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Early diagenesis and recycling of biogenic debris at the seafloor, Santa Monica Basin, California

by Richard A. Jahnke[1]

ABSTRACT

Seafloor recycling of organic materials in Santa Monica Basin, California was examined through *in situ* benthic chamber experiments, shipboard whole-core incubations and pore water studies. Mass balance calculations indicate that the data are internally consistent and that the estimated benthic exchange rates compare well with those derived from deep, moored conical sediment traps and hydrographic modeling. Pore water and benthic flux observations indicate that the metabolizable organic matter at the seafloor must be composed of at least two fractions of very different reactivities. While the majority of reactive organic compounds degrade quickly, with a half-life of ≤6.5 years, $1/4$ of the total metabolizable organic matter appears to react more slowly, with a half-life on the order of 1700 years. Down-core changes in pore water sulfate and titration alkalinity are not explained by stoichiometric models of organic matter diagenesis and suggest that reactions not considered previously must be influencing the pore water concentrations.

Measured recycling and burial rates indicate that 43% of the organic carbon reaching the basin seafloor is permanently buried. The results for Santa Monica Basin are compared to those reported for other California Borderland Basins that differ in sedimentation rate and bottom water oxygen content. Organic carbon burial rates for the Borderland Basins are strongly correlated with total organic carbon deposition rate and bulk sedimentation rate. No significant correlation is observed between carbon burial and bottom water oxygen, extent of oxic mineralization and sediment mixing. Thus, for the California Borderlands, it appears that carbon burial rates are primarily controlled by input rates and not by variations in preservation.

1. Introduction

The dominant pathway by which organic carbon is removed from the ocean is burial in continental margin sediments (Romankevich, 1984). The high organic carbon input to the seafloor adjacent to the continents may result from increased rates of surface water primary productivity and presumed particle flux near ocean boundaries (Eppley and Peterson, 1979) or export of carbon from continental shelves (Walsh *et al.*, 1981; Walsh, 1983; Malone *et al.*, 1983). While export off shelves may not be a major transport pathway for anthropogenic CO_2 (Falkowski *et al.*, 1988; Peng and Broecker, 1984), such input may still contribute significantly to the organic carbon deposition

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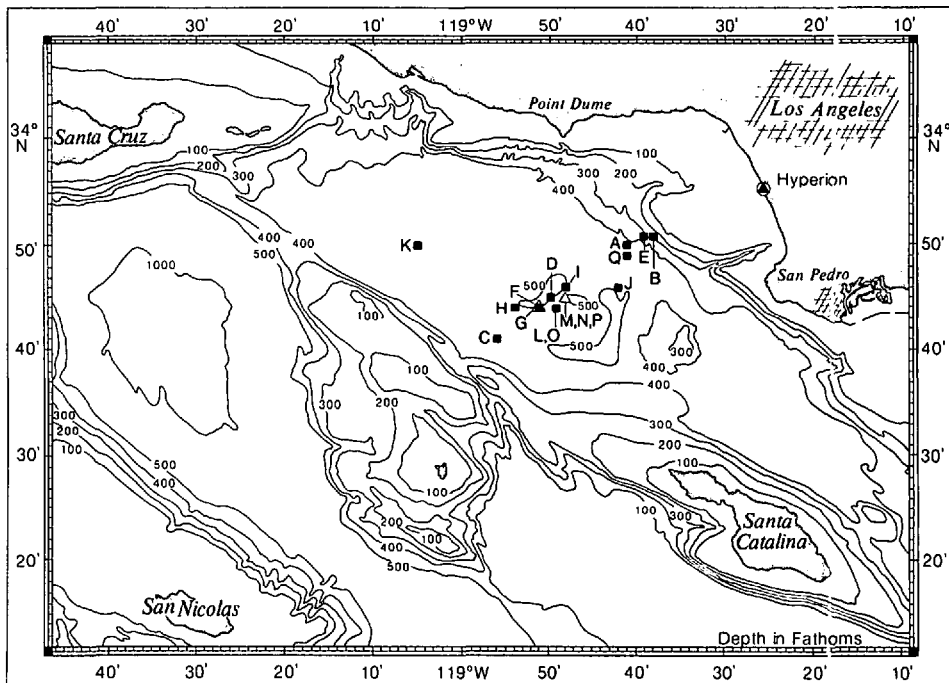
Figure 1. Sampling locations and bathymetry of Santa Monica Basin and adjacent areas.

rate. Additionally, down-core variations in the organic content of the sediment record have been interpreted as resulting either from changes in surface water productivity and, hence, input or seafloor preservation (Müller and Suess, 1979). In general, criteria have not been established by which these two possibilities can be distinguished.

As part of the Department of Energy-sponsored California Basin Study, the burial and decomposition of biogenic materials at the Santa Monica Basin seafloor has been studied. Santa Monica Basin is a deep (>900 m) steep-sided, flat-bottomed basin in the California Borderland directly adjacent to the continental shelf and offshore of Los Angeles (Fig. 1). Bottom water O_2 concentrations are less than 10 μmol kg^{-1} which severely restricts macrobenthic organism populations. Because large organisms are generally absent, bottom sediments throughout the deep basin floor are varved. Thus, in this setting, the sediment accumulation rate can be accurately assessed and has been determined to be 438 mg m^{-2}d^{-1} at the center of the basin (Huh, personal communication). Because the deep portion of the basin is completely enclosed (sill depth is 737 m), particulate materials transported off of the continental shelf and down the slope are trapped on the basin floor. Thus, the physical characteristics of this basin provide an important framework in which to investigate the decomposition and burial of organic matter at the seafloor and lateral transport of materials from the adjacent continental shelf.

Pore water and *in situ* and shipboard benthic flux measurements of the major biogenic elements from the deep, central Santa Monica Basin seafloor are presented and discussed. The results are used to test the validity of previous models of early diagenesis and to evaluate the reactivity of organic matter at the seafloor. In the final section, the organic carbon burial rate is discussed and compared to those reported for other nearby California Borderland basins of different bottom water characteristics.

2. Methods

a. Coring and pore water sampling. Sediments were sampled by Soutar box corer (Soutar *et al.,* 1981), MANOP Lander (ML) chamber (Weiss *et al.,* 1977) and Benthic Experimental Chamber Instrument (BECI) (Jahnke and Christiansen, 1989) on five cruises aboard the R/V *New Horizon* between October 1985 and October 1987 (Table 1, Fig. 1). In calm weather, the Soutar corer is capable of retrieving sediments with minimal surface disturbance (Jahnke *et al.,* 1986). As soon as the corer was secured on deck after a coring cast, 2.4 cm, 2.9 cm, and 8.9 cm diameter subcores were removed and placed vertically in a cold room or refrigerator which maintained the sediments at their *in situ* temperature, ~4°C.

Pore waters were extracted from the 8.9 cm subcores by a pressurized core barrel technique (Jahnke, 1988). Briefly, the sediment subcore is retrieved in a coring barrel that had sampling ports drilled through the barrel wall prior to use. During subcoring, these ports are sealed with nylon screws. After subcoring the box core, pistons are placed in both ends of the core barrel, sealing the sediments between them in the coring tube. The nylon screws are removed from the depths at which pore water samples are to be retrieved, and a plastic syringe is attached to each port. The subcore is then pressurized forcing the pore waters out of the sampling ports and into the plastic syringes.

