# 15. EPISODICALLY STRONG RECYCLING OF METHANE RECORDED BY $^{13}C/^{12}C$, N/C, AND H/C RATIOS FOR KEROGENS FROM THE LAST 160,000 YEARS IN THE SANTA BARBARA BASIN AT HOLE 893A[1]

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## ABSTRACT

Organic carbon contents and kerogen properties (hydrogen/carbon, nitrogen/carbon, carbon isotopic ratios) were determined for 29 core samples from Ocean Drilling Program Site 893. The samples, which span the last 160,000 years, are bioturbated and laminated silty-clay and clayey-silt hemipelagic/pelagic deposits accumulated under oxic to suboxic conditions. Organic carbon contents average 1.5 wt% with the highest values occurring in the laminated sediments. H/C and N/C atomic ratios vary between 0.8 and 1.2 and between 0.028 and 0.063, respectively. These variations are weakly correlated. Carbon isotopic compositions ($\delta^{13}C$) for 20 of the kerogens range from –22‰ to –25‰. Four kerogens have δ values varying between –25.5‰ and –27.1‰ and the remaining five kerogens have δ values between –27.7‰ and –29.5‰. The kerogens with low δ values tend to have low H/C and N/C ratios.

Wide variations in both elemental and isotopic data indicate marked changes in the sources of the organic matter deposited in the Santa Barbara Basin. Kerogens with δ values in the range –22‰ to –24‰ reflect typical hemipelagic/pelagic debris predominantly composed of photosynthetically derived marine organic matter with elemental ratios varying in proportion to the amount of terrestrial organic matter and the degree of bioturbation. In contrast, the δ values lower than –27.0‰ are not typical of any sources of organic matter reported for the modern California shelf. Kerogen with low δ values could represent episodic inputs of $^{13}C$-depleted organic matter that was produced either by methanotrophs or by chemosynthetic bacteria (e.g., sulfide oxidizers) utilizing $^{13}C$-depleted inorganic carbon derived in part from the oxidation of $CH_4$. Reports of both high concentrations of methane and abundant gas hydrates in marine sediments from offshore northern California suggest that periodic releasing of $CH_4$ is possible, making episodic recycling of $CH_4$ plausible.

## INTRODUCTION

Modern marine settings, with high rates of sediment accumulation and low levels of benthic oxygenation, are well suited for studying the cumulative effects of paleoceanographic conditions and diagenetic sediment transformation. Limited disruption of sediment microstructure by benthic macrofauna results in partially to pervasively laminated fabrics in many suboxic settings. The open slope of central and northern California and the active margin basins of the southern California Borderland have been monitored extensively to determine efficiency of nutrient recycling in the water column and fates of organic matter during early diagenesis in the sediment column (see references in Jahnke, 1990; Schimmelmann and Kastner, 1993; and Dean et al., 1994). Previously studied box and piston cores from the California Borderland basins represent a few centuries of sediment accumulation to a maximum of eight millennia (Pisias, 1978). Seasonal to decadal fluctuations in the early diagenetic environment make it difficult to assess the quantity and composition of buried organic matter at time scales of tens to hundreds of millennia. The recovery of nearly 200 m of fine-grained sediment, at Ocean Drilling Program Site 893 in the central Santa Barbara Basin, extends the paleoceanographic record in the Borderland to nearly 160,000 years (Shore-based Scientific Party, 1994) and provides an opportunity to investigate the influence of glacial-interglacial climate change on inputs and burial of organic matter in a nearshore marine basin.

Emery and Hülsemann (1962; Hülsemann and Emery, 1961) recognized that the central Santa Barbara Basin was a site of annually varved marine sediment deposited under suboxic bottom-water conditions. Their research lays a conceptual foundation for subsequent studies of sedimentological, biological, and geochemical conditions leading to the formation of these finely laminated deposits (Kaplan et al., 1963; Sholkovitz and Gieskes, 1971; Fleischer, 1972; Sholkovitz, 1973; Soutar and Crill, 1977; Pisias, 1978; Jahnke, 1990; Schimmelmann et al., 1990; Kennedy and Brassell, 1992; Schimmelmann and Kastner, 1993). Subsampling of varved sequences, with near-annual resolution, is possible because sedimentation rates for laminated, non-turbidite sediment in the central basin are about 0.8 to 1.1 cm/yr of sediment decompacted to 90% porosity (Soutar and Crill, 1977; Schimmelmann and Kastner, 1993). The central portion of the modern Santa Barbara Basin is approximately 590 m deep and 120 m below sill depth. Flow over the sill contributes colder, denser water from the East Pacific oxygen minimum zone to the lower Santa Barbara Basin. A high oxygen demand from central basin sediment with organic carbon contents in the range of 3–8 wt% (Reimers et al., 1990; Schimmelmann and Kastner, 1993) further reduces dissolved oxygen contents below the sill depth. Following the event of a spillover, nitrate and oxygen contents are rapidly reduced by degradation of organic matter. Oxygen contents in the basin bottom waters vary seasonally from maximum values of 0.5 mL/L to minimum values of less than 0.03 mL/L (Reimers et al., 1990). Suboxic benthic conditions, in the lower Santa Barbara Basin, limit the activity of benthic macrofauna and favor the development of filamentous bacterial mats on the seafloor (Soutar and Crill, 1977; Reimers et al., 1990). These mats of sulfur-oxidizing *Beggiatoa* spp. are effective chemical traps, and the modern bottom waters in the central Santa Barbara Basin do not contain free hydrogen sulfide (Sholkovitz, 1973) despite the pres-

