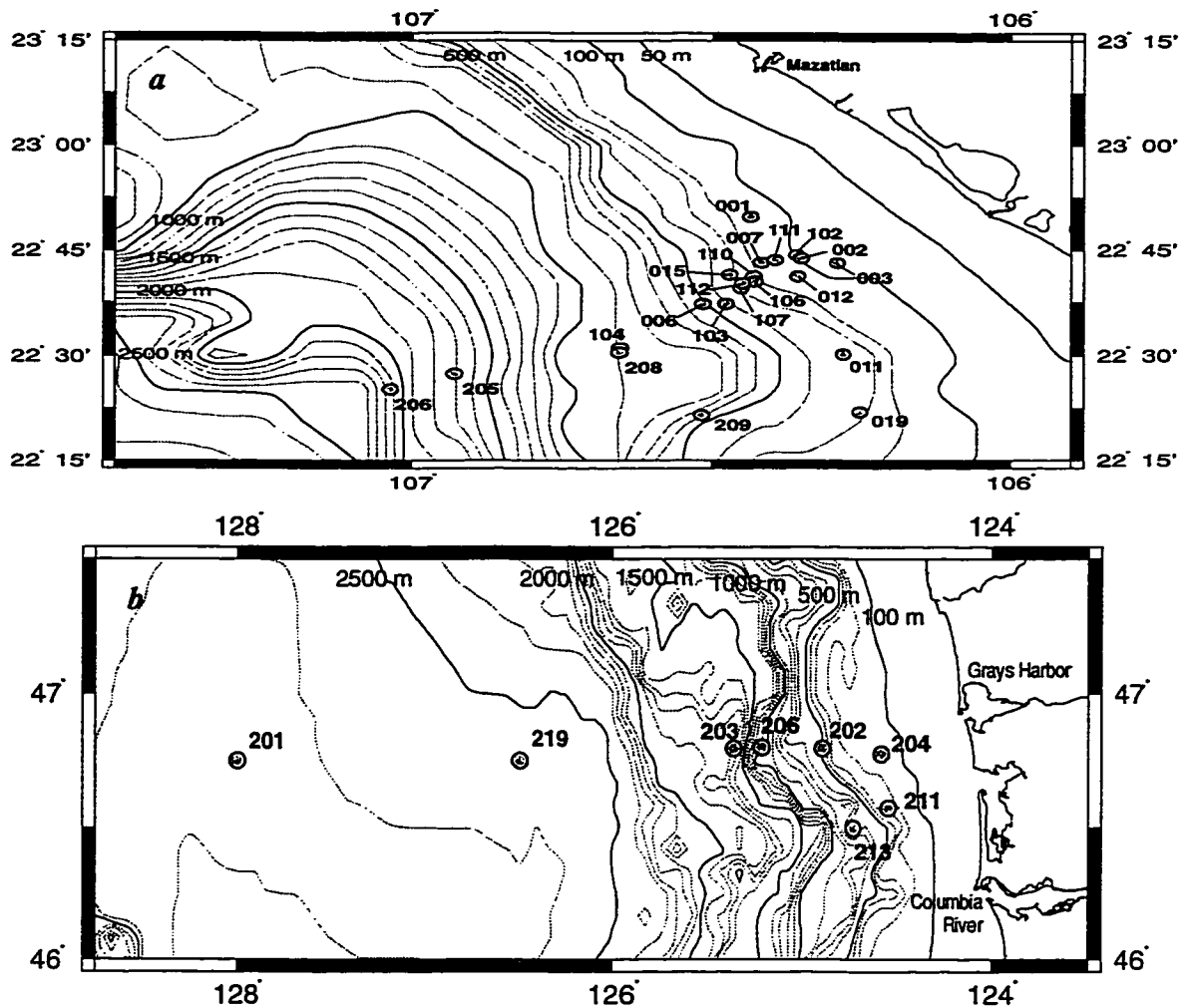


Figure 2.1 *a*) Locations of stations occupied during cruises NH90, NH93 and NH96 on the Mexican continental margin; *b*) locations of stations occupied during cruise WE94 on the Washington continental margin.

low oxygen concentrations because it is poorly ventilated by sluggish circulation due to its position in the shadow zone of the sub-tropical gyre (Huang and Russell, 1994; Luyten et al., 1983). In addition, the source waters for the ODZ include a component of North equatorial counter-current water that is relatively depleted in oxygen (Roden, 1964; Sverdrup et al., 1942). The Mexican margin has a somewhat narrow continental shelf with a shelf break at a water depth of ~200 m and a fairly steep continental slope

Table 2.1 Location, depth (m), distance from shore (nm), bottom-water oxygen concentration (μM), and surficial sediment, 0-0.5 cm, organic carbon content (wt. %) for stations from the NW Mexican and Washington state continental margins. Mexican margin station numbers are 000-series for NH90, 100-series for NH93, and 200-series for NH96. Washington margin stations have WE 200-series numbers.

Station	Latitude	Longitude	Depth	Distance offshore	$[\text{O}_2]_{\text{BW}}$	OC
NW Mexico						
NH 019	22° 22.0'	106° 15.1'	97	27.22	23	3.76
NH 003	22° 43.2'	106° 17.4'	100	8.17	6	2.50
NH 001	22° 55.9'	106° 26.2'	110	6.54	5	3.19
NH 011	22° 30.2'	106° 17.0'	135	20.17	3	3.70
NH 002	22° 43.8'	106° 21.1'	140	9.65	3	4.30
NH 102	22° 44.29'	106° 21.50'	145	9.04	1	5.47
NH 007	22° 43.2'	106° 25.1'	190	11.96	0	5.83
NH 111	22° 43.59'	106° 23.70'	220	10.79	0	6.91
NH 110	22° 41.19'	106° 25.86'	235	14.26	0	7.96
NH 106	22° 40.49'	106° 25.73'	250	14.85	0	7.69
NH 112	22° 40.27'	106° 26.97'	310	15.84	0	7.79
NH 012	22° 41.3'	106° 21.7'	322	11.86	0	6.87
NH 107	22° 39.60'	106° 27.10'	345	16.57	0	8.85
NH 015	22° 41.5'	106° 28.2'	420	15.81	0	8.98
NH 103	22° 37.30'	106° 28.60'	500	19.70	0	11.6
NH 006	22° 36.9'	106° 30.9'	620	21.42	0	10.7
NH 209	22° 21.50'	106° 31.06'	800	36.11	1	9.99
NH 104	22° 31.09'	106° 39.07'	1020	34.72	4	9.85
NH 208	22° 30.43'	106° 39.12'	1020	35.39	4	9.53
NH 205	22° 27.44'	106° 55.76'	1500	60.45	44	6.07
NH 206	22° 25.24'	107° 02.11'	2050	114.29	92	4.24
Washington						
WE 204	46° 46.63'	124° 35.27'	105	21.11	104	1.70
WE 211	46° 34.50'	124° 33.42'	219	19.90	106	2.26
WE 202	46° 47.83'	124° 54.41'	440	33.88	60	1.60
WE 213	46° 29.88'	124° 43.75'	620	26.83	39	2.04
WE 206	46° 48.10'	125° 12.73'	1025	46.14	38	2.52
WE 203	46° 47.83'	125° 22.81'	1994	52.87	56	2.35
WE 219	46° 45.02'	126° 29.93'	2525	97.72	62	1.32
WE 201	46° 45.08'	128° 00.09'	2746	157.80	87	1.18

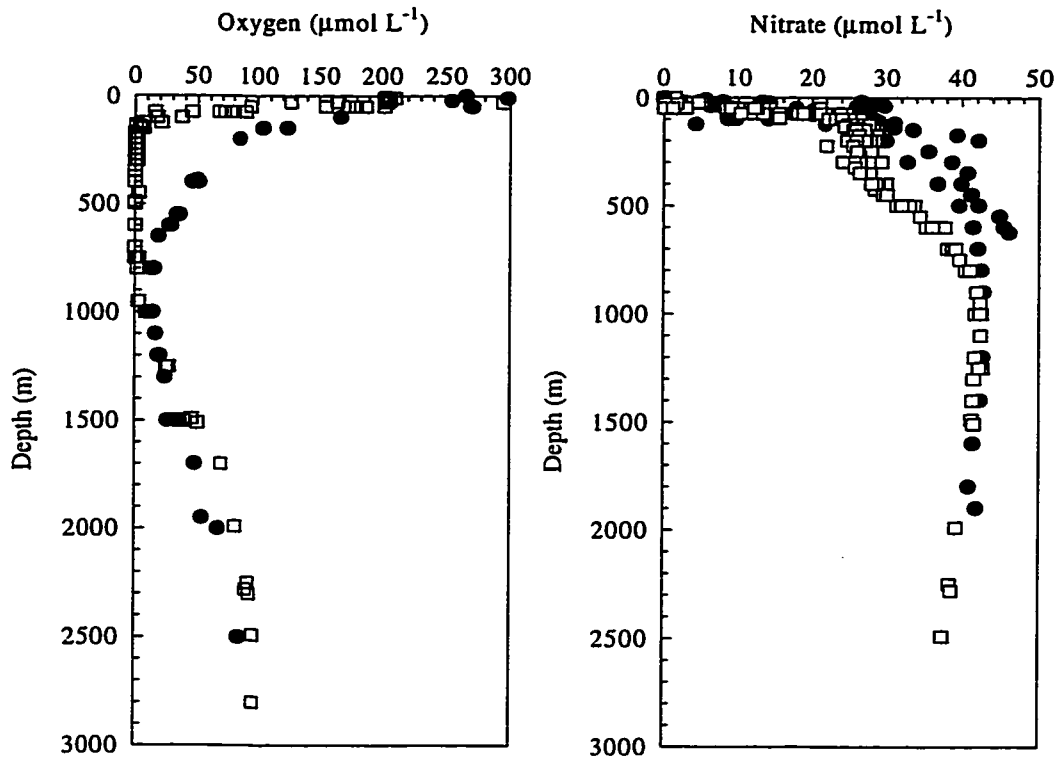


Figure 2.2 Water column oxygen and nitrate profiles for the continental margins of NW Mexico (open squares) and Washington State (filled circles). Data was collected during cruises NH90, NH93, NH96 and WE94.

(Figure 2.3). The near-shore, shallow sediments were quite sandy and had relatively low organic carbon contents (< 2 weight percent (wt. %), *see* Figure 2.4). Sediments below about 100-m were predominantly olive green silts and clays with higher organic carbon contents ranging from 2 to 12 wt. % (Hartnett et al., 1998). Deeper stations (> 1500 m) had a surficial layer of brown (oxidized) sediment with olive-green sediments below and organic carbon contents of ~ 3 to 4 wt. % in both layers.

The organic carbon contents in these sediments are substantially higher than is typical of continental margin sediments (Hedges, 1992; Hedges and Keil, 1995; Premuzic et al., 1982). Despite the observed high carbon contents, the Mexican margin, in the vicinity of the mouth of the Gulf of California, is generally less productive than typical

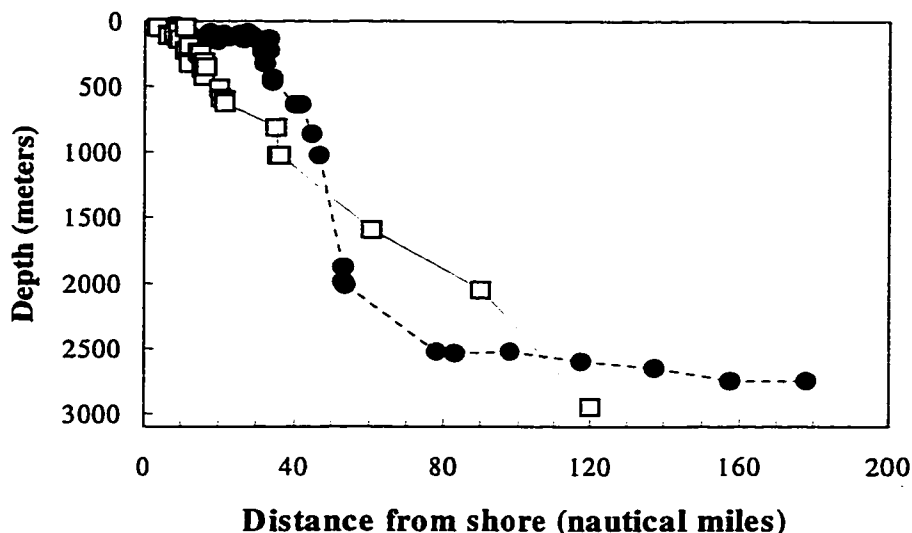


Figure 2.3 Depth vs. distance from shore for the continental margins of NW Mexico (open squares) and Washington State (filled circles).

western margins. Surface water chlorophyll (a) concentrations in this region are generally low, $<0.1 \text{ mg m}^{-3}$ in the summer and fall (Stevenson, 1970) with brief, small ($<2 \text{ mg m}^{-3}$) pigment concentration maxima in the late winter (Santamaría-del-Angel et al., 1994). Primary production rates for this region are between 51 and $91 \text{ g C m}^{-2} \text{ yr}^{-1}$ during the spring and summer (Stevenson, 1970).

The Washington margin is a typical western continental margin with seasonal, wind-driven upwelling. The margin has a broad continental shelf (Figure 2.3). The shelf break occurs at a depth of $\sim 180 \text{ m}$; the continental slope and rise extend to a depth of $\sim 2000 \text{ m}$ beyond which, the bathymetry deepens, gradually, seaward to the floor of the Cascadia Basin at about 2500 m . The sediment geochemistry of this margin has been described in detail previously by Hedges *et al.* (submitted), Devol and Christensen (1993), Archer and Devol (1992), and Gross et al., (1972) and Prahl (1985). The carbon contents in the Washington margin sediments ranged from $\sim 1 \text{ wt. \%}$ in shallow

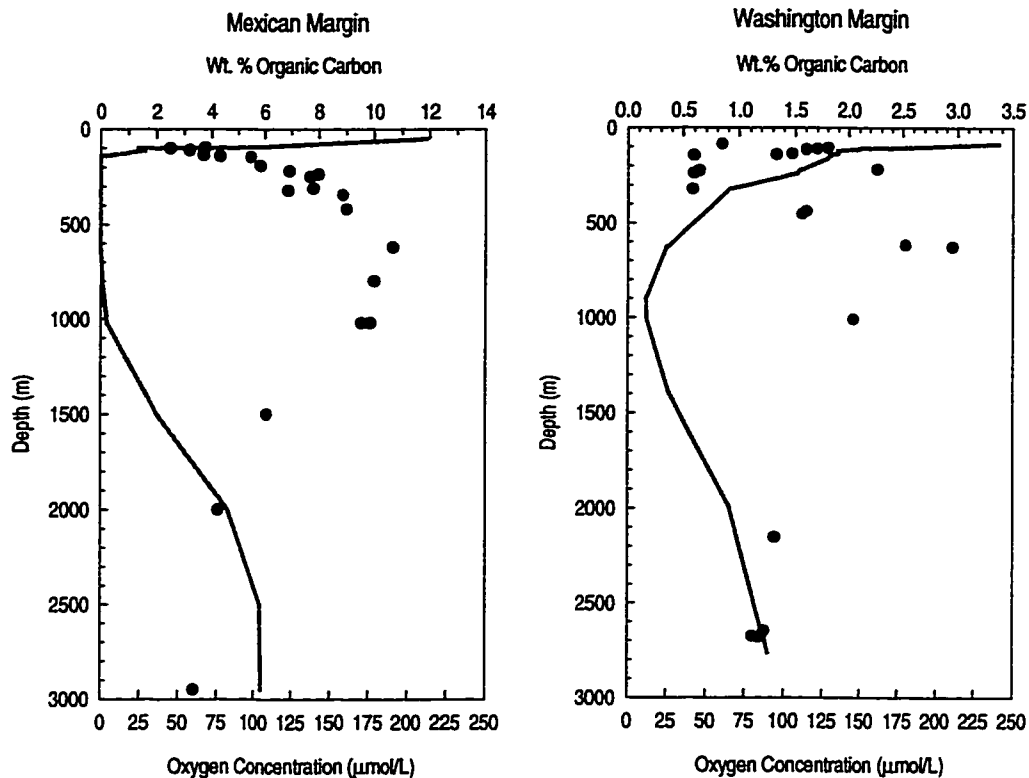


Figure 2.4 Surficial (0-0.5 cm) sediment organic carbon contents (wt. %) for (a) Mexican and (b) Washington margins. The oxygen profiles from Figure 2.2 are overlain to emphasize the position of the oxygen-deficient zone on the Mexican margin. Note difference in scales for wt. % OC in (a) and (b)

sediments up to ~3 wt. % in slope sediments. Sediments deeper than 2000 m had approximately 1 wt. % organic carbon. The Washington margin has an annual average primary production rate of $646 \text{ g C m}^{-2} \text{ yr}^{-1}$ on the shelf and $294 \text{ g C m}^{-2} \text{ yr}^{-1}$ on the continental slope (Perry et al., 1989).

BENTHIC FLUX MEASUREMENTS

Benthic fluxes of O_2 , N_2 , NO_3^- , NH_4^+ and PO_4^{3-} were measured using an *in situ* benthic flux chamber (hereafter referred to as the “lander”). The lander was deployed for 12 to 36 h with deeper stations having longer deployment times. For each deployment,

eight time-series samples were taken from the overlying water of the duplicate flux chambers; a bottom-water sample was collected at the end of each incubation. The lander was equipped with two small box cores and was usually recovered with the sediments and their overlying water intact. A detailed description of the benthic flux chamber and deployment techniques is given in Devol (1987) and Devol and Christensen (1993).

SEDIMENT TRAPS

Sediment traps were deployed at two stations (NH 104 and NH 103, 1020 and 530 m deep, respectively) on the NH93 and at station NH 206 (2050 m) on the NH96 cruise. The traps (Particle Interceptor Traps or PITs) were based on the Martin (1984) design, described in detail by Jannasch (1990). Duplicate traps were deployed as a moored subsurface array at four water depths on the NH93 cruise (220, 410, 620, and 903 m; and 150, 250, 350, and 450 m at the first and second stations, respectively) and at seven depths on the NH96 cruise (250, 500, 800, 1100, 1300, 1600, and 1800 m). The surface-most traps were below the depth of the mixed layer, which extended to approximately 50 m. Sediment traps deployments were three days long on the first cruise and four days long on the second cruise. Traps were deployed filled with filtered seawater ($0.5 \mu\text{m}$), and a brine solution ($0.02 \text{ kg NaCl L}^{-1}$) was siphoned into the bottom 10 cm of each trap. The brine provided a density barrier to prevent washout of sedimented material (Knauer and Asper, 1989). Trap material was vacuum filtered onto precombusted glass fiber filters (Whatman GF-F). Macrozooplankton (swimmers) were removed from the filters under low-power magnification. Filters were dried for 24h at 65°C and stored frozen or in a dessicator for later analysis. Samples were analyzed for organic carbon and nitrogen content on a Leeman Laboratories CHN elemental analyzer and there was no detectable difference in the two storage methods.

SEDIMENT SAMPLING

Sediment cores were collected at all stations with a Soutar box core. The box core lid sealed upon coring allowing the collection of both the sediment core and the overlying water. Great care was taken during retrieval to retain the overlying water and to preserve the sediment-water interface. Cores with a visibly disturbed sediment-water interface or that had exchanged overlying water with surface water upon recovery (as evidenced by the temperature and oxygen content of the overlying water) were discarded. Subcores for sectioning, whole-core squeezing and incubations for SO_4^- reduction rate were taken using 7.5-cm and 10-cm cast-acrylic core tubes. Core sectioning generally took place within one hour of coring. Cores were stored at approximate *in situ* temperatures (2 to 6 °C) to minimize effects due to warming. Subsectioning took place under N_2 in a glovebox at ~8 °C. Porewater was separated from the sediments by centrifugation at ~7,000 rpm for 20 min; supernatants were filtered through precombusted GFF filters before subsampling for nutrient analyses. Whole-core squeezing at *in situ* temperatures by a technique similar to that of Bender (1987) was used to obtain high-resolution pore water profiles of O_2 and NO_3^- . Porewater samples were expressed through an in-line Radiometer-style oxygen electrode (Brandes and Devol, 1995) before collection for nutrient analysis.

CHEMICAL ANALYSES

Samples for dissolved oxygen were collected from Niskin bottles and analyzed using the Carpenter (1964) modification of the standard Winkler titration (Winkler, 1888). Colorimetric low-level oxygen analyses (Broenkow and Cline, 1969) were done for ODZ stations during the NH93 cruise. Samples for O_2 and N_2 from the lander were collected with in-line nylon gas loops and analyzed by gas chromatography using a molecular sieve 5A column and a thermoconductivity detector (Devol and Christensen, 1993; Grundmanis and Murray, 1982). Lander nutrients and porewater nutrients (NO_3^- , NH_4^+ , and PO_4^{3-}) were measured on the first two cruises (NH90, NH93) with a Technicon Autoanalyzer using the methods described by Whitley et al. (1981); on the two later

cruises (NH96, and WE94) nutrients were measured manually according to the methods of Strickland and Parsons (1972). Dissolved iron and manganese were analyzed colorimetrically, using the ferrozine method for Fe, outlined by Stookey (1970) and the Brewer and Spencer (1974) formaldoxime method for Mn. Samples from the whole-core squeezer were analyzed for nitrate using a flow-injection analysis (FIA) technique based on the cadmium reduction method of Anderson (1979) and described by Lambourn et al. (1991).

SEDIMENT ANALYSES

Weight percent organic carbon and total nitrogen were determined on freeze-dried, ground sediment samples by the method of Hedges and Stern (1984) using either a Carlo-Erba model 1106 CHN elemental analyzer or a Leeman Laboratories CHN elemental analyzer. Sediment porosity was determined by the mass of water lost upon drying to a constant mass at 65 °C. Sediment accumulation rates were determined from profiles of ^{210}Pb determined according to the method of Carpenter et al. (1982). Sediment samples for radiocarbon dating were collected from the sectioned cores before centrifugation and stored in muffled, glass scintillation vials. Sediment ages (^{14}C) for determination of accumulation rate were measured at the National Oceanographic AMS facility at the Woods Hole Oceanographic Institute. Sulfate reduction rates were determined from incubations with ^{35}S -labeled SO_4^- and subsequent measurement of the ^{35}S -labeled sulfide produced (Christensen, 1989; Devol et al., 1984). The SO_4^- reduction rates were integrated over the top 30 cm of the sediment and corrected to the *in situ* temperature using a Q_{10} correction; this was generally a correction of fewer than 5 °C.

RESULTS

BENTHIC FLUXES

Benthic fluxes of oxygen, nitrate, ammonia and phosphate from lander deployments on the Mexican margin are presented in Table 2.2. Oxygen fluxes were always into the sediments (presented as negative values) and ranged from zero (unmeasurable flux) to $-2.27 \text{ mmol m}^{-2} \text{ d}^{-1}$.

Table 2.2 Benthic fluxes of oxygen, nitrate, ammonium and phosphate; bottom water oxygen (μM) and SO_4^- reduction rates (SO_4^- red.) for stations from the NW Mexican continental margin. Reported fluxes are average values for the two chambers on the lander. SO_4^- reduction rates were integrated to 30 cm and temperature-corrected. Fluxes of NH_4^+ and PO_4^3 marked with an asterisk were calculated from porewater profiles. Units for all fluxes and rates are $\text{mmol m}^{-2} \text{ d}^{-1}$.

Depth	Station	$[\text{O}_2]_{\text{BW}}$	O_2 flux	NO_3^- flux	NH_4^+ flux	PO_4^3 flux	SO_4^- red.
97	NH 019	23	-1.08	-0.61	0.03	0.03	2.53
100	NH 003	6	-0.98	-1.96	0.95	0.13	1.53
110	NH 001	5	-1.47	-1.91	0.32	0.29	0.86
135	NH 011	3	-0.86	-1.26	0.58	0.13	0.89
140	NH 002	3	-1.04	-1.24	1.17	0.14	0.92
145	NH 102	1	-0.86	-0.86	0.35	0.34	2.14
190	NH 007	0	-0.26	-2.38	0.19	0.31	1.29
220	NH 111	0	0.00	-1.61	0.39	0.12	1.88
235	NH 110	0	0.00	-0.90	0.57	0.17	1.36
250	NH 106	0	0.00	-0.70	0.33	0.25	0.86
310	NH 112	0	0.00	-1.02	0.65	0.29	1.17
322	NH 012	0	0.00	-1.03	0.37	0.73	0.89
345	NH 107	0	0.00	-1.71	0.36	0.09	1.19
420	NH 015	0	0.00	-1.12	0.34	0.34	0.87
500	NH 103	0	0.00	-1.22	0.60	0.18	0.31
620	NH 006	0	0.00	-0.78	0.12	0.02	1.29
800	NH 209	1	-0.21	-1.36	-0.12	0.06	0.67
1020	NH 104	4	-0.19	-0.18	0.15	0.00	0.61
1020	NH 208	4	-0.31	-0.44	0.03*	0.01*	0.12*
1500	NH 205	44	-1.83	-0.02	0.25*	0.02*	0.04
2000	NH 206	92	-2.27	-0.35	0.26*	0.04*	0.24*

Oxygen fluxes were unmeasurable in the Mexican oxygen deficient zone (ODZ). Nitrate fluxes, also always into the sediments, were roughly of the same magnitude as the O₂ fluxes (-0.02 to -2.38 mmol m⁻² d⁻¹) but with different distributions (*see* Table 2.2). In contrast to the O₂ fluxes, the largest NO₃⁻ fluxes were found in the ODZ. The average NO₃⁻ flux on the Mexican margin was 1.37 mmol m⁻² d⁻¹. Ammonium and phosphate fluxes were generally from the sediments to the overlying water (positive values) and ranged from -0.12 to 1.17 mmol m⁻² d⁻¹ and from 0.0 to 0.73 mmol m⁻² d⁻¹, respectively. The average NH₄⁺ flux on the Mexican margin was 0.38 mmol m⁻² d⁻¹ while the average PO₄³⁻ flux was 0.18 mmol m⁻² d⁻¹.

Oxygen fluxes on the Washington margin from the WE94 cruise ranged from -8.32 mmol m⁻² d⁻¹ in shallow shelf sediments to -0.37 mmol m⁻² d⁻¹ in deep continental rise sediments (Table 2.3). These values agree well with the range of oxygen fluxes presented in Devol and Christensen (1993) for similar sites on the Washington margin. Nitrate fluxes were also comparable to previously reported values (Devol and Christensen, 1993) and ranged from -0.06 to -1.54 mmol m⁻² d⁻¹. The average O₂ and NO₃⁻ fluxes on the Washington margin were -4.75 and -1.40 mmol m⁻² d⁻¹, respectively.

Table 2.3 Benthic fluxes of oxygen, nitrate, SO₄⁼ reduction rates (SO₄⁼ Red.) and bottom water oxygen (μM) for stations from the Washington state continental margin. Units for all fluxes and rates are mmol m⁻² d⁻¹.

Depth	Station	[O ₂] _{BW}	O ₂ flux	NO ₃ ⁻ flux	SO ₄ ⁼ Red.
105	WE 204	104	-8.32	-1.38	2.13
219	WE 211	106	-4.73	-1.54	3.22
440	WE 202	60	-2.53	-1.29	0.71
620	WE 213	39	-1.09	-0.54	0.44
1025	WE 206	38	-0.82	-0.41	0.04
1994	WE 203	56	-1.54	-0.09	0.18
2525	WE 219	62	-1.54	-0.08	0.05
2746	WE 201	87	-0.37	-0.06	0.001

ORGANIC CARBON AND TOTAL NITROGEN CONTENT AND SULFATE REDUCTION

Oxygen deficient zone sediments on the Mexican margin had organic carbon contents that ranged from ~2 wt. % at the shallowest depth sampled, 100 m, to >11 wt. % at 600 m (Figures 2.4 and 2.5). Sedimentary organic carbon contents decreased in stations deeper than 600 m to values of ~3 wt. % at 3000 m (Figure 2.4). Sedimentary total nitrogen contents ranged from 0.17 to 1.51 (Figure 2.6) and atomic carbon to nitrogen ratios, C:N(a), were relatively constant across all stations at 8.78 ± 1.4 . Down core profiles for all stations showed fairly constant organic carbon contents (Figure 2.5). On the Washington margin, carbon contents ranged from 0.5% in shallow shelf sediments

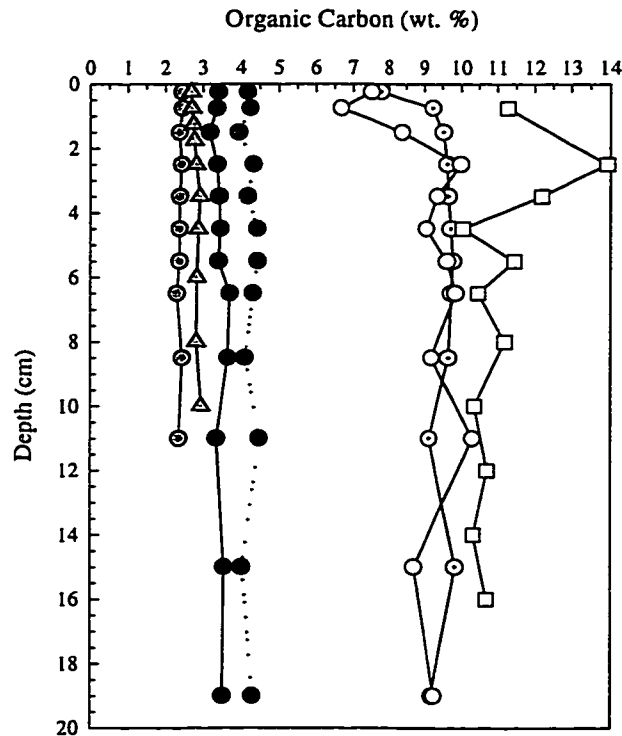


Figure 2.5 Sedimentary organic carbon (wt. %) profiles for representative stations on the Mexican margin from within (white symbols: 150–1000 m), above (gray symbols: < 100 m), and below (black symbols: >2000m) the oxygen deficient zone. Triangles are stations from NH90; squares, from NH93; and circles, from NH96.

to ~3% in slope sediments (Figure 2.4). This distribution reflects the presence of the mid-shelf silt deposit (MSSD) at ~150 m on the continental shelf. The MSSD is a depositional feature resulting from the large sediment load from the Columbia river and the local current structure and lies between the shallow (shoreward of ~60 m), inner-shelf modern sands and the non-depositional relict sands of the outer shelf (120-180 m) (*see* Nittrouer et al., 1983/1984; Nittrouer and Sternberg, 1981). The sandy sediments generally have lower organic carbon contents than do those of the MSSD. Fine-grained material with higher organic carbon contents accumulates within the MSSD and may also be transported to the continental slope. Total nitrogen concentrations for all stations ranged from 0.04 to 0.3 wt. %. The average C:N(a) ratio for the Washington margin stations was 9.59 ± 2.4 . On both margins the C:N ratio was fairly constant both down-core and across the margin (Figure 2.6).

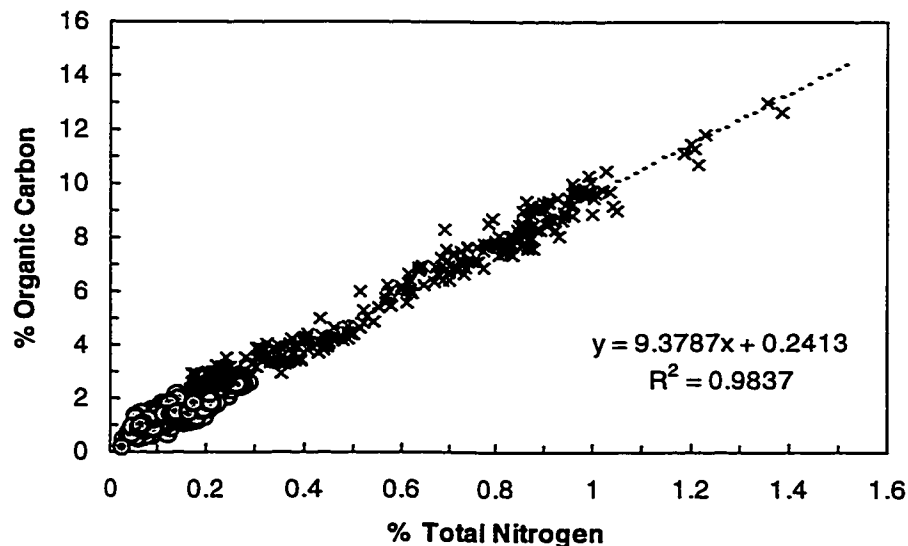


Figure 2.6 Sedimentary organic carbon (wt. %) vs. total nitrogen (wt. %) for all stations occupied during Washington (circles) and Mexican (crosses) continental margin cruises. The data from each station include samples from 0 to 36 cm depth collected at 1cm intervals. The slope of the line corresponds to an atomic C:N ratio of 8.04.

Sulfate reduction rates on the Mexican margin ranged from 2.50 $\text{mmol m}^{-2} \text{d}^{-1}$ at the shallowest station to 0.04 $\text{mmol m}^{-2} \text{d}^{-1}$ and averaged 1.06 $\text{mmol m}^{-2} \text{d}^{-1}$ (Table 2.2). Sulfate reduction rates on the Washington margin ranged from 3.22 at a shallow station to 0.001 $\text{mmol m}^{-2} \text{d}^{-1}$ at the deepest station (Table 2.3) with an average of 2.5 $\text{mmol m}^{-2} \text{d}^{-1}$. The SO_4^- reduction rates were somewhat variable but generally decreased with

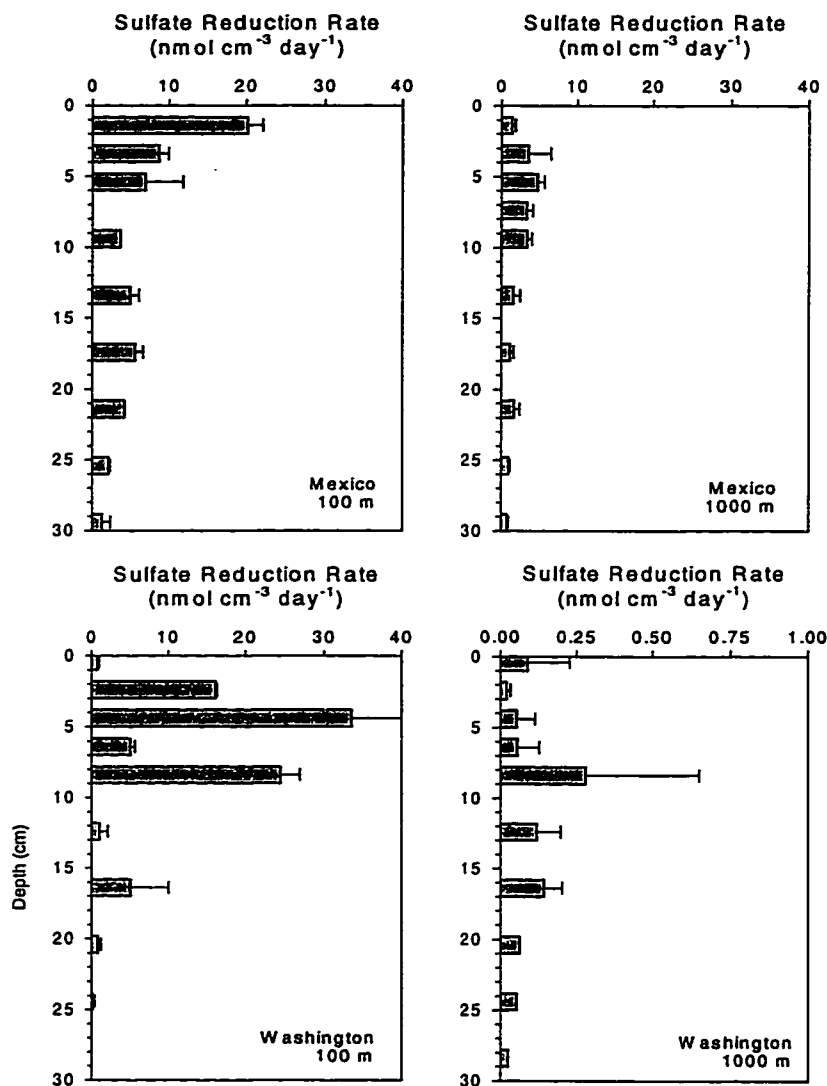


Figure 2.7 SO_4^- reduction rate profiles for representative stations from the continental margins of Mexico (upper panels) and Washington (lower panels). Units for all rates are $\text{nmol cm}^{-3} \text{day}^{-1}$ (note change in scale for the deep Washington station).

increasing water depth. Down core profiles of SO_4^- reduction (Figure 2.7) on both margins showed similar trends with a maximum between the surface and 10 cm and decreasing values deeper in the core. Sulfate reduction rates were generally quite low ($\ll 0.1 \text{ nmol cm}^{-3} \text{ d}^{-1}$) by 30 cm depth (*see also Kristensen et al., in press*).

