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Origins of lipid biomarkers in Santa Monica Basin surface sediment: A case study using compound-specific $\Delta^{14}C$ analysis

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Abstract—Compound-specific $\Delta^{14}C$ values are reported for 31 different lipid biomarker molecules obtained from Santa Monica Basin and Santa Barbara Basin surface sediments. These organic compounds represent phytoplanktonic, zooplanktonic, bacterial, archaeal, terrestrial higher plant, and fossil carbon sources. The lipid classes include the following: long-chain *n*-alkanes, fatty acids (as methyl esters; FAMEs), *n*-alcohols, C_{30} midchain ketols and diols, sterols, hopanols, and C_{40} isoprenoid side chains from the ether-linked glycerols of *Archaea*. The data show that the carbon source for the majority of the biomarkers is marine euphotic zone primary production or subsequent heterotrophic consumption of this biomass. A small amount of benthic incorporation of ^{14}C-depleted dissolved inorganic carbon was identified for the bacterial hopanols and C_{15} linear and branched-chain fatty acids. However, there is no apparent uptake of ^{14}C-depleted dissolved inorganic carbon in Santa Monica Basin by the bacteria, including filamentous *Beggiatoa* spp., that produce $C_{18:1\omega7}$ fatty acid. Two of the lipid classes did not reflect carbon originally fixed by marine photoautotrophs. These were the *n*-alkanes, for which the $\Delta^{14}C$ data are consistent with mixed fossil carbon and contemporary terrestrial higher plant sources, and the archaeal isoprenoids, for which the $\Delta^{14}C$ data are consistent with chemoautotrophic growth below the euphotic zone. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

Compound-specific isotopic measurements of individual lipids can help identify sources of organic carbon to marine sediments. This approach was developed to investigate the stable carbon isotopic ratios ($\delta^{13}C$) of organic materials in recent and ancient geological materials (Hayes et al., 1990). The large range of naturally occurring $\delta^{13}C$ values proved useful in identifying diverse carbon sources in many environments. For example, hopanols and archaeal lipids with $\delta^{13}C$ values near −100‰ indicate methanotrophy (e.g., Freeman et al., 1990; Hinrichs et al., 1999). Isorenieratene ($\delta^{13}C \sim -10$ to −15‰) records the presence of green sulfur bacteria (Kohnen et al., 1992; Sinninghe Damsté et al., 1993), and the C_{37} alkenones (37 carbon atoms, $\delta^{13}C \sim -24$‰) are used as phytoplanktonic tracers (e.g., Jasper and Hayes, 1990; Marlowe et al., 1990).

More recently, Eglinton et al. (1996) employed preparative capillary gas chromatography (PCGC) to isolate lipids in sufficient purity and abundance for compound-specific radiocarbon (^{14}C) measurement by accelerator mass spectrometry (AMS). By use of this approach, Eglinton et al. (1997) demonstrated that biomarkers extracted from a single sedimentary horizon have a wide range of ^{14}C concentrations. Despite being analogous to the wide range of values observed for ^{13}C, this heterogeneous ^{14}C distribution proved more difficult to interpret.

The goal of the present study was to generate a comprehensive, molecular-level $\Delta^{14}C$ data set to understand better the processes affecting sedimentary lipid ^{14}C concentrations. The work focuses on the upper 10 cm of a core from Santa Monica Basin (SMB), California, USA, and is supplemented by a core-top sample from the adjacent Santa Barbara Basin (SBB). These cores were chosen because of the availability of ancillary data and because they are "contemporary," meaning that the $\Delta^{14}C$ data record changes in the isotopic compositions of the carbon sources only, without significant in situ ^{14}C decay. The atmospheric ^{14}C concentration increased in the 1950s and 1960s as a result of above-ground tests of nuclear weapons. This "bomb ^{14}C" has invaded the surface ocean (e.g., Druffel et al., 1992) and terrestrial biota (e.g., Levin et al., 1985) and allows identification of recent biologic products. Marine biomarkers that exhibit no increase in their $\Delta^{14}C$ values when comparing "postbomb" and "prebomb" sediment horizons must be formed from a carbon pool physically removed from the influence of atmospheric CO_2—that is, in the deep ocean. In the case of terrestrial compounds, only carbon sequestered in soils for more than 50 yr will be free of the bomb ^{14}C influence; other, more recently synthesized plant litter will have $\Delta^{14}C$ values >0‰. Here we use this contrast between prebomb and postbomb $\Delta^{14}C$ values, or the relative rate of bomb ^{14}C uptake, as a primary tracer.

An initial phase of this study showed that the sedimentary sterols serve as excellent tracers of planktonic biomass and surface-water $\Delta^{14}C_{DIC}$ (Pearson et al., 2000). Now we combine the sterol data with compound-specific $\Delta^{14}C$ measurements obtained for additional biomarker classes from SMB sediments, including *n*-alkanes, fatty acids, *n*-alcohols, hopanols, C_{30}-alkan-15-one-1-ol, C_{30}-alkan-1,15-diol, and C_{40} isoprenoids of *Archaea*. These $\Delta^{14}C$ data, when combined with the $\delta^{13}C$

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values obtained by isotope ratio monitoring (IRM) gas chromatography (GC) mass spectrometry (MS) analysis, currently provide the most thorough carbon dual-isotopic assessment of the sources of organic carbon to marine sediments.