ence of hydrogen sulfide at high concentrations in pore waters just a few centimeters below the sediment water interface (Reimers et al., 1990).

Flooding, marine primary productivity, efficiency of recycling in the water column, and particle sinking rates determine the flux and composition of organic matter reaching the sediment surface in the near-shore basins of the California Borderland. At and near the sediment-water interface, reactive organic compounds rapidly degrade by suboxic and anoxic heterotrophic processes that generate steep benthic gradients (millimeter to centimeter scale) in concentrations of nitrate, sulfate, titration alkalinity, $Fe^{2+}$, and $Mn^{2+}$ (e.g., Jahnke 1990; Reimers et al., 1990; Schimmelmann and Kastner, 1993). The slope and position of these gradients is a dynamic property, changing seasonally in response to the flux of organic matter, supply of oxygen, and temperature of bottom water. At time scales of 1,000–100,000 years, repeated substantial changes in benthic conditions are inferred from interbedding of laminated and bioturbated sedimentary facies in the Santa Barbara Basin (Shore-based Scientific Party, 1994).

## LITHOLOGIC DESCRIPTION AND SAMPLE SELECTION

The near-shore marine deposits at Site 893 represent an upper Quaternary sequence accumulated at high sedimentation rates under oxic to suboxic conditions (Shore-based Scientific Party, 1994). Throughout the cored interval, olive-gray silt and clay are the dominant sedimentary constituents with variable abundances of diatoms and calcareous nannofossils. A single lithostratigraphic unit is recognized and divided into six subunits on the basis of sedimentary composition and structure, primarily the degree of lamination. Thin sand beds, inferred to originate as turbidites, occur intermittently within the section but are noticeably less abundant in the upper laminated (Subunit 1A) and lower laminated (Subunit 1D) sequences. The laminated sequences are marked by higher abundances of biogenic skeletal material (Shore-based Scientific Party, 1994), higher concentrations of organic carbon (Stein and Rack, this volume), and higher concentrations of total sulfur (Brüchert et al., this volume). Based on preliminary studies of pollen content and biostratigraphy of planktonic foraminifera, the sequence at Site 893 extends from near the base of isotope Stage 6 until the present day and includes two glacial and two interglacial episodes (Shore-based Scientific Party, 1994).

Ten samples used in this study of kerogens (solvent-insoluble organic matter) were taken from the sediment residues after sequential extraction of organic and inorganic sulfur species (Brüchert et al., this volume). Nineteen additional kerogen samples were prepared from unextracted sediment. The samples are distributed over the length of Hole 893A and reflect the general distribution and abundance of sediment facies with the exception of sand turbidites. Table 1 in Brüchert et al. (this volume) lists stratigraphic position, age, general lithologic character, and sedimentary textures of the samples processed for kerogen.

## ANALYTICAL METHODS

Concentrations of organic carbon ($C_{org}$) were determined using sediment samples that had been treated with hydrochloric acid (HCl). Approximately 0.25 g of air-dried sediment was powdered in an agate mortar and pestle, moistened with distilled water, and reacted overnight with 80–100 mL of 1N HCl. Insoluble residues were concentrated on Whatman GF/C glass microfiber filters, rinsed with boiling 1N HCl, washed repeatedly with distilled water, and dried for 24 hr at 60°C. Insoluble residues plus filters were combusted under flowing oxygen in a LECO CS-244 induction furnace. In this instru-

ment, yields of carbon dioxide ($CO_2$) are measured by monitoring levels of infrared absorption in comparison to yields from calibration standards. $C_{org}$ is reported as wt% of the whole sediment.

Samples of bulk organic matter were decalcified prior to isotopic analysis of the organic carbon by adding an aliquot of 10 ml of 12N HCl to 100–200 mg of wet sediment in glass centrifuge tubes. Acid and sediment were stirred and allowed to react for one hour. Acid and sediment were stirred a second time prior to removal of acid by centrifugation and aspiration. Another 10 ml of HCl was added, stirred, and allowed to react for 10 min prior to removal of acid by centrifugation and aspiration. Residual sediment was washed with distilled/deionized water until a pH of 3–4 was reached. Residual sediment was dried overnight at 65°C.