POREWATER PROFILES

High resolution porewater profiles of O_2 and NO_3^- were determined by whole-core squeezing. The sediment-water interface was determined visually from the point where the squeezing piston was first touched the sediment and the point where the piston was fully in contact with the sediment. The distance (and tilt) over which the piston expressed both porewater and overlying water was used to deconvolute the resulting profile according to Brandes and Devol (1995). Porewater profiles from the Mexican margin generally had shallow and concurrent O_2 and NO_3^- penetration depths (Figure 2.8). No O_2 was detected in the porewaters of the ODZ sediments (~150-1000 m); below that zone, porewater O_2 and NO_3^- penetration depths increased slightly and become spatially separated. Concentrations of NH_4^+ and PO_4^{3-} (as well as NO_3^-) were measured in porewaters collected from sectioned cores. Nitrate concentrations from the sectioned cores agreed well with the high-resolution squeeze core profiles (data not shown). Ammonium concentrations generally increased down core from low values (~1 $\mu\text{mol L}^{-1}$) in surface sediments to higher concentrations deeper in the core (Figure 2.8a). The three most shallow stations had the highest NH_4^+ concentrations detected (260-390 $\mu\text{mol L}^{-1}$); maximum NH_4^+ concentrations were considerably lower (15 and 63 $\mu\text{mol L}^{-1}$) in sediments from the deeper stations. Phosphate profiles in the Mexican margin sediments were similar in shape to the NH_4^+ profiles and exhibited high phosphate maxima (70 to 150 $\mu\text{mol L}^{-1}$) in the shallower stations compared to the deeper stations (14-25 $\mu\text{mol L}^{-1}$; Figure 2.8).

In general, the continental shelf sediments had O_2 and NO_3^- concentrations that decreased simultaneously to penetration depths of less than 1 cm; concentrations of NH_4^+

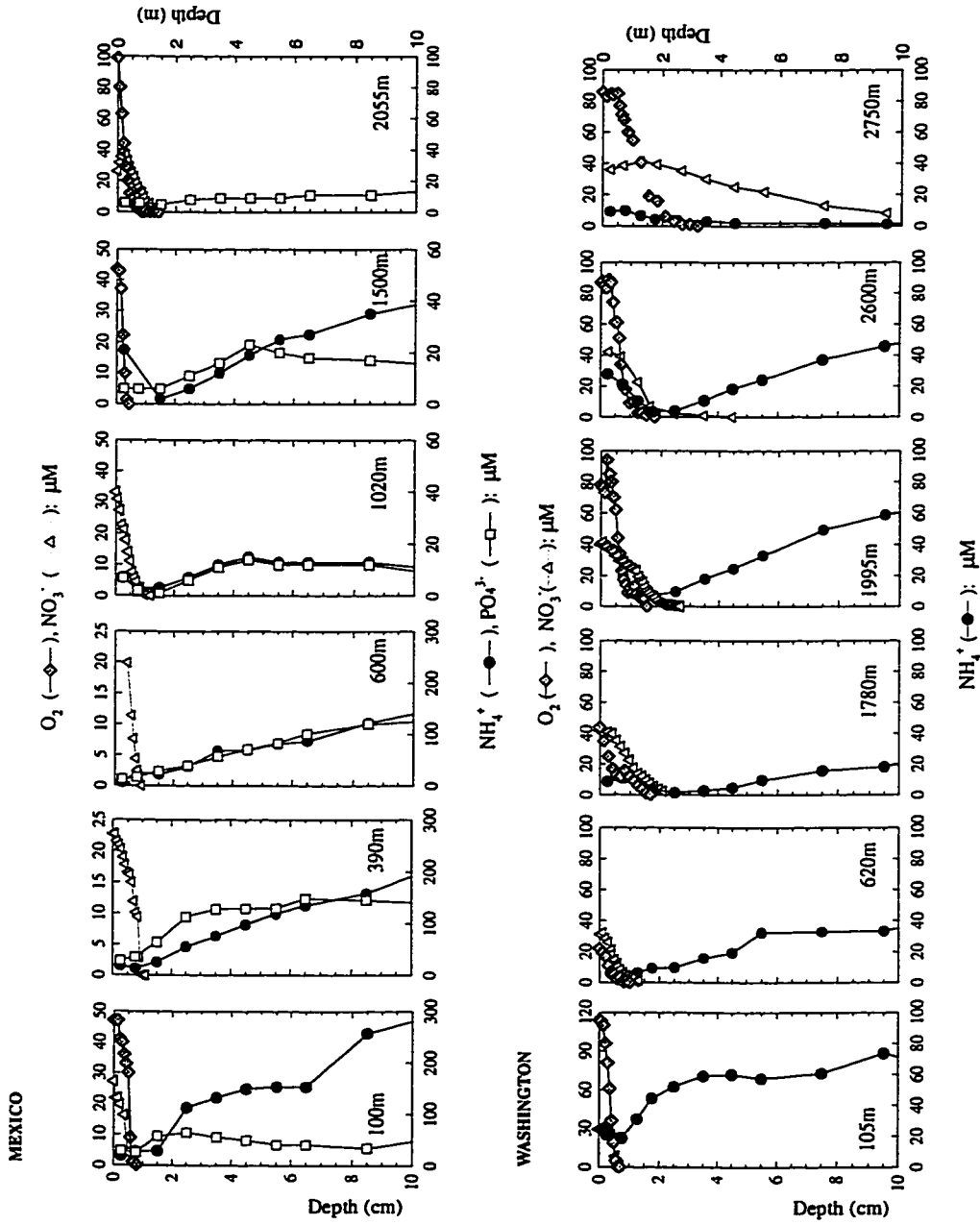


Figure 2.8 Top panels: Porewater profiles of O_2 (diamonds), NO_3^- (triangles) NH_4^+ (circles) and PO_4^{3-} (squares) for representative stations from the Mexican margin; bottom panels: Porewater profiles of O_2 (diamonds), NO_3^- (triangles) and NH_4^+ (circles) from the Washington margin. O_2 profiles are generated by whole-core squeezing; note that there is no measurable porewater O_2 at the Mexican margin ODZ stations (390, 600, and 1020 meters).

and PO_4^{3-} increased with depth in the sediments. Phosphate concentrations were rarely greater than $\sim 15 \mu\text{M}$; this is in strong contrast to the high PO_4^{3-} concentrations in the Mexican margin sediments. Washington margin stations above ~ 2000 m had shallow oxygen and nitrate penetration depths (Figure 2.8). The deep Washington margin stations had O_2 and NO_3^- penetration depths that were greater than 1 cm and the O_2 and NO_3^- profiles began to become spatially separated (Figure 2.8). Subsurface NO_3^- maxima were observed in the stations deeper than 2500 m on the Washington margin. Porewater nutrient profiles for the Washington margin have also been reported previously (Archer and Devol, 1992; Brandes and Devol, 1995; Devol and Christensen, 1993) and the data presented here agree very well with previous results.

SEDIMENT TRAPS

Fluxes of organic carbon derived from sediment traps off the coast of Mexico (Table 2.4) ranged from $7.6 \text{ mmol m}^{-2} \text{ d}^{-1}$ to $4.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ between 150 and 900 m on the NH93 cruise. The trap derived carbon fluxes on the NH96 cruise agreed very well with the earlier fluxes, ranging from 5.9 to $3.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ between 250 and 1800 m. For both cruises, the carbon flux decreased by a factor of approximately two over the depth range of the deployments.

Table 2.4 Organic carbon fluxes derived from sediment traps on the Mexican continental margin. NH93a and b refer to two different trap deployments during the 1993 cruise. All depths are in meters and carbon fluxes in $\text{mmol m}^{-2} \text{ d}^{-1}$.

NH96		NH93a		NH93b	
Depth	C flux	Depth	C flux	Depth	C flux
250	5.9	200	7.6	150	6.3
500	4.2	400	6.1	250	5.4
800	3.2	600	5.4	350	3.5
1100	3.5	900	4.7	450	4.4
1300	3.6				
1800	3.4				

DISCUSSION

CARBON OXIDATION RATES

Carbon oxidation rates are driven both by the availability of oxidizing power in the form of terminal electron acceptors (O_2 , NO_3^- , and SO_4^{2-} , in order of decreasing free energy yield) and by the supply of organic matter from the surface ocean. In continental margin sediments the rates of organic matter degradation are generally high enough to deplete sediment pore waters of O_2 and often NO_3^- within the top centimeter of the sediment column (Archer and Devol, 1992; Canfield et al., 1993; Jahnke, 1990; Reimers et al., 1992).

Maximum and minimum estimates of the total carbon oxidation rate were determined (C_{oxid} I and C_{oxid} II, respectively). The maximum estimate of the oxidation rate was calculated as the sum of the oxidation rates from the three main electron acceptor pathways: O_2 consumption, denitrification, and SO_4^{2-} reduction:

$$C_{oxid} \text{ I} = O_2 \text{ consumption} + \text{denitrification} + SO_4^{2-} \text{ reduction}$$

This estimate assumes that all removal of O_2 was due to aerobic organic matter decomposition. The minimum estimate, a more conservative estimate of the total carbon oxidation rate, and was calculated as the sum of denitrification the O_2 consumption rate or the SO_4^{2-} reduction rate, whichever was greater:

$$C_{oxid} \text{ II} = \left\{ \begin{array}{l} \text{denitrification} + O_2 \text{ consumption} \\ \text{or} \\ \text{denitrification} + SO_4^{2-} \text{ reduction} \end{array} \right.$$

This estimate assumes that some portion of the measured O_2 flux was due to oxidation of inorganic reduced species (*e.g.*, sulfide, iron or manganese). If there was significant

reoxidation of reduced species, then including the total O₂ consumption rate in the carbon oxidation rate estimate would significantly over estimate the amount of carbon removed (Canfield, 1993; Jørgensen, 1977). Put another way, if an oxygen molecule was used to oxidize a sulfide molecule, including the O₂ consumption rate as carbon oxidation would effectively double its contribution to the carbon oxidation rate. In the extreme, I assumed that if the SO₄⁼ reduction rate was greater than O₂ consumption rate, then all of the O₂ flux was due to sulfide reoxidation. If the O₂ flux was larger, I assumed that all the sulfide was reoxidized and the “leftover” O₂ was used for carbon oxidation. This parameterization implicitly assumes the maximum possible reoxidation including reoxidation of reduced metal species (Fe and Mn). I have chosen to use the more conservative estimate of the total carbon oxidation rate (C_{oxid II}) in this discussion as I do not have a quantitative estimate of the amount of sulfide or metal reoxidation occurring at the shallow sites. In practice, when either the O₂ consumption or the SO₄⁼ reduction rate is substantially larger than the other one, the two estimates of the total carbon oxidation rate (C_{oxid I} and C_{oxid II}) are similar. This was the case for deep sediments on both margins where the O₂ consumption rate was much larger than the SO₄⁼ reduction rate. This was also the case off Mexico, in the ODZ, where the two estimates were identical because there was no O₂ flux to consume either organic carbon or sulfide. Theoretically, the two estimates can vary by as much as 50%. The extreme case occurs when the O₂ consumption and SO₄⁼ reduction rates are identical and large relative to the denitrification rate. Generally, in the shallow shelf sediments there were significant rates of denitrification, and dissimilar rates of SO₄⁼ reduction and O₂ consumption. Under these conditions the two estimates tended to differ by ~ 30% (compare C_{oxid I} and C_{oxid II} in Table 2.5). The differences were most significant for the Washington shelf sediments above about 400 m; for the Mexican margin the differences were usually small (< 20 %) even at shallow stations because of the low O₂ flux in the ODZ.

The total carbon oxidation rate in the Mexican margin sediments ranged from 5.77 to 0.93 mmol m⁻² d⁻¹ with average values of 4.01 ± 1.2 mmol m⁻² d⁻¹ for depths

Table 2.5 Carbon oxidation rates ($\text{mmol m}^{-2} \text{d}^{-1}$) attributable to oxygen consumption (O_2), denitrification (NO_3^-) and sulfate reduction (SO_4^{2-}) for stations from the NW Mexican and Washington state continental margins. Total C_{oxid} I was calculated as the sum of the three individual rates; C_{oxid} II is a lower estimate that accounted for the contribution of reoxidation of inorganic species (*see text*).

Depth	Station	$[\text{O}_2]_{\text{BW}}$	O_2	NO_3^-	SO_4^{2-}	Total C_{oxid} I	Total C_{oxid} II
NW Mexican Margin							
97	NH 019	23	0.83	0.77	5.00	6.60	5.77
100	NH 003	6	0.76	2.47	3.06	6.28	5.53
110	NH 001	5	1.13	2.40	1.72	5.25	4.12
135	NH 011	3	0.66	1.58	1.78	4.03	3.36
140	NH 002	3	0.80	1.56	1.84	4.19	3.40
145	NH 102	1	0.66	1.09	4.28	6.03	5.37
190	NH 007	0	0.20	2.99	2.58	5.77	5.57
220	NH 111	0	0.00	2.02	3.76	5.78	5.78
235	NH 110	0	0.00	1.13	2.72	3.85	3.85
250	NH 106	0	0.00	0.88	1.72	2.60	2.60
310	NH 112	0	0.00	1.28	2.34	3.62	3.62
322	NH 012	0	0.00	1.30	1.78	3.08	3.08
345	NH 107	0	0.00	2.15	2.38	4.53	4.53
420	NH 015	0	0.00	1.40	1.74	3.14	3.14
500	NH 103	0	0.00	1.53	0.62	2.15	2.15
620	NH 006	0	0.00	0.97	2.58	3.55	3.55
800	NH 209	1	0.16	1.48	1.33	2.97	2.81
1020	NH 104	4	0.15	0.23	1.22	1.59	1.45
1020	NH 208	4	0.23	0.69	0.24	1.17	0.93
1500	NH 205	44	1.08	0.53	0.07	1.68	1.61
2000	NH 206	92	1.44	0.41	0.47	2.32	1.85
Washington Margin							
105	WE 204	104	6.39	1.55	4.26	12.21	7.95
219	WE 211	106	3.63	1.73	6.44	11.80	8.17
440	WE 202	60	1.95	1.45	1.42	4.81	3.39
620	WE 213	39	0.84	0.60	0.88	2.32	1.48
1025	WE 206	38	0.63	0.46	0.07	1.16	1.09
1994	WE 203	56	1.18	0.10	0.35	1.63	1.28
2525	WE 219	62	1.18	0.10	0.10	1.38	1.28
2746	WE 201	87	0.28	0.07	0.002	0.35	0.35

above 1000 m and $1.46 \pm 0.34 \text{ mmol m}^{-2} \text{ d}^{-1}$ for depths below 1000 m (Figure 2.9). On the Washington margin, the total carbon oxidation rate ranged from 8.17 to $0.35 \text{ mmol m}^{-2} \text{ d}^{-1}$. The average total carbon oxidation rate in sediments from the upper 1000 m was $5.25 \pm 3.0 \text{ mmol m}^{-2} \text{ d}^{-1}$ and the average rate for sediments below 1000 m was 1.00 ± 0.44 . The total carbon oxidation rates for the Washington margin stations below 1000 m are also quite similar in magnitude to rates presented for other deep continental margins of the western north Pacific. Values for the total carbon oxidation rate for the central and southern California margin at depths between 1000 and 4000 m range from 0.4-1.8 $\text{mmol m}^{-2} \text{ d}^{-1}$ (Berelson et al., 1996; Jahnke et al., 1990; Reimers et

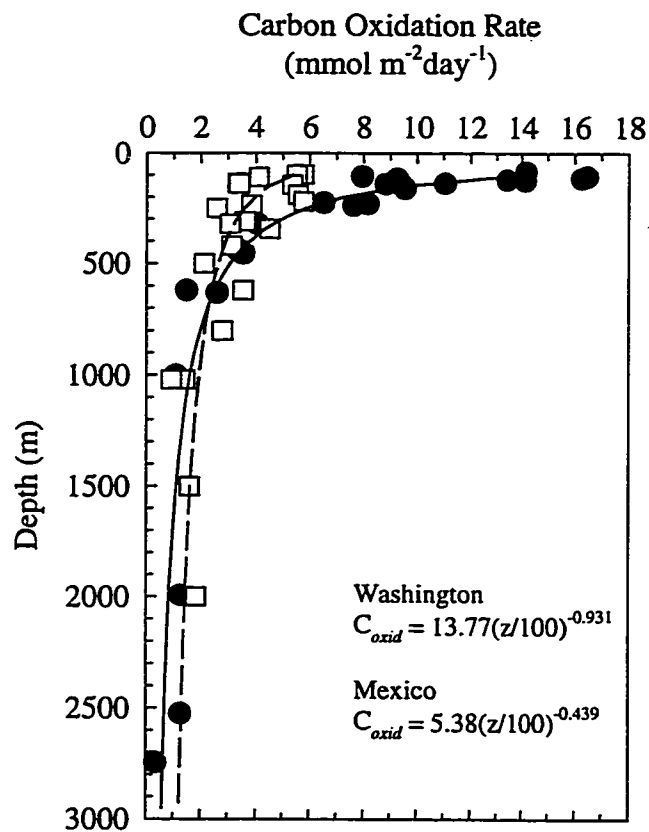
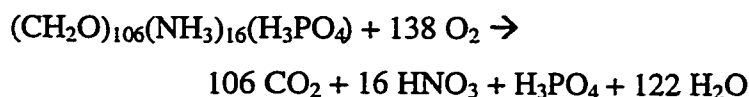


Figure 2.9 Total carbon oxidation rate ($\text{mmol m}^{-2} \text{ d}^{-1}$) for the Mexican (open squares) and Washington (solid circles) continental margins. The Washington profile includes carbon oxidation rate data recalculated (*see text*) from Devol and Christensen (1993). The lines are the best fit to the indicated power functions.

al., 1992). I recalculated the total carbon oxidation rate presented in Devol and Christensen (1993) for the 100-600 m stations using the stated assumptions about the reoxidation of reduced species (*i.e.*, C_{oxid} II) and obtained an average carbon oxidation rate for sediments above 1000 m of $9.79 \pm 4.3 \text{ mmol m}^{-2} \text{ d}^{-1}$ which compares reasonably well with the value of $5.25 \text{ mmol m}^{-2} \text{ d}^{-1}$. The average total carbon oxidation rate for Washington margin sediments below 1000 m was $1.00 \pm 0.44 \text{ mmol m}^{-2} \text{ d}^{-1}$. The Washington margin data in Figure 2.9 includes the carbon oxidation rate data from both this work and that of Devol and Christensen (1993). The following discussion of the carbon oxidation rates will treat the data from the WE94 cruise and the data from Devol and Christensen (1993) as one composite data set for the Washington continental margin.

O₂ consumption

Remineralization by oxygen is often considered to be the primary pathway for organic carbon oxidation in sediments. Carbon oxidation due to oxygen consumption is typically calculated from the benthic O₂ flux assuming a Redfield stoichiometry for organic matter degradation (Richards, 1965):



This approach results in an O:C remineralization ratio of 138:106. It is worth pointing out that this equation implicitly assumes the 16 NH₄⁺ generated from the organic matter is oxidized to NO₃⁻ in the presence of oxygen (*i.e.*, nitrification).

The Mexican margin is unique, however, due to its strong ODZ. Because limited oxygen is available for organic matter degradation over most of the margin O₂ consumption accounts for only a small fraction of the total carbon oxidation rate (between zero and 15% in the upper 1000 m; *see* Table 2.5 and Figure 2.10). The oxygen consumption rates on this margin are likely related to O₂ availability (supply and

demand) and thus to the bottom-water oxygen concentration (Archer and Devol, 1992). On the Mexican margin, the amount of carbon oxidized by O_2 consumption was determined to be substantially lower than the amount oxidized by denitrification or by SO_4^{2-} reduction at almost all stations (Table 2.5). This finding stands in contrast to the more typical Washington margin, where carbon oxidation rates due to O_2 consumption were generally large and comparable in magnitude to the SO_4^{2-} reduction rates. The

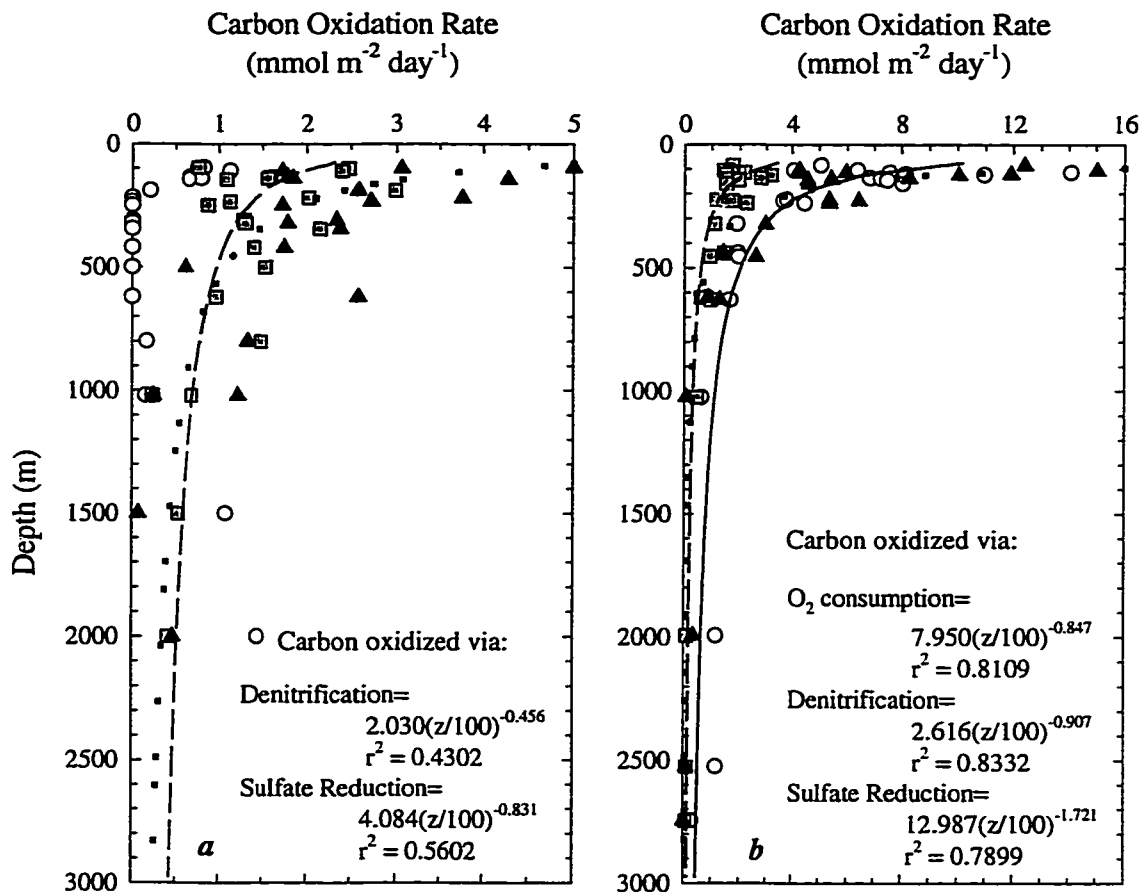


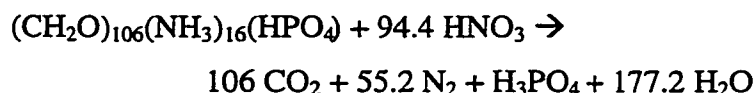
Figure 2.10 Carbon oxidation rates due to different electron acceptors for *a*, the Mexican margin and *b*, the Washington margin. O_2 consumption rates (open circles), denitrification rates (solid squares) and SO_4^{2-} reduction rates (solid triangles). Lines are best fits to the indicated power functions; oxygen consumption (solid lines), denitrification (dashed lines), sulfate reduction (dotted lines). All rates are $mmol\ m^{-2}\ d^{-1}$.

Washington margin O₂ consumption rates are also generally greater than the denitrification rates. On the Washington margin, O₂ consumption appears to follow a predictable decrease with depth and is generally the largest component of the total carbon oxidation rate, accounting for ~40 to 50% of the total (Table 2.5 and Figure 2.10).

Others have suggested that O₂ consumption is most important in deep-sea sediments and that the relative importance of NO₃⁻ and SO₄⁻ increase in continental slope and shelf sediments (Canfield, 1993; Grundmanis and Murray, 1982; Murray and Kuivila, 1990). This suggestion is borne out by this study and the fact that below 1000 m on both the Mexican and Washington margins O₂ became the most important electron acceptor. Oxygen consumption is generally the largest component of the total carbon oxidation rate in other deep margin sediments as well: Reimers et al. (1992) report O₂ consumption rates for the deep California margin that account for 60 to 80% of the total carbon oxidation rate.

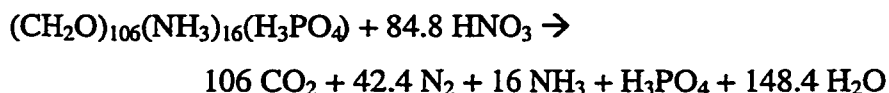
Denitrification

Denitrification is the next most energetically favorable process (after oxygen consumption) for oxidizing organic matter (Froelich et al., 1979; Richards, 1965). Nitrate was determined to be consumed relatively rapidly from the porewaters in both margins of this study indicating that significant denitrification occurs in these two regions (Figures 2.8). Classically, denitrification in sediments is assumed to follow this reaction:



In this reaction it is assumed that the 16 moles of ammonia released from the organic matter reacts with NO₃⁻ to form N₂; however, the mechanism for this reaction is not known. The C:NO₃⁻ stoichiometry of this reaction is 106:94.4 and there should be no

ammonia flux from the sediments. If there is no conversion of ammonia to N_2 , then denitrification proceeds according to the following reaction (Froelich et al., 1979):



In this case where the ammonia released from the organic matter cannot be reoxidized, the C:NO₃⁻ stoichiometry is 106:84.8. Under these conditions, one could expect to see an ammonia flux from the sediments while there is denitrification occurring. The ratio of C oxidized to NH₄⁺ regenerated is different for the two denitrification reactions and the measured NH₄⁺ fluxes and carbon oxidation rates can be used to assess which reaction is occurring in a particular sediment.

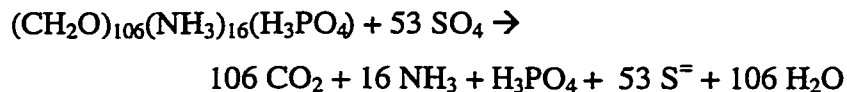
On the Washington margin where there is oxygen in the overlying water, mass balance calculations suggest there must also be a significant amount of nitrification (and subsequent denitrification) occurring (Devol and Christensen, 1993). This effect of nitrification, coupled to denitrification allows for more denitrification than can be supported by the diffusive supply of NO₃⁻ alone. Coupled nitrification–denitrification also consumes NH₄⁺ regenerated during organic carbon degradation and should therefore result in an apparent C:N regeneration ratio that is less than 106:16.

Denitrification is a much larger fraction of the total carbon oxidation rate on the Mexican margin than on the Washington margin (40% versus 15%, respectively) because the contribution to the total oxidation rate from oxygen consumption is smaller. Berelson *et al.* (1996) and Jahnke (1990) have shown that for those borderland basins off California with low bottom-water O₂, a relatively greater proportion of the carbon oxidized via denitrification (~70% and 50% in the San Pedro and Santa Monica basins, respectively). The absolute rates of denitrification in Mexican margin sediments were lower than in Washington sediments however, because coupled nitrification-denitrification in Washington sediments increased the total amount of NO₃⁻

available for denitrification. With oxygen available in the surface sediments, NH_4^+ generated by organic matter oxidation can be converted to NO_3^- and subsequently denitrified to N_2 . In addition, irrigation by macrobenthic infauna is a potentially important process in the oxygenated Washington margin sediments. Irrigation brings bottom water with relatively high O_2 and NO_3^- to greater depths in the sediment than can be attained by diffusion alone. This enhances the rates of O_2 consumption and denitrification by as much as a factor of four (Archer and Devol, 1992). By contrast, the amount of organic carbon that can be consumed via denitrification in Mexican margin sediments, where bioturbation appears to be minimal, is limited to that which can be supported by the finite diffusive supply of NO_3^- from the overlying water.

Sulfate reduction

After the depletion of O_2 and NO_3^- in the porewaters, it is generally thought that sulfate reduction becomes the most significant pathway for carbon oxidation. In both the Washington and Mexican margin sediments rates of SO_4^{2-} reduction can be as large or larger than the O_2 consumption rates. Sulfate reduction is generally assumed to be a strictly anaerobic process that can be represented by the following reaction (Froelich et al., 1979; Richards, 1965):



The rate of carbon oxidation due to SO_4^{2-} reduction is therefore two times the measured SO_4^{2-} reduction rate (Table 2.5). The SO_4^{2-} reduction rates in both the Mexican and the Washington margin sediments were generally highest in shallow sediments and decreased with increasing water depth (Figure 2.10). Sulfate reduction was the largest contributor to the total carbon oxidation rate in the Mexican margin sediments (~60% in the upper 1000 m, Table 2.5). There are a few reports for other regions where the SO_4^{2-} reduction

rate accounts for such a significant fraction of the total carbon oxidation rate (Canfield, 1994; Jørgensen, 1983). In the Washington margin sediments the SO_4^- reduction rate was the second largest component of the total carbon oxidation rate, after O_2 , accounting for ~30% of the total carbon oxidation rate (Table 2.5). Berelson et al., (1996) reported that SO_4^- reduction in the low oxygen basins of the California borderlands accounts for no more than 40% of the total carbon oxidation. The absolute SO_4^- reduction rates on the Washington and Mexican margins are comparable to rates reported for the Gulf of Maine (Christensen, 1989) and for the California margin (Berelson et al., 1996; Reimers et al., 1992) determined by similar radio-assays. Sulfate reduction rates off Mexico are relatively more important than denitrification (and O_2 consumption) in the overall carbon oxidation rate. This may be due to the fact that the extent of denitrification is limited by the diffusive supply of nitrate from overlying-waters with low NO_3^- concentrations while there is a virtually infinite diffusive supply of SO_4^- for SO_4^- reduction; however the absolute rates carbon oxidation by SO_4^- reduction and denitrification are lower within the ODZ than the rates reported here for Washington (Tables 2.2 and 2.3) and rates reported for the California margin (Reimers et al., 1992; Berelson et al., 1996).

When integrated over the upper 30 cm of the sediment column, the measured sulfate reduction rates generally decreased with depth or passed through a maximum before decreasing (Figure 2.7). The measured SO_4^- reduction rates (integrated down to 30 cm in each core) were quite low ($<1 \text{ nmol cm}^{-3} \text{ d}^{-1}$) and although the ultimate depth to which SO_4^- reduction extended may have been greater than 30 cm, the depth-integrated SO_4^- reduction rate is likely to account for the majority of the sulfate reduction at these sites. For the deepest stations, there is the possibility for the measured rates to be artificially low due to the effects of decompression on the resident bacterial populations (Parkes et al., 1994). In fact, decompression effects on anaerobic bacteria in the deep-sea are poorly known; aerobic bacteria isolated from sediments taken at depths from 1000 to 2000 meters seem to be relatively unaffected by the effects of decompression (Glud et al., 1994; Yayanos, 1995).

For stations where radio-labeled incubation assays for determining SO_4^- reduction rate were not available, the SO_4^- reduction rates have been calculated from the porewater NH_4^+ flux (Reimers et al., 1992). The ammonium flux ($F_{\text{NH}_4^+}$) was calculated from the porewater NH_4^+ profiles, the measured porosity and an assumed sedimentary diffusion coefficient for ammonium (Lehrman, 1979). Furthermore, the entire NH_4^+ flux was assumed to be due to sulfate reduction, and the SO_4^- reduction rate, stoichiometrically related to the ammonium flux:

$$C_{\text{oxid-SO}_4\text{Red.}} = \frac{106}{16} (F_{\text{NH}_4^+})$$

Because this calculation ignores any contribution to the NH_4^+ flux from iron or manganese oxide reduction it represents an upper-bound for the estimated SO_4^- reduction rate. The calculation does not explicitly address the effect of irrigation beyond the fact that irrigation will influence the porewater ammonium profiles determined from the sectioned cores. The calculated SO_4^- reduction rates for the four deepest Mexican margin stations (Table 2.6) agreed reasonably well with the measured rates; the rates were quite low ($\ll 1 \text{ mmol m}^{-2} \text{ d}^{-1}$), regardless of the method by which they were determined.

Table 2.6 Comparison between SO_4^- reduction rates measured with the ^{35}S -labeling assay (*na* = not available) and calculated from fluxes of NH_4^+ determined from porewater profiles. Units for all rates are $\text{mmol m}^{-2} \text{ d}^{-1}$.

Depth (m)	Station	SO_4^- reduction rate	
		Measured	Calculated
800	NH 209	1.22	0.46
1020	NH 104	<i>na</i>	0.24
1020	NH 208	0.07	0.34
1500	NH 205	<i>na</i>	0.78
2050	NH 206	0.47	0.25

It is worth pointing out that at these depths (>1000 m) the SO_4^{2-} reduction rate was generally a very small component of the total carbon oxidation rate (see Table 2.5 and data in Berelson et al., 1996; Reimers et al., 1992).

DEPTH ATTENUATION OF THE CARBON OXIDATION RATE

The sedimentary carbon oxidation rate is determined largely by the supply of organic carbon from the surface ocean, which decreases with depth due to the loss of labile organic matter during transit through the water column (Martin et al., 1987). This decrease in the flux of carbon to the sediments is well documented, and is usually expressed empirically as an inverse power function of depth (Bender et al., 1992; Berger et al., 1988; Betzer et al., 1984; Christensen, 1989; Devol and Christensen, 1993; Jahnke, 1996; Martin et al., 1987; Pace et al., 1987; Suess, 1980). Quantitatively, the organic carbon rain rate (the rate of input of organic carbon to the sediments) is generally expressed as a fraction of primary productivity or a fraction of the carbon flux through 100 m (e.g., $\text{Flux}_z = a \cdot \text{PP} \cdot z^{-\alpha}$ where a and α are constants, PP is the primary production rate, and z is depth or $\text{Flux}_z = \text{Flux}_{100\text{m}} (z/100)^{-\alpha}$). In either case, the attenuation coefficient (α) dictates how rapidly the flux of organic carbon decreases with depth. The reported values of the attenuation coefficient from a variety of regions (summarized in Table 2.7) have been derived both from sediment trap studies of the carbon flux and from studies of the sedimentary carbon oxidation rate. Interestingly, a very similar degree of attenuation in the carbon flux to sediments with depth is observed over much of the ocean. The fact that different workers have arrived at similar values using several different approaches (i.e., carbon oxidation rates, sediment traps, global models) suggests that the average value of -0.86 for the attenuation coefficient is fairly robust.

In order to compare the differences in the carbon oxidation rate with respect to depth for the Washington and Mexican margins, I fit the carbon oxidation rate data from both margins to a power function of depth similar to that used in Martin et al. (1987). In

this parameterization the carbon oxidation rate at any depth is equal to the carbon oxidation rate at 100 m, times the depth raised to a negative attenuation coefficient (α):

$$C_{oxid} = (C_{oxid, 100\text{ m}}) (\text{Depth}/100)^\alpha$$

The attenuation in the oxidation rate with depth differed on the two margins (Table 2.7). The carbon oxidation rates for the Washington margin were fit quite well by an equation with $\alpha = -0.93$ ($r^2 = 0.911$), a degree of attenuation consistent with other reported values for the depth-attenuation of the carbon oxidation rate (Berelson et al., 1996, Jahnke, 1996 #352; Devol and Christensen, 1993). It is also encompassed by the range in attenuation coefficients (-0.833 to -0.973) that reported for the VERTEX sediment trap transect off of Monterey Bay, California (Martin et al., 1987).

Table 2.7 Compilation of attenuation coefficients for carbon flux relationship with depth. Carbon input fluxes determined from sediment trap results and from benthic carbon oxidation rates are denoted Trap. and C oxid., respectively.

Region	Method	Attenuation Coefficient	Source
Global ocean composite	Trap	-1.000	Suess, 1980
Equatorial Pacific	Trap	-0.628	Betzer <i>et al.</i> , 1984
Global ocean composite	Trap	-1.000	Berger <i>et al.</i> , 1987 (simple fit)
Global ocean composite	Trap	-0.800	Berger <i>et al.</i> , 1987 (best fit)
Global ocean composite	Trap	-1.000	Berger <i>et al.</i> , 1987 (refractory C model)
Vertex, NE Pacific	Trap	-0.734	Pace, 1987
Vertex, open ocean composite	Trap	-0.858	Martin <i>et al.</i> , 1987
Continental shelf composite	C oxid.	-0.717	Christensen, 1989
JGOFS N.Atlantic Bloom Exp.	Trap	-1.138	Bender, 1992
Washington shelf	C oxid.	-0.910	Devol and Christensen, 1993
Global composite, 2 coefficients		-1.00, -0.50	Berger <i>et al.</i> , 1988; Jahnke, 1996
Average		-0.86 ± 0.18	
Washington Margin	C oxid.	-0.931	(this study)
Mexican Margin	Trap/Coxid.	-0.439	(this study)

Similar values for the attenuation factor were also obtained for sediment trap data from the equatorial Pacific, the deep Atlantic, and a composite of continental shelf regions (*see* Table 2.7). A similar study of carbon oxidation rates made in California shelf and upper

slope sediments off Monterey Bay shows that such a VERTEX-style attenuation coefficient ($\alpha \approx -0.85$) is sufficient to describe the decrease in oxidation rate with depth in this continental margin region as well (Berelson et al., 1996). The Mexican margin data, however, were best fit by an equation with $\alpha = -0.439$. Even though the relationship was not well constrained ($r^2 = 0.589$), the attenuation coefficient is one of the smallest of any of the reported values in the recent literature (Table 2.7). A similarly low attenuation coefficient derived from sediment traps deployed in the Peru margin ODZ has been reported by Martin et al. (1987). The carbon oxidation rates on the Mexican margin decreased by only a factor of 1.8 between 100 m and 1000 m, whereas off Washington, the rates decrease by more than a factor of 10 over the same depth range. Further examination of Figure 2.10 suggests that the Mexican carbon oxidation rates do not decrease very much at all between ~100 and 500 m which, to a large degree, accounts for the poor fit to the power function. On the Washington margin, each of the individual carbon oxidation rates was fit reasonably well by a power function similar to that for the total carbon oxidation rate (O_2 consumption: $\alpha = -0.847$, $r^2 = 0.813$; denitrification: $\alpha = -0.906$, $r^2 = 0.834$; SO_4^{2-} reduction: $\alpha = -1.72$, $r^2 = 0.792$). Off Mexico, carbon oxidation rates attenuated minimally between ~200 and 800 m (*see* Figures 2.9 and 2.10), as reflected by the poor fit to the power function ($\alpha = 0.456$, $r^2 = 0.430$ and $\alpha = 0.831$, $r^2 = 0.560$ for the denitrification and SO_4^{2-} reduction rates, respectively). Thus, it appears standard parameterizations of the carbon oxidation rate with respect to depth do not adequately represent the relation between these factors on the Mexican margin.