Pore waters were also retrieved from a separate 8.9 cm diameter subcore that was sectioned into 0.5 to 2 cm intervals. The wet sediments from each interval were placed in 50 cc centrifuge tubes and centrifuged at 15,000 g for 3 min. The resulting pore waters were decanted and filtered through 0.45 μm Gelman membrane filters. All manipulations were performed at *in situ* temperatures and in an inert atmosphere (N_2).

To evaluate gradients near the sediment surface, the 2.4 cm diameter subcores were sectioned into 2 mm intervals. The wet sediments were packed into 1.9 ml microfuge tubes and centrifuged in a Beckman microfuge. Pore waters were again decanted and filtered through 0.45 μm Gelman membrane filters. All manipulations were performed at *in situ* temperatures and in an inert atmosphere.

b. Benthic flux experiments. In situ benthic chamber experiments were performed with the ML in 1986 and the BECI in 1987 and 1988 (Jahnke and Christiansen, 1989).

The chamber and sampling system used on both vehicles for these deployments were identical.

The chamber consists of a 30 × 30 cm box, constructed from thin-walled (0.159 cm) titanium which is open at the top and bottom. A lid, constructed from polyvinylidene fluoride (a trace-metal clean, low gas permeability plastic) with a backing of PVC and aluminum for strength, is hinged on one of the top edges. A butyl rubber gasket is used to insure that a complete seal is made when the lid is closed against the top of the box.

Attached to the inside of the chamber lid is a stirring mechanism which consists of four, 10 cm rods secured to a central hub. This assembly is magnetically coupled to a stepper motor that can be driven at speeds from 1 to 10 rpm. A speed of 5 rpm was used for the deployments discussed here. This corresponds to a friction velocity (u_*) of ~0.2 cm sec^{-1} at a nominal chamber water height of 10 cm (Buchholtz-ten Brink *et al.*, 1989). Hinged to the sides of the chamber assembly is a scoop that closes off the bottom of the chamber when rotated to its vertical position. Thus, the bottom sediments are retrieved at the end of each experiment.

The sampling system consists of 20 spring-actuated syringes. Each syringe can be configured to either withdraw a 50 ml sample from the chamber or inject into the chamber a tracer, which had been loaded into the syringe prior to deployment. Each sampling/injection operation is controlled by a simple, central timer circuit. A single, thick-walled, 0.8 mm (1/32″) I.D. Tygon tube leads from the chamber lid to the sampling syringes. Thus, after the first sampling, the dead volume within the system is less than 0.2% of the sample volume. Once the sample has been withdrawn, the syringe plunger is locked in position, minimizing any exchange that could occur between the samples and chamber water during vehicle recovery. The volume of water withdrawn from or injected into the chamber is balanced by bottom water that exchanges with the chamber water through a 30 cm long, 30 mm I.D. Tygon tube.

In 1986, this same chamber and sampling system were deployed using the ML instrument frame. The most important difference between the instruments is that the ML is much larger and capable of deploying three benthic chambers simultaneously. To accommodate this, the chambers were positioned around the perimeter of the instrument frame and the expendable weight, which consisted of a 1.5 m diameter steel plate, was located in the center. Because the chambers extended approximately 25 cm below the frame and ballast plate, it was originally thought that sediment disturbance was minimized. Additionally, thin skirts, which extended downward approximately 10 cm, were attached to the ballast plate adjacent to the chambers to direct the bow wave away from the chambers. As will be discussed in the Results section, the ballast plate used in this instrument design produced such a large bow wave that these precautions were not enough to prevent measurable sediment disturbance.

Benthic fluxes were also estimated by incubating sediment subcores on board ship. Subcores of boxcores with approximately 15 cm of bottom water still overlying the sediment surface were recovered and placed upright in a cold room. A piston was

positioned in the subcore so that no air space remained between the piston and overlying bottom water. The water was occasionally stirred manually and periodically sampled through ports in the coring barrel. The volume of sample removed during sampling was compensated by moving the piston closer to the sediment surface. The final flux estimates were corrected for the change in volume caused by the piston movement.

c. Analytical methods. At sea, pore water and chamber samples were analyzed for PO_4^{3-} ($\pm 2\%$), $Si(OH)_4$ ($\pm 2\%$), and NH_4^+ ($\pm 3\%$) using procedures described by Strickland and Parsons (1972), pH ($\pm .03$) by glass electrode (NBS buffer scale), titration alkalinity (T.A.) ($\pm .5\%$) by Gran titration (Edmond, 1970). Pore water samples were further analyzed for SO_4^{2-} ($\pm 1.5\%$) by the turbidometric method of Tabatabi (1974), Fe^{2+} ($\pm 5\%$) by the ferrozine method (Stookey, 1970), Mn^{2+} ($\pm 5\%$) by the dioxime method (Brewer and Spencer, 1971), and F^- ($\pm 3\%$) by the alizarin complexone method of Greenhalgh and Riley, (1961). Calcium ($\pm .05\%$) and NO_3^- ($\pm 2\%$) were also determined on chamber samples by the EGTA titration (Tsunogai *et al.*, 1968) and Cd reduction (Strickland and Parsons, 1972) methods, respectively. ATP measurements were performed using the procedure reported in Craven *et al.* (1986).

3. Results

a. Pore waters. The locations at which pore water sampling and benthic flux measurements were performed are summarized in Table 1 and Figure 1. Little spatial variability was observed; pore water results for all cores from the center of the basin (denoted F, H, I, L, and O in Table 1) are plotted in Figure 2. No consistent temporal variations were observed in the pore water data.

The pH levels decreased markedly from bottom water values to a minimum value of approximately 7.2 a few centimeters below the sediment surface. A slight increase in pH was observed with increasing sediment depth over the remainder of the pore water depths sampled. Titration alkalinity increases nearly linearly from values of approximately 2.4 meq kg^{-1} at the sediment surface to 7 meq kg^{-1} at 40 cm sediment depth. Over the same depth range pore water NH_4^+ also increases linearly from near-zero levels at the sediment surface to 300 μmol kg^{-1} at depth. In contrast, SO_4^{2-} decreases with sediment depth from bottom water values of approximately 28 mmol kg^{-1} to 23 mmol kg^{-1}.

Extremely steep near-surface gradients are observed for pore water PO_4^{3-} and $Si(OH)_4$. Below 20 cm, $Si(OH)_4$ levels appear to have nearly reached an asymptotic value of approximately 400 μmol kg^{-1}; PO_4^{3-} continues to increase slightly with depth. Elevated levels of Fe^{2+} and Mn^{2+} are observed at all pore water sampling depths. The occurrence of these reduced metals indicates that the pore waters are anoxic throughout the depths sampled. A small but significant subsurface maximum in pore water F^- is also observed.

Table 1. Sampling locations. Date of collection is included in the expedition label. For example, NH1085 indicates that samples were obtained from the R/V *New Horizon* (NH) in October 1985. Other abbreviations are: BC - box corer, ML - MANOP Lander, BECI - Benthic Experimental Chamber Instrument.