Kerogen was isolated from sediment samples that were demineralized with multiple acid treatments. Approximately 5 g of sediment was air-dried, powdered in an agate mortar and pestle, moistened with distilled water, and reacted overnight with 100 mL of 12N HCl. Sediment residue was concentrated by centrifugation, the supernatant was decanted, and the residue was resuspended in distilled water. These steps were repeated until the pH of the supernatant solution was ≥3. Sediment residue was resuspended in 100 mL of concentrated hydrofluoric acid (HF) and reacted overnight. Insoluble products of this treatment were concentrated and neutralized following the procedure described for the initial acid treatment, then reacted overnight with 12N HCl. Final sediment residue (kerogen) was concentrated on a Whatman GF/C glass microfiber filter, washed repeatedly with distilled water, and dried overnight at 60°C. Kerogen was carefully lifted from the filter and powdered in an agate mortar and pestle. Kerogen was soaked for 30 min at room temperature with dichloromethane to remove bitumen.

Carbon isotopic compositions ($\delta^{13}C$) of bulk organic matter and kerogen were determined using carbon dioxide ($CO_2$) produced by sealed-tube combustion. Approximately 1.5 g of cupric oxide (CuO) wire was added to 15–30 mg of residual sediment or 2 mg of prepared kerogen and sealed under vacuum in quartz tube (9 mm diameter, 15 cm length). Sealed tubes were heated overnight at 850°C and the resulting $CO_2$ was purified by cryogenic distillation. The isotopic composition of purified $CO_2$ was determined using a Finnigan Mat 252 mass spectrometer. Values of $\delta$ are reported in per mil units (‰) relative to the Peedee belemnite (PDB) standard:

$$\delta^{13}C \ (‰) = 1000[(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{pdb} - 1].$$

Concentrations of carbon (C), hydrogen (H), and nitrogen (N) in kerogen were determined using a Carlo Erba 1106 elemental analyzer. Kerogen samples were stored in a desiccator before they were loaded into tin vessels for combustion in the elemental analyzer. In this instrument, a constant helium flow is briefly enriched with oxygen to assure rapid combustion at 1020°C. Combustion products are further oxidized by reaction with granular chromic and cobaltic oxides ($Cr_2O_3$ and $Co_2O_3$) and carried through a copper reduction reactor at 650°C to absorb excess oxygen and reduce nitrogen oxides. $N_2$, $CO_2$, and $H_2O$ are separated in a chromatographic column at 130°C and quantified using a thermal conductivity detector. The elemental analysis system was calibrated using an acetanilide standard. Elemental data for kerogen are reported as atomic ratios of N/C and H/C.

## ANALYTICAL RESULTS

The 29 sediment samples analyzed in this study are representative of the clayey silt and silty clay (pelagic/hemipelagic deposits) accumulated under suboxic to oxic benthic conditions in the central portion of the Santa Barbara Basin. No samples from the thin to medium-thick beds of sand (turbidites), which are intermittently present in the sediment sequence at Hole 893A, were included in this

study. Each of the analyzed sediments is characterized as either laminated or bioturbated/structureless on the basis of the dominant sedimentary fabric in the sample interval (table 1 in Brüchert et al., this volume). Relatively large samples were required for the companion study of sulfur isotopic budgets (Brüchert et al., this volume); therefore, the samples used here span core intervals of 4–10 cm in depth. A thin slice of sediment, cut perpendicular to layering and thus incorporating all strata in the sample, was homogenized prior to determination of $C_{org}$ and preparation of kerogen. Homogenization of several centimeters of sediments dilutes the influence of unusual thin layers and laminae.

Homogenized large samples of sediment from the sequence at Hole 893A have average contents of $C_{org}$ of approximately 1.5 wt%, with maximum values of 2.5 to 3 wt% occurring in Subunit 1A, near the base of Subunit 1C, and in Subunit 1D. Similar values are reported by Stein and Rack (this volume) for average contents of $C_{org}$, but they report higher maximum values (3.5 to 4.5 wt%) for contents of $C_{org}$ from small samples of sediment. The highest contents of $C_{org}$ reported in this study and in Stein and Rack (this volume) occur in well-laminated sediment from Subunit 1A (isotope Stage 1) and Subunit 1D (isotope Stage 5).

Bulk organic carbon is enriched in $^{13}C$ relative to kerogen by up to 7.3‰ for Santa Barbara sediments from Hole 893A (Table 1). The bulk material must, therefore, include a fraction that is enriched $^{13}C$ relative to the kerogen and which is solubilized during the acid treatments (isolation and purification of kerogen requires several days of treatment with concentrated hydrochloric and hydrofluoric acids for the dissolution of carbonate and silicate minerals). Such large isotopic differences between bulk organic matter and kerogen are generally not observed for sediment or rock that has undergone diagenesis and burial for millions of years. For upper Quaternary sediment in the Santa Barbara basin, however, the δ value of bulk organic matter ranges from –24.4‰ to –21.8‰ and averages –22.6‰ and that of kerogen prepared from the same samples ranges from –29.‰ to –22.2‰ and averages –25.4‰. The wide range in isotopic compositions for kerogen and narrow range for bulk organic matter indicate substantial variation in the proportion of acid-soluble organic matter. Given good correlations between kerogen elemental ratios and $\delta^{13}C_{kerogen}$ (Figs. 1 and 2), the isotopic composition of kerogen appears to be a sensitive indicator of variations in the deposition of an isotopically distinct component of organic matter.