If sedimentary carbon oxidation decreases less on the Mexican margin it is reasonable to assume that there is either a) an additional source of organic matter to these sediments other than overlying primary production, or b) some factor that inhibits the degradation of the organic material during transit through the water column or in the sediments. Potential explanations for the smaller depth-attenuation of the carbon oxidation rate on the Mexican margin include: chemolithotrophic production of organic matter in the water column below ~100 m depth, or off-shelf or horizontal transport of

organic matter to the continental slope; and decreased degradation of organic matter as it transits the O₂-deficient water column.

Karl et al. (1984) presented evidence from the Vertex III transect that suggests that chemolithotrophic production associated with sinking particles may be a source of organic carbon to the deep ocean. I have no data with which to assess the presence of chemolithotrophic production in the water column of the Mexican margin; however, I can evaluate the amount of chemolithotrophic production that would be required in the Mexican water column to account for the discrepancy in the relative amount of carbon reaching 1000 m on the Mexican and Washington margins. The calculated Mexican margin carbon flux at 100 m is $\sim 1 \text{ mmol m}^{-2} \text{ d}^{-1}$. If the flux at 100 m ($5.5 \text{ mmol m}^{-2} \text{ d}^{-1}$) were attenuated with the same -0.85 that is observed for the Washington margin, the flux at 1000 m would be only $\sim 0.015 \text{ mmol m}^{-2} \text{ d}^{-1}$. This difference implies an *in situ* production rate of roughly $0.98 \text{ mmol m}^{-2} \text{ d}^{-1}$ (or $11.8 \text{ mg C m}^{-2} \text{ day}^{-1}$, or roughly half of the Mexican margin primary production rate). This is roughly two orders of magnitude greater than the production rate reported for the Vertex III site. In addition, Karl et al. (1984) reported a maximum rate of chemolithotrophic production of $0.04 \text{ mmol m}^{-2} \text{ d}^{-1}$ due to nitrification; if it is assumed that all of the proposed autotrophic production is a result of nitrification, a production rate of $0.98 \text{ mmol C m}^{-2} \text{ d}^{-1}$ would require an unrealistically large supply of NH₄⁺ ($22 \text{ mmol m}^{-2} \text{ d}^{-1}$). The measured benthic NH₄⁺ flux from this margin is also not large enough to supply this amount of NH₄⁺. It seems unlikely that this degree of production is occurring on the Mexican margin, especially since the oxygen deficient zone off Mexico is an unlikely place for a significantly aerobic process like nitrification.

Off-shelf transport is another potential source of organic rich material to the Mexican continental slope. Jahnke et al. (1990) and Reimers et al. (1992) have suggested that there may be anomalously high rates of carbon oxidation in continental slope sediments resulting from horizontal transport of organic-rich material from the shelf to the slope. While I cannot rule out off-shelf transport as a source of organic matter to the

Mexican slope, the Mexican margin appears less likely than the Washington margin to be strongly influenced by horizontal processes. The Washington margin, for example receives a large input of sediment from the Columbia River and is a higher energy environment subject to periodic sediment mass flows from the shelf to the slope (Nittrouer and Sternberg, 1981). The carbon oxidation rates at the base of the continental slope on the Washington margin (~2000 m) are somewhat underestimated by the power function approximation (Figure 2.9). This enhanced rate of degradation may be fueled by off-shelf transport of organic material.

A third alternative for the reduced attenuation is decreased removal of organic carbon during transit through the water column. Particles falling through the water column will have an associated population of bacteria. Large particles which sink relatively rapidly (~20-50 m d⁻¹; Brewer et al., 1980) will take roughly 30 days to transit the ODZ. The strictly aerobic population of bacteria will not be able to degrade organic carbon during transit; however, I would expect there to be an active population of facultative anaerobes present as well. There is also a reduced population of zooplankton in the water column of the ODZ that may contribute to the lower rates of oxidation and thus to greater throughput of organic matter to the sediments (King et al., 1978; Wishner et al., 1995).

The sedimentary carbon oxidation rates for the Washington and Mexican margins normalized to the oxidation rates at 100 m are presented in Figure 2.11. The gray lines in the figure are the normalized carbon fluxes calculated using the attenuation coefficients presented in Table 2.7. The carbon oxidation rates at 2500 m on the Mexican margin are approximately 25% of the rates at 100 m. On the Washington margin the oxidation rates at 2500 m are less than 10% of the 100-m rates, suggesting that more organic matter is remineralized during water column transit. The attenuation of the carbon oxidation rate is analogous to the attenuation in the carbon input flux. It appears that the Mexican margin ODZ allows the passage of a substantially larger fraction of the export production to reach the deep-sea and be remineralized than is typical in oxygenated water columns (Figure 2.11). The normalized data from the sediment trap studies of Suess (1980) and

Martin et al., (1987) suggest that ~2-15% of the carbon flux at 100 m remains by 2500 m, so the Washington margin data appear to be in line with previous results. Currently, oxygen deficient zones comprise less than 2% of the worlds oceans. If the areal extent of oxygen deficient zones were to increase, a consequence of one scenario for glacial-interglacial climate change (Boyle, 1988; Boyle and Keigwin, 1987; Sarmiento and

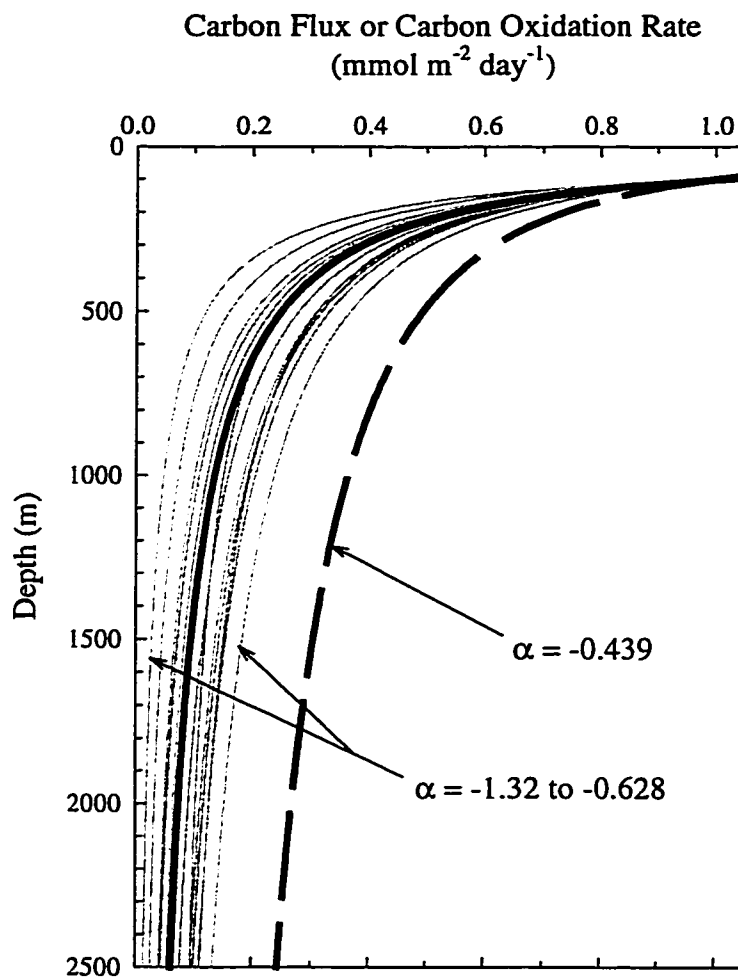


Figure 2.11 Carbon oxidation rates normalized to the oxidation rates at 100 m for the Washington (solid black line) and Mexican (dashed black line) continental margins. Gray lines are the normalized carbon flux calculated using the previously reported values for the attenuation coefficient summarized in Table 2.7.

Sundquist, 1992), there is the potential for a much greater percentage of primary production to be preserved in the to the deep-sea. If more carbon reached the deep sea and was subsequently buried, there would also be fundamental implications for the dynamic balance between the global cycles of carbon and oxygen, as burial of organic carbon balances the supply of oxygen to the atmosphere (Bernier, 1982; Hartnett et al., 1998; Holland, 1978).

CARBON INPUT RATES

Carbon oxidation rates in Mexican margin sediments are lower than those on the Washington margin. In addition, primary productivity estimates for the Mexican margin suggest that the carbon flux to the sediments should be low in comparison to that of other margin regions with higher productivity. If there is a relationship between carbon oxidation and carbon input, it should be possible to estimate the carbon input rate from the rate of carbon oxidation and carbon burial. This calculated rate can then be compared to a sediment trap-derived carbon input rate. Differences between the calculated and measured input rates may provide insight to the mechanisms controlling the amount of organic matter reaching the sediments. I estimated the organic carbon flux to the sediments of the Mexican margin as the sum of the carbon burial rate (the amount of carbon preserved in the sediments) and the total carbon oxidation rate (the rate of carbon degradation or removal; Berelson et al., 1996; Hartnett et al., 1998; Reimers et al., 1992):

$$\text{Carbon Input} = \text{Carbon Burial} + \text{Carbon oxidation}$$

The carbon burial rate was estimated from the sediment accumulation rate and the organic carbon content at depth (15 cm) in the sediment:

$$\text{Carbon Burial} = [\text{OC}]_{15\text{cm}} (S_{\text{acc}})$$

This parameterization of the input rate assumes that the carbon content at 15 cm is representative of the carbon content at greater depths in the core. The relatively constant carbon contents in the Mexican margin sediments (Figure 2.5) suggest that this is a reasonable assumption for this location. The carbon input to the sediments was calculated for the stations where I measured both sediment accumulation rates and carbon oxidation rates (Figure 2.12). Sediment traps provide a direct estimate of the carbon flux and its attenuation with depth. The carbon flux to the Mexican margin sediments, measured directly in two different years using sediment traps, was comparable to the calculated carbon input rate (Figure 2.12). Both the trap-derived carbon flux and the calculated carbon flux decreased with depth by a factor of 1.7 and could be approximated using the same power function relation (*i.e.*, $F_z = F_{100}(Z/100)^\alpha$) with $\alpha = -0.35$. Again, this was substantially less attenuation with depth than had been determined from other sediment trap studies in the North or equatorial Pacific. As was the case for the carbon oxidation rates, the carbon flux to the sediments did not decrease as rapidly in Mexican margin sediments as it did in other regions. Sedimentary processes are driven in part by carbon supply from the surface. Thus, it is not surprising that the calculated carbon input rate should resemble the sediment trap flux. While this is not a formal attempt to balance the carbon rain rate against benthic processes, the agreement between the two estimates of carbon input suggests that over most of the Mexican margin, carbon input was primarily a result of vertical particle transport. It is difficult to assess the impact of horizontal processes with this data set; however, at 620 m the calculated carbon flux was larger than the sediment-trap derived flux which may indicate the influence of off-shelf transport to this continental slope region. With the exception of the 620 m datum it appears that the sediment trap flux and the calculated flux based on carbon oxidation and burial rates are in good agreement. This agreement suggests that my parameterization of the carbon oxidation rate provided an appropriate estimate of the total oxidation rate on this margin. It also implies that the carbon oxidation rate was not integrating a large horizontal transport signal over longer time scales that was missed by the sediment traps operating on short time scales.

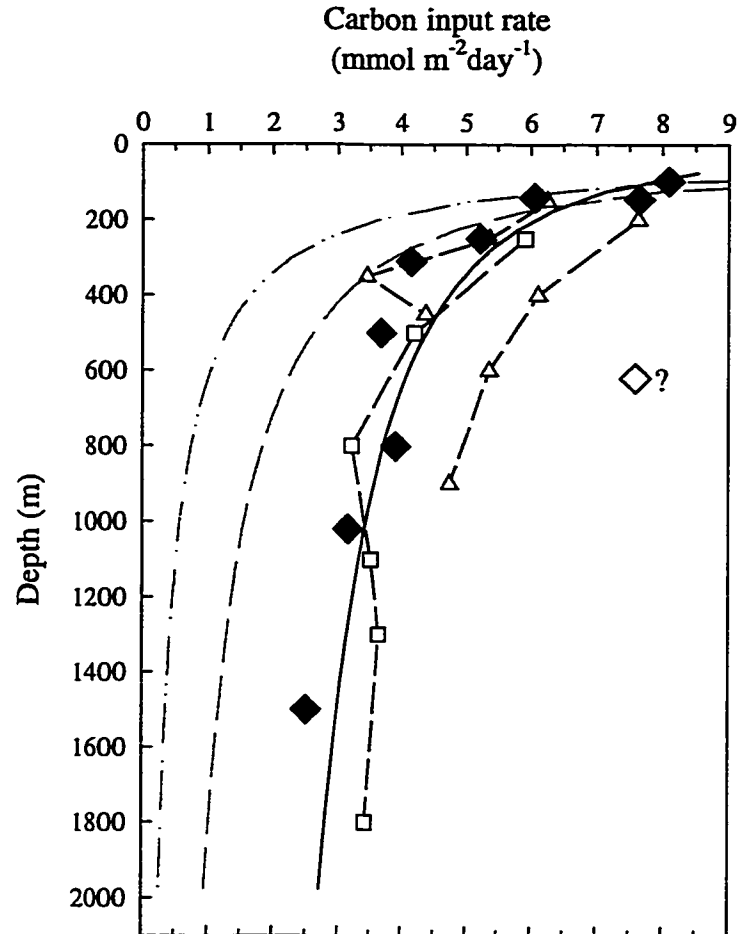


Figure 2.12 Organic carbon input flux ($\text{mmol m}^{-2} \text{d}^{-1}$) to the sediments of the Mexican continental margin. Solid diamonds are carbon input rates calculated from burial and oxidation; open symbols are sediment trap-derived carbon fluxes for three trap deployments (squares, NH93 and triangles, NH96). The solid curve is a power function relation fit to the calculated carbon fluxes with an attenuation coefficient (α) of -0.35 ($r^2 = 0.90$); the gray curves are modeled carbon input fluxes using an attenuation coefficient of -1.14 (dash-dotted line, Bender et al., 1992) and an attenuation coefficient of -0.72 (dashed line, Christensen, 1989).

Reimers et al. (1992) estimated carbon input rates for the deep California margin off Monterey and compared those rates to a similar set of power function relations. In comparing the calculated input rates to the rates predicted by the attenuation models of Martin et al. (1987) and Betzer et al. (1984) they concluded that there must have been a

horizontal component to the input flux because the calculated input rates significantly exceeded the model derived input rates. Most of the power function models fit the measured data best over the top 1000 m, characterized by a significant decrease in the carbon flux. The Reimers et al. (1992) data set only included data from stations deeper than ~ 800 m, where the changes in the carbon input flux were very small. However, Berelson et al. (1996) reported reasonably good agreement between calculated carbon input rates and the Martin et al. (1987) model for stations from the same part of the California margin between 100 and 3000 m. The Berelson et al. (1996) data set shows the majority of the attenuation in the carbon flux occurring between the surface and 1000 m. However, closer examination of the data from Reimers et al. (1992), Berelson et al. (1996) and this study suggests that below 1000 m there is little variation in the carbon flux to the sediments at any of the four locations (Figure 2.13). The Reimers et al. (1992) data set indicates a slight increase in the carbon oxidation rate at depths between 3000 and 4000 m, which they attribute to carbon input to the sediments via horizontal transport processes at the base of the continental slope on this margin. The Washington margin data may also show a slight increase at about 2000 m which is at the base of the continental slope (*see* Figure 2.13). It is possible that the power function models do not describe the data very well below 1000 m, where the attenuation is small. The power function models predict a change of about a factor of two in the carbon oxidation rate between 1000 m and 4000 m (*see* Figure 2.11), a prediction that does not appear to be supported by the available data.

ELEMENTAL NUTRIENT REGENERATION RATIOS

A higher percentage of the surface primary production appeared to have reached the Mexican margin sediments, possibly as a result of decreased oxidation during transit through the water column. If the organic matter that reaches the sediments has a Redfield-like composition (C:N:P of 106:16:1) then one would expect N and P to be regenerated in similar proportions. Differences between observed regeneration ratios and the theoretical ones may be suggestive of the pathways for carbon and nitrogen cycling in

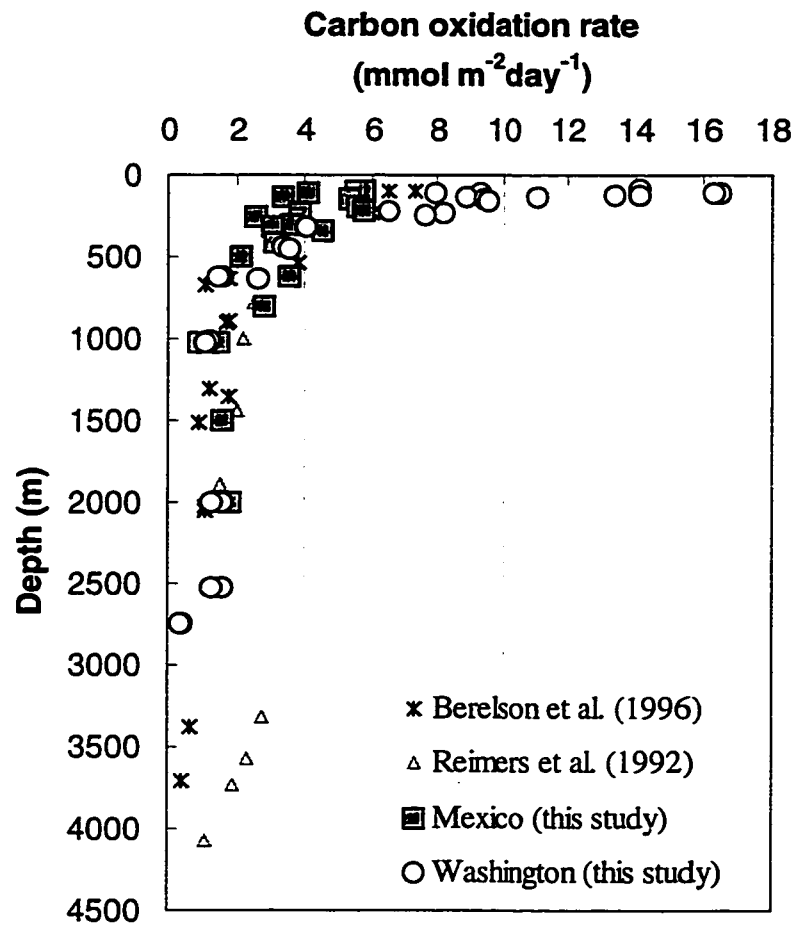


Figure 2.13 Carbon oxidation rates from the California margin (data from Reimers et al., 1992; Berelson et al., 1996), the Mexican margin and the Washington margin. Note the lack of attenuation in the oxidation rates below 1000 m.

sediments. I evaluated the nutrient regeneration ratios by calculating the average, observed C:N, N:P and C:P ratios from the average carbon oxidation rate and the average measured lander fluxes of PO_4^{3-} and NH_4^+ on each margin:

$$\text{C:N}_{\text{regen}} = \text{C}_{\text{oxid}} / \text{benthic NH}_4^+ \text{ flux}$$

$$C:P_{regen} = C_{oxid} / \text{benthic } PO_4^{3-} \text{ flux}$$

The regeneration of nitrogen and phosphorus resulting from organic matter diagenesis, like the absolute rate of oxidation, showed distinct differences between the two margins (Table 2.8) and from Redfield stoichiometry. On the Mexican margin, N:P ratios and C:P ratios were much smaller than a Redfield stoichiometry would predict (1.9 vs. 16 and 20.2 vs. 106, respectively) while the C:N ratio of 10.2 was relatively close to the Redfield value of 6.6 and virtually identical to the C:N ratio of the sediments (see Figure 2.3). Thus, the first striking result is that the C:N ratio was very close to the Redfield prediction, implying the amount of NH_4^+ escaping the system was roughly the same as the amount released from organic matter oxidation. Nitrogen regeneration appears to be tightly coupled to carbon oxidation with little nitrification occurring in these sediments. If nitrification were consuming regenerated NH_4^+ in these sediments, the observed C:N ratio would be larger than the Redfield prediction. The second significant result is the implication from the low C:P and N:P ratios that a great deal more phosphorus was escaping the sediments than could be supplied via organic matter decomposition. Other evidence to suggest the presence of excess P in Mexican margin sediments includes the high porewater PO_4^{3-} concentrations, particularly in the ODZ (Figure 2.8), and the well known presence of phosphorites in the shelf sediments (Ingall and Jahnke, 1994). In the ODZ, with little or no oxygen to oxidize Fe and Mn^{2+} , the reduced metals may be completely mobilized and diffuse out of the sediment (Nameroff, 1996). The elevated porewater PO_4^{3-} levels may be due, in part, to the absence of precipitated metal-oxides that ordinarily could bind with and sequester phosphorus (Ingall et al., 1993). Ultimately, however, it is not at all clear how to explain a C:P ratio of 20, which is substantially lower than the ratio of 106 predicted by Redfield stoichiometry. The presence of high C:P ratios in the sediments near the Mexican ODZ has also been discussed but not resolved by Schuffert et al. (1994)

Table 2.8 Nutrient regeneration ratios for the Washington and Mexico continental margins. Washington margin ratios are calculated from regenerated N and P derived from NH_4^+ and PO_4^{3-} data presented in Devol and Christensen (1993).

	Mexico	Washington	Redfield
C:N	10.2	22.5	6.63
N:P	1.99	11.6	16
C:P	20.2	259	106

For comparison, I also calculated the Washington margin nutrient regeneration ratios from data presented in Devol and Christensen (1993; *see* Table 2.8). The C:N regeneration ratio of 22.5 was much larger than the Redfield ratio of 6.63. This discrepancy is consistent with the presence of nitrification and subsequent denitrification in these sediments. Devol and Christensen (1993) have estimated that coupled nitrification-denitrification consumes as much as half of the remineralized organic nitrogen on the Washington margin. Also notable, is the Washington margin C:P ratio (more than twice Redfield), suggesting a potentially large phosphorus sink in these sediments. One possible explanation is the adsorption of regenerated P to iron oxy-hydroxides (Schulz et al., 1994; Suess, 1979). Phosphorous burial, which would also increase the observed C:P regeneration ratio, has been shown to be more efficient in oxic sediments (Ingall and Jahnke, 1994; Ingall et al., 1993). The presence of coupled nitrification-denitrification and the large C:N regeneration ratio on the Washington margin, taken together with the near-Redfield C:N regeneration ratio on the Mexican margin, suggests not only the absence of nitrification in the Mexican sediments but also that the denitrification reaction does not include the conversion of NH_4^+ to NO_3^- or N_2 .

A CARBON BUDGET FOR THE MEXICAN AND WASHINGTON MARGINS

The attenuation of the flux of organic carbon with depth on both margins examined in this study indicated that a larger percentage of the export flux from the surface ocean reaches the sediments on the Mexican margin. About 25% of the export flux reaches the Mexican margin vs. 5% for the Washington margin, although, the

Mexican margin input rates are lower in an absolute sense than the Washington rates. The carbon input rates on the Mexican margin were measured directly using sediment traps as well as calculated from determinations of carbon burial and carbon oxidation; the two estimates agreed quite well (*see* Figure 2.11 and Table 2.9). Using measured carbon burial and oxidation rates, and calculated carbon input rates an organic carbon budget can be constructed for the Mexican margin sediments.

Table 2.9 Carbon budget for sediments above, within, and below the Mexican margin ODZ and for the Washington shelf/slope (<1000 m depth) and the deep Washington slope (>1000 m depth). All rates and fluxes are in $\text{mmol m}^{-2} \text{d}^{-1}$, sediment accumulation rate S_{acc} is cm yr^{-1} and burial efficiency in percent.

	Mexico			Washington	
	Oxic Shelf	ODZ	Oxic Slope	Shelf/Slope	Deep Slope
O ₂ consumption	0.94 ± 0.3	0.00 ± 0.001	0.94 ± 0.7	5.58 ± 3.4	0.82 ± 0.4
Denitrification	1.47 ± 0.6	1.13 ± 0.3	0.37 ± 0.1	1.65 ± 0.6	0.18 ± 0.2
SO ₄ ²⁻ reduction	1.45 ± 0.6	1.05 ± 0.4	0.25 ± 0.2	5.95 ± 3.8	0.45 ± 0.3
Total C _{oxid} rate	4.7 ± 0.99	3.5 ± 0.99	1.6 ± 0.34	9.4 ± 4.4	1.5 ± 0.6
POC (wt. %)	4.1 ± 2	8.6 ± 1	7.94 ± 3	1.5 ± 0.7	1.95 ± 0.5
S _{acc} Rate	0.06 ± 0.03	0.031 ± 0.01	0.015 ± 0.01	0.09 ± 0.04	0.01 ± 0.01
C Burial	1.4 ± 0.2	1.7 ± 0.74	0.5 ± 0.3	2.4 ± 1.1	0.21 ± 0.2
C Input (Oxid.+Bur.)	6.13	5.31	2.06	11.8	1.66
C Input (Traps)	6.1 ± 0.9	4.7 ± 1.4	2.7 ± 0.3		
Burial Efficiency	19.3	38.2	18.5	19.5	12.4
Oxidation Efficiency	80.7	61.8	81.5	80.5	87.6

This budget cannot be a perfectly closed estimate because it is based on independent estimates of carbon burial and carbon input but it serves to illustrate the differences in the extent of degradation and preservation within, above, and below the ODZ. A similar budget for the Washington margin can also be developed for comparison (Table 2.9). The Mexican margin budget and the deep Washington slope estimates are based on results from this study, while the Washington shelf/slope estimates have drawn heavily from the results presented by Archer and Devol (1992) and Devol and Christensen

(1993). The Mexican margin has low input rates because the primary production rate in this region is relatively low. The input rates, relative the primary production rate, are higher than they would be in other regions because carbon flux to the sediments does not attenuate as sharply through the ODZ as it does in other locations (*see* Chapter 2). The relatively low carbon oxidation rates on the Mexican margin allow more of the input flux to be buried especially within the ODZ where burial efficiencies (burial expressed as a percentage of the carbon input rate) are as high as $38 \pm 10\%$. The 10% error in the burial efficiency was estimated using a Montecarlo-style simulation of the analytical errors (Bevington and Robinson, 1992). The Washington margin is a more typical continental margin with higher carbon input and oxidation rates and burial efficiencies of approximately $20 \pm 10\%$. In the deeper sediments of the Washington slope the burial efficiencies were lower (Table 2.9), approaching conditions more typical of the deep sea. The depth at which the Washington margin burial efficiencies dropped to low levels (<10%) occurred at relatively shallow water depths because the Cascadia Basin (the local abyssal plain) is only about 2800 meters deep. Conditions that allow for carbon oxidation to balance carbon input, however, are dependent upon not only water depth, but also carbon supply, and oxygen exposure which are related to distance from shore as well as water depth. The burial and oxidation efficiencies from Washington margin carbon budget for the deep stations (>600 m) were very similar to burial efficiencies reported for the California margin (Reimers et al., 1992). The California margin sediments between depths of 500 and 4500 m had an average carbon burial efficiency of 13% based on an input rate of $2.03 \pm 0.43 \text{ mmol m}^{-2} \text{ d}^{-1}$ and a burial rate of $0.29 \pm 0.23 \text{ mmol m}^{-2} \text{ d}^{-1}$. The California margin primary production rates (Reimers et al.; 1992) were roughly comparable to those off the Washington slope (54 vs. 67 $\text{mmol m}^{-2} \text{ d}^{-1}$) and the carbon oxidation rates attenuated similarly; this comparison suggests that Washington and California margins are both representative of typical carbon burial conditions along the eastern north Pacific Ocean. Furthermore, I suggest that the general similarity in the budgets for Washington, California, and the oxic portions of the Mexican margin highlights the presence of unusually high burial efficiencies in the ODZ off Mexico.

SUMMARY

The sedimentary carbon oxidation rates on the Mexican continental margin were lower and attenuated less with depth in the water column than those of the Washington continental margin. The lower carbon oxidation rates were due in part to lower productivity in the surface waters, but more importantly, they also appeared to be a function of reduced oxidation in the ODZ. The rain rate attenuation coefficient of $\alpha = 0.43$ was much smaller than the 1.1-0.7 that is typical of most oceanic regimes. The smaller depth attenuation appeared to result from decreased organic matter degradation within the oxygen deficient water column between 150 and 1000 m. Sediment trap fluxes of organic carbon from this region which agreed well with calculated carbon input rates, demonstrated a markedly reduced attenuation in the carbon flux to the sediments.

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Although the Mexican margin carbon oxidation rates are lower in an absolute sense than those of the Washington margin, a greater percentage (relative to the primary production rate) of the organic carbon rain reached these sediments because there is less degradation in the anoxic water column during transit to the sediments.

The Mexican margin ODZ appeared to have an effect on the relative importance of the different electron acceptors in the total carbon oxidation rate and the regeneration of N and P. The C:N stoichiometry of NH_4^+ regeneration on the Mexican margin was ~ 10.0 , roughly comparable to the theoretical ratio of 6.62, implying no nitrification in this system. By comparison, the Washington margin had a significant component of coupled nitrification-denitrification and a regeneration ratio much greater than the theoretical ratio. The Mexican margin sedimentary denitrification rate was relatively low compared to that of oxic continental margin regions. The absence of a significant amount of nitrification will limit the denitrification rate to that which can be supplied by the diffusive NO_3^- flux. The regeneration ratios lent support to the assumption of a C:N stoichiometry of 106:84.8 for the denitrification reaction in the Mexican sediments and suggest that there is no oxidation of NH_4^+ occurring in the sediments.

The results from the study of the attenuation in the carbon flux and the carbon budget calculations suggested that the oxygen-deficient zone may operate to increase the rate of organic matter burial (relative to the primary production rate) in Mexican sediments in two ways. First by allowing a greater fraction of the export flux from the surface ocean to reach the sediments, and second by decreasing the efficiency with which carbon is oxidized after it is deposited on the seafloor. Why organic matter oxidation should be less efficient in this region remains a question for further study.

CHAPTER 3: THE EFFECTS OF OXYGEN AND PHYSICAL MIXING ON ORGANIC MATTER DEGRADATION IN SEDIMENT INCUBATION EXPERIMENTS

INTRODUCTION

The long established controversy over the role of oxygen in organic matter preservation has inspired many investigations of microbial organic matter decomposition under both aerobic and anaerobic conditions. Early work suggested that aerobic carbon oxidation was the most important form of respiration in typical sediments (Jørgensen and Sorensen, 1985; Sorensen et al., 1979) and implied that anaerobic bacteria were fundamentally less efficient at oxidizing organic matter because the diagenetic reactions using non-oxygen electron acceptors (*i.e.*, NO_3^- , FeOOH , MnO_2 , or SO_4^{2-}) yield less energy on a per-mole basis than the aerobic degradation reaction (Froelich et al., 1979). Most experiments evaluating organic matter degradation under oxic and anoxic conditions indicated that there was no intrinsic difference in the rate of organic matter degradation by aerobes and by anaerobes; however, these studies often relied on fresh plankton or small easily degradable organic molecules as substrates (Canfield, 1989; Foree and McCarty, 1970; Jewell and McCarty, 1971; Lee, 1992). More recently, it has been recognized that aerobic pathways of organic matter degradation favor the production of CO_2 as an end-product while anaerobic conditions favor the production of DOC from organic matter (Hansen and Blackburn, 1991). This may be due to the fact that the first step in degradation by anaerobic consortia likely requires the hydrolysis of complex organic molecules to the smaller, low-molecular weight organic acids that can then be mineralized to CO_2 by various electron acceptors or due to the inherent production of low molecular weight organic acids during fermentation processes. Aerobes, by contrast, may be able to mediate both the hydrolysis and mineralization of complex molecules (Kristensen et al., 1995). It has been suggested that fresh organic

material is equally available to all metabolic pathways (aerobic and anaerobic alike) but that recalcitrant or highly degraded material is more readily mineralized by aerobic bacteria (Andersen, 1996; Canfield, 1994; Hedges and Keil, 1995; Kristensen et al., 1995).

Bioturbation and physical mixing also have a significant impact on the rates and extent of organic matter decomposition. Mixing and irrigation processes whether as a result of macrofaunal activity or of turbulence events will increase the supply of oxidizing power to depths in the sediment that cannot be achieved by diffusion alone (Aller, 1982; Berner, 1980). Mechanical (*i.e.*, non-biological) mixing alone has been shown to enhance the rates of microbial activity in inter-tidal sediments (Deming, personal communication, Ritzrau and Deming, submitted, and Ritzrau, 1988). Recently, Aller (1994) has suggested that bioturbation is fundamentally linked to the role of oxygen in the degradation of organic matter because the mixing process changes the redox potential of the sediments from oxic to anoxic on short time scales. Aller's (1994) work provides evidence that degradation rates in incubations that oscillated between oxic and anoxic conditions are higher than rates in incubations with uniformly oxic conditions and higher than rates in incubations that were only "oscillated" once. Intrinsically, bioturbation must also be related to the presence of oxygen as the large, sediment-moving animals have metabolic oxygen requirements that prevent them from surviving very long at low oxygen concentrations.

Length of exposure to oxygen has been hypothesized as a control on organic matter preservation (Hartnett et al., 1998; Hedges et al., in press; Hedges and Keil, 1995; Keil et al., 1994a). Oxygen exposure time (OET) is a function of both oxygen concentration and the depth of oxygen penetration in the sediments. The oxygen exposure time is generally parameterized as a function of sedimentation rate; however, it can also be considered as a residence time within the oxic region that is influenced both by sedimentation and by mixing. Organic carbon preservation appears enhanced in regions with short oxygen exposure times and decreases with increasing length of oxygen exposure (Table 3.1). The sediments of the Mexican margin in the oxygen deficient zone

(ODZ) have burial efficiencies as high as 55% and exposure times of less than one month, while Washington margin sediments have burial efficiencies of less than ~20% and exposure times that are longer than a year (Hartnett et al., 1998). This suggests that oxygen exposure times on the order of months to years are sufficient to reduce burial efficiencies from >50% to the more typical values seen on the Washington margin.

Table 3.1 Organic carbon burial efficiency (%), oxygen exposure time (years) and organic carbon: mineral surface-area ratios ($\text{m}^2 \text{g}^{-1}$) for the Mexican and Washington continental margins. Data taken from Hartnett et al. (1998) and Hedges et al. (in press).

	Burial Efficiency	O ₂ Exposure Time	Approximate OC:SA
Mexico			
oxic shelf/slope	7.42-21.2	0.16-0.59	1
ODZ	21.5-53.1	<0.005	4
Washington			
shelf/upper slope	3.0-28.2	1.18-14.5	1
lower slope/rise	4.7-20.1	34.9-678	<1

If the critical O₂ exposure time for significant organic matter degradation is on the order of months, it should be possible to evaluate the effect of O₂ exposure through an oxygen manipulation experiment. I conducted a series of sediment slurry experiments and core incubation experiments under oxic and anoxic conditions to evaluate the potential for physical mixing and exposure to oxygen to enhance the rate and/or extent of organic matter degradation in sediments. The slurry experiments were designed to assess the effects of physical mixing only and do not address the effects of macrofaunal activity that may impart some chemical signature (*i.e.*, gut passage). The core incubation experiments require less manipulation of the system and therefore, might be more representative of natural conditions in the sediment column. The cores maintain the natural vertical zonation and diffusion limitation within the sediments that the slurries do not. These were experiments of potential, and were designed to provide information about the possibility for a change in redox or mixing conditions to influence organic matter degradation rather than to provide realistic models for the *in situ* rates of organic

matter oxidation. That said, they do allow for the manipulation of sediments in a controlled way that is likely to illuminate a bulk change in the system as a result of the experimental treatments.

The Mexican margin sediments in the ODZ have high organic carbon contents (in addition to high burial efficiencies) and low rates of carbon oxidation (*see* Chapter 2) they are also devoid of large macrofauna; the sediments are varved, confirming the absence of bioturbation. The organic matter in these sediments has clearly been resistant to the levels of *in situ* degradation imposed by anaerobic processes in the general absence of mixing over at least the last several hundred years. By comparing similar experiments on the Washington margin, where the sedimentary organic matter has been mixed and reprocessed by larger animals it should be possible to evaluate the effects of increasing oxygen exposure and physical mixing on the organic matter reactivity in Mexican margin sediments.

METHODS

SAMPLING SITES

Sediment cores were collected during cruises to the Washington margin in the summer of 1997 (WE 97) and the Mexican margin during the fall of 1996 (NH 96; *see* Chapter 2 for a more detailed description of the study sites, especially Figure 2.4). Cores were taken at stations above the oxygen minimum zone (100 meters) and within the oxygen minimum zone (350 meters off Mexico and 620 meters off Washington) on each margin (Figure 3.1). The 100-meter Mexican station had 3.1% organic carbon (by weight) and a bottom-water oxygen concentration of $25 \mu\text{mol L}^{-1}$. The oxygen deficient zone (ODZ) station, at 350 m, had unmeasurable bottom-water O_2 and 7.5% organic carbon. The Washington margin stations (120 and 630 meters) had 140 and 25 $\mu\text{mol O}_2 \text{ L}^{-1}$ and 1.7 and 2.8 % organic carbon, respectively (Table 3.2).