Designation	Number & Type	Latitude	Longitude	Depth (m)
A	NH1085-BC12	33°50'N	118°41'W	750
B	NH1085-BC40	33°51'N	118°38'W	398
C	NH1085-BC89	33°41'N	118°56'W	908
D	NH1085-BC102	33°45'N	118°50'W	908
E	NH1085-BC113	33°51'N	118°39'W	572
F	NH0586-BC1	33°44'N	118°51'W	908
G	NH0586-ML	33°44'N	118°51'W	908
H	NH0487-BC1	33°44'N	118°54'W	910
I	NH0487-BC4	33°46'N	118°48'W	907
J	NH0487-BC6	33°46'N	118°42'W	908
K	NH0487-BC8	33°50'N	119°05'W	880
L	NH0987-BC2	33°44'N	118°49'W	907
M	NH0987-BECI2	33°45'N	118°48'W	908
N	NH1087-BECI3	33°45'N	118°48'W	907
O	NH1087-BC1	33°44'N	118°49'W	908
P	NH1087-BECI4	33°45'N	118°48'W	907
Q	NH1087-BC3	33°49'N	118°41'W	855
R	NH0988-BECI5	33°45'N	118°49'W	908
S	NH0988-BECI6	33°45'N	118°49'W	908

To examine the sediment-water interface region more closely, pore water samples were also recovered at 2 mm depth intervals (Fig. 3). In general, the overall pore water characteristics and profile shapes measured at the large sampling intervals are observed at these finer-scales. The subsurface pH minimum is well resolved. While the T. A. profile between 2 and 10 cm is similar to that displayed in Figure 2 the profile becomes nearly vertical in the upper 2 cm. A hint of a more vertical profile is also observed for total inorganic carbon (T.I.C.). Since the latter was not measured directly but was calculated from pH and T. A., the discussion will focus on T. A. The possible thickening of the diffusive sublayer during core recovery and processing may contribute to the upward curvature of the profiles by restricting the diffusional exchange rate. However, because the pore waters were extracted within 90 minutes of core recovery, this effect cannot account for all of the observed curvature in the profile, which extends to >2 cm in the sediment core.

b. Benthic chamber results. Selected results of *in situ* benthic chamber experiments performed in the center of the basin are displayed in Figures 4 and 5. Because the volume of water removed during sampling is replaced with bottom water, there is a
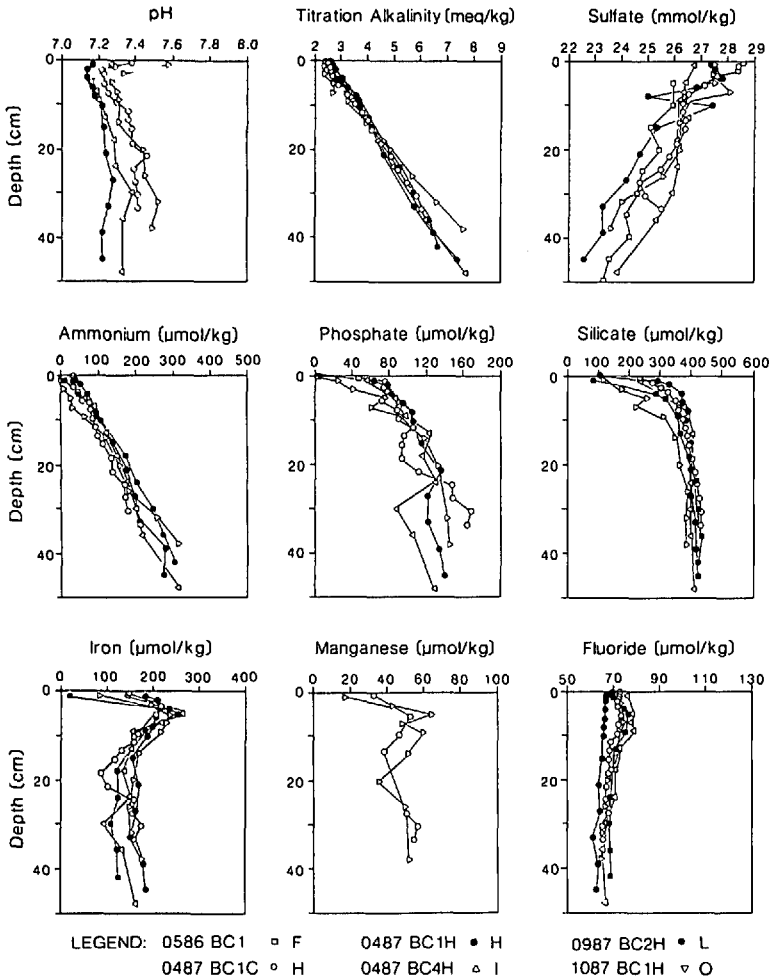
Figure 2. Pore water distributions of the indicated solutes at the center of the basin.

small (~0.5%) dilution of chamber waters. The results presented here have been corrected for this dilution which accounts for the negative O_2 concentrations displayed. Lines are drawn through the data to accentuate the trends observed. The chamber water concentrations of metabolic oxidants such as O_2 and NO_3^- decrease during the experiment, indicating a flux of these constituents into the sediments. Conversely, solutes released during the dissolution or metabolic breakdown and oxidation of biogenic debris such as PO_4^{3-}, $Si(OH)_4$, and T. A. increase in concentration during the experiment, indicating a flux out of the sediment.

The triangles on each figure indicate concentrations determined on bottom water samples obtained with a Niskin bottle mounted on a Soutar box corer. Because these results are from different casts and, hence, slightly different locations and water
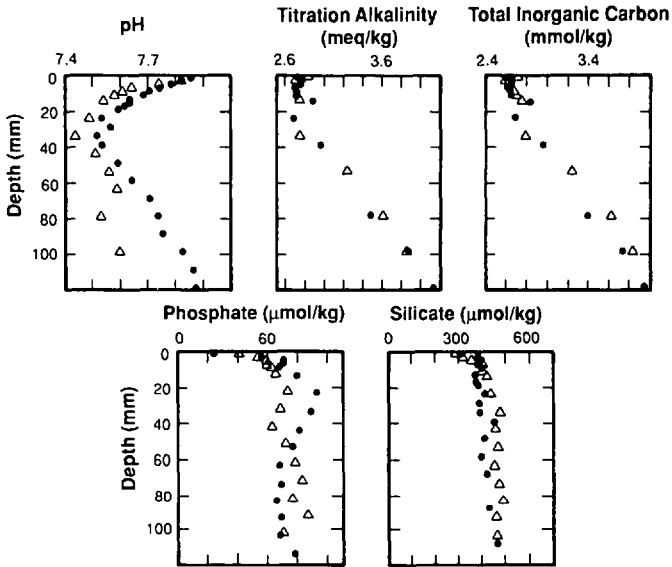
Figure 3. Pore water distributions of indicated solutes at 2-mm depth intervals at locations D (△) and C (●).

depths, small differences are to be expected. In general, the benthic chamber results are in good agreement with the Niskin bottle values, suggesting that there is little contamination from the sampling system. The differences which do occur are generally smaller than the changes observed during the experiment, suggesting that the system is adequate to estimate benthic fluxes.

The chamber samples were not poisoned, filtered, or preserved in any manner *in situ* and one might expect some alteration of the sample during storage due to microbial activity. However, the first sample withdrawn has the longest storage time in the syringes and ampules and hence the greatest probability of being significantly altered. The reasonably good agreement between the early chamber samples and the Niskin samples suggests that changes to the sample while it resides in the syringes and ampules are generally negligible relative to the changes observed during the experiment.