Carbon isotopic compositions of kerogen span a substantial range of δ values (Table 1 and Fig. 3). Twenty of the kerogen samples have isotopic compositions in the range of –22‰ to –25‰. The remaining nine samples have more negative δ values with four samples in the range of –28‰ to –29.6‰. Isotopic compositions for kerogen more depleted in $^{13}C$ than –27‰ are problematic. Values of $\delta^{13}C$ reported for bulk organic matter from rivers in central and northern California and from the Columbia River in Washington range from –24‰ to –27‰ (Peters et al., 1978; Hedges et al., 1984). Carbon isotopic compositions for bulk organic matter from near-surface sediment samples and sediment traps in the California Borderland basins and on the continental margin of northern California range from –21‰ to –24‰ (Peters et al., 1978; Crisp et al., 1979; Schimmelmann and Tegner, 1991; Dean et al., 1994). Additional distinct sources of organic matter for the Borderland basins include northern Pacific phytoplankton ($\delta^{13}C$ range from –18‰ to –22.5‰; Rau et al., 1982), Pacific coastal kelp ($\delta^{13}C$ range from –11‰ to –20‰; Schimmelmann and Tegner, 1991), and Miocene kerogen and bitumen derived from the Monterey Formation ($\delta^{13}C$ range from –22‰ to –26‰; see references in Schimmelmann and Tegner, 1991).

Elemental compositions of kerogen from Hole 893A span a substantial range (Table 1 and Fig. 3). The 29 kerogens analyzed in this study are markedly depleted in both nitrogen and hydrogen compared to organic matter collected from sediment traps in the overlying water column (Crisp et al., 1979) and, as shown in Figure 4, variations in
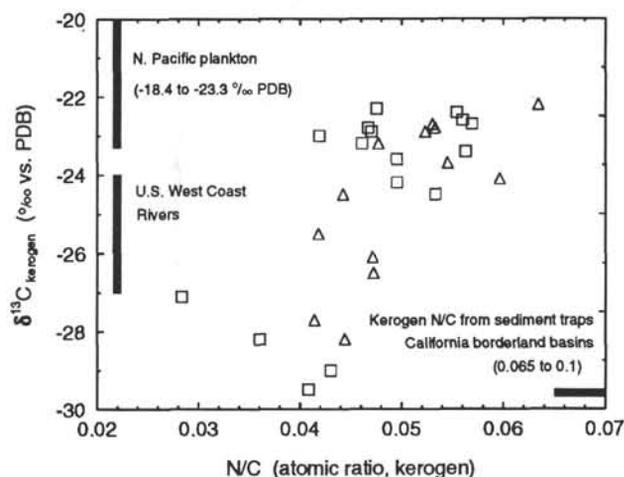


Figure 1. Plot of $\delta^{13}C$ vs. N/C for kerogens from Hole 893A. Reference values for the isotopic composition of terrigenous organic matter were taken from Hedges et al. (1984) for the Columbia River and from Peters et al. (1978) for California rivers. Reference values for the isotopic composition of marine organic plankton were taken from Rau et al. (1982). Reference values of atomic H/C ratios are for kerogens prepared from modern organic matter recovered in sediment traps (Crisp et al., 1979). Open squares = bioturbated/structureless sediments; open triangles = laminated sediments.
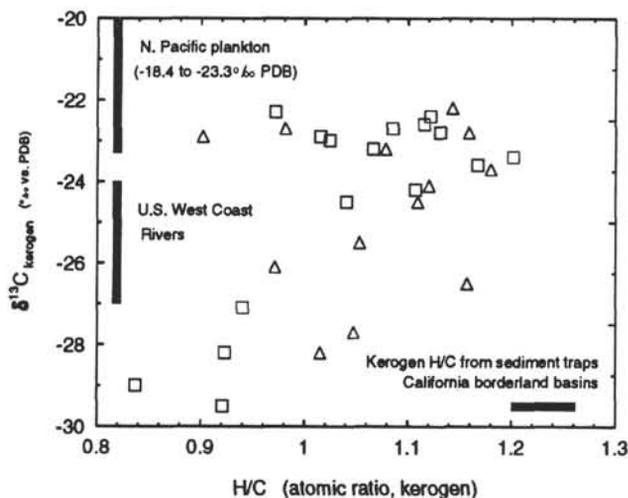


Figure 2. Plot of $\delta^{13}C$ vs. H/C for kerogens from Hole 893A. Reference values for the isotopic composition of terrigenous organic matter in northern California rivers were taken from Hedges et al. (1984). Reference values for the isotopic composition of marine organic plankton were taken from Rau et al. (1982). Reference values of atomic H/C ratios are for kerogens prepared from modern organic matter recovered in sediment traps (Crisp et al., 1979). Symbols as in Figure 1.