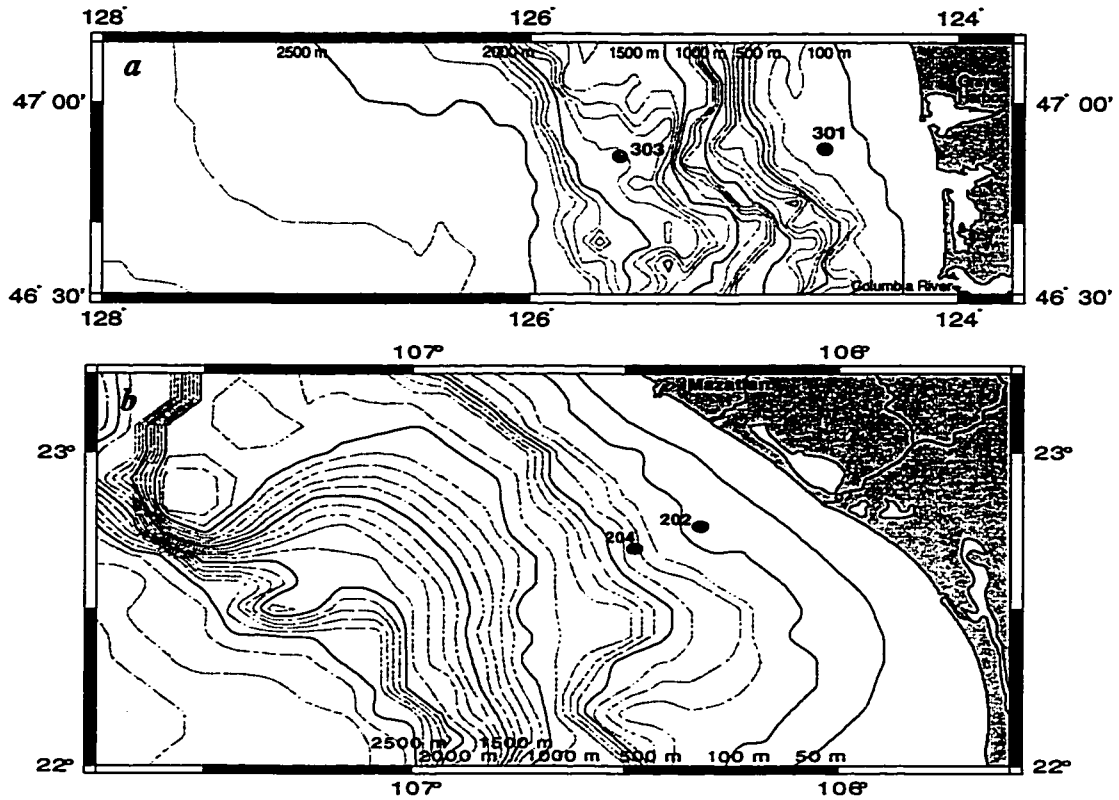


Figure 3.1 Charts with station locations for sediment slurry and core incubation experiments for the Washington (*a*) and Mexican (*b*) continental margin.

Table 3.2 Location, depth (meters), particulate organic carbon (POC) content (wt. %) and bottom-water oxygen concentration ($\mu\text{mol L}^{-1}$) for stations with slurry and core incubation experiments.

Station	Depth	Latitude	Longitude	POC	$[\text{O}_2]_{\text{bw}}$
Mexico					
NH 202	103	22° 46.01'	106° 19.16'	3.1	23
NH 204	360	22° 41.78'	106° 28.61'	7.5	0
Washington					
WE 301	119	46° 48.60'	124° 37.20'	1.7	140
WE 302	640	46° 49.69'	125° 05.82'	2.8	97

EXPERIMENTAL SET-UP

Slurry Incubations

Sediment cores were obtained with a Soutar box corer at each station, two subcores were collected from each box core with 12.8 cm I.D. acrylic core tubes. Each subcore was comprised of a 12-14 cm column of sediment with 6-8 cm of overlying water. Sediments and overlying water were homogenized in a large glass Erlenmeyer flask and sterile (autoclaved) seawater was added to bring the total volume to ~2400 ml. Temperature and O₂ concentration were measured to confirm that the core was recovered with bottom water and not surface seawater overlying the core. The slurries had a final porosity of between 0.90 and 0.96 (determined by mass of water lost upon drying to a constant mass at 65 °C) and generally contained ~ 1800 mg organic carbon (Table 3.3). The slurry was partitioned into 300-ml aliquots in sterile, glass 500-ml Erlenmeyer flasks with a Teflon-coated magnetic stir-bar and covered loosely with aluminum foil (Figure 3.2). The anoxic slurries were put into a N₂ filled glove bag while the oxic slurries were left open to the atmosphere. Oxygen concentrations were monitored using an oxygen microelectrode, and the slurries were completely anoxic within 18 hours of being placed in the glove bag. The oxic slurries remained within 50 % of saturation throughout the experiment. Slurries were mixed twice each day for four hours on magnetic stirring plates at low speed (~80 rpm). Incubations were kept in the dark at *in situ* temperatures (~8 °C) in a cold room. Every two days, O₂ concentrations were measured and 5 ml samples for DOC and POC were withdrawn with a Teflon syringe. Care was taken to maintain DOC “clean” conditions and to prevent contamination of the bacterial populations in the various incubations. Slurries were well stirred before collecting the samples to insure that a representative sample (both solid and liquid phases) was taken. Samples were centrifuged for 15 minutes at ~3,000 rpm to separate the water from the sediments.

Table 3.3 Slurry incubation set-up for each station: sedimentary organic carbon content (mg gdw^{-1}), total slurry volume (ml), volume of sediment (ml), porosity and organic carbon content (mg) in each slurry.

	Depth	OC	Total volume	Sediment volume	Slurry porosity	OC in slurry
Mexico						
NH 202	100	31.2	2,413	210	0.93	1747
NH 204	360	74.1	2,841	78	0.97	2002
Washington						
WE 301	120	17.0	2,261	369	0.90	2001
WE 302	630	28.0	2,180	203	0.91	1774

Sediments were frozen and returned to the laboratory for organic carbon analysis. Water samples were acidified with 2N HCl and dissolved organic carbon was analyzed on board ship by high-temperature oxidation. Slurry incubations lasted for 21 days on the Mexican margin cruise and for 19 days on the Washington margin cruise.

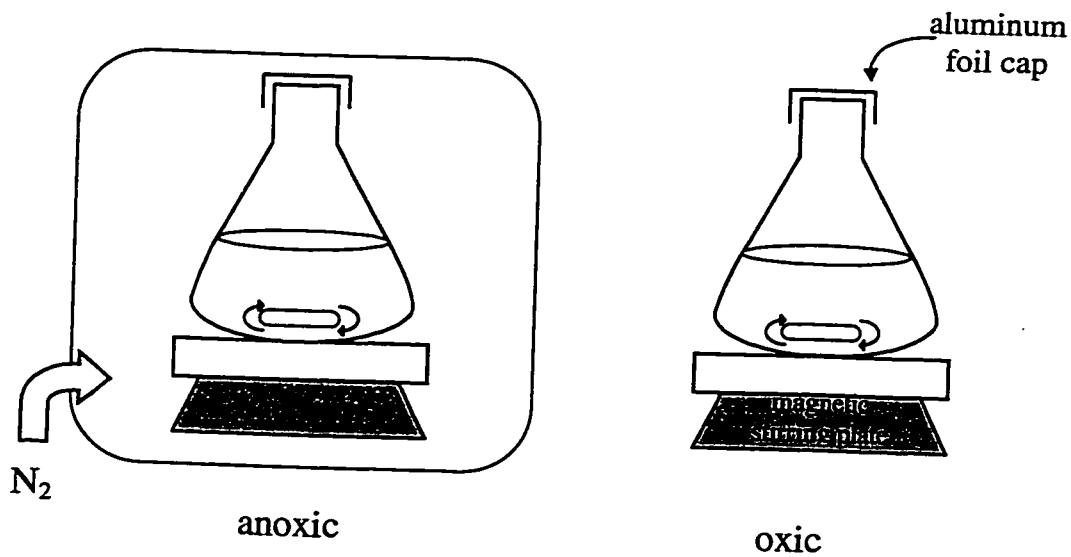


Figure 3.2 Schematic of the experimental set-up for the sediment slurry incubations. Anoxic conditions were maintained by keeping flasks in a N₂-filled glove bag.

Core Incubations

At each station, six subcores were collected in 12.8-cm I.D. acrylic core tubes for whole-core incubation experiments. Care was taken to collect cores that were as undisturbed as possible, based on visual inspection of the box core. The subcores contained roughly 10-12 cm of sediment and 12 cm of overlying water. Cores were closed with rubber stoppers and left with a 1-cm headspace (the overlying water was not in contact with the stoppers during the incubation experiments. The rubber stoppers were leached with seawater for 5 days prior to reduce to amount of DOC that might be associated with the stoppers. In half the cores the headspaces were flushed continuously with O₂ to maintain oxic conditions. In the other half, headspaces were flushed with nitrogen (Figure 3.3) and kept in an N₂-filled glove bag. The cores were incubated in the dark at *in situ* temperature (~ 8 °C) in a cold room. During the Mexican margin cruise, the overlying water was stirred with a Teflon-coated stir bar suspended from the rubber stopper and driven by an external rotating magnet at 60-80 rpm. On the Washington cruise, the overlying waters were bubbled gently with O₂ or N₂ rather than stirred. Under both conditions, there was no oxygen measured in the overlying water of the anoxic cores and the oxic cores were maintained at close to saturation oxygen concentrations. Oxygen concentrations were monitored by electrode every two days and samples were collected (2 ml) for dissolved organic carbon analysis. The experiments were conducted for approximately 20 days on both cruises. At the end of the experiment on the Mexican margin cruise, microscale subcores were taken from the incubation cores with a modified 60-cc syringe barrel and sliced at 1-mm intervals. Sediments from each interval were frozen, dried and analyzed for particulate organic carbon content.

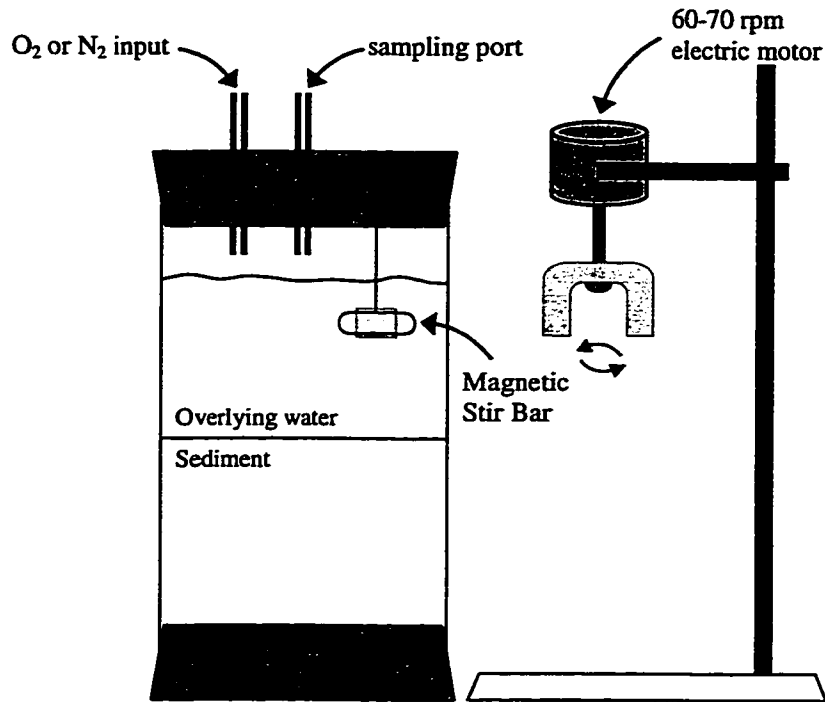


Figure 3.3 Schematic diagram of experimental set-up for whole core incubations. Anoxic conditions were maintained by keeping cores in a N_2 -filled glove bag and by flushing the headspace with N_2 .

MEASUREMENTS

Oxygen contents were determined in the slurries and cores using an oxygen microelectrode. The electrode was calibrated using air-saturated equilibrated seawater and either N_2 -purged seawater or an oxygen-free solution of saturated sodium sulfide in seawater as the saturation extremes. Sediment porosity was determined from the mass of water lost upon drying to a constant weight at $65^\circ C$. Organic carbon contents were determined after freeze-drying of the samples according to the methods of Hedges and Stern (1984). Dissolved organic carbon was determined by high-temperature oxidation using a Shimadzu TOC 5000 analyzer. Sediment mineral surface-areas were determined

by N₂ adsorption using a Quantachrome surface area analyzer (Keil et al., 1994c; Mayer, 1994b).

RESULTS

SLURRY INCUBATIONS

Dissolved Organic Carbon

Concentrations of DOC in the slurries increased over the course of the experiments. On both margins there were significant differences in the amount of DOC produced in slurries from the two different stations, but there was no difference (within the analytical uncertainty of the analysis,) in the DOC concentrations of the oxic and anoxic slurry treatments. The Mexican margin slurries (Figure 3.4a) from the 360-m station had the highest DOC production with DOC concentrations increasing rapidly from about 7 mg L⁻¹ to 25 mg L⁻¹ in the first 4 days and then increasing more slowly to a concentration of 40 mg L⁻¹ after 18 days. At the 100-m station, DOC concentrations in slurries from both treatments increased from 5 to 12-14 mg L⁻¹ after 7 days and remained fairly constant over the remainder of the experiment. The Washington margin slurries had more variable DOC concentrations over time, with less marked increases or differences between stations. The DOC concentrations increased slightly in the Washington margin oxygen minimum zone slurry (630 m) and were generally higher than the DOC concentrations at the 120-m slurry which showed little or no increase (Figure 3.4b). The slurries from the 120-m station had fairly high initial DOC concentrations of ~12 mg L⁻¹; at this station, DOC in the anoxic slurry increased rapidly to ~18 mg L⁻¹ and then decreased again. The oxic slurry initially decreased from 12 to ~3 mg L⁻¹ and then increased again. After day 6 both the oxic and anoxic slurries from this station behaved similarly with DOC concentrations showing concomitant increases and decreases of the same magnitude as the initial changes. After day 6, the average DOC concentration for both treatments at this station was roughly 11 mg L⁻¹. The slurries from the 630-m Washington margin station had initial DOC concentrations of ~5 mg L⁻¹; in both

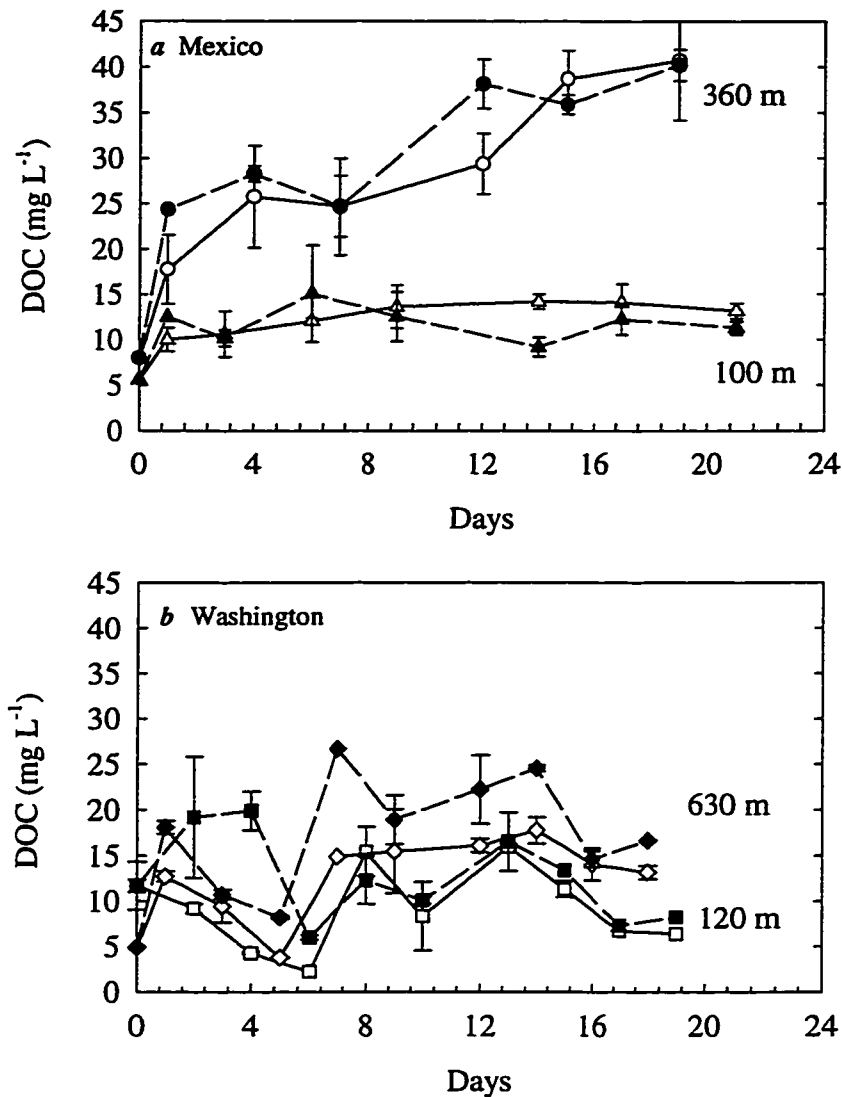


Figure 3.4 *a*) Concentrations of DOC (mg L⁻¹) over the course of sediment slurry incubations from the Mexican margin (360 m, circles; 100 m, triangles). *b*) DOC concentrations over the course of sediment slurry experiments from the Washington margin (630 m, diamonds; 120 m, squares). Solid symbols/dashed lines indicate anoxic treatments; open symbols/solid lines indicate oxic treatments. Error bars are the standard deviation of triplicate incubations at each station.

treatments, the DOC concentrations showed an initial rapid increase and then decreased until day 5. After day 5, the DOC concentrations increased again and leveled out after

about day 9 at $\sim 22 \text{ mg L}^{-1}$ and 16 mg L^{-1} in the anoxic and oxic treatments, respectively. At the end of the incubations, the DOC concentrations in slurries from the shallow stations on both margins were roughly the same (~ 9 to 11 mg L^{-1}), the Washington margin oxygen minimum zone station (630-m) had slightly higher DOC concentrations at roughly 20 mg L^{-1} , and the Mexican margin ODZ station (360 m) had the highest DOC concentrations (40 mg L^{-1}).

Particulate Organic Carbon

Particulate organic carbon contents generally decreased over the course of the slurry experiments under both oxic and anoxic conditions (Figure 3.5). Weight percent organic carbon in the slurries from the Mexican margin decreased from 3.10 wt. % to 2.63 ± 0.15 wt. % at the 100-m station. At the 360-m station organic carbon decreased from 7.45 wt. % to 7.10 ± 0.15 wt. % (Figure 3.5 a, b). These decreases correspond to the removal of 180 to 260 mg of carbon from the 100-m slurry and 34.6 to 138.4 mg of carbon from the 360-m slurry. The oxic and anoxic slurries showed similar behavior at both stations. At the 100-m station $12.7 \pm 1.8\%$ of the initial carbon was consumed in the oxic slurry and $12.6 \pm 2.3\%$ of the initial POC was consumed from the anoxic slurry. At the 360-m station, less organic matter was consumed, with $3.6 \pm 1. \%$ and $5.7 \pm 1.7\%$ of the initial being removed from the oxic and anoxic slurries respectively (Table 3.4). Assuming an exponential removal of carbon, it is possible to calculate $\tau_{1/2}$, a half-time, for the organic matter in the slurry. The half-times for the Mexican slurry experiments ranged from 233 to 373 days in the ODZ station slurry and from 101 to 103 days in the 100-m station. This calculation assumes that all of the organic matter in the slurry was reactive, which is not likely to be correct; however, the rates of degradation were fast and would have been faster still if the model had included a fraction of non-reactive carbon.

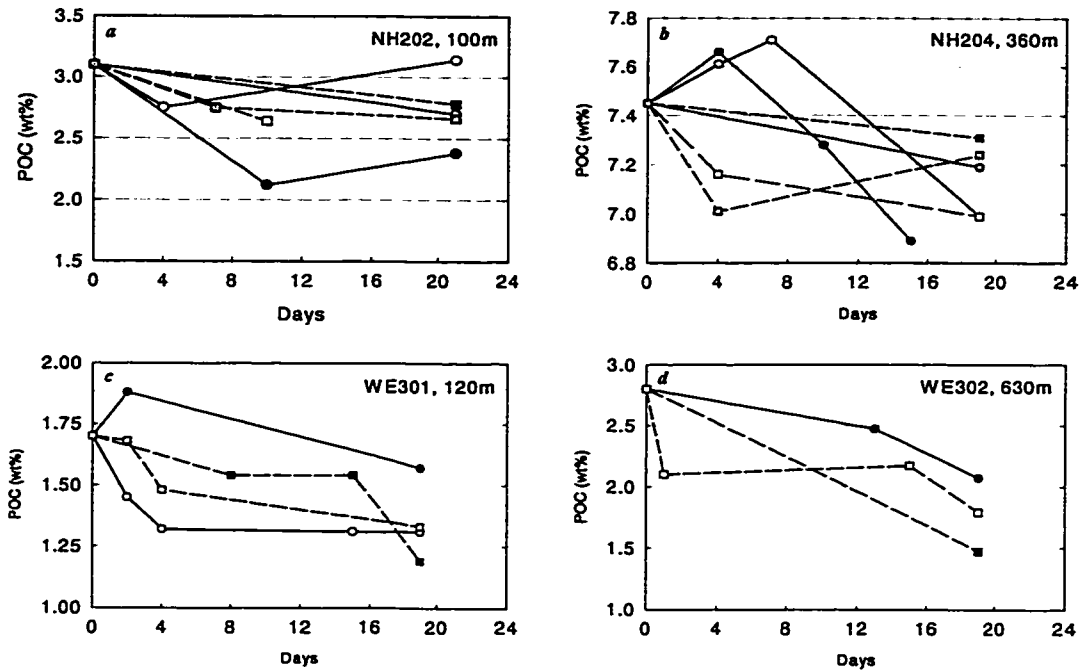


Figure 3.5 Particulate organic carbon content (wt. %) during sediment slurry incubations from the Washington and Mexican margins: *a*) NH 202, 100m; *b*) NH 204, 360 m; *c*) WE 301, 120 m; *d*) WE 302, 630 m. Round symbols with solid lines indicate oxic incubations; and square symbols with dotted lines indicate anoxic incubations.

On the Washington margin, POC in the slurries decreased from 1.74 wt. % to 1.34 ± 0.11 wt. % at the 120-m station and from 2.8 wt. % to 1.8 ± 0.25 wt. % at the 630-m station. The oxic and anoxic slurries showed quite similar degrees of carbon removal ($25.9 \pm 4.1\%$ vs. 22.9% of the initial carbon lost, respectively). At the 120-m station, these decreases correspond to 459-634 mg of organic carbon mineralized from the slurry (Figure 3.5 c, d) and half-times of 46 days and 53 days in the oxic and anoxic slurries respectively. At the 630-m station, there were 518-943 mg of organic carbon mineralized during the experiment with $41.8 \pm 5.7\%$ of the organic carbon removed from the oxic incubations and 26.1% of the carbon removed from the anoxic incubations (*see* Table 3.4). Half-times for the 630-m slurry were 25 days in the oxic slurry and 45 days in the

anoxic slurry. The Washington slurries had faster degradation rates than the Mexican slurries with half times of less than two months. The shallow stations on both margins showed roughly similar degradation rates between the two treatments while the deeper stations apparently had larger differences between oxic and anoxic treatments.

Table 3.4 Particulate organic carbon contents (mg), POC loss (mg), percentage of initial organic carbon consumed and $\tau_{1/2}$ (days) in sediment slurry experiments from the Washington and Mexican margins.

	Depth (m)	POC Initial	POC loss		% POC _i consumed		$\tau_{1/2}$	
			Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic
Mexico								
NH 202	100	1747	220 ± 56	223 ± 36	12.7 ± 1.7	12.6 ± 2.3	103	101
NH 204	360	1841	67 ± 41	105 ± 34	3.6 ± 1.8	5.7 ± 1.7	373	233
Washington								
WE 301	120	2113	547 ± 123	485	25.9 ± 4.1	22.9	46	53
WE 302	630	1987	830 ± 161	517	41.8 ± 5.7	26.1	26	46

CORE INCUBATIONS

Dissolved Organic Carbon

Dissolved organic carbon concentrations in the overlying water of the core incubations were quite variable over the course of the experiments. Generally, DOC concentrations increased from the beginning of the experiments (Figure 3.6a, b), but this was not always the case, nor did replicate cores from the oxic and anoxic treatments at each station always show the same trends. The Washington margin core incubations from the 120-m station had larger overlying water DOC increases in the anoxic cores than in the oxic cores, while the DOC concentrations in the anoxic cores were consistently higher than those of the oxic cores over the 13-day experiment (Figure 3.6). The initial DOC values from this station were quite low ($\sim 1 \text{ mg L}^{-1}$), indicating that there was little or no disturbance of the core and the surface sediments during subcoring. The incubated cores from the 630-m station did not show any appreciable increase in overlying water DOC concentrations over the 18-day incubation period under either oxic

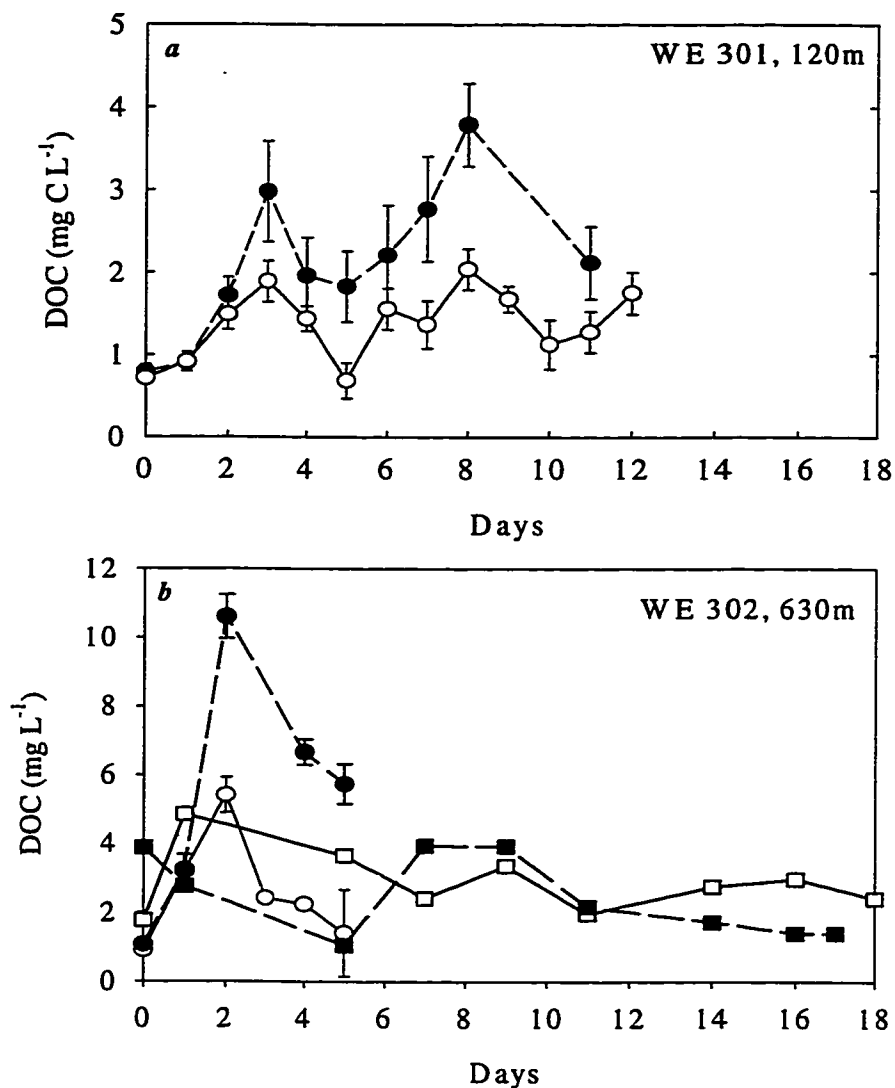


Figure 3.6 Concentrations of DOC (mg L^{-1}) during Washington margin core incubations at: *a*) 120 m, where symbols for oxic incubations are open circles/solid lines, and anoxic incubations are solid circles/dashed lines; and *b*) 630 m, where squares are long term incubations, circles are short (5-day) experiments; open symbols/solid lines are oxic treatments, and solid symbols/dashed lines are anoxic treatments.

or anoxic conditions. The initial DOC concentrations in the anoxic core were somewhat elevated, suggesting that the cores may have been disturbed during collection. Two pairs of short-term core incubations at this station (from a different box core) showed higher

DOC concentrations in the overlying water of the anoxic cores (Figure 3.6b). Core incubations from the Mexican margin all had somewhat elevated initial DOC concentrations in the overlying water (3-5 mg L⁻¹; Figure 3.7a, b), indicating that the

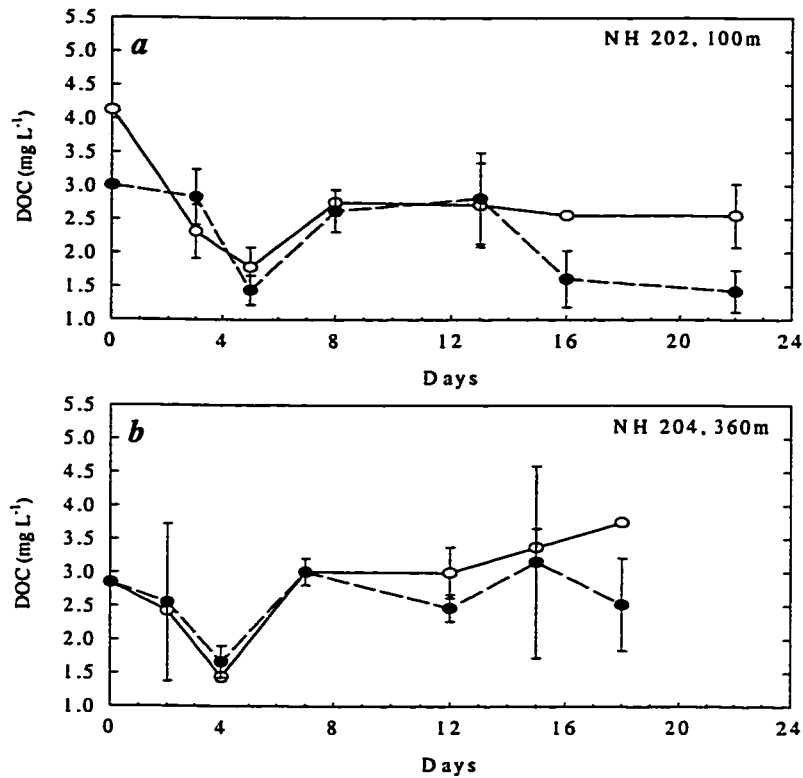


Figure 3.7 Concentrations of DOC (mg L⁻¹) during Mexican margin core incubations at: *a*) 100m and *b*) 360 m. Symbols for oxic incubations are open circles/solid lines and symbols for anoxic incubations are shaded circles/dashed lines. The point at which the incubations appear to have adjusted to the effects of sampling is indicated by the vertical dashed line.

surface sediments were disturbed either during recovery of the box core or during subcoring. Dissolved organic carbon concentrations initially decreased; after 5 days, they had dropped to ~1.5 mg L⁻¹ (a typical value for bottom-water DOC). After 5 days, the DOC concentrations generally showed a small increase with little or no difference

between the oxic and anoxic incubation conditions. There was slightly more DOC produced in the cores from the deeper station after 16 days (Figure 3.7), but no significant difference in DOC production between the oxic and anoxic cores from either Mexican station.

Particulate Organic Carbon

Particulate organic carbon was measured at 2-mm intervals throughout the top 3 cm of the sediments of the incubated cores from the Mexican ODZ station. Organic carbon contents in the surface sediments of the incubated cores were lower (6.2 wt. % in the oxic core and 6.5 wt. % in the anoxic core) than those determined from the core collected and processed for carbon analysis immediately upon retrieval (Figure 3.8). In the top 1 to 2 cm of the core, both the oxic and the anoxic incubated cores the POC contents were lower than 7.0 wt. %; below ~2.5 cm, organic carbon contents increased, approaching the 7.0 wt. % in the sectioned core. The decrease in organic carbon at the top of the core may indicate increased organic matter degradation in the incubated cores; however, the rates in the core incubations may also be enhanced due to disturbance of the system during sampling.

DISCUSSION

SLURRY INCUBATIONS

Under the initial hypothesis that organic matter preserved in sediments under anoxic conditions can be extensively degraded by exposure to O₂ and mixing, I expected to see the greatest carbon losses in the oxic slurry of the Mexican ODZ sediments (360 m). I further expected that there would be less carbon removed in the Washington slurries as a whole because presumably the sedimentary organic carbon had been more degraded by exposure to O₂ and mixing *in situ*. As expected, the sediment slurries had high rates of organic matter degradation. In undisturbed sediments, diffusion governs the supply of oxidants and removal of metabolic byproducts which may inhibit

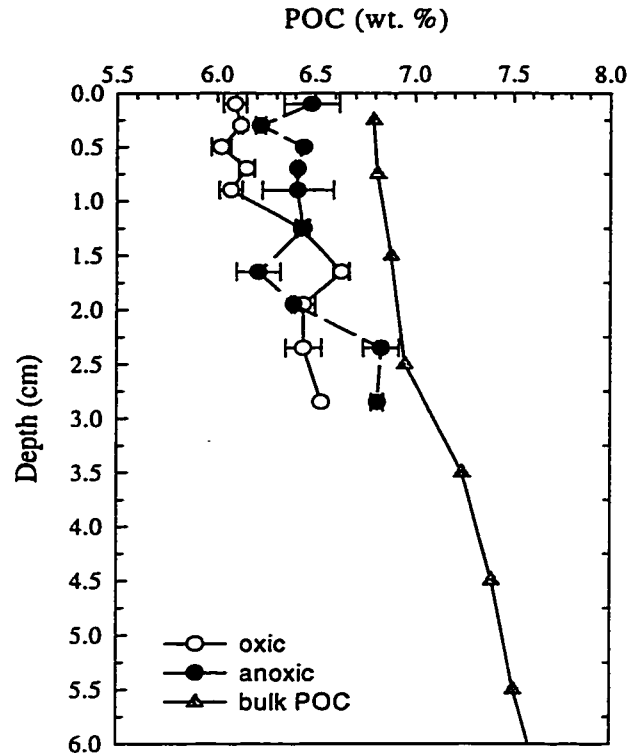


Figure 3.8 Particulate organic carbon profiles in sediments from the 630-m Mexican margin core incubation. Open circles/solid line indicate the oxic core, and solid circles/dashed line indicate the anoxic core. Sedimentary organic carbon profile from 360 m is shown as well. (shaded triangles). The error bars represent the standard deviation of duplicate determinations of the POC content.

degradation rates. Physical mixing of sediments can reduce limitation due to diffusion by reducing the gradients around microorganisms attached to particles, thereby increasing degradation rates.

To evaluate the rate and extent of carbon loss under the different incubation conditions, I calculated carbon degradation as the bulk POC loss over the time of the incubation. The POC loss was taken as the difference between the average final POC for each treatment and the initial POC value. It is clear from figure 3.5 that changes in the POC content were not always linear (or even monotonic), so that this calculation is clearly a simplification of the processes occurring in the experiment. Production of DOC

was calculated in a similar way, assuming that the DOC concentrations at the final time point (*see* Figure 3.4) represented the change over the course of the experiment. Again, the DOC time-course data indicate both increases and decreases in the DOC concentration; suggesting that this is a rough estimate of net DOC production. The POC removal rates ranged from 0.98 to 12.1 $\mu\text{mol C cm}^{-3} \text{d}^{-1}$ (Table 3.5). DOC production rates ranged from 0.041 to 0.173 $\mu\text{mol cm}^{-3} \text{d}^{-1}$. The rates of DOC production in the slurries from both Washington margin stations and the shallow Mexican margin station were $<2\%$ of the POC removal rates. Only at the Mexican 360-m station, in heart of the ODZ, did DOC production account for a larger fraction of the organic carbon removal; 18 and 11% of the carbon removal in the oxic and anoxic slurries, respectively. If one assumes that total CO_2 (TCO_2) production is calculated as the difference between POC loss and DOC production; it is clear from Table 3.5 that the DOC produced in the slurries at all stations was only a small percentage of the total carbon oxidized.

Table 3.5 Average rates of POC consumption, DOC and TCO_2 production in slurries incubations. All rates are in $\mu\text{mol cm}^{-3} \text{d}^{-1}$.

		POC Removal	DOC Production	TCO_2 Production
Mexico				
100	Oxic	2.9 ± 0.7	0.048 ± 0.004	2.85 ± 0.7
100	Anoxic	2.9 ± 0.5	0.041 ± 0.003	2.82 ± 0.6
360	Oxic	1.6 ± 0.5	0.173 ± 0.04	1.37 ± 0.5
360	Anoxic	0.98 ± 0.5	0.171 ± 0.02	0.81 ± 0.5
Washington				
120	Oxic	7.9 ± 1.8	0.059 ± 0.01	7.81 ± 1.8
120	Anoxic	7.0	0.061 ± 0.003	6.91
630	Oxic	12.1 ± 2.5	0.070 ± 0.007	11.9 ± 2.5
630	Anoxic	7.5	0.097 ± 0.005	7.43

Based on previously reported work (Hansen and Blackburn, 1991; Kristensen et al., 1995), I expected to see more DOC production in the anoxic slurries, but the data indicate that roughly the same amount of DOC was produced in each treatment for a given station.