In ML Chamber 1 (Fig. 4a) the stirring speed was increased from 6 rpm to 10 rpm during the experiment at the time indicated by the vertical dashed line. These rates correspond to diffusive sublayer thicknesses of approximately 200 μm and 120 μm, respectively. The results appear insensitive to chamber stirring rate, at least over this relatively narrow range of conditions. This observation agrees with measurements of Berelson and Hammond (1986) at two other sites in the California Borderland.

To assess whether disturbance of the sediment surface could affect the chamber results, chamber emplacement by the BECI tripod was directly observed with a deep-sea video camera system. No significant disturbance was observed. The integrity
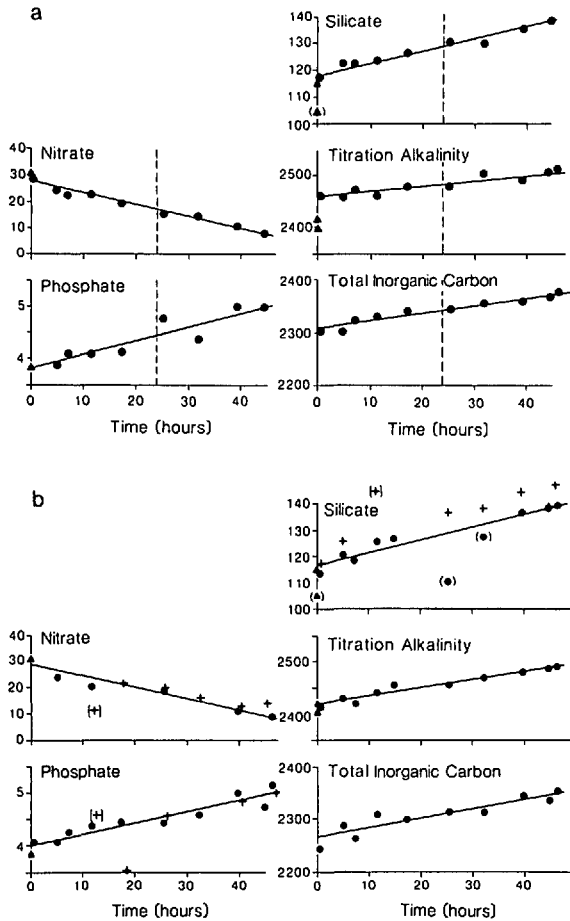
Figure 4. (a) Benthic chamber results from chamber 1 of the MANOP Lander. Dashed lines indicate when stirring rate was changed. (b) Benthic chamber results from chamber 2 (+) and chamber 3 (●) of the MANOP Lander. Triangles represent bottom water concentrations. Concentrations are in $\mu mol\ kg^{-1}(\mu eq\ kg^{-1}$ for T.A.).

of the sediment surface in the chambers was also assessed by comparing the near-surface distribution of ATP in sediments recovered by Soutar box corer and the benthic chambers (Fig. 6). The overall agreement between the box core and BECI results suggests that chamber emplacement with the BECI tripod caused little disturbance. A loss of 2 mm of surface sediment would be observable.

Significant differences in surface ATP distributions were observed between ML chamber sediments and Soutar box corer samples. Three profiles from ML chamber 1 were all similar and suggest a loss of approximately 3 mm of sediment from the entire surface. Chambers 2 and 3, on the other hand are quite variable. Profiles from subcores removed from near the outside wall of the chambers suggest little sediment disturbance
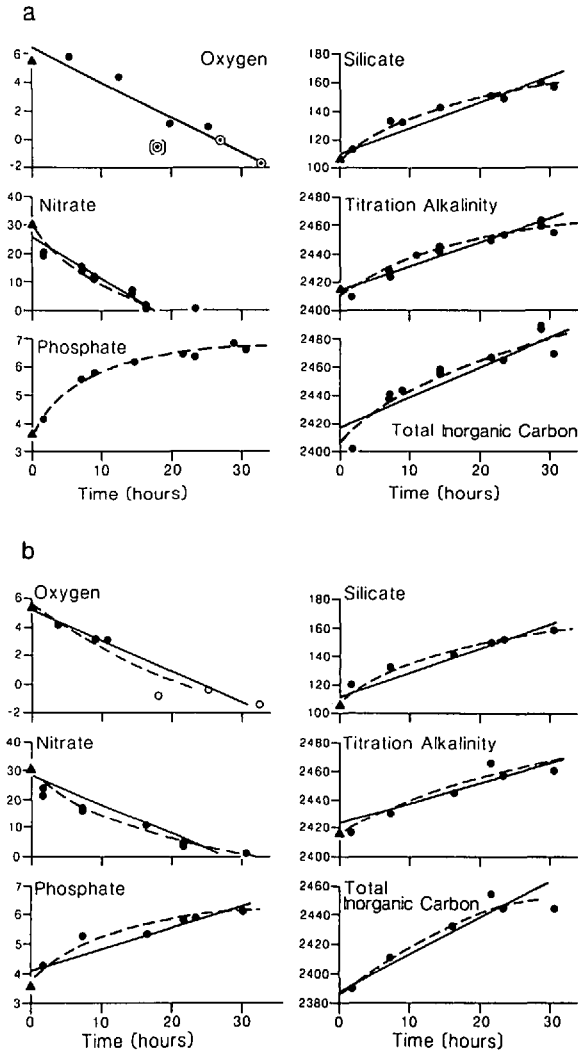
Figure 5. Benthic chamber results from the BECI tripod for (a) site M, BECI 2 and (b) site N, BECI 3. Triangles are bottom water concentrations. Concentrations are in $\mu mol\ kg^{-1}$ ($\mu eq\ kg^{-1}$ for T.A.).

while profiles from near the inner wall suggest sediment losses of 4 to 6 mm. This disturbance is probably due to the bow wave which proceeds the large ballast plate used on the ML instrument.

4. Discussion

a. Accuracy of benthic flux measurements. The benthic flux estimates for the major biogenic elements are listed in Table 2. The pore water fluxes were calculated from the
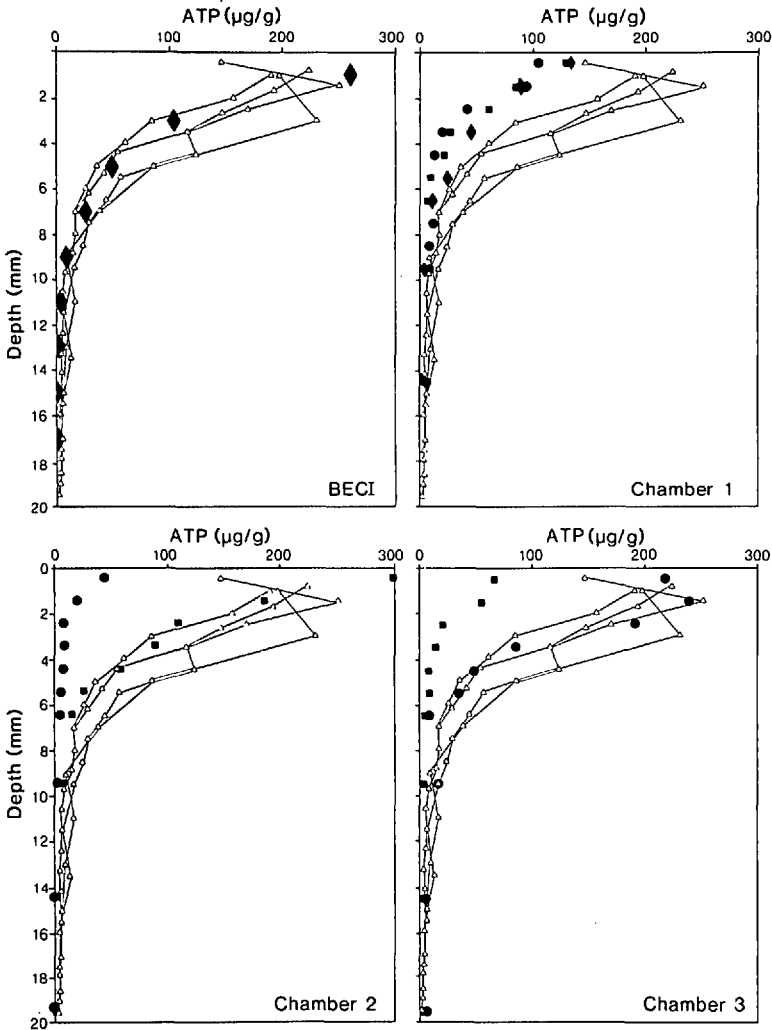
Figure 6. ATP distributions in Santa Monica Basin from Soutar cores recovered over a two-year period (△), from the BECI sediments (♦), and MANOP Lander chambers (1–3). Different symbols for the MANOP Lander data represent profiles determined for different locations within the chambers.