N/C and H/C atomic ratios are correlated. Marked variations in the N/C and H/C ratios occur in the upper 50 m of this sequence (Fig. 3), with elemental compositions becoming less variable down sequence. The lowest N/C and H/C ratios occur in kerogens from bioturbated/structureless sediments, but there is no clear separation of these from laminated sediment samples on a crossplot of kerogen atomic ratios (Fig. 4).

**Table 1. Geochemical data from this study.**

| Core, section, interval (cm) | Depth (mbsf) | Age (k.y.) | Total $C_{org}$ (wt%) | $\delta^{13}C_{org}$ (‰ PDB) | $\delta^{13}C_{kerogen}$ (‰ PDB) | H/C$_{kerogen}$ atomic ratios | N/C$_{kerogen}$ atomic ratios |
|---|---|---|---|---|---|---|---|
| 146-893A- | | | | | | | |
| 1H-1, 82–98 | 0.9 | 0.5 | 2.50 | –21.8 | –23.7 | 1.180 | 0.055 |
| 1H-4, 82–97 | 5.4 | 3.2 | 2.19 | –22.1 | –24.1 | 1.120 | 0.060 |
| 2H-3, 83–99 | 10.4 | 6.3 | 1.71 | –22.0 | –22.2 | 1.143 | 0.063 |
| 2H-7, 62–80 | 15.7 | 9.7 | 1.69 | –22.0 | –27.7 | 1.048 | 0.041 |
| 3H-3, 73–88 | 19.8 | 12.4 | 1.53 | –22.6 | –29.0 | 0.837 | 0.043 |
| 3H-4, 82–94 | 21.2 | 13.4 | 1.31 | –22.7 | –23.4 | 1.202 | 0.056 |
| 4H-4, 4–16 | 29.6 | 19.1 | 1.46 | –22.3 | –29.6 | 0.921 | 0.041 |
| 5H-5, 71–77 | 41.1 | 27.0 | 1.56 | –22.4 | –28.2 | 0.923 | 0.036 |
| 6H-3, 83–98 | 47.8 | 32.2 | 1.39 | –22.1 | –24.5 | 1.041 | 0.053 |
| 6H-5, 112–128 | 50.9 | 34.4 | 1.17 | –22.5 | –22.9 | 0.902 | 0.052 |
| 7H-3, 103–128 | 55.9 | 38.1 | 0.66 | –22.8 | –27.1 | 0.940 | 0.028 |
| 7H-5, 61–74 | 58.2 | 39.7 | 1.35 | –22.2 | –24.2 | 1.107 | 0.050 |
| 9H-4, 71–85 | 77.4 | 54.0 | 1.44 | –22.6 | –22.7 | 1.085 | 0.057 |
| 10H-4, 45–59 | 87.4 | 62.4 | 1.06 | –23.0 | –23.2 | 1.066 | 0.046 |
| 12H-3, 90–102 | 105.2 | 80.7 | 1.62 | –22.3 | –22.4 | 1.122 | 0.055 |
| 13H-6, 44–55 | 117.0 | 90.7 | 1.32 | –22.7 | –22.9 | 1.015 | 0.047 |
| 14H-2, 45–56 | 122.5 | 96.5 | 2.26 | –22.5 | –22.6 | 1.115 | 0.056 |
| 15H-3, 92–104 | 133.7 | 108.5 | 1.90 | –22.7 | –28.2 | 1.015 | 0.044 |
| 15H-5, 117–129 | 137.0 | 112.1 | 1.63 | –22.6 | –22.7 | 0.981 | 0.053 |
| 16H-2, 22–33 | 140.9 | 116.2 | 0.92 | –24.4 | –24.5 | 1.109 | 0.044 |
| 16H-3, 26–40 | 142.4 | 117.7 | 2.83 | –22.2 | –26.5 | 1.157 | 0.047 |
| 17H-3, 110–122 | 153.1 | 125.2 | 1.40 | –22.4 | –22.3 | 0.972 | 0.048 |
| 18H-4, 84–96 | 163.8 | 133.2 | 1.36 | –23.3 | –22.8 | 1.159 | 0.053 |
| 18H-5, 81–93 | 165.2 | 134.5 | 1.20 | –23.0 | –23.2 | 1.078 | 0.048 |
| 19H-2, 130–141 | 170.7 | 139.5 | 1.72 | –23.1 | –26.1 | 0.971 | 0.047 |
| 19H-5, 66–77 | 174.5 | 142.9 | 1.12 | –23.1 | –23.0 | 1.024 | 0.042 |
| 20H-4, 41–53 | 182.2 | 149.8 | 1.10 | –22.7 | –22.8 | 1.131 | 0.047 |
| 21H-2, 134–146 | 189.2 | 156.1 | 1.49 | –22.4 | –23.6 | 1.167 | 0.050 |
| 21H-4, 124–136 | 192.3 | 158.9 | 1.44 | –22.4 | –25.5 | 1.053 | 0.042 |
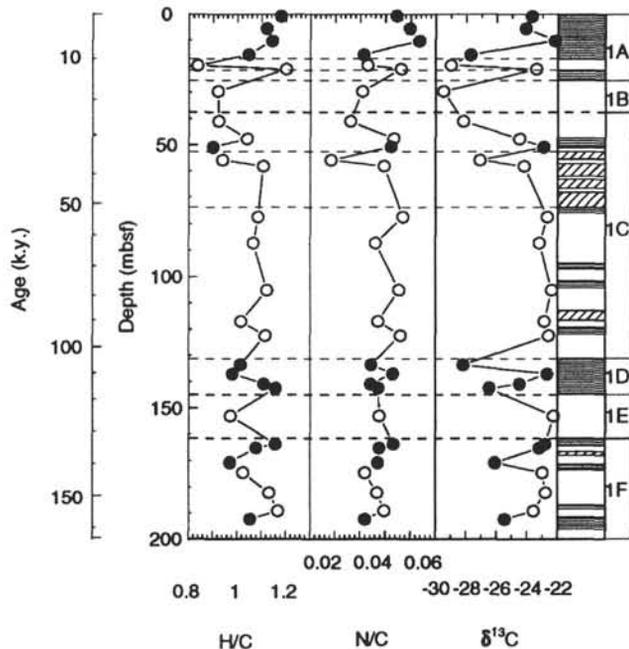