Production of CO₂ was highest in Washington margin slurries. Carbon oxidation (POC loss) was greatest at the 630-m station and averaged 12.1 $\mu\text{mol cm}^{-3} \text{d}^{-1}$ in the oxic slurries and 7.5 $\mu\text{mol cm}^{-3} \text{d}^{-1}$ in the anoxic slurries. At the 120-m station, carbon oxidation rates were 7.9 and 7.0 $\mu\text{mol cm}^{-3} \text{d}^{-1}$ in the oxic and anoxic slurries respectively. On the Mexican margin, oxic POC removal rates were 2.9 $\mu\text{mol cm}^{-3} \text{d}^{-1}$ in the 100-m slurry and 1.6 $\mu\text{mol cm}^{-3} \text{d}^{-1}$ in the 360-m slurry. The loss of POC in the anoxic slurries was 2.9 and 0.98 $\mu\text{mol cm}^{-3} \text{d}^{-1}$ at the 100 and 360-m stations respectively. Contrary to expectations, the Mexican ODZ sediments did not show more enhanced degradation in the oxic slurry. The Washington slurries, which were expected to be the least susceptible to the effect of mixing, showed the highest degradation rates and the largest carbon loss. These results suggest that the Mexican ODZ carbon may be less reactive than the carbon at all of the other stations. This apparently low reactivity is not altered by mixing or by exposure to O₂.

Physical disturbance in the samples did enhance the rates of organic matter degradation on a relative scale. The degree of enhancement was estimated by comparing the slurry rates to the carbon oxidation rates in unstirred, anaerobic jar incubations of sediments from the Washington and Mexican continental margins presented by Kristensen et al. (in press), and to the *in situ* carbon oxidation rates from the same locations (see Chapter 2). Production of TCO₂ in anaerobic jar incubations from the Mexican margin was 0.027 $\mu\text{mol cm}^{-3} \text{d}^{-1}$ at 140 m and 0.022 $\mu\text{mol cm}^{-3} \text{d}^{-1}$ at 350 m; on the Washington margin jar incubation rates were 0.037 $\mu\text{mol cm}^{-3} \text{d}^{-1}$ at 110 m and 0.023 $\mu\text{mol cm}^{-3} \text{d}^{-1}$ at 620 m (Kristensen et al., in press). These jar rates are 30-300 times lower than the slurry rates (Table 3.6). The *in situ* carbon oxidation rates determined by the benthic lander are also substantially lower than the slurry rates. I assumed that the lander integrates over the top 10 cm of the sediment column and calculated rates that range from 0.23 to 0.79 $\mu\text{mol cm}^{-3} \text{d}^{-1}$ (Table 3.6). In general, the *in situ* rates were of the same magnitude as the jar rates. The jar rates were slightly lower than the *in situ* rates, probably because they reflect only anaerobic organic matter degradation (essentially SO₄⁼ reduction), whereas the *in situ* rates also included the

contributions of oxic and sub-oxic degradation pathways (O_2 consumption, denitrification, Fe and Mn-oxide reduction). At the two shallow stations, the *in situ* rates were about twice the jar rates, possibly due to irrigation enhancement of the benthic flux (Archer and Devol, 1992). The comparison between the slurry rates and the *in situ* or jar-incubation rates cannot be precise, since they are very different determinations, but rather is meant to emphasize the degree of enhancement in the slurry degradation rates. The main point is that the rate of organic carbon degradation was greatly enhanced at all stations, on both margins, whether under oxic or anoxic conditions when the sediments were mixed.

Table 3.6 Comparison of total CO_2 production in slurry incubations to *in situ* carbon oxidation rates and jar incubation TCO_2 production rates. The lander rates are calculated assuming they integrate over the top 10 cm of sediment; the jar rates are calculated from the integrated rates presented in Kristensen et al. (in press).

		Total CO_2 Production ($\mu\text{mol cm}^{-3} \text{d}^{-1}$)		
		Slurries	<i>In situ</i>	Jar incubation
Mexico				
100	Oxic	2.85	0.060	
100	Anoxic	2.82		0.027
360	Oxic	1.37		
360	Anoxic	0.81	0.045	0.022
Washington				
120	Oxic	7.81	0.079	
120	Anoxic	6.91		0.037
630	Oxic	11.9	0.023	
630	Anoxic	7.43		0.023

It was surprising that the Mexican ODZ sediments with the highest carbon contents were the most resistant, despite the extensive degradation in the slurry experiments. These ODZ sediments had the slowest oxidation rates and the least carbon removal. In addition, I did not expect to see the largest differences between the two margins, regardless of treatment, rather than between the different oxygen treatments (Figure 3.9). These results may be consistent, however, with the trends in bulk organic carbon content on these two margins in that the ODZ sediments have the highest carbon and thus should be the least

degraded. The slurry-incubation experiments imply that carbon availability or reactivity is an important parameter and that the organic matter in the Mexican margin sediments from the ODZ is somehow less susceptible to microbial attack than the organic matter from above the ODZ or than the organic matter from the Washington margin.

It appears that whatever is causing the Mexican ODZ organic matter to escape degradation in the sediments was not affected by the slurring procedure or by the addition of oxygen. This organic carbon appeared to be less reactive than the organic carbon at the other stations. One explanation for this low reactivity is some physical protective mechanisms such as sorption to mineral surfaces (Keil et al., 1994b; Keil et al., 1994c; Mayer, 1994a; Mayer, 1994b). Surface protection has been suggested as a mechanism for the preservation of high levels of organic carbon in sediments from the Peru Margin ODZ (Bergamaschi et al., 1997). The Mexican ODZ sediments have high

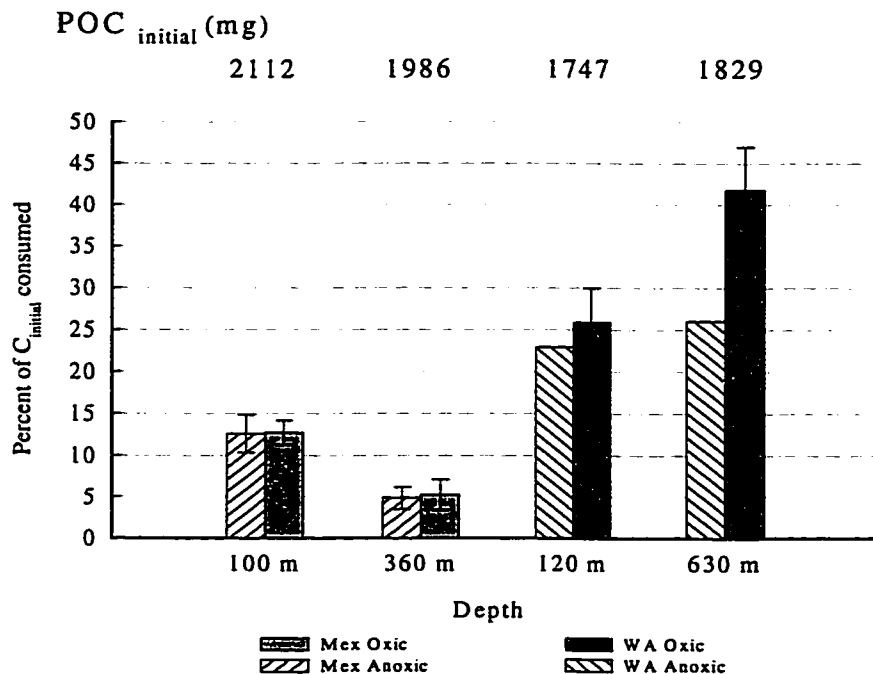


Figure 3.9 Histogram of percent of initial carbon removed from each slurry. Error bars are standard deviations of final POC values in replicate slurries

OC:SA ratios, a finding that further suggests a role for surface-associated protection. The apparent lack of reactivity also suggests that the organic matter preserved in the Mexican ODZ sediments is more degraded; however, Keil et al. (1998) have presented amino acid and organic carbon data that suggest the ODZ organic matter is relatively fresh and less degraded than the organic matter outside the ODZ.

CORE INCUBATIONS

The whole-core incubations were designed to evaluate carbon degradation under oxic and anoxic conditions in a relatively undisturbed system, the results of which could then be compared to the manipulated slurry incubations. As it turned out, the small changes in DOC concentration and somewhat variable time-course results for both set of incubations made the comparison challenging. Part of the difficulty was due to the fact that DOC concentrations in overlying water were lower than porewater concentrations (Keil and Devol, unpublished data) by a factor of 5 to 10. Contaminating the overlying water with high concentrations of porewater-DOC is easy, if the sediment is at all disturbed during retrieval or subcore collection. Such contamination is generally not the case for dissolved species that have decreasing porewater profiles (*e.g.*, O_2 and NO_3^-). Significant amounts of DOC may also be associated with the surface 'fluff' layer, which is difficult to collect intact from the ocean floor. The initial decreases in overlying-water DOC were likely due to a combination of consumption by bacteria in the overlying water, and adsorption to fine grained material that settled back to the sediments. Microbial populations are known to respond rapidly to physical disturbances by increasing metabolic rates and biomass; relatively shortly after the "disturbance event" they will return to normal conditions (Findlay et al., 1985).

The Washington margin core incubations from the 120-m station showed the clearest increases in overlying-water DOC concentrations and was the only station with differences in DOC production between the oxic and anoxic cores. This was also the only station where the overlying water was not initially contaminated during sampling. Porewater DOC concentrations were generally higher than bottom-water DOC

concentrations at both the Washington and the Mexican stations (~ 12 and ~ 4 mg L⁻¹ in the porewater vs. 1 mg L⁻¹ in the overlying water; Keil and Devol, unpublished data). This concentration difference should support a diffusive flux of DOC to the overlying water. The initial change in overlying water DOC with time can be used to estimate the flux from the sediments; the estimate will be conservative, given the assumption that no DOC consumption occurs in the overlying water. Using the rate of change in DOC over the first three days of incubation, the average DOC flux was 6.2 mmol m⁻² d⁻¹ from the anoxic cores and 2.7 mmol m⁻² d⁻¹ from the oxic cores (Table 3.7). Calculating the flux for day 1 through day 3 clearly over estimates the total amount of DOC produced (*see* Figure 3.6). Over the course of the entire experiment, however, there was both gain and loss of DOC from the overlying water, suggesting that the DOC flux from the sediments was readily degraded in the overlying water. An estimate of the net flux of DOC can be

Table 3.7 Calculated DOC fluxes from Washington margin core incubation experiments. The initial flux (days 1-3) was calculated using the concentration change over the first three days; the overall flux (final-initial) was calculated using the net concentration change over the entire experiment. Units for all fluxes in mmol m⁻² d⁻¹.

		DOC flux (days 1 - 3)	DOC flux (final - initial)
Washington			
120 m	Anoxic	6.24 ± 1.7	1.53 ± 1.1
120 m	Oxic	2.70 ± 0.3	1.39 ± 0.9

made by calculating a flux based on the concentration change from the beginning to the end of the experiment; however, this is likely to underestimate the flux, particularly at the beginning of the experiment. The DOC concentration changes in the Mexican margin core incubations were smaller than those from the Washington margin, implying that the fluxes were also lower; however, it was difficult to calculate a flux from the time course data in Figure 3.7. I expected to see more DOC produced in the cores incubated under anoxic conditions at all stations. No difference in the DOC concentrations between the

oxic and anoxic treatments was observed for either of the Mexican margin stations or the deep Washington station.

The DOC flux calculated here is lower than the total carbon oxidation rate at this station ($\sim 8 \text{ mmol C m}^{-2} \text{ d}^{-1}$, *see* Chapter 2) but it is of similar magnitude to the total carbon oxidation rates at deeper stations. Martin and McCorkle (1993) suggest that DOC fluxes can potentially account for over half the total organic carbon oxidation in sediments (although the magnitude of their DOC flux estimate depends heavily upon the value assumed for the diffusivity of DOC). The most conservative estimate they present suggests that the DOC flux can be as little as 12-23% of the carbon oxidation; while the highest diffusivity would predict the DOC flux to account for 60-140% of their total carbon oxidation. The ratio of the DOC flux to the total carbon oxidation rate for the 120-m Washington margin core incubation ranges from 0.19 to 1.82. This range is comparable to the range in the DOC:DIC flux presented in Martin and McCorkle (1993). The Washington core incubations from 120-m represented a relatively undisturbed system, thus it is possible that the initial DOC fluxes were representative of the *in situ* DOC flux; however, the oxidation rates in the core incubations may have been enhanced by the incubation process, just as the slurry rates were enhanced.

The DOC concentrations did suggest that there was slightly more DOC production in the anoxic incubations. This is consistent with data in the literature that suggest anaerobic processes favor DOC production over CO_2 production (Andersen, 1996; Hansen and Blackburn, 1991; Kristensen et al., 1995). Never-the-less, as was the case for the slurry incubations, the highest concentrations were found at those stations with the highest oxidation rates and the lowest organic carbon contents (*i.e.*, the Washington margin stations). The Mexican ODZ station showed the smallest response during the incubation, again suggesting that DOC production (and by inference, carbon oxidation) was dependent on the amount of organic matter available and did not appear to respond to the addition of oxygen.

While the DOC fluxes may have initially appeared to be a reasonable estimate of the *in situ* DOC flux, because they are of the similar magnitude as those presented in

Martin and McCorkle (1993), the changes in particulate organic carbon from the 360-m Mexican core incubation indicated that even in these relatively unmanipulated core incubations, the carbon oxidation rates were higher than expected for natural conditions. This discrepancy suggests that the calculated DOC flux may have overestimated the *in situ* DOC flux. The *in situ* carbon oxidation rates at this station (*see* Chapter 2, Table 2.5 and relevant discussions) were not high enough to measurably decrease the weight percent organic carbon over the course of 20 days. In the absence of any carbon input, the *in situ* carbon oxidation rate of $3.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ could remove only about $3.3 \text{ } \mu\text{mol}$ of carbon from the top centimeter of the core over 19 days. This loss corresponds to $\sim 0.46 \text{ mg g}^{-1}$ or a decrease in the organic carbon content of about 0.05% by weight. The POC decrease in the upper centimeter of the incubated cores was approximately 0.5 wt. %. Suggesting that the carbon oxidation rates in the incubated cores were about 10X the *in situ* rate. If true, then the DOC flux estimate from the Washington margin is 10X too high and not in good agreement with the results from Martin and McCorkle (1993). This would further imply that Martin and McCorkle's estimates of the DOC flux from core incubations may also be too high. The changes in POC were most pronounced in the oxic core, possibly indicating a difference in organic matter reactivity under oxic and anoxic conditions. It appears, that of the carbon fraction available to the microbial population, more was degraded by aerobes than by anaerobes.

SUMMARY

The carbon oxidation rates in sediment incubations were generally higher than the *in situ* rates, with the slurry rates being as much as two orders of magnitude higher. Rates were enhanced equally under both oxic and anoxic conditions at most stations. Carbon oxidation was greater in the Washington margin slurries than in the Mexican slurries suggesting that the organic matter in Washington margin sediments was more reactive. This suggestion is not in general agreement with the hypothesis that sediments with the most organic matter also have the freshest, most reactive carbon. My preliminary hypothesis predicted the greatest carbon loss from the station with the most

organic matter when subjected to mixing and oxygenation. Further, I expected that the stations with the most organic matter would have the most reactive organic matter. However, in both the slurry and core experiments, the results indicated that there was more degradation in the Washington sediments and shallow Mexican sediments than in the Mexican ODZ sediments. DOC production in the slurries was not a significant fraction of the total carbon loss, suggesting that at very high oxidation rates CO_2 production was favored over DOC production under both aerobic and anaerobic conditions. The whole-core incubations, which were less invasive and therefore potentially more representative of natural conditions, also demonstrated greater DOC production in Washington cores than in Mexican cores. Both the slurry and core incubation experiments point to the reactivity of the sedimentary organic carbon as an important factor in the extent to which that carbon can be oxidized. More importantly, despite the relatively intense degradation conditions in these experiments (especially in the slurries) the organic carbon from the Mexican ODZ sediments was apparently less reactive than the organic carbon from all the other stations.

CHAPTER 4: CARBON LIMITATION, OXIDANT STRESS AND THE FRACTIONATION OF OXYGEN AND NITROGEN DURING SEDIMENTARY RESPIRATION

INTRODUCTION

Organic carbon degradation rates are dependent upon a combination of factors that range from carbon content and organic matter reactivity to oxidant supply and sediment redox conditions. In any given location one of these factors must ultimately limit the oxidation of organic carbon. At one endmember condition lies the deep ocean, where carbon oxidation rates are slow and limited by the amount of available organic carbon; in other words, bacterial activity in these sediments causes the reactive sedimentary organic carbon to run out before the oxygen is exhausted. Under these conditions, other electron acceptors (NO_3^- , oxides of Mn and Fe, or SO_4^{2-}) do not contribute to the degradation of organic carbon (Emerson, 1985a; Murray and Kuivila, 1990). At the other extreme, in shallow sediments from continental shelves and estuaries, organic carbon is abundant and degradation rates are high enough to completely consume the oxygen before the organic carbon is removed (Brandes and Devol, 1995; Canfield, 1989; Reimers et al., 1992). In these sediments, oxygen (and often times nitrate) is completely removed from the porewaters within a few millimeters of the sediment surface. When O_2 is completely removed before organic carbon is remineralized, the uptake of O_2 is limited by the available oxygen concentration and the oxidation of carbon can be said to be occurring under conditions of oxygen stress. The shift in sedimentary regime from the continental margin to the deep-sea involves distinct and correlated changes in water depth, organic carbon supply (or rain rate), mineral grain size, nutrient availability and sediment redox potential (Jahnke et al., 1990). At some point along the continental margin sediments must switch from being primarily oxygen- (oxidant-) limited on the shelf and slope to the substrate-limited mode that is found in deep-sea

sediments. Murray and Kuivila (1990) suggest, based on the ratio of porewater oxygen to POC in sediments off California, that the switch from carbon-limited conditions to oxygen-limited conditions must exist shoreward of ~ 4500 meters water depth and that oxygen penetration depths of less than 10 cm may be indicative of oxygen-limited sediments.

In contrast, continental margin sediments are regions of high organic carbon input that drives high carbon oxidation rates. Oxygen concentrations in sediment porewaters are drawn down rapidly. Shallow continental shelf sediments often have oxygen penetration depths of only a few millimeters (Archer and Devol, 1992; Berelson et al., 1996; Reimers et al., 1992). Reimers et al., in their 1992 study of California slope sediments show that oxygen penetration depths for sediments between 2000 and 4000 meters on the same margin are generally between 1 and 3 cm. A compilation of oxygen penetration depths in North Pacific sediment from the literature shows that in margin sediments, O₂ penetration is rarely greater than 3.5 cm, even at depths up to 4000 m (Figure 4.1). This shallow penetration suggests that margins sediments, where rates of carbon input and carbon oxidation are highest, will be oxygen-limited, even though they may lie in fairly deep waters. On each of the margins examined in this study, O₂ penetration depths did not increase above ~2.5 cm until depths beyond the base of the continental slope. That depth was slightly different for each margin depending upon the local bathymetry (*see* Chapter 2, Figure 2.3). In this case, I mean oxygen-limited in the sense that oxygen runs out long before carbon runs out.

Microbial activity discriminates between the heavy and light isotopes of oxygen during the aerobic degradation of organic matter. This discrimination is based on a slight energetic advantage in using the light isotope of oxygen for metabolizing organic carbon. The ability to fractionate hinges upon a sufficient supply of oxygen, such that the microorganisms can afford to be “choosy” about which isotope they utilize. When the diffusive oxygen flux is insufficient to balance the respiratory demand, all oxygen molecules are consumed and there is no distinction between the heavy and light isotopes (Bender, 1990; Brandes and Devol, 1997; Grande et al., 1989). In a sense, when O₂

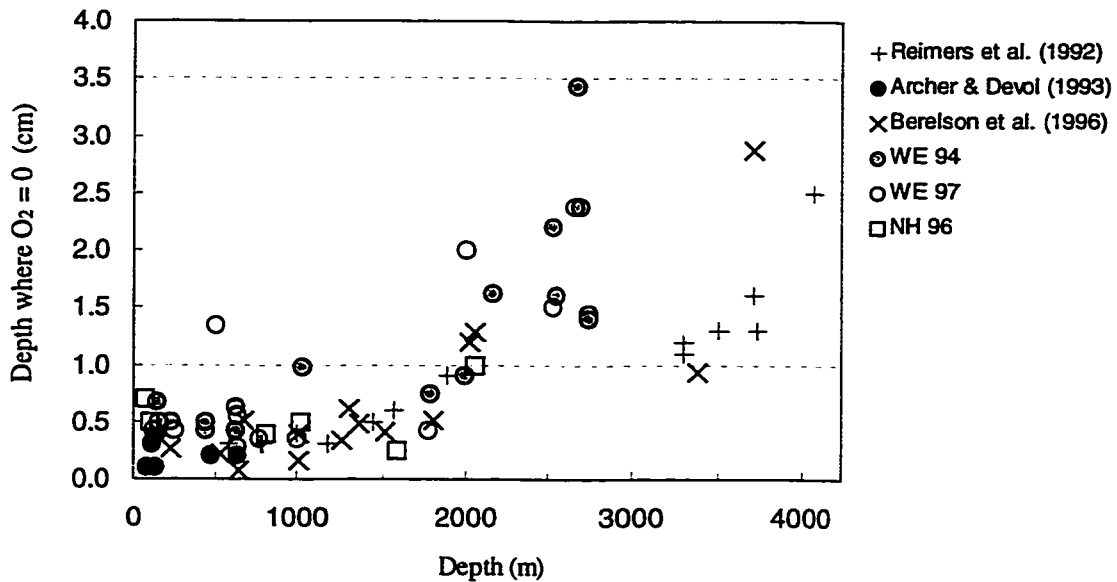


Figure 4.1 Compilation of oxygen penetration depths for stations along the North Pacific continental margin. Circles are from the Washington coast, crosses and plus signs from the California margin near Monterey and squares are from the Mexican margin

concentrations at the site of enzymatic activity are vanishingly small, the microbes are oxygen-stressed; they will take up every possible oxygen molecule.

The fractionation factor for oxygen consumption (α_{O_2}) during respiration by marine bacteria has been determined and averages 0.980 for cultures of free-living bacteria (Kiddon et al., 1993). The apparent oxygen isotope fractionation factor for community respiration in deep-sea sediments has a predicted value of $\alpha_{O_2app} = 0.991$ (or $\epsilon_{O_2app} = 9\text{‰}$, where $\epsilon = (1 - \alpha) \cdot 10^3$; Bender, 1990). This value is based on a model of sediment oxygen consumption that satisfies the assumption of first order kinetics with respect to carbon (*i.e.*, a porewater profile where oxygen decreases exponentially with depth below the sediment-water interface) and implies that the rate of organic matter oxidation is carbon-limited. Bender suggests the semi-infinite slab geometry of the

sediments (a partially closed, essentially two-dimensional diffusive system) prevents the expression of the full microbial respiration fractionation. The apparent fractionation in sediments ($\alpha_{O_2app} = 0.991$) has a square-root relation to the fractionation factor for bacterial cultures as a result of the assumption of first order degradation kinetics.

Brandes and Devol (1997) have presented oxygen isotope fractionation results for benthic chamber deployments in Puget Sound, Washington. They report an apparent fractionation factor of $\alpha_{O_2app} = 0.997$ for sedimentary respiration. The Puget Sound sediments are sites of rapid organic matter diagenesis; O_2 is completely consumed within the top half centimeter of the sediments. Brandes and Devol (1997) argued that the apparent fractionation is dramatically reduced from Bender's value of 0.997 due to complete oxygen removal and the diffusive limitation of the sedimentary geometry. Their model parameterizes intense diagenesis in discrete sediment micro-sites wherein oxygen is completely consumed. The apparent fractionation is small because oxygen concentrations approach zero at the micro-site. They suggest that this small fractionation arises as a result of oxidant limitation.

Based on results from Brandes and Devol (1997) and predictions from Bender (1990) I hypothesized that oxygen fractionation will be fully expressed only when the microbial population is not oxygen-stressed. Under these conditions, organic carbon (or more specifically, microbially available organic carbon) is likely to limit organic matter degradation rates. Otherwise, high consumption rates will decrease O_2 concentrations rapidly and the fractionation will be small to non-existent. Nitrogen is also potentially useful as an indicator of oxidant vs. substrate limitation in sediments because, after O_2 , NO_3^- is the next most energetically favorable electron acceptor (Froelich et al., 1979). In the presence of reactive carbon, NO_3^- will then become the limiting factor for the rate of organic matter degradation. Fractionation of the nitrogen in NO_3^- during denitrification is analogous to the fractionation of O_2 during oxygen consumption. In addition, ammonium uptake during nitrification is known to be a fractionating process. These nitrogen fractionations are poorly known for free-living bacteria and virtually unknown in

sediments; however, the metabolic pathways that utilize nitrogen as an electron acceptor (denitrification) and that fix ammonia into NO_3^- (nitrification) are known to favor the light nitrogen isotope (Cline and Kaplan, 1975; Delwiche and Stein, 1970; Liu and Kaplan, 1989; Mariotti et al., 1981). The fractionation is likely to be fully expressed only when nitrate or ammonium is available in excess.

In order to investigate the fractionation of oxygen and nitrogen I conducted a variety of incubation experiments to measure changes in oxygen and nitrogen species and fractionations of oxygen and nitrogen during sediment respiration. Previous results from shallow, estuarine sediments demonstrate very small to undeterminable fractionation factors (Brandes and Devol, 1997). I have attempted to measure the fractionation of oxygen and nitrogen under conditions that may allow for larger fractionations (*i.e.*, carbon-limited degradation). The oxygen incubations were specifically designed to address the effect of carbon limitation on the apparent fractionation of oxygen during sediment respiration by increasing the supply of oxygen during the experiment. The nitrogen isotope experiments were conducted using sediments from a range of depths to evaluate changes in the degree of fractionation along an off-shore transect that would indicate a shift from oxidant to carbon limitation. The nitrogen isotope experiments included measurements of $\delta^{15}\text{N-N}_2$, $\delta^{15}\text{N-NO}_3^-$ and $\delta^{15}\text{N-NH}_4^+$ in an attempt to constrain the magnitude of the fractionations during nitrification and denitrification. Information about the relative contributions of nitrification and denitrification and their isotopic signatures were expected to allow the evaluation of differences in nitrogen-cycling pathways by comparing sediments from different regions.

METHODS

SAMPLING LOCATIONS

Continental margin stations on the Mexican and Washington coasts were occupied during cruises in fall of 1996 on the R/V New Horizon (NH96) and summer of 1997 on the R/V Wecoma (WE97), respectively (Table 4.1; *see* Chapter 2 for a more

detailed description of the two margins). On both margins, stations were occupied at depths from 100 to ~2000 meters along transects roughly perpendicular to shore (Figure 4.2). The Washington margin is a typical western continental margin, characterized by seasonal wind-driven up-welling and moderate rates of primary productivity. The Mexican margin has weaker seasonal upwelling, lower productivity and a pronounced oxygen deficient zone located between ~150 and 1000 meters water depth (*see* Chapter 2, Figure 2.2).

OXYGEN INCUBATIONS

Oxygen fractionations were determined from the changes in oxygen concentration and isotopic composition during core incubation experiments. Samples were collected for oxygen incubations during the Washington margin cruise (WE97). Sediment cores were collected from stations at depths of 800, 1,770, 2,000 and 2,500 meters using a Soutar box corer. Four sub-cores were taken from each core in three-inch I.D. acrylic core liners and capped with #14 rubber stoppers. The subcores consisted of ~25 cm of sediment and 25 cm of overlying water. Cores were stored with their overlying water at *in situ* temperature (~2 °C) for return to the laboratory. Prior to beginning the experiment, overlying water was removed and replaced with seawater that had been equilibrated with the atmosphere (at 2 °C) by bubbling with air for five days. The cores were equilibrated with the atmosphere for 72 hours after the overlying water was replaced to allow the porewater to equilibrate with the new overlying water. At the start of the experiment, oxygen concentration in the reservoir of air-equilibrated seawater was determined using the standard Winkler titration (Carpenter, 1964; Winkler, 1888). Duplicate samples were collected for O₂ isotope measurements. The initial oxygen concentrations in the subcores were measured with an Orion™ electrode. The cores were sealed again with rubber stoppers and plastic electrical tape. Initial and final oxygen concentrations in the cores were also collected in nylon gas loops and analyzed by gas chromatography (Devol and Christensen, 1993; Grundmanis and Murray, 1982). The initial O₂ concentrations measured with the electrode and by gas chromatography agreed

Table 4.1 Station locations, water depth (meters), core top (0-0.5 cm) organic carbon content (wt. %), bottom-water oxygen concentration ($\mu\text{mol L}^{-1}$), and types of samples (lander incubations, L and core incubations, C) for Washington and Mexican margin stations occupied during R/V Wecoma cruise (WE97) and R/V New Horizon cruise (NH96).

Station	Depth	Latitude	Longitude	Org Carbon	[O ₂] _{bw}	$\delta^{18}\text{O-O}_2$	Incubation type				N/Ar ^{air} $\delta^{15}\text{N-N}_2$
							$\delta^{15}\text{N-NO}_3^-$	$\delta^{15}\text{N-NH}_4^+$	$\delta^{15}\text{N-N}_2$	$\delta^{15}\text{N-N}_2$	
Washington Margin											
WE 301	120	46° 48.60'	124° 37.20'	1.61	140		C, L		C		L
WE 311	247	46° 34.24'	124° 33.24'	2.26	97		C		C		
WE 308	396	46° 32.30'	124° 39.64'	0.58	54		C		C		
WE 309	503	46° 47.49'	124° 54.87'	1.60	38		C		C		
WE 306	630	46° 29.60'	124° 43.22'	1.56	25		C		C		
WE 312	800	46° 23.80'	124° 45.89'	2.41	15	C	C		C		
WE 307	997	46° 26.61'	124° 47.22'	2.52	14		C		C		
WE 313	1770	46° 32.75'	125° 12.16'	2.47	50	C	C		C		
WE 303	2000	46° 46.71'	125° 23.47'	1.32	66	C	C, L		C		L
WE 304	2500	46° 45.50'	126° 00.58'	1.23	83	C					
WE 305	2664	46° 44.97'	127° 59.96'	1.12	90		C				
Mexican Margin											
NH 202	100	22° 46.01'	106° 19.16'	2.85	23		L		L		
NH 204	360	22° 41.78'	106° 28.61'	8.13	0		L		L		L
NH 203	587	22° 39.65'	106° 31.96'	8.92	0		C, L				L
NH 209	800	22° 21.50'	106° 31.06'	9.99	1		L				L
NH 208	1020	22° 30.43'	106° 39.12'	9.53	4		C, L				L
NH 205	1500	22° 27.44'	106° 55.76'	6.07	44		C, L		L		L
NH 206	2050	22° 25.24'	107° 02.11'	4.24	92		L		L		L

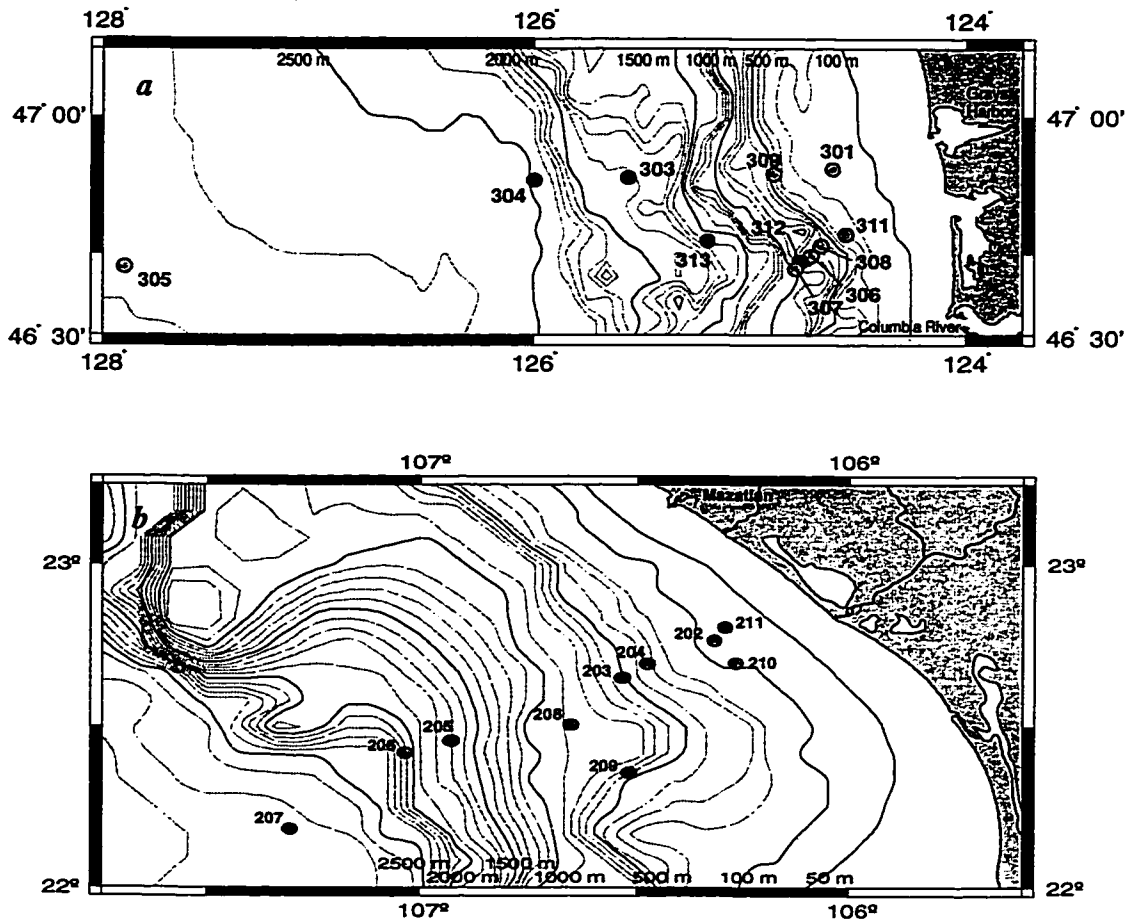


Figure 4.2 Charts with station locations for a) the Washington and b) the Mexican continental margins. Black symbols in represent stations with oxygen isotope experiments, gray symbols represent stations with nitrogen isotope experiments.

reasonably well with the Winkler titrations. In one core from each station, subsamples for oxygen were collected at 12 and 24 hours in addition to the initial and final time points to more accurately determine the oxygen consumption rates. The mid-point samples were removed without atmospheric contamination of the incubation set-up by drawing samples into the gas loops with a 60-cc syringe and then replacing the sample volume with water from a reservoir in a separate syringe. The experiments were ended after 48 hours, at which point roughly 30% of the oxygen had been consumed. A core

from the 2500 m station was allowed to incubate for 72 hours in order to increase the percentage of initial oxygen consumed. Samples for oxygen isotope determinations were collected at the end of the experiment by siphoning water via 1/8-inch O.D. nylon tubing into evacuated, glass sample bottles equipped with high-vacuum Viton O-ring stopcocks (Louwers-Haupt). Atmospheric contamination was prevented by flushing the sample bottle necks with CO₂ and by collecting the sample slowly enough that water was continually overflowing the sampling apparatus as water entered the evacuated bottle. The evacuated bottles were pre-poisoned with 100 µl of saturated HgCl₂ to prevent any subsequent O₂ consumption. For a detailed description of the sampling method see Emerson et al. (1991), Quay et al. (1993), and especially, Brandes (1996). The water was equilibrated with the headspace volume at 20 °C to extract the dissolved O₂; the headspace gas was purified cryogenically to remove water and CO₂. The δ¹⁸O of the dissolved oxygen was determined on a Finnigan 251 dual-inlet Isotope Ratio mass Spectrometer (IRMS) in the U.W. Stable Isotope Laboratory (U.W. S.I.L.) using the method detailed by Emerson et al. (1991).

NITROGEN INCUBATIONS

Samples for the N₂/Ar gas ratio, nitrate and ammonium concentrations and the nitrogen isotope compositions of nitrogen gas, nitrate and ammonium (δ¹⁵N-N₂, δ¹⁵N-NO₃⁻, and δ¹⁵N-NH₄⁺) were collected using an *in situ* benthic flux chamber ('lander', Brandes, 1996; Devol, 1987) as well as from core incubation experiments. The lander was deployed for 12-48 hours, depending upon the estimated magnitude of the flux at each station, during which time-series samples for O₂, N₂ and nutrient concentrations were collected. Samples at the final time point were collected for gas ratios and stable isotopes in vacuum-tight sample loops constructed of grade 2 seamless titanium connected in-line with the lander sampling system (Brandes, 1996). The sample loop valves were closed immediately upon recovery of the lander to isolate the samples. The water samples were extracted on board ship from the titanium loops into evacuated glass sample bottles using the method detailed in Brandes (1996). Initial concentrations and

isotopic compositions were determined from a bottom-water sample collected at ~1 m above the seafloor. The initial sample for N_2/Ar and $\delta^{15}N-N_2$ was collected using the same method outlined above for oxygen isotope sampling except, that the nylon sample tube was connected directly to a Niskin bottle and water was gravity-fed to the evacuated sample bottle rather than siphoned. The sample bottles were poisoned with $HgCl_2$ for storage and return to the laboratory. Samples for $\delta^{15}N-N_2$ were then processed using the same method as outlined above for $\delta^{18}O$ and analyzed on a Finnigan 251 IRMS. Nitrogen and ammonium concentrations were measured colorimetrically according to the methods outlined in Strickland and Parsons (1972). Gas ratio and $\delta^{15}N-N_2$ samples were not collected from core incubation experiments.