measured pore water gradients and an effective pore water diffusion coefficient approximated as the molecular diffusion coefficient multiplied by the square of the porosity. The pore water flux listed for O_2 assumes that the pore waters are devoid of O_2 at depths > 1 mm. The values listed for each chamber and shipboard incubation are means of the fluxes estimated from a linear regression of each entire data set and of the first three data points of each set. The latter calculation procedure estimates the flux in

Table 2. Benthic flux summary (mmol m^{-2}d^{-1})

Pore Water		O_2 (−0.6)	NO_3^- —	SO_4^{2-} −0.4 ± 0.08 n = 7	TCO_2 —	T.A. —	$Si(OH)_4$ 1.9 ± 0.5 n = 4	PO_4^{3-} —
MANOP	Ch1	—	−1.09	—	4.4	3.2	1.20	0.073
Lander	Ch2	—	−0.81	—	—	—	1.38	0.055
	Ch3	—	−0.94	—	4.3	3.7	1.10	0.054
Shipboard Incubation		—	−0.81	—	—	2.6	1.24	—
BECI	#2	−0.2	−1.10	—	1.63	1.30	1.37	—
	#3	−0.25	−0.88	—	2.50	1.93	1.32	0.073
	#4	−0.35	−1.10	—	—	—	1.53	0.104
	#5	−0.34	−1.72	—	1.44	0.90	2.02	0.162
	#6	−0.66	−1.47	—	1.95	1.45	1.81	0.157
Average Measured *in situ* Fluxes		−0.36 ± 0.18	−1.10 ± 0.31	—	2.70 ± 1.33	2.15 ± 1.04	1.47 ± .31	0.097 ± 0.046
Calculated Based on O_2, NO_3^-, SO_4^{2-} Fluxes					2.36	1.98		

the initial stage of the experiment and may better represent the *in situ* benthic flux in cases where significant curvature is observed (Bender *et al.*, 1989).

Silicate fluxes calculated from surface pore water gradients compare favorably with those estimated from *in situ* ML and BECI benthic chamber incubations and the shipboard subcore incubation. The results suggest that there has been no major disruption of sedimentary processes during the *in situ* chamber deployments. It appears that the dissolution rate of opal in these sediments is slow enough that the pore water sampling intervals employed were sufficient to resolve the surface gradient. This is not the case with other biogenic elements of interest such as T. A. and PO_4^{3-} and prevents further pore water gradient—benthic flux comparisons. The fact that the ML $Si(OH)_4$ flux results agree reasonably well with the others despite the known surface sediment disturbance is in itself an indication that the silicate pore water gradients are not extremely steep at the sediment surface. The observation that the flux calculated from the surface pore water gradient tends to be slightly larger than the other estimates may be caused by using too large a diffusion coefficient. We have estimated the effective diffusion coefficient in the surface sediments by multiplying the molecular diffusion coefficient by the square of the porosity. Because there is a bacterial mat at the sediment surface, the extremely high porosities (and water contents) measured may not actually correspond to ·quivalently high pore space and/or permeabilities.

The NO_3^-, T.I.C., and T.A. benthic flux estimates for the different incubations may also be compared. Similar NO_3^- fluxes are estimated from all of the techniques. On the other hand, the T.I.C. and T.A. fluxes measured with the ML are approximately a factor of two greater than the other estimates. The discrepancy between the results

may be caused in some way by the known disturbance of the surface sediments in the ML chambers. However, the discrepancy may also represent a seasonal variation in the fluxes because the ML deployments were in May whereas the BECI deployments were in September and October. Without conclusive evidence to discount their validity, the ML results are included in the following interpretations.

If we assume that the oxidation of organic matter controls the overall fluxes of O_2, NO_3^-, SO_4^{2-}, T.I.C. and T.A., we can predict the T.I.C. and T.A. fluxes out of the sediments from the flux of oxidants in. Several assumptions need be made to do so. First, we assume that organic matter oxidation proceeds with Redfield stoichiometry. Furthermore, we assume that there is no $CaCO_3$ dissolution in the central basin sediments. While this is in direct conflict with Berelson *et al.* (1987) who used benthic chamber measurements to evaluate $CaCO_3$ dissolution kinetics in the nearby adjoining San Pedro Basin, several observations support this assumption. Sediment trap fluxes determined for a total of 437 collection days between February 1986 and October 1987 indicate that the $CaCO_3$ particulate flux to the sediments is generally less than 10% of the organic carbon flux (A. Soutar, personal communication). Thus, even if all of the $CaCO_3$ were to dissolve, it would only contribute a small portion of the T.A. and T.I.C. flux. Also, there was no detectable change in the Ca^{2+} concentration in the *in situ* benthic chamber incubations, suggesting a maximum Ca^{2+} flux from the sediments of ≤ 0.3 mmol m^{-2}d^{-1}. Finally, geological evidence suggests that there is little $CaCO_3$ dissolution in the central basin sediments (R. Douglas, personal communication). With these assumptions, the T.I.C. and T.A. fluxes from the sediments were predicted (Table 2). In general, these fluxes are close to the measured values and suggest that we have an internally consistent set of measured benthic fluxes.