Figure 3. Stratigraphic profile of variations in H/C and N/C atomic ratios and carbon isotopic compositions in kerogens prepared from sediment samples of Hole 893A, Santa Barbara Basin. Open circles = bioturbated/structureless sediments; closed circles = laminated sediments. Columns on right show variation in sedimentary fabric, from laminated (laminated pattern) to non-laminated/structureless sediments (no pattern). Subunit 1C contains several sand layers (diagonal line pattern). Division of cored interval into Subunits 1A through 1F was adopted from Kennett, Baldauf, et al. (1994). Age assignments are based on biostratigraphy, pollen events, and $^{14}C$ chronology (Kennett, Baldauf, et al., 1994).
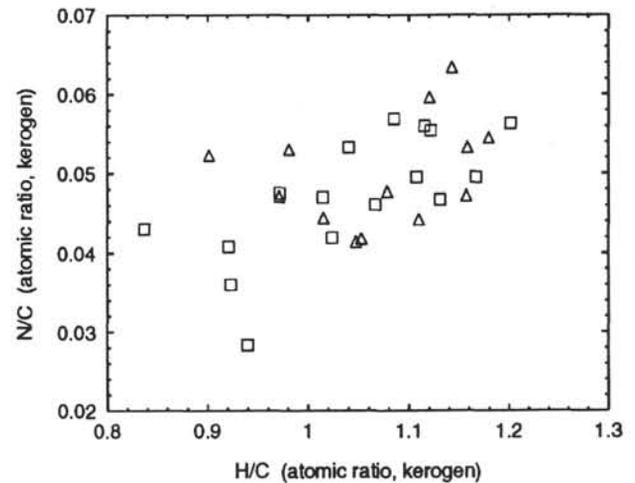


Figure 4. Graph showing positive correlation between the atomic ratios of N/C and H/C in Santa Barbara kerogens from Hole 893A. Symbols as in Figure 1.

## DISCUSSION

Carbon isotopic compositions ($\delta^{13}C$) and elemental ratios (N/C and H/C) of kerogens from the sedimentary sequence recovered at Hole 893A record marked variations in sources of organic matter accumulating in hemipelagic/pelagic sediments in the central Santa Barbara Basin during the past 160,000 years. Even though no samples from interbedded sandy turbidites in Hole 893A were included in this study, large differences in isotopic and elemental compositions occur. Notably, $\delta$ values for six of the 29 kerogens are lower than –27‰. These low values cannot be explained by the sources of organic matter considered thus far for the modern California shelf (e.g., Schimmelmann and Tegner, 1991; Dean et al., 1994), all of which have $\delta$ values > –27‰.

As shown in Figure 1, values of $\delta_{kerogen}$ and N/C are roughly covariant. In contrast, two different trends are suggested when $\delta_{kerogen}$ is plotted vs. H/C (Fig. 2). First, there is a general trend of positive covariance between $\delta_{kerogen}$ and H/C for kerogens with $\delta < -24‰$. Second, isotopic compositions are independent of H/C atomic ratios for kerogens with $\delta$ values between $-22‰$ and $-24‰$. The six kerogen samples with anomalously low $\delta$ values have N/C atomic ratios ranging from 0.028 to 0.044 and are thus depleted in N compared to other kerogens from this site. Ratios of H/C for these samples range from 0.84 to 1.05, which are intermediate to low values compared to other kerogens from this site.