The isotopic analysis of NO_3^- and NH_4^+ requires a larger volume of water (1 to 2 liters) than can be collected in a lander sample loop. Nitrate and ammonium samples were collected either from overlying water in the lander or from overlying water in shipboard core incubations. Core incubations were used not only to complement the *in situ* incubation experiments but also as an independent measure at those stations where no lander was deployed. The lander is equipped with small box cores and is usually recovered with the sediments and their overlying water intact. After each lander recovery, final samples for $\delta^{15}N-NO_3^-$ and $\delta^{15}N-NH_4^+$ were collected by siphoning two liters of the box-core overlying water into HDPE bottles (Nalgene). Samples were poisoned with 2 ml of saturated $HgCl_2$ solution and stored cold or frozen until analysis. Core incubation experiments were conducted with duplicate subcores collected from box cores using 5-inch O.D. plastic core lines. The core liners were large enough to enclose ~2 liters of overlying water and 10 cm of sediment. The cores were capped and stored at 8 °C in a cold room and maintained in the dark during incubation. Samples were collected daily to monitor nitrate consumption; incubations were ended after roughly 30% of the nitrate was removed (~3 to 4 days). At the end of the incubation, final nutrient samples were collected, and 2-liter water samples were siphoned into HDPE bottles and poisoned with saturated $HgCl_2$. Initial samples for NO_3^- and NH_4^+

concentrations and nitrogen stable isotope compositions were taken from the box-core overlying water prior to subcoreing.

The nitrogen isotope analysis has been detailed by Brandes (1996) and Brandes and Devol (1997). Briefly, ammonium was collected from a one liter sample by hot, basic distillation into acid solution (Velinsky et al., 1989) and then adsorbed to ion sieve (Union Carbide, W-85); the ion sieve was filtered on to quartz fiber filters (Whatman, QF-A) and stored in a dessicator. After removal of ammonium, nitrate was then converted to ammonium using Devarda's alloy (Cline and Kaplan, 1975); subsequent distillation and adsorption procedures were identical to those outlined above for ammonium. The ammonium trapped in the ion sieve was analyzed by coupled elemental analyzer–isotope ratio mass spectrometer (Finnigan Delta plus EA-IRMS). This method allowed rapid and direct determination of the amount of nitrogen trapped on the ion sieve and the isotopic composition of the trapped nitrogen. This method represents a significant advantage over the previous “in-tube combustion” method for measuring the $\delta^{15}\text{N-NO}_3^-$ and $\delta^{15}\text{N-NH}_4^+$ which required the ion sieve to be sealed (under high-vacuum) into quartz tubes followed by high-temperature combustion of the NH_4^+ to N_2 in the presence of Cu and CuO and finally cryogenic purification of the N_2 gas and analysis by dual-inlet IRMS (Brandes, 1996).

The EA-IRMS method allows the analysis of a significantly larger number of samples per day (up to 30 samples in a single over-night run, as compared to ~5 samples per day). While the distillation method is still somewhat time-consuming (four samples per day if both NH_4^+ and NO_3^- are collected), the improvement in the mass spectrometry technique has cut the processing time for an individual sample by more than half. Standard solutions of KNO_3 and procedural blanks were processed using the Devarda's alloy reduction each week during sample processing. The KNO_3 standard solutions had an average $\delta^{15}\text{N-NO}_3^-$ of $5.95 \pm 0.2 \text{ ‰}$ ($n = 18$; Table 4.2 and Figure 4.4), which compares extremely well with the standard values presented in Brandes (1996) using the in-tube combustion method ($5.5 \pm 0.3 \text{ ‰}$; $n = 20$). Direct combustion of the KNO_3 in the

EA-IRMS yielded an isotopic composition of $6.50 \pm 0.1 \text{ ‰}$; within measurement error, this value is identical to the $6.30 \pm 0.2 \text{ ‰}$ from Brandes (1996).

Table 4.2 Comparison of stable isotopic composition (‰) of KNO_3 standards and nitrogen content (μg) and isotopic composition (‰) of blanks by EA-IRMS and by in-tube combustion methods.

	EA-IRMS	In-tube combustion/ Dual-inlet IRMS
KNO_3 standard		
Direct measurement	$6.50 \pm 0.1 \text{ ‰}$	$6.3 \pm 0.2 \text{ ‰}$
Devarda's alloy reduction	$5.95 \pm 0.2 \text{ ‰}$	$5.5 \pm 0.3 \text{ ‰}$
Blank		
Isotopic composition	$-0.31 \pm 3.88 \text{ ‰}$	$\sim -2 \text{ ‰}$
Nitrogen content	$2.76 \pm 2 \text{ } \mu\text{g N}$	$\sim 2.5 \text{ } \mu\text{g N}$

The difference between the $\delta^{15}\text{N}$ of the directly combusted KNO_3 salt and the KNO_3 standard reduced with Devarda's alloy confirmed that the fractionation associated with the reduction method was approximately -0.6 ‰ . The blank contributions were small: $\sim 2 \text{ } \mu\text{g N}$ per sample or less than 5 % of the nitrogen in the sample (Figure 4.3).

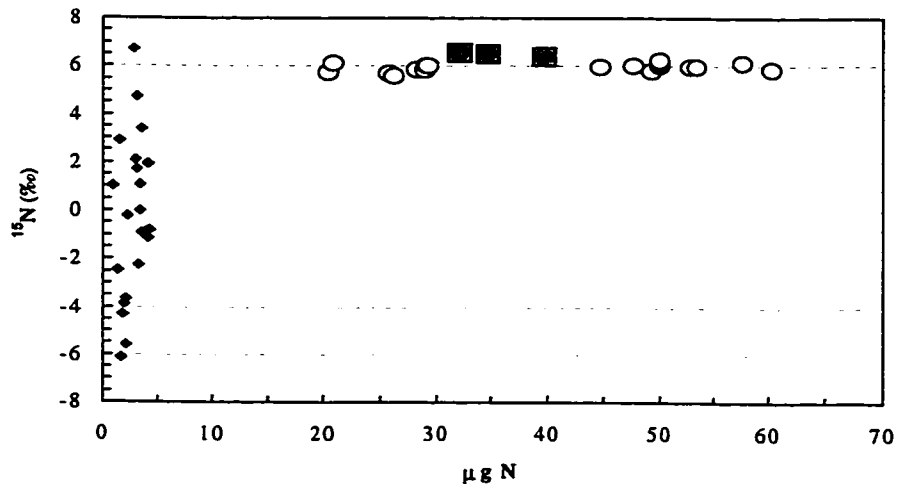


Figure 4.3 Isotopic compositions of standards and blanks run on the EA-IRMS: procedural blanks (small filled diamonds), KNO_3 by direct combustion (large shaded squares), and KNO_3 reduced with Devarda's alloy (open circles).

RESULTS

OXYGEN INCUBATIONS

Dissolved oxygen concentrations in the overlying water of all the core incubations decreased, while the $\delta^{18}\text{O}$ of the dissolved oxygen increased over the course of the experiments (Table 4.3, Figure 4.4). The initial overlying water had an oxygen concentration of $338 \mu\text{mol L}^{-1}$ and an isotopic composition of 0.51‰ . At the end of the experiment, oxygen concentrations ranged from 199 to $327 \mu\text{mol L}^{-1}$, while the final overlying water $\delta^{18}\text{O}$ ranged from 2.21 to 6.40‰ . The fractional change in O_2 concentration was calculated as:

$$\Delta\text{O}_2 = (\text{O}_2 \text{ final} / \text{O}_2 \text{ initial}) - 1$$

Table 4.3 Oxygen concentrations and stable isotope compositions for Washington margin oxygen isotope fractionation experiments

Sample	Depth	O_2 ($\mu\text{mol L}^{-1}$)		$\delta^{18}\text{O}\text{-O}_2$ (‰)		ΔO_2	$\Delta \delta^{18}\text{O}$
		Initial	Final	Initial	Final		
WE 312a	800	339	230	0.51	3.26	-0.37	2.75
WE 312b	800	339	285	0.51	3.46	-0.20	2.95
WE 313a	1770	339	310	0.51	2.89	-0.22	2.38
WE 313b	1770	339	213	0.51	4.97	-0.43	4.46
WE 303a	2000	339	199	0.51	6.4	-0.55	5.89
WE 303b	2000	339	220	0.51	4.11	-0.46	3.60
WE 304a	2500	339	312	0.51	2.21	-0.24	1.70
WE 304b	2500	339	327	0.51	2.22	-0.17	1.71
WE 304c	2500	338	242	0.51	3.17	-0.28	2.36

The decrease in oxygen concentration represented a consumption of 17 to 55% of the initial oxygen. The per mil fractionation, or the change from the final $\delta^{18}\text{O}$ to the initial $\delta^{18}\text{O}$ over the course of the experiment, ranged from 1.70 to 5.89‰ (Table 4.3). Positive per mil fractionations result when the final isotopic composition is greater than the initial

isotopic composition (*i.e.*, $\delta^{18}\text{O}_f - \delta^{18}\text{O}_i$); in other words, when the overlying-water oxygen pool becomes enriched over the course of the experiment.

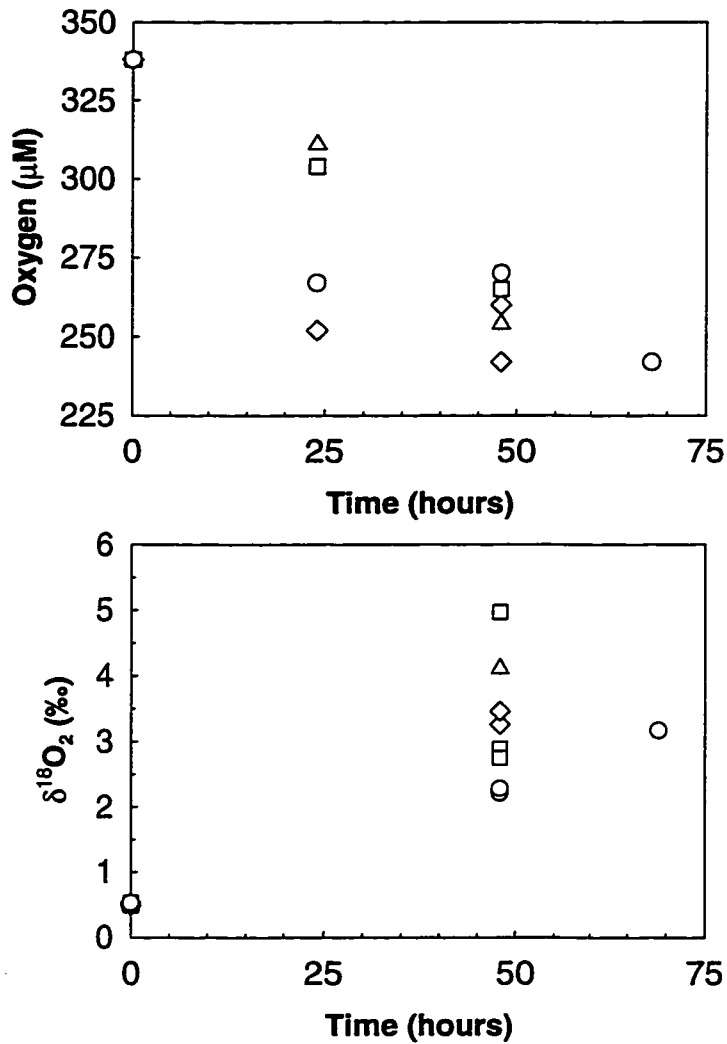


Figure 4.4 Oxygen concentration and $\delta^{18}\text{O}$ of dissolved oxygen during core incubation experiments. Symbols for station depths are as follows: diamond, 800 m; squares, 1770 m; triangles, 2000 m; and circles, 2600 m.

NITROGEN SPECIES

Nitrogen gas

Changes in the concentration of nitrogen gas during lander incubations were determined from changes in the N_2/Ar_{sat} ratio at two Washington margin stations and at six Mexican margin stations. The N_2/Ar_{sat} ratio is the N_2/Ar ratio measured at a given temperature and salinity, normalized to the N_2/Ar ratio at saturation. At saturation, the normalized N_2/Ar ratio should equal one; increases in N_2 will be reflected as increases in the normalized N_2/Ar ratio. Initial N_2/Ar_{sat} ratios on the Washington margin were approximately 1.018; on the Mexican margin they were more variable, ranging from 1.025 to 1.032 (Table 4.4). The elevated, initial N_2/Ar_{sat} ratios in the lander are in line with water column N_2/Ar_{sat} ratios from the North Pacific, which are not well understood but have been described by Emerson et al. (1991) and Brandes et al. (in press). The Mexican margin had higher water-column nitrogen gas concentrations as a result of production via denitrification in the oxygen-deficient zone (Brandes, 1996). Nitrogen gas was produced in the lander chambers at all stations; final N_2/Ar_{sat} ratios ranged from 1.028 to 1.064 on the Washington margin and from 1.041 to 1.100 on the Mexican margin. The increase in nitrogen over time of the lander deployment was estimated from the change in N_2/Ar_{sat} :

$$[N]_{increase} = (N_2/Ar_{final} - N_2/Ar_{initial}) \cdot [N]_{(T, S)}$$

Where $[N]_{(T, S)}$ is the equilibrium nitrogen concentration at the sample temperature and salinity predicted from the Weiss (1970) solubility estimate. On the Washington margin nitrogen increases were between 5.9 and 24.8 $\mu\text{mol L}^{-1}$ while Mexican margin N_2 production ranged from ~4.8 to 12.7 $\mu\text{mol L}^{-1}$ (Table 4.5). Nitrogen gas production can be also estimated from the lander NO_3^- flux, assuming the only source of N_2 is denitrification of NO_3^- diffusing into sediments from overlying-water.

Table 4.4 Initial and final N_2/Ar (normalized to saturation), NO_3^- and NH_4^+ concentrations ($\mu\text{mol L}^{-1}$) and nitrogen isotope compositions (‰) for Mexican and Washington lander experiments.

Station	Depth(m)	N_2/Ar_{sat}		$\delta^{15}N-N_2$		NO_3^-		$\delta^{15}N:NO_3^-$		NH_4^+		$\delta^{15}N:NH_4^+$	
		Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Mexico													
NH 202	100					22.0	3.3	8.94	5.10	0.25	8.74		12.4
NH 202	100					22.0	8.5	8.94	6.33				
NH 204	360	1.025	1.058	0.330	-0.008	29.0	10	14.6	13.39	0.27	16.13		15.8
NH 204	360	1.025	1.048	0.330	-0.028								
NH 203	587	1.032	1.056	0.633	0.578	35.2	18.5	10.75	2.33				
NH 203	587	1.032	1.041	0.633	0.443								
NH 209	800					34.7	10.2	9	6.68				
NH 209	800					34.7	5.7	9	5.97				
NH 208	1020					50.0	18.0	8.26	10.64				
NH 208	1020					50.0	20.6	8.26	9.16				
NH 205	1500	1.025	1.041	0.624	0.330	44.5	32.5	6.75	4.46	0.0	5.45		8.20
NH 205	1500					44.5	36.0	6.75	7.01				
NH 206	2050	1.033	1.046	0.700	0.657								
NH 206	2050					39.0	30.0	6.50	1.66	<0.3	4.34		7.01
Washington													
WE 301	120	1.017	1.064	0.59	-0.16	35.4	26.0	6.96	4.70				
WE 301	120					35.4	25.2	6.96	5.04				
WE 303	2000	1.018	1.028	0.48	0.39	46.4	17.5	6.32	4.37				
WE 303	2000	1.020	1.039	0.48	0.34	46.4	21.3	6.32	3.99				

Table 4.5 Nitrogen gas production ($\mu\text{mol L}^{-1}$), expected N_2 production (calculated from the lander NO_3^- changes in $\mu\text{mol L}^{-1}$), normalized NO_3^- consumption, NH_4^+ production ($\mu\text{mol L}^{-1}$), per mil fractionations ($\Delta \delta^{15}\text{N-N}_2$ and $\delta^{15}\text{N-NO}_3^-$) and final $\delta^{15}\text{N-NH}_4^+$ in Mexican and Washington lander experiments.

Station	Depth (m)	N_2 Production	Expected N_2 Production	$\Delta \delta^{15}\text{N-N}_2$	NO_3^- Consumption	$\Delta \delta^{15}\text{N-NO}_3^-$	NH_4^+ Produced	$\delta^{15}\text{N-NH}_4^+$
Mexico								
NH 202	100		9.5		-0.85	-3.83	8.49	12.4
NH 202	100		13.5		-0.61	-2.60		
NH 204	360	16.3	9.5	-0.34	-0.66	-1.21	15.8	15.8
NH 204	360	11.3		-0.36				
NH 203	587	12.7	8.4	-0.06	-0.47	-8.42		
NH 203	587	4.8		-0.19				
NH 209	800		12.3	-0.15	-0.71	-3.01		
NH 209	800		14.5	0.18	-0.84	-3.72		
NH 208	1020		16.0	-0.18	-0.64	2.38		
NH 208	1020		14.7	-0.16	-0.59	0.90		
NH 205	1500	9.2	6.0	-0.29	-0.27	-2.29	5.45	8.20
NH 205	1500		4.3	-0.47	-0.19	0.26		
NH 206	2050	7.7	4.5	-0.04	-0.23	-4.84	4.04	7.01
NH 206	2050							
Washington								
WE 301	120	24.8		-0.75	-0.27	-2.26		
WE 301	120				-0.29	-1.92		
WE 303	2000	5.9		-0.09	-0.62	-1.94		
WE 303	2000	11.3		-0.14	-0.54	-2.33		

In the Mexican ODZ the measured N_2 gas fluxes were only slightly larger than predicted values (Table 4.5). Outside the ODZ and on the Washington margin, the N_2 gas flux was substantially larger than the NO_3^- flux, indicating that an additional source of NO_3^- had contributed to the pool of denitrified NO_3^- . In general, the final $\delta^{15}N-N_2$ values at all stations were lighter than the initial $\delta^{15}N-N_2$ values. Washington margin $\delta^{15}N-N_2$ values started at approximately +0.5‰, while final $\delta^{15}N-N_2$ values ranged from -0.16‰ to 0.39‰ (Figure 4.5); these values represent per mil fractionations of -0.09 to -0.75‰ (Table 4.5). On the Washington margin N_2 production was larger at the 100-m shelf station than at the 630-m slope station. Larger N_2 production was also associated with a larger per mil fractionation. Initial $\delta^{15}N-N_2$ values for the Mexican margin ranged from 0.33 at 360 m to 0.70 at 2000 m. These values reflect the pronounced minimum in $\delta^{15}N-N_2$ in the ODZ due to denitrification (Brandes, 1996). The nitrogen produced in the Mexican margin lander experiments had $\delta^{15}N$ compositions ranging from -0.01 to 0.68‰. These

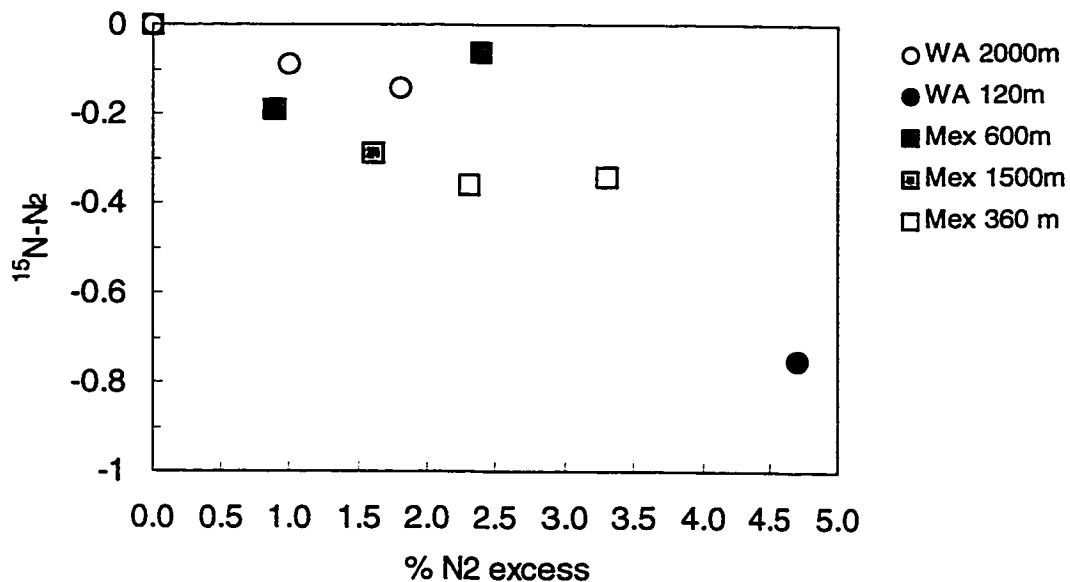


Figure 4.5 Isotopic composition of N_2 in lander overlying water from Mexican and Washington margin stations.

isotopic changes corresponded to per mil fractionation that ranged from -0.47 to +0.18; the largest per mil fractionations tended to occur at those stations with the largest N_2 production (*see* Tables 4.4 and 4.5).

Ammonium

Changes in ammonium concentration and the $\delta^{15}N$ of ammonium were determined from lander incubation experiments at four Mexican margin locations and from core incubation experiments at four Washington margin locations (*see* Table 3.1). The initial NH_4^+ concentrations were determined from bottom-water samples. At the shallow Washington margin station the bottom-water NH_4^+ concentration was $0.7 \mu\text{mol L}^{-1}$. Initial NH_4^+ concentrations for all other stations were less than $0.3 \mu\text{mol L}^{-1}$ (Tables 4.4 and 4.6). Final ammonium concentrations in the Washington margin core incubations were higher than initial concentrations and ranged from 1.58 to $4.54 \mu\text{mol L}^{-1}$. The smallest NH_4^+ increase was seen at the shallowest station (120 m) while the deeper stations all had roughly comparable increases in NH_4^+ (an average increase of $3.5 \mu\text{mol L}^{-1}$). The Mexican margin lander incubations generally had much larger increases in NH_4^+ with final NH_4^+ concentrations ranging from 4.04 to $15.86 \mu\text{mol L}^{-1}$. On the Mexican margin the smallest increase in NH_4^+ occurred at the deepest station (2050 m) and the largest increase in NH_4^+ was seen at the 360-m ODZ station. The initial $\delta^{15}N-NH_4^+$ compositions were assumed to be equal to the ^{15}N composition of the sedimentary organic matter at each station. The Washington margin organic matter $\delta^{15}N$ was estimated to be ~ -7 based on the assumptions that no fractionation of nitrogen occurred during aerobic organic matter degradation and that organic matter $\delta^{15}N$ is ~ 1 ‰ heavier than typical water column $\delta^{15}N-NO_3^-$ values (Brandes and Devol, 1997; Velinsky et al., 1991). Ammonium produced during Washington margin core incubations was enriched relative to the organic matter source; final $\delta^{15}N-NH_4^+$ values ranged from 9.01 to 6.38 ‰ (Table 4.6 and Figure 4.6). The Mexican margin sedimentary organic matter $\delta^{15}N$ values ranged from 8.8 to 9.25 ‰

(organic matter $\delta^{15}\text{N}$ was measured on bulk sediments with the EA-IRMS). In general the $\delta^{15}\text{N}$ of organic matter on the Mexican margin was lightest in shallow sediments and heavier in deep sediments; a broad peak in $\delta^{15}\text{N}$ -OM in sediments was also observed near the top of the ODZ (Devol, unpublished data).

Table 4.6 Initial and final NO_3^- and NH_4^+ concentrations ($\mu\text{mol L}^{-1}$) and nitrogen isotope compositions (‰) for Washington margin whole-core incubation experiments.

Station	Depth	NO_3^-		$\delta^{15}\text{N}\text{-NO}_3^-$		NH_4^+		$\delta^{15}\text{N}\text{-NH}_4^+$	
		Initial	Final	Initial	Final	Initial	Final	Initial	Final
WE 301	120	26.8	20.1	6.33	5.14				
WE 301	120	26.8	21.4	6.33	2.88				
WE 311	247	23.2	9.6	6.22	3.88	0.0	3.53		14.2
WE 311	247	23.2	14.5	6.22	3.18	0.0	3.18		16.4
WE 308	396	13.7	21.8	5.72	6.08				
WE 308	396	13.7	20.5	5.72	6.73				
WE 309	503	21.3	30.6	6.62	6.59				
WE 309	503	21.3	32.1	6.62	7.02				
WE 306	630	27.8	33.9	6.69	6.89				
WE 306	630	27.8	33.2	6.69	6.79				
WE 312	800	30.8	31.3	6.72	7.12				
WE 312	800	30.8	33.2	6.72	7.03				
WE 307	997	31.8	37.7	6.29	6.75				
WE 307	997	31.8	36.0	6.29	4.83	0.0	4.54		9.01
WE 313	1770	31.7	31.3	5.90	1.57				
WE 313	1770	31.7	23.2	5.90	6.42				
WE 303	2000	24.2	29.9	5.77	1.08	<0.3	2.53		11.6
WE 303	2000	24.2	29.3	5.77	1.08	<0.3	3.83		12.7
WE 305	2664	40.0	46.9	5.52	6.96				
WE 305	2664	40.0	47.9	5.52	6.32				

The Mexican margin $\delta^{15}\text{N}\text{-NH}_4^+$ values at the end of the lander incubations were sometimes heavier and sometimes lighter than the organic matter source and ranged from 7.01 to 15.8 ‰ (Table 4.5). The absolute $\delta^{15}\text{N}\text{-NH}_4^+$ values were roughly similar at the end of the experiments on both margins. The Mexican margin stations generally had larger $\delta^{15}\text{N}\text{-NH}_4^+$ values associated with larger NH_4^+ production; off Washington the relation between the amount of NH_4^+ produced and the isotopic composition of the NH_4^+ was less clear.

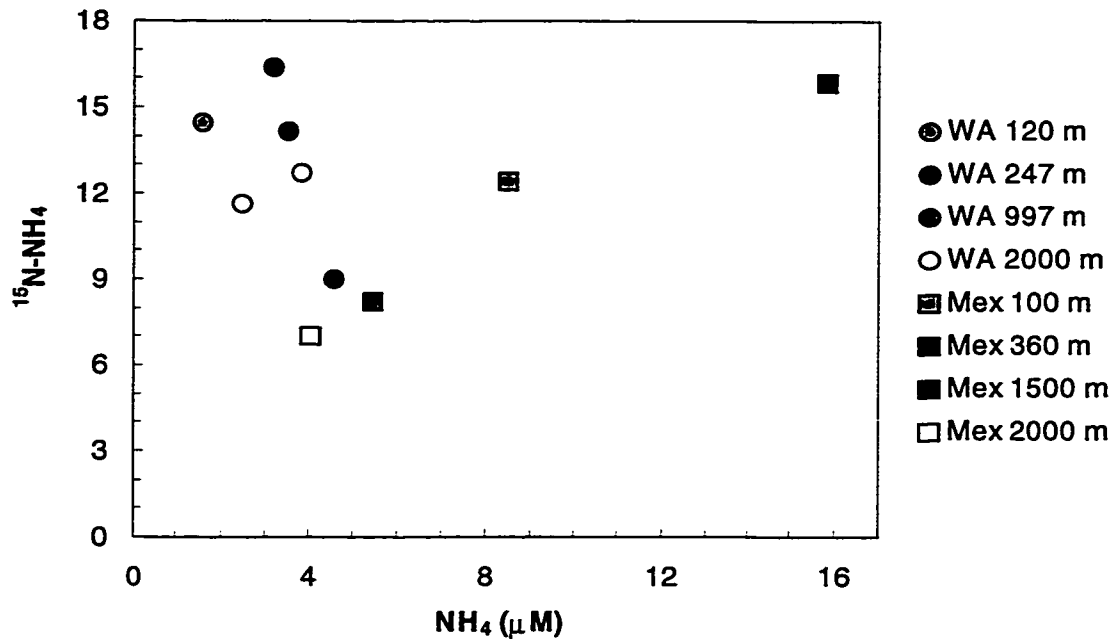


Figure 4.6 Per mil change in NH_4^+ isotopic composition during Washington margin core incubations (circles) and Mexican margin lander experiments (squares). Initial NH_4^+ isotopic compositions were taken as the $\delta^{15}\text{N}$ of the organic matter at each station.

Nitrate

Changes in nitrate concentration and the $\delta^{15}\text{N}$ of nitrate were determined from two lander incubations and ten core incubations at Washington margin stations and from seven lander incubations and three core incubations at Mexican margin stations. The nitrate concentrations in lander incubations from the Washington margin and Mexican margins (Table 4.4) as well as in core incubations from the Mexican margin (Table 4.8) decreased over the course of the experiments. Initial concentrations ranged from 17.5 to $\sim 50 \mu\text{mol L}^{-1}$ and were in general agreement with water-column nitrate values from both margins (*see* Chapter 2, Figure 2.2).

Final concentrations ranged from 3.3 to 36 $\mu\text{mol L}^{-1}$. The changes in nitrate are presented as NO_3^- concentration normalized to the initial nitrate concentration:

$$\text{NO}_3^- \text{ consumption} = \Delta\text{NO}_3^- = (\text{NO}_3^-_{\text{final}} / \text{NO}_3^-_{\text{initial}}) - 1$$

The normalized NO_3^- changes and per mil fractionations in lander experiments and core incubations, presented in Tables 4.5, 4.7 and 4.8, ranged from -0.19 to -0.85 $\mu\text{mol L}^{-1}$.

Generally, the $\delta^{15}\text{N-NO}_3^-$ became lighter over the course the incubations. The Washington margin core incubations showed both increases and decreases in overlying water NO_3^- concentration (Table 4.6). At many of the Washington margin stations,

Table 4.7 Normalized change in NO_3^- concentration, per mil fractionation ($\Delta \delta^{15}\text{N-NO}_3^-$), increase in NH_4^+ concentration ($\mu\text{mol L}^{-1}$), and final $\delta^{15}\text{N-NH}_4^+$ determined for Washington margin nitrogen-isotope fractionation experiments.

Station	Depth (m)	ΔNO_3^-	$\Delta \delta^{15}\text{N-NO}_3^-$	ΔNH_4^+	$\delta^{15}\text{N-NH}_4^+_f$
WE 301	120	-0.25	-1.19	1.58	14.4
WE 301	120	-0.20	-3.45		
WE 311	247	-0.59	-2.34	3.53	14.2
WE 311	247	-0.37	-3.05	3.18	16.4
WE 308	396	0.59	0.37		
WE 308	396	0.50	1.01		
WE 309	503	0.44	-0.03		
WE 309	503	0.51	0.40		
WE 306	630	0.22	0.20		
WE 306	630	0.19	0.10		
WE 312	800	0.02	0.41		
WE 312	800	0.08	0.31		
WE 307	997	0.19	0.45		
WE 307	997	0.13	-1.47	4.54	9.01
WE 313	1770	-0.01	-4.33		
WE 313	1770	-0.27	0.53		
WE 303	2000	0.24	-4.69	2.50	11.6
WE 303	2000	0.21	-4.69	3.80	12.7
WE 305	2664	0.17	1.44		
WE 305	2664	0.20	0.81		

Table 4.8 Initial and final NO_3^- concentrations ($\mu\text{mol L}^{-1}$) and stable isotope compositions (‰), normalized NO_3^- change, and per mil fractionation ($\Delta \delta^{15}\text{N-NO}_3^-$) for Mexican margin core incubation experiments.

Station	Depth	NO_3^-		$\delta^{15}\text{N-NO}_3^-$		ΔNO_3^-	$\Delta \delta^{15}\text{N}$
		Initial	Final	Initial	Final		
NH203	587	17.5	5.5	13.13	0.34	-0.69	-12.79
NH203	587	17.5	5.0	13.13	5.21	-0.71	-7.92
NH208	1020	55.0	11.0	8.25	6.85	-0.80	-1.40
NH209	1500	44.5	22.3	6.75	8.46	-0.50	+1.71

the initial NO_3^- concentrations were lower than the bottom-water concentrations (*see* Chapter 2, Figure 2.2) suggesting that the Soutar box core was not sealing properly and allowed the exchange of overlying water with surface water during recovery. While these cores may not represent *in situ* conditions, they still provide information as to the processes that contribute to nitrogen fractionation during respiration. The possible exchange of surface-water for bottom-water may have been a significant artifact in the NO_3^- experiments. It should be noted that these same cores are less biased for the ammonium experiments, because the initial NH_4^+ concentrations were essentially zero and dilution with surface water did not change the NH_4^+ concentration. The normalized NO_3^- consumption was calculated using the initial concentration as measured in the core and the NO_3^- concentration at the end of the experiment; they ranged from -0.59 to +0.59.

DISCUSSION

FRACTIONATION OF OXYGEN

Dissolved oxygen in the overlying water of the cores became heavier over the course of the experiment indicating that isotopically light molecules of O_2 were removed preferentially during respiration. The apparent fractionation factor ($\alpha_{\text{O}_2\text{app}}$) can be modeled from the changes in oxygen concentration and isotopic composition using Rayleigh fractionation kinetics. The Rayleigh model is defined only for a closed system.

The core incubation set-up is assumed to mimic a closed system in that the overlying water is the only source of oxygen and aerobic sedimentary respiration is the only sink for oxygen. The Rayleigh approximation states that the ratio of initial to final isotopic composition at any time, t , is related to the concentration change over the same time, through the fractionation factor α ; thus:

$$\delta^{18}\text{O}_{(t)} = \delta^{18}\text{O}_{(t=0)} \cdot F^{(\alpha-1)}$$

Where $\alpha = {}^{18}\text{R} / {}^{16}\text{R}$ and F is the fraction of the initial oxygen remaining at time t (*i.e.*, $[\text{O}_2]_t / [\text{O}_2]_{t=0}$) and ${}^{16}\text{R}$ and ${}^{18}\text{R}$ are reaction rates of the light and heavy isotopes of oxygen respectively. The fractionation factor (α) is a ratio with a value close to one. In the following discussion α will be presented as a ratio rather than in per mil notation (ϵ , where $\epsilon = (1 - \alpha) / 1000$) to avoid confusion with the per mil fractionation that I have used to describe net isotopic changes during the incubation experiments.

The Rayleigh model predicts that the per mil fractionation for a given degree of oxygen consumption will increase dramatically as the fractionation factor gets larger. In terms of α , larger corresponds to a number further away from (in this case, less than) 1.000. The change in $\delta^{18}\text{O}$ composition is plotted in Figure 4.7 as a function of the fraction of the normalized change in O_2 concentration. Model-derived vectors of $\delta^{18}\text{O}$ as a function of O_2 consumption for specific values of the fractionation factor (α) are plotted as well. The $\alpha_{\text{O}_2\text{app}}$ values from the incubation experiments fall within a narrow band between 0.994 and 0.991 with a mean of 0.992 ± 0.0015 . This value is remarkably close to the value of 0.991 predicted for the apparent fractionation factor (Bender, 1990). The data from Brandes and Devol (1997) plotted in the figure for comparison reflect a much smaller apparent fractionation, with $\alpha_{\text{O}_2\text{app}}$ greater than 0.996.

This experiment was designed to examine O_2 fractionation under conditions where O_2 stress was not affecting the degradation of organic carbon. Under *in situ* conditions, O_2 in these sediments was still removed relatively rapidly ($[\text{O}_2]$ goes to zero

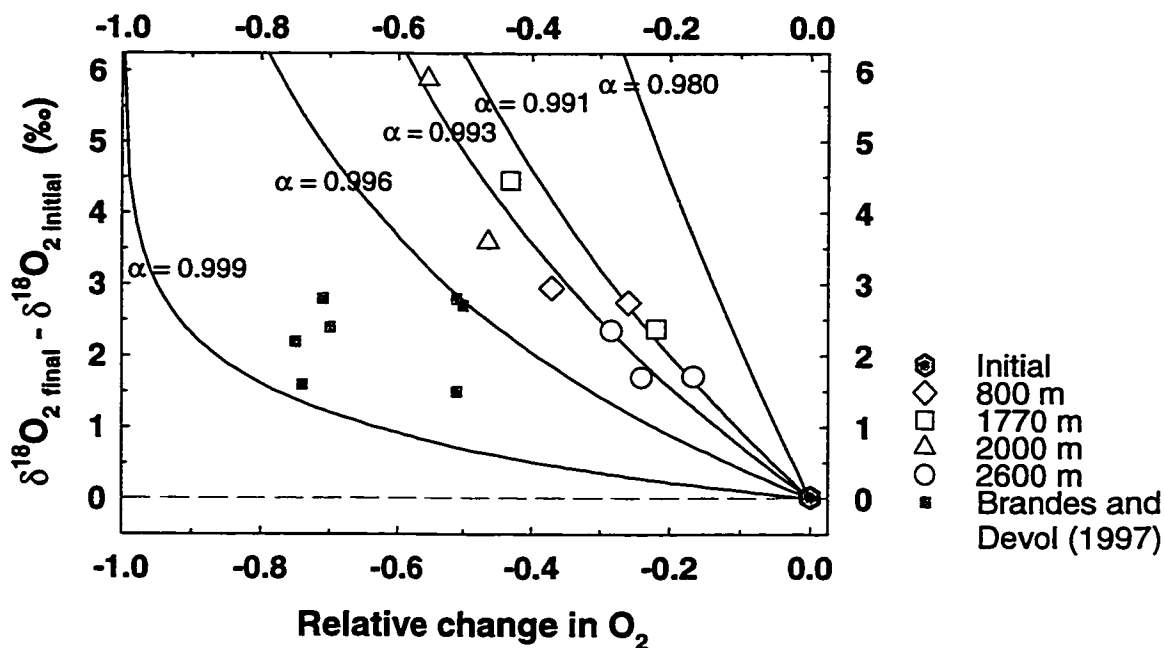


Figure 4.7 Fractionation of dissolved oxygen during sediment core incubations. Per mil fractionation of dissolved oxygen in the overlying water is plotted versus normalized oxygen concentration. Lines indicate predicted $\delta^{18}\text{O}$ compositions based on Rayleigh fractionation kinetics for the indicated values of the fractionation factor (α). Open symbols are data from this study and shaded squares are replotted from Brandes and Devol, 1996.

at ~1 to 2 cm). The potential for oxygen stress to affect the measured fractionations was minimized by equilibrating the overlying water with the atmosphere. The initial oxygen concentration in the experiment ($339 \mu\text{mol L}^{-1}$) was four to twenty times the *in situ* concentrations for the four depths sampled (*see* Table 4.1 and Chapter 2, Figure 2.2). The experimental conditions attempted to reflect conditions approaching those in the carbon-limited deep sea. Because oxygen concentration in this experiment was set at a substantially elevated level and the sedimentary organic carbon contents were all roughly similar, it is not possible to assess off-shore changes in the fractionation of O₂ under true

substrate-limited conditions. Rather the cores taken together represent a generic “pseudo-substrate-limited” condition in that they appear to have had sufficiently high oxygen concentrations over the duration of the experiment to preclude oxygen stress. Implicit to Bender’s (1991) prediction of an apparent fractionation of 0.991 is a system that is not stressed by the availability of oxygen; *i.e.*, deep-sea sediments. In my substrate- (carbon-) limited experimental system with the oxygen stress relieved, the isotopic fraction approached Bender’s theoretical value of 0.991. Based on data in Brandes and Devol (1997), continental margin sediments appear to be oxygen stressed and to have small apparent fractionations. My experimentally derived fractionation factor of 0.992 is more representative of sediments in which carbon oxidation is substrate- (*i.e.* carbon-) limited.