As a final check, benthic exchange rates were compared to estimates of deep basin respiration rates based on hydrographic models of basin-water residence time and composition and to deep-moored sediment trap and burial flux estimates. Deep water column microbial decomposition is of only minor significance in this basin. The hydrographic model, sediment trap plus burial, and benthic flux estimates are in general agreement (Jackson *et al.*, 1989). Thus, the models support the benthic flux measurements and suggest that the measured fluxes are reasonably representative of the deep basin floor.

b. Stoichiometry of organic matter diagenesis. As has been commonly reported for many marine pore waters, the major profile features may be attributed to processes and reactions related to the heterotrophic breakdown of organic matter. Because the bottom water contains little O_2 ($\sim 5\mu M$), oxic and suboxic reactions are limited to the upper few mm of the sediments and anoxic processes dominate throughout the depths sampled. The evidence for this is the decrease in SO_4^{2-} and increase in T.A. and NH_4^+ with increasing sediment depth and the elevated concentrations of Fe^{2+} and Mn^{2+} which occur throughout the profiles. Thus, qualitatively the profile shapes reflect the
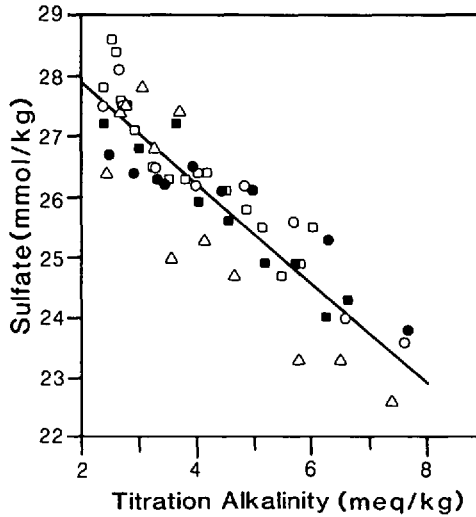
Figure 7. Pore water SO_4^{2-} vs. T.A. for the central basin. The slope of the regression line is $-.826$ (r = .89). H, centrifuged ($\square$); H, pressurized core ($\blacksquare$); I (O); L ($\triangle$); O ($\bullet$).

dominance of SO_4^{2-} reduction in the sediments. The minimum in pH just below the sediment surface may be due to the release of CO_2 during organic matter oxidation. Although there was no detectable H_2S odor, some of the drop in pH below the interface may also be caused by the release of H^+ during the oxidation of sulfides.

If the average oxidation state of organic matter undergoing decomposition is that of carbohydrate, then for every mole of SO_4^{2-} reduced to S^{2-}, two moles of CO_2 and 2.3 equivalents of T.A. should be produced (Emerson *et al.*, 1980; 1982). Assuming that SO_4^{2-} and HCO_3^- do not significantly adsorb onto sediment particles (Berner, 1977) and correcting for differences in molecular diffusion rates, one would expect the Δ T.A.:Δ SO_4^{2-} ratio down-core to be -2.1 (where Δ T.A.:Δ SO_4^{-2} is the ratio of the change in pore water T.A. to the change in pore water SO_4^{2-}). Note that if $CaCO_3$ dissolution were also contributing to the down-core increase in T.A., the expected value should be more negative than -2.1. In the center of the basin, the Δ T.A.:Δ SO_4^{2-} ratio is only -1.21 (inverse of the slope in Fig. 7). This value contrasts significantly with ratios near -2.0 reported for Long Island Sound (Martens *et al.*, 1978) but is similar to those measured in Puget Sound (Grundmanis and Murray, 1986). The latter study suggested that bioturbation increased the flux of oxidants into the Puget Sound sediments maintaining a redox state such that $S_2O_3^{2-}$ and not sulfide (S^{2-}) was the terminal S product of SO_4^{2-} reduction. Thiosulfate was not measured in the present study but Santa Monica Basin sediments are varved and devoid of macrobenthic organisms. Thus, bioturbation cannot be invoked to transport oxidants downward in the sediments.

Another possible explanation is that reactions other than sulfate reduction are

occurring and influencing pore water T.A. Because the pore water did not smell of H_2S, the most likely possibility is the removal of HS^- as a Fe^{2+} mineral. It is difficult to assess this possibility in quantitative terms. No consistent down-core variation in Fe or S in the sediments was observed (Finney and Huh, 1989). If we assume that all S^{2-} is produced at a rate equivalent to the downward pore water SO_4^{2-} flux and that all of the S^{2-} produced is removed to the sediments as FeS, the sediments should contain approximately 3% FeS-sulfur (at the measured sediment accumulation rate of 438 mg $m^{-2}d^{-1}$). Finney and Huh (1989) have reported that the total S contents of the sediments are relatively constant with depth and in the range of 0.4 to 0.7% (wt/wt). It is unlikely, therefore, that the formation of FeS in the sediments can completely account for the observed $\Delta T.A.:\Delta SO_4^{2-}$ ratio.

Recently, it has been suggested that the mean oxidation state of C in organic matter may be significantly different than Redfield ratio (Takahashi *et al.*, 1985; Martin *et al.*, 1987). The results suggest that in the extreme case, organic matter may be better represented as C_2H_4 (C^{2-}) as opposed to the more common representation, CH_2O (C^0). Sulfate reduction of the more reduced material can be described as follows:

$$(C_2H_4)_{53} + 79.5\ SO_4^{2-} \rightarrow 106\ CO_2 + 106H_2O + 79.5\ S^{2-}$$
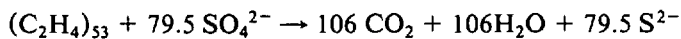
While the use of more reduced organic matter alters the $\Delta T.I.C.:\Delta SO_4^{2-}$ relationship, the $\Delta T.A.:\Delta SO_4^{2-}$ relationship remains essentially unchanged. The precipitation of $CaCO_3$ at depth, of course, would remove T.A. from the system and lower pore water T.A. levels. However, pore water Ca^{2+} concentrations vary by <0.1 mmol/kg from bottom water values. Because a downcore decrease of pore water Ca^{2+} of nearly 2 mmol/kg would be required to fully account for the "missing" T.A., $CaCO_3$ precipitation cannot explain the results. Thus, it remains unclear as to why an approximate 1:1 variation in T.A. and SO_4^{2-} is observed in the pore waters.

c. Benthic N fluxes. Based on the measured benthic fluxes, there is a large NO_3^- flux into the sediments (Table 2), most probably the result of denitrification in the sediments. No significant flux out of the sediments of other forms of fixed N, NH_4^+, NO_2^-, and combined and free amino acids (P.M. Williams, personal communication) has been observed in the benthic chamber experiments. Thus it appears that these sediments represent a sink for fixed nitrogen. Deep particulate N fluxes measured via deep moored sediment traps over a two year collection period are 0.36 mmol N $m^{-2}d^{-1}$ (Jackson *et al.*, 1989). The diffusive flux of bottom water NO_3^- into the sediments exceeds the particulate flux by approximately a factor of three. Thus, although this basin is >900 m deep, the dominant mechanism for transporting NO_3^- from the water column to the sediments is by the direct diffusion of the dissolved NO_3^- and not by the particulate rain of biogenic materials. Summing these two fluxes, the sediments of this basin are consuming approximately 1.5 mmol N $m^{-2}d^{-1}$.

Although only an isolated basin, this location may be reasonably representative of upper slope sediments in the eastern Pacific where organic inputs are relatively high and bottom water O_2 is low due to the occurrence of the O_2 minimum zone. The total area of seafloor between 500 and 1000 m is estimated to be $9.7 \times 10^{12} m^2$ (Sverdrup *et al.*, 1942). If even 10% of this area is similar to Santa Monica Basin, this region would consume 7.4 Tg N yr^{-1} ($1Tg = 1 \times 10^{12}$ g). Recently, Christensen *et al.* (1987) reviewed the oceanic fixed nitrogen cycle and concluded that denitrification in shelf sediments is much larger than previously estimated, accounting for the consumption of $>50Tg$ N yr^{-1}. The consequence of this observation is that the oceanic fixed N budget appears to be unbalanced with removal exceeding input by 60–90 Tg yr^{-1}. However, sedimentary denitrification on the continental slope was not considered by Christensen *et al.* (1987). If we add our estimated denitrification rate for upper slope sediments, the imbalance increases.

d. Reactivity of sedimentary organic matter. Most previous kinetic models of organic matter diagenesis have assumed that metabolizable organic matter consists of different fractions that have different reactivities and that the rate of reaction of each fraction can be described as a first-order process (the multi-G model: Berner, 1974; Westrich and Berner, 1984). From the ATP profiles (Fig. 6), it is clear that much of the microbial biomass and presumed activity are concentrated in the upper 1 cm of the sediments. As discussed previously, even at a 2 mm sampling interval, we are unable to resolve the curvature in the T.A. profile near the sediment surface from which to estimate reaction rates. Because of this limitation, vertical fluxes will be compared at three depth horizons; the sediment surface (measured by benthic chamber), and the 2 cm and 40 cm depth horizons (estimated by pore water diffusion calculations).