## Indicators of Episodic Methane Recycling

Carbon isotopic compositions of organic matter in near-surface marine sediments from numerous locations in the modern northeastern Pacific range between $-21‰$ and $-24‰$ (Peters et al., 1978; Schimmelmann and Tegner, 1991; Dean et al., 1994). Sixteen out of 29 kerogen samples from Hole 893A are within this narrow range of values for $\delta^{13}C$. The other 13 record episodic, marked excursions to lower values of $\delta^{13}C$. Such depletions are typical of (1) products of chemosynthetic organisms growing in an environment where oxidation of methane is an important source of inorganic carbon (Paull et al., 1992, and references therein) and (2) products of aerobic methanotrophic bacteria (Freeman et al., 1990, and references therein). Aerobic or anaerobic oxidation of methane can produce $^{13}C$-depleted $CO_2$ in near-surface pore water and in poorly mixed bottom water (Scranton et al., 1993, and references therein), leading to highly variable $\delta^{13}C$ values for organic matter produced chemosynthetically at or near the oxic/anoxic interface. Aerobic methane consumption leads to organic matter that is strongly depleted in $^{13}C$ as the result of direct incorporation of carbon from methane. The extent of methane contribution to $CO_2$ and/or direct incorporation of carbon from methane is indicated by the magnitude of excursions to lower values of $\delta^{13}C$ for kerogen.

Chemosynthetic production of organic matter by mats of *Beggiatoa* spp. is well documented in the modern Santa Barbara Basin (Soutar and Crill, 1977; Reimers et al., 1990). Growth of these benthic bacterial mats has been inferred to play an important role in the formation of annual laminations that occur in discrete intervals within Hole 893A. Methanotrophic bacteria are not reported from the modern Santa Barbara Basin but probably are present during times of methane release to oxic environments in the sediment or water columns. Events of methane release are likely, given the high concentration of methane in Hole 893A (Shore-based Scientific Party, 1994) and the presence of gas hydrates in marine sediments from offshore northern California (Brooks et al., 1991). Negative isotopic shifts of several per mil could occur if even a small proportion of the total sedimentary organic matter in Hole 893A was sourced episodically from methane-influenced chemosynthetic or methanotrophic organisms. The lowest value of $\delta^{13}C_{kerogen}$ reported from Hole 893A is $-29.6‰$. Typical hemipelagic/pelagic organic matter in the Santa Barbara Basin has an isotopic composition of $-23‰$. This difference of $-6.5‰$ in isotopic compositions could be explained with the input of 15% chemosynthetic or methanotrophic organic matter with an isotopic composition of $-66‰$. Organic matter with values of $\delta^{13}C$ in the range $-50‰$ to $-75‰$ are typical of tissues, sedimentary organic matter, and individual bacterial biomarkers from environments with strong methane cycling (Freeman et al., 1990; Paull et al., 1992).

## CONCLUSIONS

1. Changes in carbon isotopic abundances ($\delta^{13}C$) and elemental atomic ratios (N/C, H/C) for kerogen from Hole 893A cannot be explained by mixing of normal marine and terrestrial sources of organic matter or by differences in the degree of sedimentary lamination or bioturbation.

2. Values of $\delta^{13}C$ for bulk organic matter are systematically higher than kerogen as a result of the removal of acid-soluble organic constituents enriched in $^{13}C$ during the preparation of kerogen.

3. Sediment samples with values of $\delta^{13}C_{kerogen}$ in the range of $-22‰$ to $-24‰$ reflect typical hemipelagic/pelagic debris composed predominantly of photosynthetically derived marine organic matter. Elemental ratios for this hemipelagic/pelagic organic matter vary in proportion to both the amount of terrestrial organic matter and the degree of sediment bioturbation.

4. Sediment samples with values of $\delta^{13}C_{kerogen}$ lower than $-24$ reflect episodically strong recycling of methane in the benthic environment of the Santa Barbara Basin. Elemental ratios for the methane-influenced organic matter vary in proportion to the degree of sediment bioturbation. Kerogen samples with lowest ratios of both N/C and H/C from Hole 893A occur in bioturbated samples with low values of $\delta^{13}C_{kerogen}$.

## REFERENCES

Brooks, J.M., Field, M.E., and Kennicutt, M.C., II, 1991. Observations of gas hydrates in marine sediments, offshore Northern California. *Mar. Geol.*, 96:103–109.

Crisp, P.T., Brenner, S., Venkatesan, M.I., Ruth, E., and Kaplan, I.R., 1979. Organic chemical characterization of sediment-trap particulates from San Nicolas, Santa Barbara, Santa Monica, and San Pedro Basins, California. *Geochim. Cosmochim. Acta*, 43:1791–1801.