Taken together, these data and those of Brandes and Devol suggest sediments will become progressively less oxidant stressed with distance from shore; *i.e.*, with greater oxygen supply and a more refractory pool of available organic carbon. The switch from oxidant to substrate limitation should therefore be accompanied by an increase in the fractionation of oxygen during benthic metabolism, assuming a continuum from oxidant limitation in shelf and upper-slope sediments to substrate limitation in sediments from deeper waters. A compilation of data from the literature and from Chapter 2 for O₂ flux and bottom-water oxygen concentrations indicated that shallow regions show a fairly linear relationship between oxygen flux and bottom-water oxygen concentrations (Figure 4.8). The deep ocean, in contrast, appears to have little relationship between O₂ flux and bottom-water O₂ content. The shallow stations in this plot should exhibit little or no isotopic fractionation of oxygen; I would predict that those (deep) stations falling in the lower right hand portion of this plot, where there is no apparent relationship between O₂ flux and bottom-water oxygen should exhibit a larger isotopic fractionation of oxygen. An *in situ* measurement of the fractionation of oxygen during respiration remains as a final confirmation of the effective fractionation in carbon-limited sediments. In addition, an off-shore transect of δ¹⁸O incubations would allow the establishment of point along the margin where the shift from oxidant stress to substrate limitation occurs.

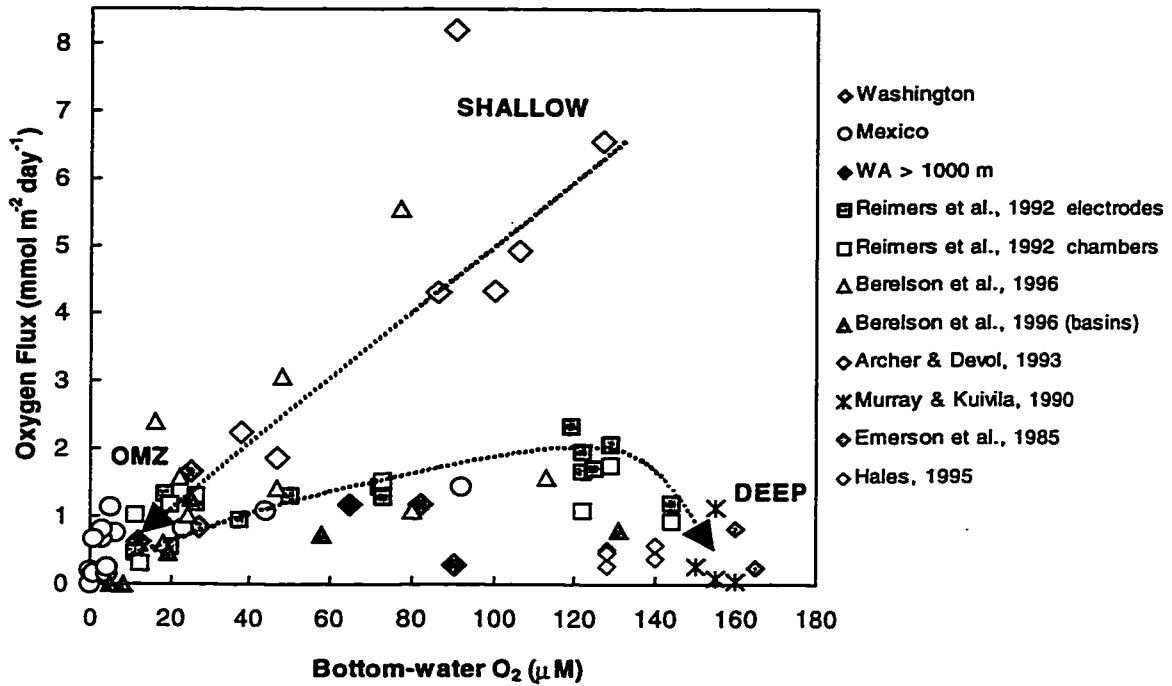


Figure 4.8 Relationship between diffusive oxygen flux and bottom-water O₂ concentration based on literature values for sediments from the North Pacific Ocean.

FRACTIONATION OF NITROGEN

Contrary to expectations based on the O₂ fractionation experiments, the ¹⁵N-isotopic composition of the nitrate in the overlying water became isotopically lighter in almost all incubation experiments (Figure 4.9). At first glance, this finding would appear to contradict the expected microbial fractionation that favors the light isotope of nitrogen in the uptake of NO₃⁻ or NH₄⁺. The results also appeared to differ from those of Brandes and Devol (1997) for Puget Sound, where no significant change in the isotopic composition of the lander NO₃⁻ was observed. The measured changes in δ¹⁵N-NO₃⁻ and δ¹⁵N-NH₄⁺ in my studies were robust; based on changes in concentration and isotopic

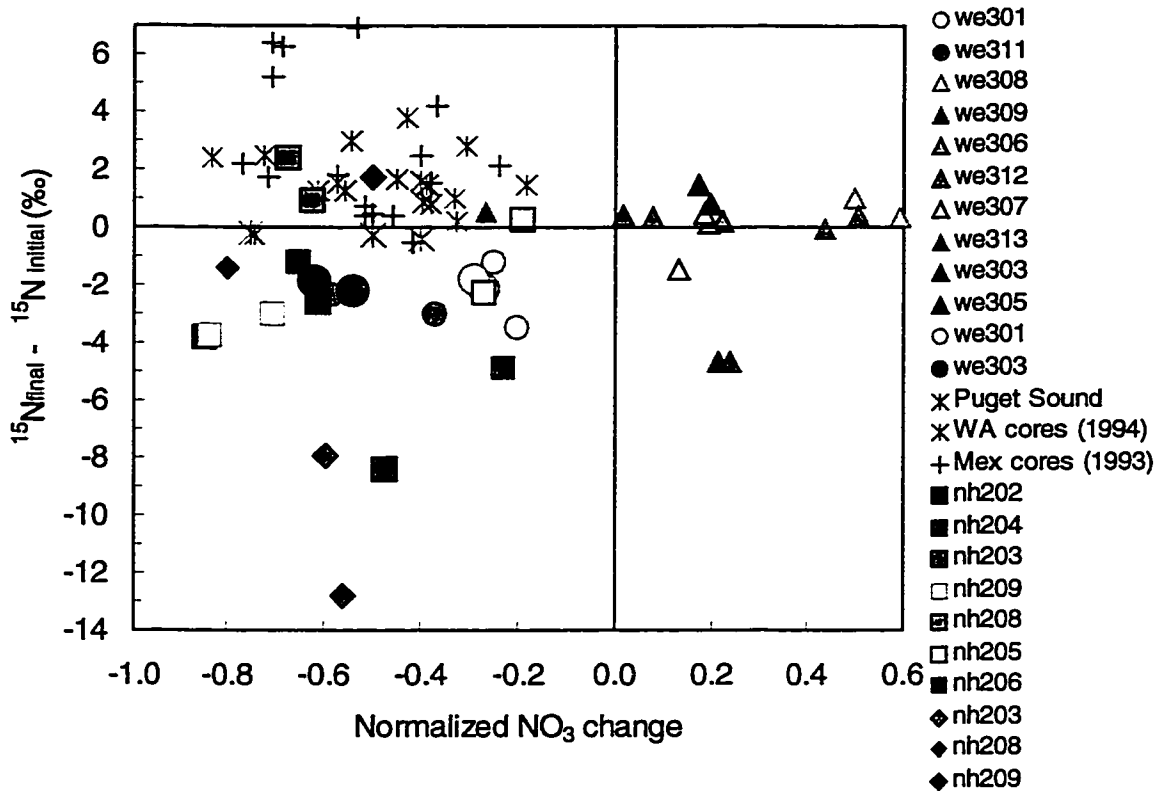


Figure 4.9 Per mil change in NO_3^- isotopic composition for Mexican margin lander experiments (squares) and core incubations (diamonds), Washington margin lander experiments (large circles) and core incubations (small circles). Data from Brandes and Devol (1997) is included for comparison: Washington margin core incubations (asterisks), Mexican margin core incubations (plus signs); Puget Sound lander experiments (crosses).

composition of NH_4^+ and NO_3^- in the lander samples, a number of artifacts that could produce the isotopically light NO_3^- values can be ruled out.

Contamination with surface water during lander recovery and insufficient poisoning of the samples after collection could both have produced isotopically light NO_3^- . Surface-water contamination would decrease the lander NO_3^- and NH_4^+ concentrations, because the surface ocean is depleted in both NO_3^- and NH_4^+ .

Furthermore, surface water addition should drive $\delta^{15}\text{N}-\text{NO}_3^-$ toward the surface water

value of $\sim +6\text{‰}$. At the Washington margin lander stations, neither NO_3^- nor NH_4^+ concentrations supported the addition of surface water. The final $\delta^{15}\text{N-NO}_3^-$ at these stations were actually lighter than $+6\text{‰}$, a result that cannot derive from addition of surface water. The Washington margin core incubations (triangles in Figure 4.9) showed increasing NO_3^- concentrations and final $\delta^{15}\text{N-NO}_3^-$ values that were isotopically heavy. These results can be explained by surface water dilution of the box core overlying water during recovery: low NO_3^- concentrations in the overlying water would have created a gradient and a flux out of the sediments. It is also possible that nitrification could also have occurred in the core incubations but the sediments were collected from a range of depths where I expected denitrification to dominate and therefore to observe net NO_3^- consumption in the overlying waters. The Mexican lander $\delta^{15}\text{N-NO}_3^-$ values were heavier than $+6\text{‰}$, a result that could have been affected by the addition of isotopically light surface water NO_3^- . However, surface-water dilution would also affect NH_4^+ concentrations and NH_4^+ values were very low. Low NH_4^+ concentrations and would have diluted any NH_4^+ signal, which does not appear to have been the case. The Mexican NH_4^+ concentrations in the lander overlying water were instead consistent with the lander time-course samples eliminating the possibility of surface water dilution. The presence of NH_4^+ at concentrations large enough for isotope determinations also argues against significant dilution by surface water.

Insufficient poisoning of the samples might also have had a predictable effect on the concentrations and isotopic compositions of NO_3^- and NH_4^+ . Nitrification is the process most likely to have occurred in the bottles. Isotopically, nitrification should have increased the $\delta^{15}\text{N-NH}_4^+$ and decreased the $\delta^{15}\text{N-NO}_3^-$; these changes are roughly in the direction seen in the lander data. However, nitrification would decrease the NH_4^+ concentrations and increase the NO_3^- concentrations, directions not evidenced by the data. Any denitrification in the bottles would have lowered the NO_3^- concentrations but increased the $\delta^{15}\text{N-NO}_3^-$; patterns not supported by the data.

In an effort to describe a scenario in which overlying water NO_3^- could both decrease in concentration and become isotopically light, I calculated the isotopic composition of the nitrate flux (*i.e.*, the $\delta^{15}\text{N}$ of the NO_3^- diffusing into the sediments) from the change in the NO_3^- concentration and the $\delta^{15}\text{N}\text{-NO}_3^-$ in the lander chamber:

$$\left(\frac{^{15}\text{N}}{^{14}\text{N}}\right)_{\text{NO}_3 \text{ flux}} = \frac{[\text{NO}_3]_{\text{final}} \cdot \left(\frac{^{15}\text{N}}{^{14}\text{N}}\right)_{\text{NO}_3, \text{final}} - [\text{NO}_3]_{\text{initial}} \cdot \left(\frac{^{15}\text{N}}{^{14}\text{N}}\right)_{\text{NO}_3, \text{initial}}}{\Delta[\text{NO}_3]}$$

where $(^{15}\text{N}/^{14}\text{N})$ is the isotopic composition of the NO_3^- at the beginning and end of the experiment and ΔNO_3^- is the change in the NO_3^- composition over the deployment. The isotopic composition of the N_2 gas and NH_4^+ fluxes were calculated in the same way. In the calculation of the isotopic composition of the NH_4^+ flux, I assumed an absence of NH_4^+ initially. In general, the lander NO_3^- flux was isotopically heavy compared to the overlying water NO_3^- (Table 4.9). The NH_4^+ flux was also generally heavy relative to the organic matter source; in contrast, the N_2 gas fluxes were isotopically light compared to overlying water N_2 .

The apparent fractionation for denitrification could not be determined from the simple Rayleigh model because the sediments were not a closed system with respect to NO_3^- consumption, as was the case for O_2 consumption: an additional source of NO_3^- within the sediments could have arisen from nitrification. Further complicating this system, nitrification has an associated N-fractionation, but this fractionation is not well known (Figure 4.10).

Table 4.9 Isotopic composition of the lander fluxes of NO_3^- , NH_4^+ and N_2 . The ratios marked with and asterisk were determined from core incubation experiments.

	$(^{15}\text{N}/^{14}\text{N})$ Ratio of Benthic Flux		
	NO_3^-	NH_4^+	N_2
Mexico			
100	1.01010	1.01243	
360	1.01524	1.01583	0.98676
587	1.02008		0.98843
808	1.00968		
1007	1.00741		
1500	1.00930	1.00820	0.98150
2000	1.02263	1.00701	0.99724
Washington			
120	1.01246	1.01444*	0.98361
200		1.01528*	
997		1.00901*	
2000	1.00790	1.01219*	0.99203

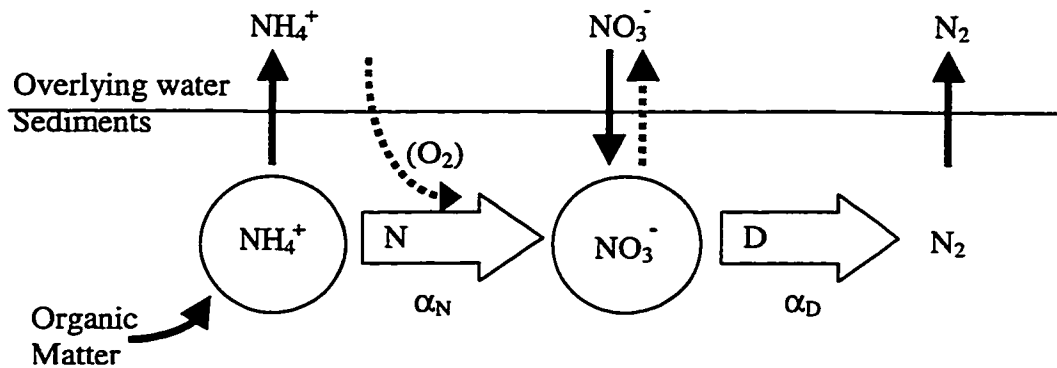


Figure 4.10 Schematic of nitrogen cycle in sediments with sources and sinks for NH_4^+ , NO_3^- and N_2 ; Large circles represent sedimentary pools, arrows represent measured fluxes and the large arrows represent processes that potentially fractionate the nitrogen pools (nitrification, N and denitrification, D).

A simple mass balance for the sediment NO_3^- pool can be constructed assuming that the measured flux of NO_3^- is a function of NO_3^- loss due to denitrification (**D**) and NO_3^- gain from nitrification (**N**):

$$\text{Net } \text{NO}_3^- \text{ flux} = F_{\text{NO}_3^-} = -\text{D} + \text{N}$$

The flux is driven by the gradient between the overlying water nitrate concentration and that in the sediment, a function of **N** and **D**. An isotopic mass balance can be constructed in the same way, including the isotopic composition ($^{15}\text{N}/^{14}\text{N}$) of each pool and the fractionations (α_{D} and α_{N}) associated with denitrification and nitrification, respectively:

$$F_{\text{NO}_3^-} \cdot \left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{NO}_3^- \text{ flux}} = -\text{D} \cdot \alpha_{\text{D}} \cdot \left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{denitrified NO}_3^-} + \text{N} \cdot \alpha_{\text{N}} \cdot \left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{nitrified NH}_4}$$

Using this conceptual model, a scenario can be constructed in which an isotopically heavy NO_3^- flux is generated, as was observed in the incubations. If the net effect of nitrification and denitrification is to isotopically deplete the sedimentary $\delta^{15}\text{N}\text{-NO}_3^-$ pool relative to the overlying water pool, and the denitrification rate is larger than the nitrification rate, there must be an isotopically heavy NO_3^- from the overlying water in order to balance the $^{15}\text{NO}_3^-$ and $^{14}\text{NO}_3^-$ gradients.

This heavy NO_3^- flux, which leaves the remaining overlying water NO_3^- isotopically lighter, can be described qualitatively using the Washington margin lander data from the 100-m station. The measured nitrate flux was isotopically heavy (12.46 ‰) relative to the overlying water NO_3^- (6.96 ‰; see Table 4.9). An isotopically heavy flux implies that the sediment NO_3^- pool was lighter than the overlying water pool. The N_2 gas flux measured at this station was isotopically light (-16.4 ‰) relative to the overlying

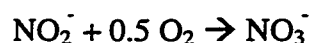
water N_2 (+0.33 ‰) so that any N_2 produced must also have been isotopically light. The N_2 flux was also substantially lighter than either the NO_3^- flux or the pool of overlying water NO_3^- ; therefore, if I assume that α_D must be relatively small (*i.e.*; close to 1.000), then there must have been an additional source of light NO_3^- . In the extreme, with no fractionation due to denitrification (Brandes and Devol, 1997), nitrification is the obvious source of light NO_3^- that would not only isotopically deplete the sediment NO_3^- pool, but also supply light NO_3^- for denitrification, producing light N_2 . Published values for fractionation due to nitrification are relatively large, although the precise value is not well known ($\alpha_N = \sim 0.980$, Delwiche and Stein, 1970; Mariotti et al., 1981) so that supply of light NO_3^- to the sediments by this mechanism should be possible. The Washington margin core incubation from this station is not directly comparable to the *in situ* experiment; however, the NH_4^+ flux from the core incubation was isotopically heavy, implying fractionation during nitrification to produce light NO_3^- . The NH_4^+ flux from the core incubation was 14.4 ‰, heavier than the sedimentary organic matter source (compare values for $\delta^{15}\text{N-NH}_4^+$ from Table 4.8 and 4.10, with 7 ‰ or 1.007 for $\delta^{15}\text{N-organic matter}$). The heavy NH_4^+ flux suggests that the fractionation during nitrification was large. The Washington margin data from the 2000-m lander station and 2000-m core incubation experiments were also consistent with a source of light nitrate from nitrification, a loss of NO_3^- with little or no fractionation to denitrification, and subsequent production of light N_2 gas. In both cases the N_2 gas was isotopically light because the pool of NO_3^- in the sediments was light and not because of a large fractionation associated with sedimentary denitrification. This qualitative assessment of the necessity for nitrification and denitrification to contribute to both the observed NO_3^- flux and the isotopic composition of the NO_3^- flux has assumed that α_D is equal to 1.000. There is no *a priori* requirement that denitrification not be a fractionating process, only that the fractionation not be so large as to enrich the sediment NO_3^- pool isotopically with respect to the overlying water NO_3^- . For all of the stations studied, the NO_3^-

concentrations in the porewater are drawn down to concentrations approaching zero within the top few centimeters (*see* Chapter 2, Figure 2.8) implying that denitrification will be limited by the supply of NO_3^- . By analogy, to oxygen stress or limitation described earlier, α_D must be fairly small as a result of this NO_3^- limitation.

The changes in the $\delta^{15}\text{N-NO}_3^-$ values during the Mexican margin lander and core experiments suggested there must also be nitrification and denitrification occurring in these sediments. The N_2 gas data indicate that there must be a light N_2 flux as well (*see* Table 4.11). The Mexican $\delta^{15}\text{N-NH}_4^+$ data, however, are less straightforward to interpret. At all stations, there was a net NH_4^+ flux from the sediments to the overlying water; but at two stations that flux was isotopically heavy while at the two others it was isotopically light with respect to the $\delta^{15}\text{N}$ of organic matter. A heavy NH_4^+ flux suggests nitrification, a process classically considered to requires O_2 (Kaplan, 1983):



and



Because it is generally assumed that nitrification does not occur in the absence of oxygen, there should be no nitrification in the Mexican ODZ sediments. In addition, the ratio of NH_4^+ regenerated to oxidized organic carbon in the Mexican margin sediments does not indicate a significant loss of regenerated NH_4^+ to nitrification. Never-the-less, the isotopic evidence from the 360-m station suggests that NH_4^+ is being removed from the sediments by a fractionating process. Reactions between NH_4^+ and MnO_2 , producing N_2 gas and between NO_3^- and Mn^{2+} to produce MnO_2 have been proposed by Murray et al. (1995) and Luther et al. (1997) as possible mechanisms for N_2 production. These possible reactions are particularly interesting to consider in the Mexican margin sediments because they would allow the oxidation of NH_4^+ in the absence of O_2 . If the reactions between MnO_2 and NH_4^+ and are mediated microbially, there is likely to be an associated isotopic fractionation that produces light N_2 and leaves behind heavy NH_4^+ .

Porewater Mn^{2+} profiles from the Mexican margin indicate that there are low, but non-zero, Mn^{2+} concentrations at all depths in the Mexican margin ODZ sediments; thus there is the possibility for Mn^{2+} and NO_3^- to co-exist in these sediments. Solid phase Mn profiles from Nameroff (1996) indicate slight surface enrichments that could be due to the presence of manganese oxides. The data available cannot provide direct evidence of NH_4^+ oxidation by MnO_2 ; however, it may be possible Mn^{2+} may oxidize to MnO_2 in the presence of NO_3^- which could facilitate NH_4^+ oxidation. If manganese is acting in some catalytic role, a large concentration of either dissolved or solid phase Mn in the sediments may not necessarily be needed; merely a rapid conversion between the two species. This coupled NH_4^+ and manganese cycling is not well understood and warrants further research.

IMPLICATIONS FOR THE $\delta^{15}\text{N}$ OF NITROGEN IN THE OCEANS.

The changes in the $\delta^{15}\text{N}$ of the lander NO_3^- are not necessarily inconsistent with the results presented in Brandes and Devol (1997) for Puget Sound sediments. In both their data set and mine, a fractionation during nitrification is required to balance the flux of isotopically light N_2 gas. Brandes and Devol (1997) had the additional constraint of not having measured a change in the isotopic composition of the lander NO_3^- , thus putting a limit on the degree of fractionation during nitrification. They predicted a fractionation of $\sim 5\%$ during nitrification, since no larger fractionation could be supported in the absence of an observed change in the lander $\delta^{15}\text{N}\text{-NO}_3^-$ values. If nitrification had contributed more to the NO_3^- pool of these Puget Sound sediments or if the fractionation during nitrification had been larger, the NO_3^- in the sediments would have become depleted isotopically relative to the overlying water and the measured NO_3^- flux would have become isotopically heavy relative to the overlying water NO_3^- . It is possible to generate a NO_3^- flux that is isotopically very heavy or very light with respect to the overlying water NO_3^- given only small changes in the relative contribution of nitrification and denitrification. If nitrification has a large α_{N} , then clearly the sedimentary pool

becomes lighter and the NO_3^- flux must be relatively heavy. If denitrification is large relative to nitrification, then even a small α_D will eventually leave the sedimentary NO_3^- pool isotopically heavy and the NO_3^- flux isotopically light. The isotopic composition of the organic matter relative to that of the overlying water NO_3^- will also affect how much nitrification and α_N will affect the isotopic difference between overlying water NO_3^- and porewater NO_3^- .

It follows from these results that it is possible for nitrate in the bottom waters to become isotopically lighter as a result of nitrification and denitrification in the sediments. While the sediments in most continental margin regions are a net sink for nitrate, the processes which contribute to the nitrate flux from the sediments can also combine to leave the remaining nitrate in the bottom water isotopically depleted in ^{15}N . I would suggest that in shelf and upper slope sediments, denitrification rates are typically NO_3^- limited (subject to nitrate stress, such that no fractionation occurs during denitrification), therefore α_D is generally likely to be ~ 1.000 . Under these conditions, the fractionation due to nitrification and the $\delta^{15}\text{N}$ of organic matter will be the most important factors in determining the effect of sedimentary processes on oceanic ^{15}N distributions. Deeper on the continental slope, conditions may allow for a fractionation during denitrification as both oxygen and nitrate stress are relieved and organic carbon becomes limiting to organic matter degradation.

SUMMARY

The nitrogen isotope fractionations that occur in continental margin sediments favor the light isotope of nitrogen, but determining the fractionation factors for nitrification and denitrification is difficult because the two processes are tightly coupled in most margin sediments. It is entirely possible for the two reactions to combine to make the sediments a net sink for NO_3^- yet leave the remaining NO_3^- isotopically light; conversely, denitrification can consume NO_3^- with a small fractionation such that the

overlying water NO_3^- becomes isotopically heavy. The isotopic effects of sedimentary processes on NH_4^+ and N_2 are simpler to describe as they are only affected by one process (nitrification and denitrification, respectively). Nitrogen gas from sedimentary denitrification appears to be an isotopically light source of N_2 , while NH_4^+ regenerated from organic matter is generally isotopically heavy due to a loss to nitrification, particularly in the Washington margin sediments. In regions where little or no denitrification occurs (*i.e.*, the deep sea) the NO_3^- source from the sediments is likely to resemble the isotopic composition of the organic matter source.

The apparent fractionation of oxygen during sedimentary respiration is dependent upon the conditions which control degradation of the organic matter. When respiration is limited by the amount of reactive organic carbon, the apparent fractionation ($\alpha_{\text{O}_2\text{app}}$) is 0.992. This value is significantly smaller than the oxygen fractionation that occurs during water column respiration (*see* Figure 4.12). Under carbon-limited conditions, typical of the deep sea, sedimentary respiration could significantly increase the $\delta^{18}\text{O}$ of the local bottom water. In margin regions, however, O_2 is not fractionated during uptake so that $\delta^{18}\text{O}$ in shallower water (<1000 m) will reflect the fractionation by bacteria in the water column ($\alpha = 0.980$). Models for glacial-interglacial climatic changes that invoke increases in high latitude productivity predict increased bottom-water anoxia (Sarmiento and Sundquist, 1992; Sarmiento and Toggweiler, 1984); such increases may imply a change in the areal extent of oxidant-limited and substrate-limited respiration in marine sediments. If the more of the oceans sediments were subjected to oxygen stress in the past, then one might expect the deep-ocean $\delta^{18}\text{O}$ signal to have been isotopically heavier, reflecting the full microbial fractionation rather than the reduced fractionation that is indicative of the carbon-limited sedimentary respiration typical in much of the contemporary deep ocean.

CHAPTER 5: IMPLICATIONS OF INPUT AND DEGRADATION STUDIES FOR PRESERVATION OF ORGANIC MATTER IN CONTINENTAL MARGIN SEDIMENTS

DEGRADATION AND PRESERVATION

There is an inherent relationship, albeit not always a clear one, between organic carbon degradation and preservation. While it is true that these are in a sense “opposite” processes (Hedges and Keil, 1995), it is also true that when a significant amount of carbon is lost during water-column transit and early diagenesis, less organic carbon is preserved in sediments. Conversely, if more organic matter escapes degradation in the water column and survives diagenesis in surface sediments preservation will be higher; thus, a better understanding of the what controls the extent of degradation will shed some light on the potential for organic matter to be preserved in sediments. Often the relation between degradation and preservation is difficult to quantify because the time scale over which organic carbon degradation occurs is much shorter than that over which preservation operates. In assessing the relation between organic matter degradation and preservation the “investigative time scale” will often dictate the rates which can be measured. An experiment sampled every two days will not reflect processes that occur on the time scale of minutes, while one that lasts for 30 days will not be able to identify changes that occur over the course of decades.

This work has addressed the issues of investigative time scale in several ways: by incorporating measure that integrate over different degradative time scales; by manipulating oxygen exposure times, thereby accelerating the time over which slower processes occur; and by employing sensitive stable isotope techniques to measure processes that respond to degradation over short time scales. In Chapter 2, the measures of carbon oxidation include not only fast reactions using O_2 and NO_3^- but also measurements of SO_4^{2-} reduction rate that integrate over a greater depth in the core and

therefore over a longer time scale (order of decades). This time scale begins to be comparable to the time scale beyond which carbon is permanently buried because carbon contents did not appear to change below the depth of measurable SO_4^- reduction (~ 10-15 cm) in the regions studied. In Chapter 3, the issue of investigative time-scale was approached in two ways. First, I chose to conduct the experiments over the course of ~30 days; an intermediate experimental length that tends to be less well studied. Short time-scales (order of hours) are suited to *in situ* lander studies and have been widely applied (Devol and Christensen, 1993; Jahnke, 1990). Longer time-scales can be addressed easily in down core studies of organic matter changes and in sediment studies from the deep sea, where oxidation rates and accumulation rates are very slow (Emerson, 1985a; Grundmanis and Murray, 1982; Murray and Kuivila, 1990). Intermediate length studies, on the scale of weeks to months, may improve our understanding of the differences between regions since the differences in oxygen exposure time between region of high and low levels of preservation are on the order of a few months (Hartnett et al., 1998). The second method that I employed at an intermediate time scale involved manipulating the exposure to oxygen, and assuming that changing the O_2 concentration effectively altered the length of exposure time. Oxidic sediments were removed from an O_2 source while anoxic sediments were exposed to high O_2 concentrations. Since most of the sediments studied were sub-oxic to anoxic within ~ 1 cm of the surface, the effect of oxygen exposure was expected to be substantial and thus easily detected. In Chapter 4, I described changes in the isotopic composition of oxygen and nitrogen in short-term incubation experiments, that reflected processes influencing the rate and time scale of organic matter degradation. Such changes (especially for O_2) must also have implications for processes that operate over longer time scales. Oxygen can only be fractionated when there is sufficient oxygen present and, by inference, when oxygen exposure times are long. Similarly, the nitrogen experiments indicated that changes in the isotopic composition of the various N species were, in part, dependent on the amount of organic matter that was available for respiration and thus, must reflect processes that occur on a variety of time-scales. All of these experiments were conducted with natural

sedimentary organic matter under *in situ* temperatures in order to prevent elevation of degradation rates by temperature-driven changes in metabolic rate or substrate reactivity. While it is difficult to conclude exactly how preservation follows from degradation, as degradation proceeds over time the remaining organic matter should begin to reflect what is preserved in the sediments. In the following discussion, I have attempted to further constrain the processes that may control preservation by interpreting the results from Chapters 2 through 4 in light of carbon burial efficiency and exposure time. The new analysis provides an improved understanding of how much carbon can be degraded and under what conditions, which may in turn provide information about the potential for organic matter to be preserved.

HOW ARE INPUT AND DEGRADATION RELATED TO PRESERVATION?

The attenuation of carbon flux through the water column or oxidation rate in the sediments with depth has generally been expressed as a power function of depth (*see* Chapter 2, Figures 2.9, 10, and 11 and Table 2.7). This strictly empirical model does not attempt to provide a mechanism for the attenuation, short of the relation with water depth. A more mechanistic parameterization of carbon flux (or oxidation rate) can be described by a 'Berner-style' multi-G model (Berner, 1980; Westrich and Berner, 1984). The multi-G model provides information necessary to describe regional differences in attenuation in terms of organic matter reactivity. I have fit the Washington and Mexico carbon oxidation rate data to an equation of the form:

$$\text{Flux or Rate} = G_{1o} e^{-K_1 z} + G_{2o} e^{-K_2 z} + G_{NR}$$

In this equation, two fractions of the organic carbon, G_1 and G_2 , are reactive with first-order kinetics (K_1 and K_2 , where $K = k/\omega$; k is the first-order degradation rate constant and ω is the particle settling velocity) and a third fraction is non-reactive, G_{NR} (Figure 5.1). The data (normalized to the oxidation rate at 100 m) were best fit by the following equations:

$$C_{oxid} - \text{Washington} = 8.12e^{-0.00698(z-100)} + 4.23e^{-0.00285(z-100)} + 0.9307$$

$$C_{oxid} - \text{Mexico} = 3.58e^{-0.00209(z-100)} + 4.69 \cdot 10^{-8} e^{-5.5 \cdot 10^{+6}(z-100)} + 1.376$$

Although empirical fits to the data, these equations allow a mechanistic relation of the attenuation in carbon flux to different components of more or less reactive organic matter. Generally, the equations indicate a larger non-reactive flux off Mexico than off Washington; a greater percentage of the carbon flux at 100 m reaches the Mexican margin sediments. The most reactive component of the Mexican margin carbon oxidation rate is only as reactive as the less reactive component of the Washington oxidation rate ($K_1\text{-Mex.} = -0.00209$ and $K_2\text{-WA} = -0.00285$). The less reactive component of the Mexican oxidation rate is essentially zero and the Mexican rates only require a non-reactive fraction and a relatively less reactive fraction to fit the data. The Mexican data does not require any component that is as reactive as the Washington margin reactive fraction. The relatively large reactive flux off of Washington is consistent with the faster attenuation in the carbon oxidation rates on this margin. The oxidation rates at 100 m predicted by the multi-G model are 4.96 and 13.28 mmol m⁻² d⁻¹, respectively. These rates are in good agreement with the measured oxidation rates at 100 m. Since the exponents in these equations are the ratio of k/ω , with estimates of the settling velocity they could be used to determine a degradation rate constant. In spite of the empirical best fit, the multi-G model still does not describe attenuation in the Mexican carbon oxidation rates very well ($r^2 = 0.581$). Lack of attenuation in the data may be related to a factor other than reactivity of the organic matter (e.g., reduced bacterial consumption due to the presence of the ODZ or lower macrofaunal activity). It is also possible that off-shelf transport of organic matter contributes to the pattern in carbon oxidation rates, but the model does not address lateral advection. Statistically the carbon oxidation rate data from both margins are fit almost equally well by the power function relation as by the multi-G model, even though the multi-G model has more

fitting parameters. However, the potential mechanistic information that can be obtained with more degrees of freedom justifies use of the multi-G model; more information can be obtained that relates to reactivity of the organic matter flux.

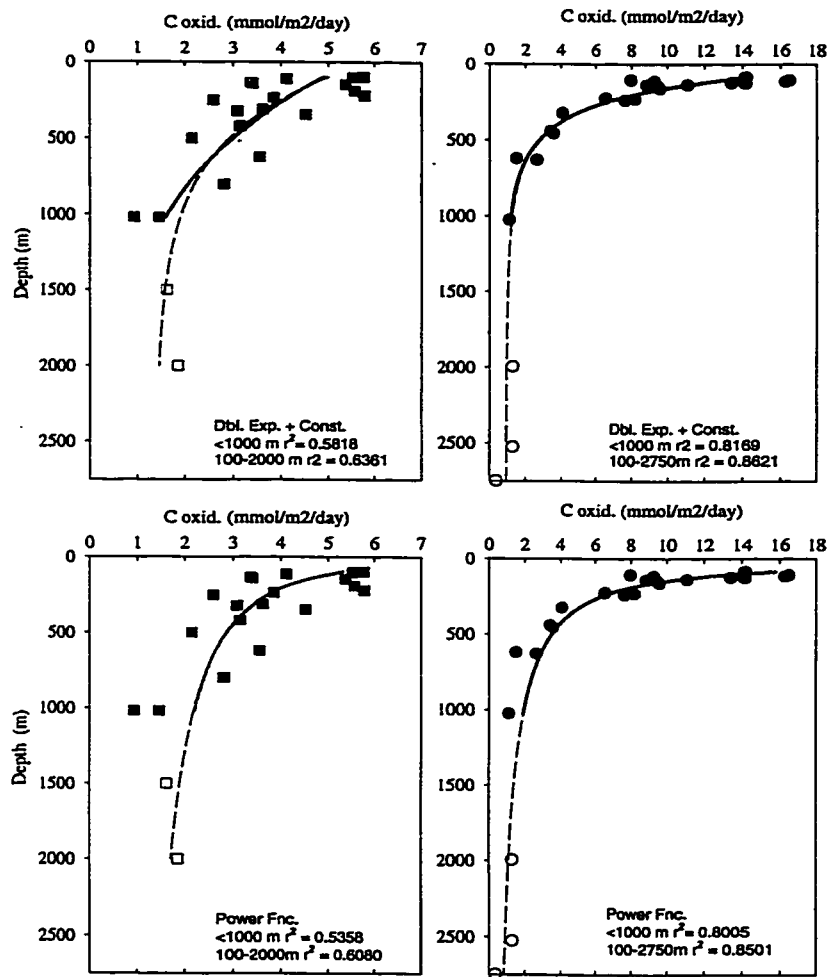


Figure 5.1 Multi-G model and power function curve fits for Washington (circles) and Mexico (squares) carbon oxidation rate data. The upper panels are multi-G model fits and the lower panels are the power function fits. Solid lines are fits to stations above 1000 m and dotted lines are fits to all data for each margin.