The estimated T.A. flux across the 2 cm depth horizon (0.46 meq $m^{-2}d^{-1}$) accounts for only 22% of the total benthic flux of 2.15 meq $m^{-2}d^{-1}$ as estimated by benthic chamber measurements (Table 2). Thus, the majority (78%) of the T.A. production and presumed organic matter mineralization occurs in the upper 2 cm of the sediments. Interestingly, the calculated pore water flux at 40 cm is 0.25 meq $m^{-2}d^{-1}$ which is more than one-half (54%) of the 2 cm flux and 12% of the total flux. To the extent that T.A. production is a surrogate for organic matter decomposition (a reasonable assertion for these sediments as discussed previously), we conclude that 78% of the metabolizable organic C is decomposed within 2 cm of the sediment surface, 10% is decomposed between 2 cm and 40 cm and 12% is decomposed below 40 cm.

Because the sediment accumulation rate is known for this location and sediment mixing is negligible, we can estimate maximum lifetimes of the organic matter in the sediment. At the measured sediment accumulation rate of 438 mg $m^{-2}d^{-1}$ and mean porosity of 0.93, 22 years are required to accumulate the upper 2 cm of the sediments. Accounting for the down-core change in porosity, ~1700 years are required to accumulate the top 40 cm. Thus, it appears that 78% of the metabolizable compounds

are degraded within 22 years of deposition whereas 12% are decomposed after 1700 years of burial.

The results cannot be represented by the first-order decomposition of a single organic fraction. If only one type of organic matter was present and 78% was degraded within the first 22 years after deposition, one would expect less than 0.001% to survive to a depth of 40 cm. Since >10% survives to 40 cm, the metabolizable organic matter must be composed of at least 2 fractions of very different reactivity. Subtracting the flux across the 40 cm depth horizon from the total flux yields a minimum estimate of the more reactive fraction (2.15 meq m^{-2}d^{-1} − 0.25 meq m^{-2}d^{-1} = 1.90 meq m^{-2}d^{-1}). 89% of this fraction (1.69 meq m^{-2}d^{-1}/1.90 meq m^{-2}d^{-1} × 100%) is decomposed above the 2 cm depth horizon. This corresponds to a half-life of this fraction ≤6.5 yrs ($k_1 > 0.15$ yr^{-1}). The remaining reactive fraction must degrade slowly. Since a minimum of ½ of this material is not oxidized until burial to 40 cm, a minimum estimate of the half-life of this less-reactive fraction is 1700 years ($k_2 \sim 0.0006$ yr^{-1}).

Westrich and Berner (1984) have studied the decomposition of planktonic materials directly in the laboratory. They observed that the decomposition of fresh and "aged" plankton remains could be described reasonably well by a two-component, multi-G model with first-order degradation rate constants of approximately 8 yr^{-1} and 1 yr^{-1}. The larger rate constant determined for Santa Monica Basin is in the same range as values reported from field studies of 0.44 yr^{-1}, 0.58 yr^{-1} and 0.95 yr^{-1} by Turekian *et al.* (1980), Berner (1980) and Billen (1982), respectively. Because the rate constant determined for the most reactive organic fraction in Santa Monica Basin is a minimum estimate, these values are reasonably similar. Thus, a large portion of the organic matter reaching the 900 m deep basin floor is quite reactive. The resolution of the pore water data are such that the existence of the very rapidly reacting fraction ($k_1 \sim 8$ yr^{-1}) reported by Westrich and Berner (1984) cannot be verified. It is also clear, however, that approximately ¼ of the metabolizable fraction is reacting more slowly than reported in the previous studies.

The response of benthic fluxes to seasonal variations in sedimentation rate have been modeled by Martin and Bender (1988). Seasonally-varying benthic fluxes are favored by a large portion of the deposited organic matter having very rapid decomposition rates (>1–2 yr^{-1}). Because of limited resolution, we cannot rule out degradation rate constants in this range for some fraction of the deposited organic matter. However, the observation that a significant portion (¼) of the metabolizable organic matter has a degradation rate constant much slower than 1 yr^{-1} suggests that benthic fluxes can vary by no more than a factor of 3 over the annual cycle.

For comparison, <1% of the Si dissolution occurs below 40 cm and 90% to 97% occurs above the 2 cm depth horizon. Using the same line of reasoning as above, this implies a Si dissolution rate constant of 0.19–0.28 yr^{-1}. This is significantly less than rate constants reported by Hurd (1973), Grill and Richards (1964) or Vanderborght *et al.* (1977) which tend to range between 6–15 yr^{-1}. While there is no direct evidence, it

Table 3. Carbon burial summary for the California borderland sediments. All burial and flux rates are in mg $m^{-2}d^{-1}$.

Basin	O_2(B.W.) μM	Sediment Accumulation Rate	Organic Carbon Content %	C Burial	C Recycled	Total Organic Carbon Input	% Burial
San Clemente	55	274–411[f]	2.0[h]	5.5–8.2	14.8[c]	20.3–23.0	27–36%
San Nicolas	22	383[d]	6.0[a]	23.0	15.6[a]	38.6	59.6%
Santa Catalina	15	465[e]	6.5[b]	30.3	28.6[b]	58.9	51%
San Pedro	7	904[d]	5.0[g]	45.2	19.2[a]	64.4	70.2%
Santa Monica	5	438	5.5	24	32	56	43%

[a]Berelson *et al.* (1987)
[b]Smith *et al.* (1987)
[c]Bender *et al.* (1989)
[d]Bruland *et al.* (1981)
[e]Emery (1960)
[f]Emery and Bray (1962)
[g]Craven *et al.* (1986)

is possible that organic coatings associated with the surface bacterial mat, or iron coatings formed by the intense rate of iron cycling at the surface, slow dissolution.