Dean, W.E., Gardner, J.V., and Anderson, R.Y., 1994. Geochemical evidence for enhanced preservation of organic matter in the oxygen minimum zone of the continental margin of northern California during the late Pleistocene. *Paleoceanography*, 9:47–61.

Emery, K.O., and Hülsemann, J., 1962. The relationships of sediments, life and water in a marine basin. *Deep-Sea Res. Part A*, 8:165–180.

Fleischer, P., 1972. Mineralogy and sedimentation history, Santa Barbara Basin, California. *J. Sediment. Petrol.*, 42:49–58.

Freeman, K.H., Hayes, J.M., Trendel, J.M., and Albrecht, P., 1990. Evidence from carbon isotope measurements for diverse origins of sedimentary hydrocarbons. *Nature*, 343:254–256.

Hedges, J.I., Turin, H.J., and Ertel, J.R., 1984. Sources and distributions of sedimentary organic matter in the Columbia River drainage basin, Washington and Oregon. *Limnol. Oceanogr.*, 29:35–46.

Hülsemann, J., and Emery, K.O., 1961. Stratification in recent sediments of Santa Barbara Basin as controlled by organisms and water character. *J. Geol.*, 69:279–290.

Jahnke, R.A., 1990. Early diagenesis and recycling of biogenic debris at the seafloor, Santa Monica Basin, California. *J. Mar. Res.*, 43:413–436.

Kaplan, I.R., Emery, K.O., and Rittenberg, S.C., 1963. The distribution and isotopic abundance of sulphur in Recent marine sediments off southern California. *Geochim. Cosmochim. Acta*, 27:297–331.

Kennedy, J.A., and Brassell, S.C., 1992. Molecular records of twentieth century El-Niño events in laminated sediments from the Santa Barbara basin. *Nature*, 357:62–64.

Kennett, J.P., Baldauf, J.G., et al., 1994. *Proc. ODP, Init. Repts.*, 146 (Pt. 2): College Station, TX (Ocean Drilling Program).

Paull, P.K., Chanton, J.P., Neumann, C.A., Coston, J.A., and Martens, C.S., 1992. Indicators of methane-derived carbonates and chemosynthetic organic carbon deposits: examples from the Florida escarpment. *Palaios*, 7:361–375.

Peters, K.E., Sweeney, R.E., and Kaplan, I.R., 1978. Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. *Limnol. Oceanogr.*, 23:598–604.

Pisias, N.G., 1978. Paleoceanography of the Santa Barbara Basin during the last 8000 years. *Quat. Res.*, 10:366–384.

Rau, G.H., Sweeney, R.E., and Kaplan, I.R., 1982. Plankton $^{13}C/^{12}C$ ratio changes with latitude: differences between northern and southern oceans. *Deep-Sea Res.*, 29:1035–1039.

Reimers, C.E., Lange, C.B., Tabak, M., and Bernhard, J.M., 1990. Seasonal spillover and varve formation in the Santa Barbara Basin, California. *Limnol. Oceanogr.*, 35:1577–1585.

Schimmelmann, A., and Kastner, M., 1993. Evolutionary changes over the last 1000 years of reduced sulfur phases and organic carbon in varved sediments of the Santa Barbara Basin, California. *Geochim. Cosmochim. Acta*, 57:67–78.

Schimmelmann, A., Lange, C.B., and Berger, W.H., 1990. Climatically controlled marker layers in Santa Barbara basin sediments, and fine-scale core-to-core correlation. *Limnol. Oceanogr.*, 35:165–173.

Schimmelmann, A., and Tegner, M.J., 1991. Historical oceanographic events reflected in $^{13}C/^{12}C$ ratio of total organic carbon in Santa Barbara basin sediment. *Global Biogeochem. Cycles*, 5:173–188.

Scranton, M.I., Crill, P., de Angelis, M.A., Donaghay, P.L., and Sieburth, J.M., 1993. The importance of episodic events in controlling the flux of methane from an anoxic basin. *Global Biogeochem. Cycles*, 7:491–507.

Sholkovitz, E., 1973. Interstitial water chemistry of the Santa Barbara Basin sediments. *Geochim. Cosmochim. Acta*, 37:2043–2073.

Sholkovitz, E.R., and Gieskes, J.M., 1971. A physical-chemical study of the flushing of the Santa Barbara Basin. *Limnol. Oceanogr.*, 16:479–489.

Shore-based Scientific Party, 1994. Site 893. *In* Kennett, J.P., Baldauf, J.G., et al., *Proc. ODP, Init. Repts.*, 146 (Pt. 2): College Station, TX (Ocean Drilling Program), 15–50.

Soutar, A., and Crill, P.A., 1977. Sedimentation and climatic patterns in the Santa Barbara Basin during the 19th and 20th centuries. *Geol. Soc. Am. Bull.*, 88:1161–1172.