BURIAL EFFICIENCY AND OXYGEN EXPOSURE TIME

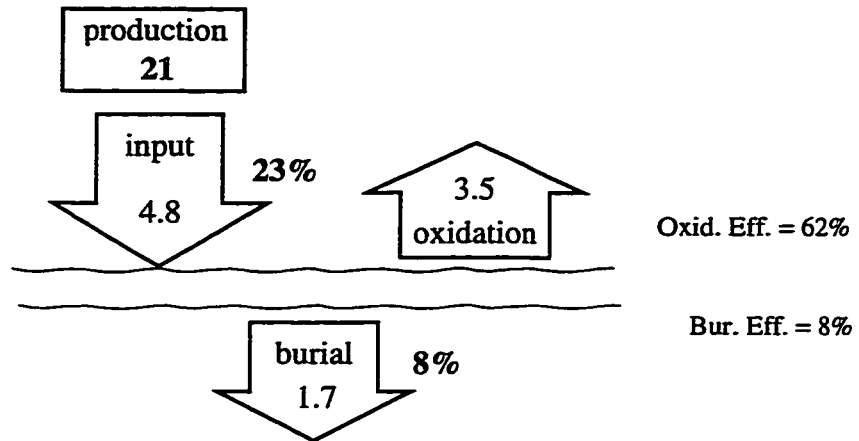
The degree of preservation can be compared among regions by calculating the burial efficiency of organic carbon (Betts and Holland, 1991; Canfield, 1994; Hartnett et al., 1998; Henrichs and Reeburgh, 1987). This parameterization of carbon burial, relative to carbon input, essentially normalizes the amount of organic matter preserved and removes the effect of sedimentation rate on the carbon burial term which varies from region to region:

$$\text{Burial Efficiency} = C_{\text{burial}} / C_{\text{input}}$$

where carbon input is either the sum of carbon burial rate plus total carbon oxidation rate, (*i.e.*, the sum of what remains in sediments and what was removed by degradation; *see* Chapters 2 and 4), or a measured estimate of the carbon input rate (*e.g.*, a sediment trap flux). Previously reported calculations of burial efficiency indicate a greater degree of preservation in Mexican margin sediments than in Washington margin sediments (Hartnett et al., 1998). The carbon budget presented in Chapter 2 suggested that the burial of organic matter was more efficient in the Mexican margin ODZ sediments. A closer examination of the budget for the oxygen deficient zone reveals that approximately 8% of the primary production on the Mexican margin survives passage through the water column and oxidation in the sediments (Figure 5.2). In contrast, approximately 1% of the primary production survives to be buried in Washington margin sediments. The budget in Figure 5.2 is constructed for the Mexican ODZ stations and the Washington margin stations between depths of 100 and 600 m in order to emphasize the differences in burial and oxidation efficiency on the two margins.

Compelling evidence to suggest that oxygen is a controlling factor in the preservation of organic carbon includes: a correlation between high sediment organic carbon contents and low bottom-water oxygen (Canfield, 1994; Demaison and Moore, 1980; Hedges and Keil, 1995); a relation between benthic oxygen flux (and by inference, organic carbon oxidation) and bottom-water oxygen (Archer and Devol, 1992; Jahnke et

MEXICO
(ODZ)



WASHINGTON
(100-600 m)

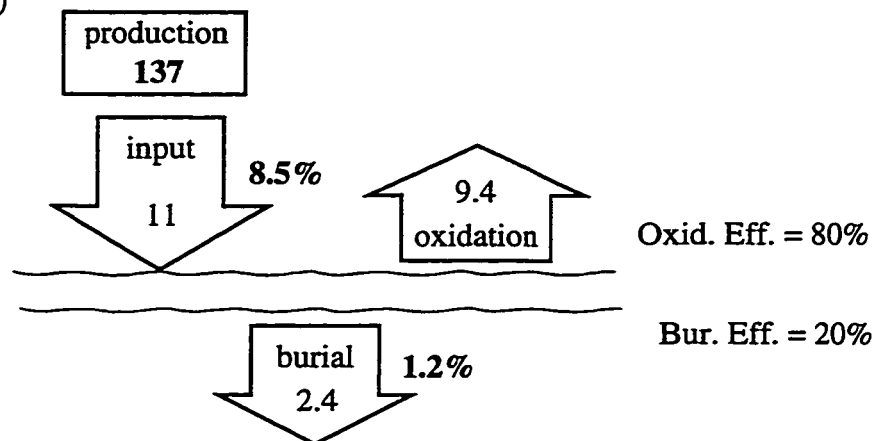


Figure 5.2 Schematic carbon budget for the Mexican margin ODZ and the Washington margin between depths of 100 and 600 m. Boxes indicate primary production rates for the two margins; arrow indicate rates of carbon input oxidation, and burial. Units for all fluxes and rates are in $\text{mmol m}^{-2} \text{d}^{-1}$. Bold faced numbers indicate the percentage of the primary production represented by the indicated rates.

al., 1990); and the relationship between burial efficiency and oxygen exposure time (Hartnett et al., 1998). In addition, a number of results from this study point to a significant role for oxygen in the degradation and preservation of organic matter. Results from Chapter 2 indicated that reduced exposure to oxygen in the Mexican ODZ allowed

the passage of a much larger percentage of the export carbon flux from the surface ocean to reach the sediments. The carbon arriving at the seafloor appeared to be resistant to degradation and thus was buried in the sediments. Results of the slurry and core incubation experiments in Chapter 3 also suggested an oxygen effect because the rates of degradation in the presence of O₂ were high. Carbon may also have been more completely mineralized of carbon in the oxic core incubations as evidenced by lower DOC concentrations.

Oxygen exposure time (OET) incorporates a time scale (derived from the sediment accumulation rate) that provides a mechanism for the inverse relation between oxygen exposure and organic carbon preservation (Hartnett et al., 1998; Hedges et al., in press). Oxygen exposure time is calculated from the depth at which oxygen concentrations approached zero in the sediments (O₂ penetration depth, in cm) and the sediment accumulation rate (in cm yr⁻¹):

$$\text{OET} = \text{O}_2 \text{ penetration depth} / \text{Sediment accumulation rate}$$

Oxygen exposure time generally increases with increasing water depth because both sedimentation and carbon oxidation rates decrease; decreasing oxidation rates and higher oxygen concentrations allow for deeper O₂ penetration in the sediments. A relationship between burial efficiency and exposure time has been presented for the shallow Mexican margin stations by Hartnett et al. (1998). This relation has been extended to the deep Mexican margin stations from Chapter 2 (*see* Figure 5.3); the shallow and deep portions of the Mexican margin, where there is oxygen in the overlying water, clearly follow the same trend as other western continental margin sediments. The correlation was slightly better with the inclusion of the deep Mexican margin data than without ($r^2 = 0.624$ vs. $r^2 = 0.545$, respectively).

The oxidation efficiency can be compared for the two margins as well. Similar to burial efficiency, it is calculated as the percentage of the carbon input rate that is oxidized in the sediments. The oxidation efficiencies were higher for the Washington margin than

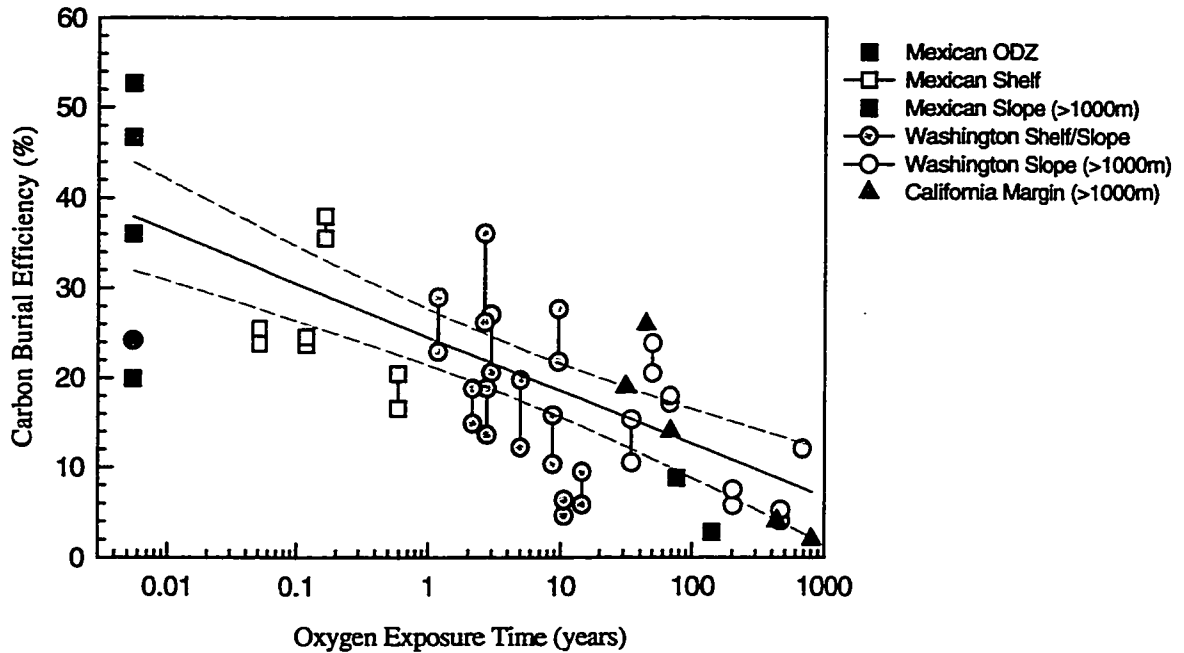


Figure 5.3 Carbon burial efficiency vs. oxygen exposure time for sediments from the continental margins of Mexico, Washington and California. O_2 exposure time is plotted on a log scale so that variations in burial efficiency at short exposure times can be distinguished. The ODZ sediments are assumed to have exposure times of ~ 0.003 years (< 2 days). Pairs of connected symbols indicate range in burial efficiency calculated from C_{oxidI} and C_{oxidII} (see text). The solid line is a least-squares fit to the data, $r^2=0.624$, $P<0.05$; the dotted lines are the 95% confidence intervals.

for Mexican margin. The reduced oxidation efficiencies in the Mexican sediments appeared to be related to the presence of the ODZ and was likely some function of the reactivity of the organic matter present in the sediments. The slurry experiments from Chapter 3. also suggested the organic matter in the ODZ sediments was intrinsically less reactive than the organic matter from oxic sediments. It seems unlikely that the ODZ organic matter is fundamentally different from the organic matter on the rest of the margin as the primary production rates are similar across the region and the stations sampled are all within about 25 km of each other. It is possible that surface adsorption of the organic matter renders it in some way less available to the microorganisms in the sediment. If the organic carbon:surface-area (OC:SA) is indicative of the amount of

microbially available organic matter there should be a relationship between carbon oxidation efficiency and the OC:SA ratio. There was an inverse relationship between carbon oxidation efficiency and OC:SA ratio for the Washington and Mexican margin sediments (Figure 5.4). Sediments from the Mexican margin with high OC:SA ratios had lower oxidation efficiencies while sediments from the Washington margin and from the deeper, oxic portion of the Mexican margin had similar, higher oxidation efficiencies and lower OC:SA ratios. The exact reasons for the apparent non-reactivity of the Mexican ODZ sediments remain to be elucidated.

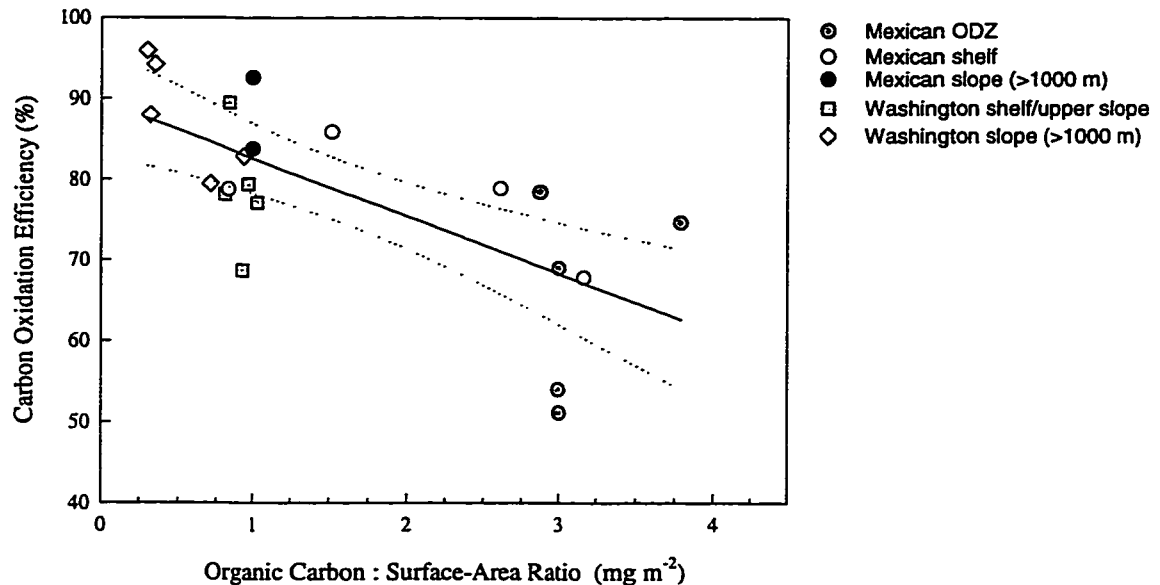


Figure 5.4 Carbon oxidation rate vs. OC:SA ratio for the Mexican and Washington continental margins. The OC:SA data for the Washington stations is taken from Hedges et al. (in press) and the Mexican stations is from Keil (unpublished data). The solid line is a least-squares fit to the data ($r^2 = 0.479$, $P < 0.05$) and the dotted lines indicate the 95% confidence intervals.

IS THERE A PROTECTIVE MECHANISM IN ADDITION TO ANOXIA?

Results from the sediment incubation experiments in Chapter 3 were surprising in that provision of oxic conditions did not lead to an enhancement of degradation of organic matter in the Mexican ODZ sediments. This result has implications for causal links between degradation and preservation of organic matter in the ODZ: some additional protective mechanism that overrides the effect oxygen exposure or mixing may be operating in the ODZ sediments.

First, it appeared that slurring enhanced the degradation of organic matter in sediments over that which occurred *in situ* (see Chapter 3). These experiments were diluted and stirred more strongly than any of the sediments would ever have been *in situ*. The relatively lower of enhancement of the ODZ sediments compared to the other stations is important because it indicates that whatever mechanism is protecting the organic matter in these sediments from degradation, it is not affected by slurring, at least on the time-scale of the experiment. It is unlikely for the apparent enhancement of degradation to be due to desorption and subsequent degradation of organic matter or due to some other dilution effect. The desorption of organic matter from sediments generally releases less DOM than I measured in the slurry experiments (Keil, personal communication). I had expected the ODZ sediments to be the most susceptible to the effects of slurring because they are rarely if ever mixed and diluted *in situ* given the absence of large bioturbating organisms. If slurring enhances degradation, and the ODZ sediments are never disturbed naturally, the associated organic material should be degraded and thus, more reactive than in sediments that are mixed and diluted through the activity of benthic macrofauna.

Second, much of the natural organic matter in these experiments was obviously accessible to the resident bacterial populations: substantial degradation of organic carbon occurred under both oxic and anoxic conditions, regardless of initial redox state of the sediments. Although no differences in amount of organic carbon degraded under oxic and anoxic conditions were apparent, the reactivity of organic matter from the ODZ

sediments appeared to be lower than that from the oxic Mexican shelf or Washington margin sediments.

Lastly, whatever factor made the carbon from ODZ sediments resistant to *in situ* degradation still operated in the laboratory incubations, despite the high carbon removal rates. The sediments with the shortest oxygen exposure times (OET) and highest carbon contents (ODZ sediments) were the least degraded whether under oxic or anoxic conditions. Sediments with long OET's and less organic carbon (Washington sediments and Mexican shelf sediments) showed the most carbon degradation. These results suggest that ODZ sediments may have the highest potential for preservation because their carbon contents are the most difficult to degrade (over intermediate time scales), even in the presence of O₂. The particulate organic carbon results from the core incubations, however, are contradictory and suggest that O₂ alone may be enough to enhance degradation. It is possible that because the slurry degradation rates were highly enhanced any small differences between the oxic and anoxic treatments were obscured.

The enhanced degradation due to slurring may be due to accelerated cycling between different redox states. The effect of redox-oscillation (switching from oxic to anoxic conditions and vice versa) is generally thought to increase the degradation of organic matter (Aller, 1982; Aller, 1990; Aller, 1994; Carpenter et al., 1982). In natural sediments, the effect of mixing and bioturbation is to redistribute sediment vertically and horizontally (Wheatcroft et al., 1990) and frequently to enhance organic matter oxidation rates as a result of porewater irrigation. Vertical bioturbation can move sediments from the surface oxic layer down into regions with little or no oxygen, as well as bring material from sub-oxic depths up to the oxic layer. During the course of this animal activity sedimentary organic matter is exposed periodically to different electron acceptors and types of bacteria thus, likely enhancing the rate at which organic matter is degraded. Vertical redistribution of sediment in a net sense will not affect oxygen exposure time if sediments are mixed upwards and downward at the same time (this simplified explanation will not hold for certain types of animal feeding behaviors that do not move sediment equally in both directions). If the effect of switching from oxic to anoxic

conditions to another can enhance degradation, then while the absolute OET may be unaffected by vertical mixing, the effect of that exposure may be functionally different if it occurs in discrete stages rather than as a single event. The slurry experiments can be thought of as a one-time switch in the redox state of the sediments. The results were similar to those of Aller (1994), and indicated that this single switch does not appear to have a significant effect on the extent or rate of organic carbon degradation. Further experiments with truly oscillating redox conditions would provide more information as to the potential for the organic carbon in the ODZ to be more fully remineralized.

DO THE ISOTOPIC RESULTS SUPPORT THE OET HYPOTHESIS?

Aerobic sedimentary respiration appears to fractionate oxygen when the system is not subject to oxygen stress; *i.e.*, when enough oxygen is available so that degradation rates do not draw O₂ concentrations to zero at the site of bacterial activity. Brandes and Devol (1997) showed that in regions of either low oxygen or extremely high respiration rates, where the oxygen concentration approaches zero at a respiring microsite, isotopic fractionation was small. In incubation experiments where very high oxygen concentrations were supplied (*i.e.*, O₂ stress removed), isotopic fractionations approached the theoretical value of 0.991. A continuum in isotopic fractionation must exist across the seafloor from near-shore sediments with low oxygen availability to deep-sea sediments with high oxygen availability. This availability is a function of both water-column O₂ concentration and reactivity of the sedimentary organic carbon to aerobic degradation. I suggest that sediments with long oxygen exposure times will also have sufficient oxygen available for a measurable fractionation of oxygen to occur during respiration.

Oxygen fractionation during respiration has implications for the preservation of organic carbon. I suggest there is a correlation between sediments with OC:SA ratios of <0.5 and sediments where O₂ is fractionated during respiration; *i.e.*, sediments with high porewater oxygen concentrations and long exposure times. Sediments with long exposure times are usually found in the deep sea and generally have OC:SA ratios ≤ 0.5

(Hedges et al. (in press), Keil et al., 1994c). A long OET generally requires O₂ to be present in the sediments below the top centimeter of the sediment. This level of O₂ is also likely to be high enough to allow expression of microbial fractionation. In sediments with a short OET the O₂ demand is high and microbial activity is apparently fast enough to reduce oxygen concentrations to zero at the site of respiration such that no fractionation occurs. High rates of respiration contribute to short exposure times and prevent expression of the O₂ fractionation. These sediments are likely to have OC:SA ratios that approach 1.0. This level of organic carbon appears to be a function of sediment surface area and is comparable across many different continental margin regions. On shelves and in estuarine regions (*e.g.*, Puget Sound) the relation between O₂ uptake without fractionation and “monolayer equivalent” carbon loadings (*sensu* Mayer, 1994) appears to be robust. In extremely low O₂ regimes, more carbon can be associated with mineral grains (‘super-monolayer’ carbon loadings), and may act in concert with an oxygen control mechanism operating to maintain high carbon in the sediments.

In light of the apparent relation between oxygen fractionation during respiration and long OET, I suggest that fractionation may correspond to reduced organic matter preservation. It also seems reasonable to hypothesize that a similar pattern may exist between nitrogen isotope fractionation, oxidant (*i.e.*, NO₃⁻) exposure and organic matter preservation; however, results of core incubation and lander experiments as well as in results from Brandes (1996) make clear that no obvious relationship exists between $\Delta\delta^{15}\text{N-NO}_3^-$ (*i.e.*, the fractionation during denitrification) and the amount of NO₃⁻ removed, or available, or the depth NO₃⁻ penetration into the sediments.

IMPLICATIONS FOR OTHER PRESERVATION MECHANISMS

Collectively the results from studies presented in Chapters 2 through 4 can be used to evaluate the various mechanisms that have been proposed to explain organic matter preservation in sediments; *e.g.*, oxygen-based mechanisms, accumulation-based mechanisms, degradation rates, selective preservation mechanisms, and surface protection. The main conclusion is that preservation in most margin sediments can be

best described by a relation to oxygen exposure time. Sediments in contact with a strong oxygen deficient zone, however, appear to be less susceptible to degradation, even in the presence of high oxygen concentrations for periods of months. The comparison of degradation rates and carbon burial efficiencies on the Washington and Mexican margins clearly indicates that processes driven solely by sediment accumulation cannot describe the distribution of organic carbon on the two margins. Rates of primary production, organic carbon flux and sediment accumulation all highest on the Washington margin, yet the Washington margin has less carbon burial. Sediment accumulation and organic carbon rain rate both influence the length of oxygen exposure by either increasing the rate at which sediments accumulate below the oxic layer or shoaling the oxygen penetration depth via rapid consumption of O₂ in the sediments. Long-term accumulation of organic matter in sediments is partly dependent on the rate at which it is removed from sediments, while the carbon oxidation rate on many margins can be related to the availability of oxygen in the sediments (Archer and Devol, 1992; Berelson et al., 1996; Jahnke et al., 1990; Reimers et al., 1992). The relation between O₂ exposure time and preservation reflects more direct control than a relation between organic matter preservation and sediment accumulation.

The selective preservation argument suggests that more recalcitrant material is buried preferentially because it cannot be degraded under *in situ* conditions (deLeeuw and Largeau, 1993; Sinninghe-Damste et al., 1989). This argument would predict Mexican margin organic carbon to be less reactive than Washington margin organic carbon because carbon burial is greater in the Mexican sediments. I have no direct evidence for assessing this hypothesis, but the slurry incubation experiments provide some indirect evidence in support of it. The ODZ slurry showed the smallest amount of carbon loss, suggesting that even under conditions that favor high rates of degradation some component of the organic matter remains non-reactive. Molecular level analyses of the preserved organic carbon are required to confirm or reject selective preservation of certain types of carbon.

Surface protection of organic matter was not addressed directly in these studies; but, again, the slurry experiments may provide indirect evidence of the role of surface associations in organic matter preservation. The dilution and mixing in the slurry experiments did not appear to displace or desorb a notable amount organic matter from the surfaces of sediments; the DOC production was a very small fraction of the amount of POC removed in the slurries. Furthermore, despite the large amount of carbon removed from the slurries via mineralization, not enough was removed to noticeably affect the OC:SA ratio of the sediments. These results imply that organic matter can remain surface-associated even under relatively intense degradation conditions and that the association is not sensitive to O₂ exposure on the short time-scales of these experiments.

DIRECTIONS FOR FURTHER RESEARCH

The overall results from these studies suggest that organic matter preservation in sediments is related to oxygen exposure time both in sediments and during water column transit. The enhanced preservation in the Mexican ODZ sediments remains to be fully explained. Further work is needed to determine what process or factor makes the ODZ organic matter resistant to microbial decomposition. Molecular level analyses of the ODZ organic matter could provide insight as to the potential reactivity of the preserved organic matter. Additional investigation of the nature of the association between organic carbon and the surfaces of mineral grains may also prove useful in determining why the organic carbon is so resistant to degradation. Detailed knowledge of the microbiological system operating in the ODZ sediments is wanting. If surface protection plays a role in the non-reactivity of the ODZ organic matter then a better understanding of how anaerobes process carbon at the extracellular level and the role of anaerobic bacterial consortia at mineral surfaces could provide insight into the degradation of carbon in these sediments.

A FINAL SYNTHESIS

The relationships between oxygen exposure time, oxygen fractionation, OC:SA, and organic carbon preservation all appear to follow a continuum that extends from shallow near-shore sediments through deeper continental margin sediments and to the deep sea (Figure 5.5). Shallow sediments generally have high carbon input and oxidation

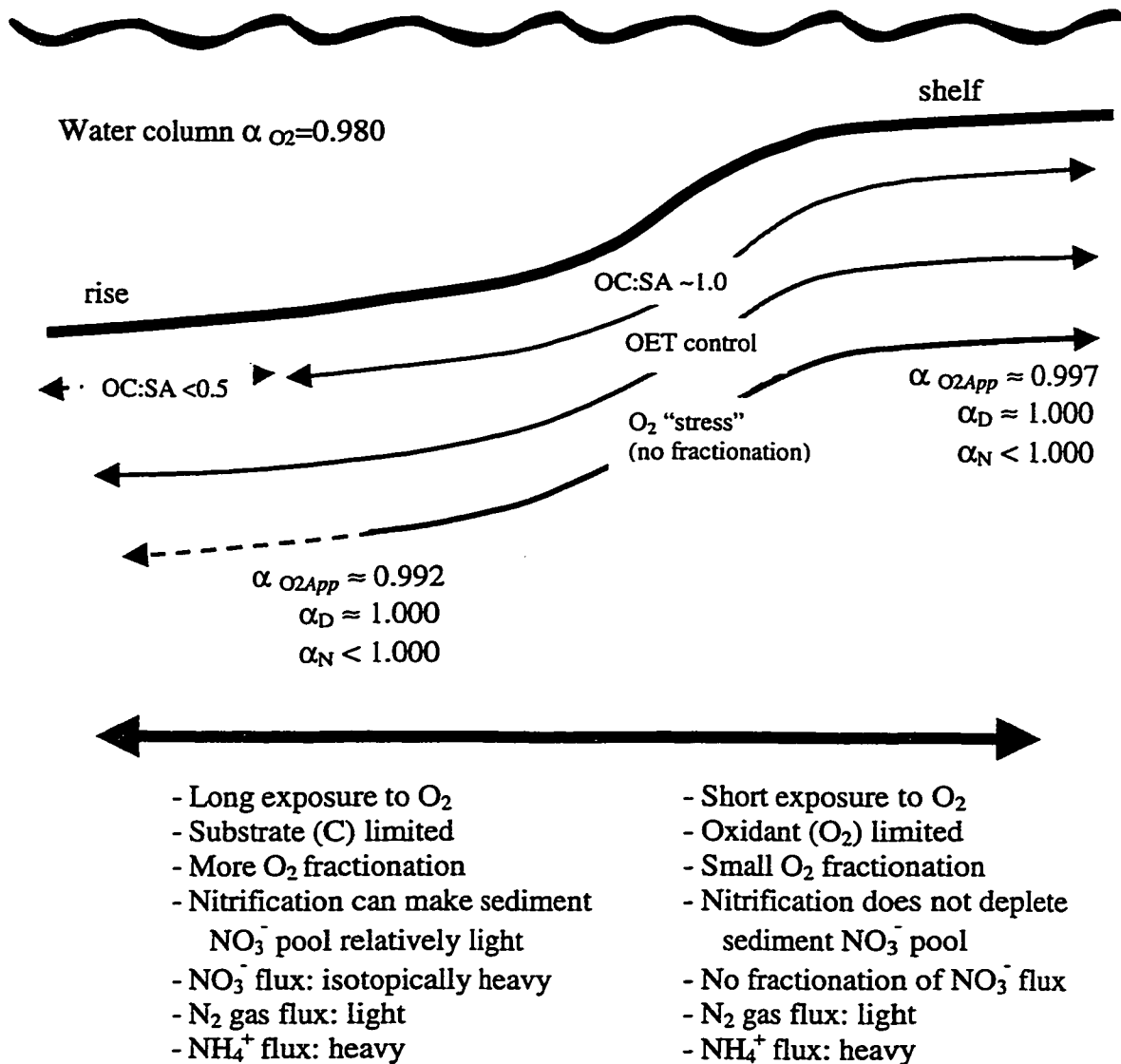


Figure 5.5 Schematic diagram of relation between oxygen exposure time, O₂ fractionation, OC:SA and organic carbon burial on continental margins.

rates which lead to short oxygen exposure times. Short O₂ exposure results in conditions that do not allow oxygen fractionation during respiration or organic carbon degradation to proceed far enough to reduce OC:SA ratios from the typical surface-area controlled level of ~ 1.0. Ultimately short exposure time allows a greater percentage of the carbon reaching the sediments to be buried permanently. As the seafloor becomes deeper, carbon input and sedimentary oxidation rates decrease; oxygen demand decreases and O₂ penetration depths (and therefore OET) increase. This increased exposure eventually is long enough to allow oxygen fractionation and degradation of surface-associated organic carbon which results in reduced burial and less preservation. The depth along the margin where this occurs is not known exactly but is likely to be related to the point where carbon oxidation rates slow enough to allow deeper penetration of O₂ and NO₃⁻. Very rapid rates of oxidation lead to simultaneous depletion of O₂ and NO₃⁻ in sediments (Brandes and Devol, 1995); as rates slow, NO₃⁻ penetration depths start to become deeper than O₂ penetration depths. On the Washington margin this effect occurs between 700 and 1000 meters. The shallow and deep sediments of the Mexican margin fit the same general pattern of high carbon input, and burial, short O₂ exposure times and OC:SA ratios approaching 1.0 in shallow, oxic sediments and lower input, lower burial and longer exposure time in deeper, oxic sediments. The sediments within and just below the Mexican ODZ are different from typical margin sediments, having some of the highest carbon contents found in marine sediments. The presence of the ODZ creates a zone of enhanced preservation on this margin that likely results from extremely short exposure times and high carbon input rates relative to primary production rates. In these sediments, as in other margin sediments, carbon input rates the carbon oxidation rates to such an extent that a large percentage of the carbon reaching the seafloor is buried permanently. I suggest that preservation in the oxygen minimum zone results from the same processes that allow organic matter to be preserved in all margin sediments, but that preservation is enhanced by the very short exposure times. It may also be possible that the ODZ allows for other preservation processes (*e.g.*, surface protection or selective

preservation) to come into play because the degradation rates are lower and the full spectrum of degradation reactions is not present.

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- 1989 Undergraduate Research Summer Institute, Environmental Chemistry, Vassar College
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PROFESSIONAL AFFILIATIONS

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 American Chemical Society, Geochemistry Division
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PUBLICATIONS

- Hartnett, H.E.** and A.H. Devol. (submitted) Organic carbon input and oxidation in the continental margin sediments of Washington and Mexico: influence of the oxygen deficient zone. *Geochim. Cosmochim. Acta*
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PRESENTATIONS AT PROFESSIONAL CONFERENCES

- 1998 8th Annual V.M. Goldschmidt Conference. Fractionation of oxygen during sedimentary respiration. Toulouse, France. Sept. 1998.
- 1998 Ocean Sciences Meeting, American Geophysical Union. DOC production in oxic and anoxic incubations of sediments from the oxygen minimum zones of Washington and Mexico. San Diego, California. Feb. 1998.
- 1996 American Chemical Society. Oxygen exposure time as a control on carbon preservation in continental margin sediments. Orlando, Florida. Aug. 1996.

- 1995 American Geophysical Union Fall Meeting. Organic carbon:surface area ratios for the Washington and Mexican Continental Margins. (poster) San Francisco, California. Dec. 1995.
- 1994 Ocean Sciences Meeting, American Geophysical Union. Carbon burial efficiencies in the continental margin sediments of Washington and Mexico. San Diego, California. Feb. 1994.

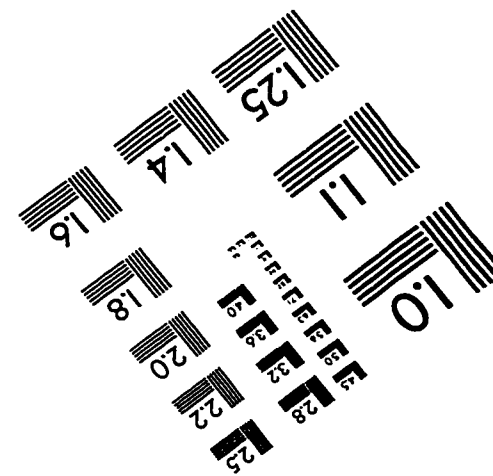
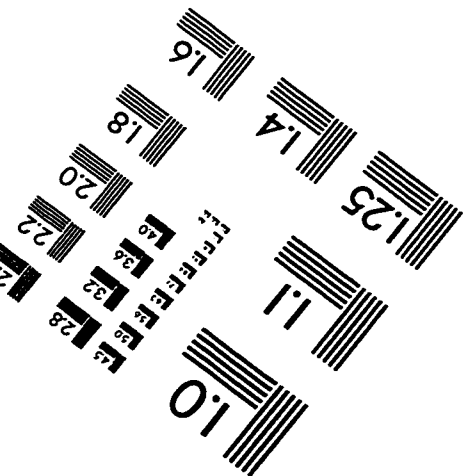
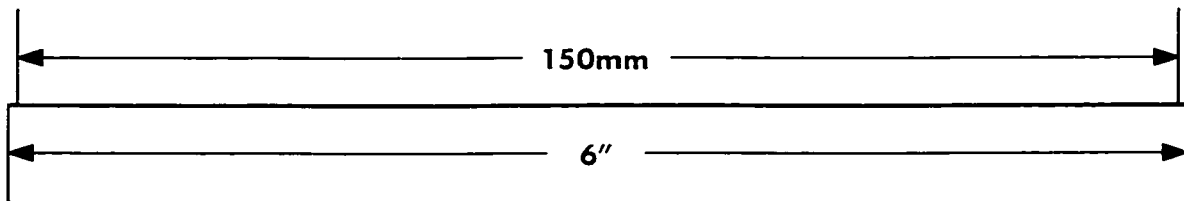
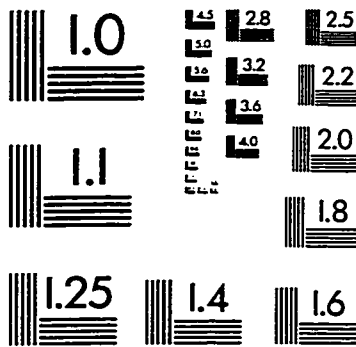
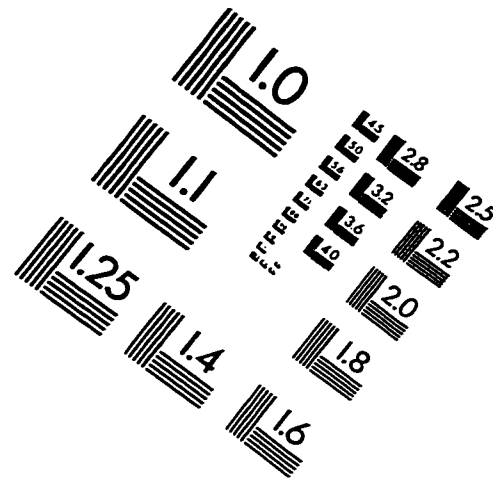
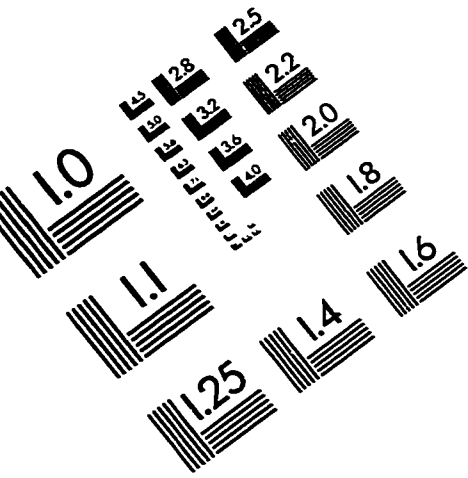
CRUISE/FIELD EXPERIENCE

- Washington Margin. *R/V Wecoma*, Aug.-Sept. 1997. Chief Scientist: Allan Devol
 Gulf of Mexico. *R/V Gyre*, June 1997. Chief Scientist: Gil Rowe
 Vancouver Island Fjords. *R/V Barnes*, May 1997. Chief Scientist: Ellery Ingall
 Mexican Margin (NiCAD). *R/V New Horizon*, Nov.-Dec. 1996.
 Chief Scientist: Allan Devol
 Pacific Coast Transect (STUPEX '96). *R/V Thomas G. Thompson*, July 1996. Co-
 Chief Scientist: **Hilairy Hartnett**
 Washington Margin. *R/V Wecoma*, August-September 1994.
 Chief Scientist: Allan Devol
 Mexican Margin (TTAN). *R/V New Horizon*, Nov.-Dec. 1993.
 Chief Scientist: Allan Devol
 Bermuda Transect. *R/V Oceanus*, October 1989. Chief Scientist: Steve Emerson
 Washington Margin. *R/V New Horizon*, June-July 1988.
 Chief Scientist: Allan Devol

OTHER INTERESTS

Mountaineering, rock climbing, rowing, cycling and all manner of human-powered outdoor activities.

IMAGE EVALUATION TEST TARGET (QA-3)



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