Another important observation is that there is a very large non-reactive organic fraction in these sediments. Approximately 43% of the organic C deposited on the seafloor is permanently buried. One possible explanation for this large fraction of carbon burial is the input of terrestrial and sewage materials from the adjacent Santa Monica shelf. These compounds may be less susceptible to microbial degradation than materials of planktonic origin. Jackson *et al.* (1989) reported estimates for the amount of terrestrial and sewage materials reaching the Santa Monica Basin seafloor based on several different tracers. They conclude that as much as 35% of the recent organic sedimentation may be comprised of terrestrial and sewage materials. However, as we will discuss in the next section, the proportion of the organic carbon rain buried in other California Borderland Basins are reported to be similarly high. Since it is unlikely that all of these basins receive similar amounts of terrestrial and sewage organic matter, other mechanisms may be responsible.

e. Carbon burial; Inter-basin comparison. The organic carbon rain and burial rates for several of the other California Borderland Basins of differing bottom water O_2 content are compared to the results for Santa Monica Basin (Table 3). In all of the studies listed, the organic carbon recycling rate was determined directly by *in situ* benthic flux chamber incubations. At all locations except Santa Catalina Basin, the estimate of organic carbon recycling rate includes the contribution of oxic, suboxic and anoxic oxidation processes. For Santa Catalina Basin, the value listed represents only oxic respiration and may, therefore underestimate total organic matter mineralization.
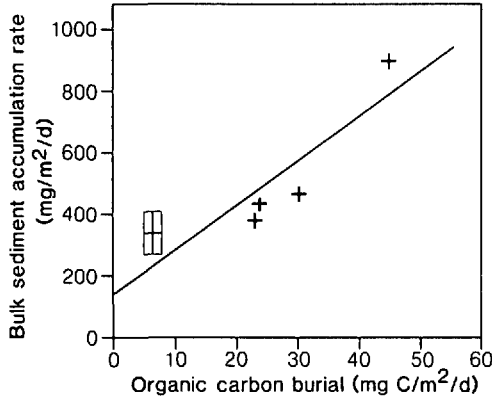
Figure 8. Bulk sediment accumulation rate vs. organic carbon burial for California Borderland Basins. Regression correlation coefficient = .91; significant at the .05 level.

While benthic fluxes can respond to changing seafloor conditions and inputs on time-scales of months (Smith and Baldwin, 1984), sediment accumulation and burial rates integrate events of years to thousands of years. Recognizing the different response times of these quantities is especially important in the Southern California Borderland region because terrigenous sediment input rates have been altered during the last several hundred years due to increased human populations and changing land use of the adjacent continental drainage areas (Schwalbach and Gorsline, 1985). To provide the most accurate comparison between benthic flux and burial, sediment accumulation rates that best respond to short-term changes in deposition, such as ^{210}Pb, are used in the Table. The only values reported for San Clemente Basin, however, are based on ^{14}C ages. Therefore, a range of values is used for this basin. For Santa Catalina Basin, accumulation rates are based on $CaCO_3$ stratigraphy (Schwalbach and Gorsline, 1985) which are also in the range suggested by ^{14}C dating (Emery, 1960). The total organic carbon input is estimated as simply the sum of the burial and recycling rates.

Previous work has suggested correlations between carbon burial and sediment accumulation (Müller and Suess, 1979), organic carbon rain rate, bottom water oxygen content and the organic matter degradation rate constant (Emerson, 1985). Despite the caveats concerning the sediment accumulation rate estimates, the results listed in Table 3 can be used to assess the influence of the suggested factors on carbon burial.

The strongest correlations with organic carbon burial are observed for bulk sediment accumulation (Fig. 8) and with organic carbon input rate (Fig. 9). As these quantities themselves tend to be correlated, it is difficult to assess whether the correlations have a mechanistic basis. For deep ocean conditions where sedimentation rates are <10 cm 10^{-3} yrs, modeling studies have suggested that organic carbon burial is insensitive to changes in bulk sediment accumulation rates (Jahnke *et al.*, 1982; Emerson 1985) and that organic carbon input rate is a major factor controlling burial. However, because
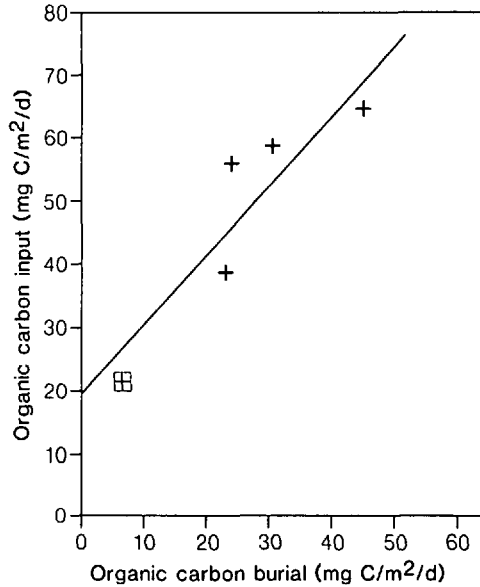
Figure 9. Organic carbon input rate vs. organic carbon burial for California Borderland Basins. Regression correlation coefficient = .92; significant at the .05 level.

sedimentation rates in the Borderland basins exceed those used in the modeling studies, further work is required to assess the mechanistic implications of the observed correlations.

At each site, the proportion of the organic matter mineralized by oxygen utilization has been estimated (Fig. 10). Because the reported benthic carbon budget for Santa
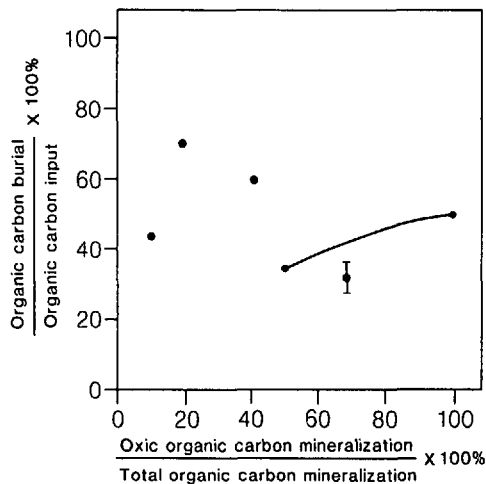

Figure 10. Proportion of total organic carbon deposited that is buried vs. the proportion of organic carbon recycled by O_2 respiration.

Catalina Basin was based solely on O_2 fluxes, total benthic mineralization may be underestimated. A range of values (represented by the line on Fig. 10) is therefore presented for this basin assuming that oxidants other than O_2 may account for as much as $1/2$ of the total benthic respiration.

A statistically significant correlation between organic carbon burial efficiency and oxygen respiration is not observed. Note that the contribution of oxic mineralization to seafloor decomposition ranges from being relatively insignificant in Santa Monica Basin (~10%) to dominating benthic recycling in San Clemente Basin (~70%) and possibly Santa Catalina Basin. The lack of a significant trend on this figure suggests that suboxic and anoxic processes decompose organic matter at rates similar to oxic processes as suggested by Henrichs and Reeburgh (1987). Oxic respiration does not appear to recycle organic matter more efficiently and the proportion of the organic rain that is buried is relatively insensitive to bottom water O_2 concentrations.

The rate at which sediments are mixed also appears to have little effect on organic carbon burial efficiency. Because the sediments in Santa Monica Basin are varved, particle mixing rates must be near zero. In Santa Catalina Basin, however, abundant macrobenthic organism populations rework surface sediments at a rapid rate, resulting in the penetration of excess ^{234}Th ($t_{1/2} = 24$ days) to depths of 4–6 cm (Smith *et al.*, 1986). No dramatic change in burial efficiency is observed, suggesting that organic carbon preservation is not sensitive to changes in bioturbation.

Thus, it appears that the overwhelming factor that determines organic C burial rate is the input rate to the sediments. Little correlation is observed between carbon burial or burial efficiency and bottom water O_2, proportion of O_2 mineralization, and sediment mixing rate. A recent analysis of geological evidence supports the conclusion that the oxygen content of bottom waters is not a major factor controlling the burial rate of organic carbon (Calvert and Pedersen, in press). If these results are substantiated, previous studies that ascribed organic carbon variations in the sedimentary record to changes in bottom water O_2 content should be re-evaluated.

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