2. MATERIALS AND METHODS

2.1. Samples

Sediments were collected in November 1996 from the central SMB (33°44.0′ N, 118°50.0′ W), California, USA. An Ocean Instruments multicorer was used to collect identical 10-cm-diameter subcores in sets of eight per deployment. Details of sediment sectioning and ^{210}Pb stratigraphy were described by Pearson (2000). Discrete detrital aggregates (separate orange, green, and black particles) and filamentous sulfur bacteria constituted the majority of the surficial material. The top 0 to 1 cm of a core from SBB (34°13.5′ N, 120°03.5′ W, 595-m water depth) was also obtained.

2.2. Lipid Analysis

For each of the horizons selected for isotopic analysis (0–0.75-cm, 0.75–1.5-cm, 4.5–5.5-cm, and 5.5–8.5-cm horizons), freeze-dried samples were Soxhlet extracted with 93:7 CH_2Cl_2/CH_3OH (Fisher GC Resolv or Burdick and Jackson GC^2). A mixture of recovery standards representing the compound classes of interest was added to the total lipid extract. These were *n*-C_{21} fatty acid ($\Delta^{14}C = -389‰$) and *n*-C_{19} alcohol ($\Delta^{14}C = -999‰$). In addition, *n*-C_{33} alkane ($\Delta^{14}C = +146‰$) was added to the polar lipid fractions just before HI cleavage and $LiAlH_4$ reduction and was recovered with the archaeal isoprenoids.

The total lipid extracts were transesterified (5% HCl/CH_3OH, 70°C for 12 h) with CH_3OH of known isotopic composition ($\delta^{13}C = -51.3‰$, $\Delta^{14}C = -992.5‰$). This treatment releases bound lipids, hydrolyzes wax esters and fatty acid side chains of phospholipids (producing fatty acid methyl esters (FAMEs)), and cleaves sterol chlorin esters. Lipids were partitioned into hexane (8 × 30 mL), dried onto quartz sand, and separated into 10 fractions on a Biotage Flash 40Mi pressurized chromatography system (column: 15 cm × 40 mm, SiO_2 gel, 32–63 μm). The solvent polarity gradient was based on methods of McCaffrey (1990). The resulting samples were split into 5% for $\delta^{13}C$ analysis and 95% for $\Delta^{14}C$ analysis.

The *n*-alkanes eluted in fraction 1 (100% hexane) and were purified by urea adduction (full methods in Pearson and Eglinton, 2000). Fractions 2 to 4 contained aromatic compounds and were not used for isotopic analysis. FAMEs and ketones coeluted in 90% hexane/10% ethyl acetate (fraction 5). The two compound classes were separated by use of Varian aminopropyl-bonded SiO_2 gel (NH_2, 40 μm). Approximately 2 g of solid was equilibrated with hexane and loaded into a gravity-flow column. The samples were added in hexane and were eluted with 15 mL hexane (FAMEs) and another 15 mL hexane (polyunsaturated FAMEs; not analyzed), finishing with 15 mL 50:50 hexane:CH_2Cl_2 (ketones; not analyzed). Fraction 6, minor unidentified alcohols, was not utilized. Dinosterol, other 4-methyl-sterols, and the hopanols were separated by urea adduction from the *n*-alcohols and alkan-15-one-1-ols, all of which eluted in 80% hexane/20% ethyl acetate (fraction 7). The 4-desmethyl-sterols eluted in 75% hexane/25% ethyl acetate (fraction 8), occasionally with a small amount of the alkan-15-one-1-ols; there was no further purification of this fraction. Ether-linked membrane lipids characteristic of *Archaea* eluted in 100% ethyl acetate (fraction 9; fraction 10, 100% methanol, was not utilized). The ether linkage was cleaved by reflux in 55% HI, followed by reduction under $LiAlH_4$ following the procedure of Hoefs et al. (1997). This generated C_{40} isoprenoid hydrocarbons and a series of even carbon number *n*-alkanes.

Hydrolysis-resistant derivatives are necessary for PCGC separation and $\Delta^{14}C$ measurement. The 95% splits of each alcohol fraction were acetylated (Alltech, lot 11689, $\delta^{13}C = -27.1‰$, $\Delta^{14}C = -997‰$). Samples were dissolved in 2:1 pyridine:acetic anhydride, purged with N_2, and stirred (25°C, 12 h), then dried and dissolved in CH_2Cl_2 for PCGC separation. The contribution of derivative carbon was removed by isotopic mass balance correction.

Trimethyl-silyl derivatives of the alcohols also were prepared for accurate determination of compound-specific $\delta^{13}C$ by IRM-GC-MS. BSTFA + 1% TMS (Alltech, lot 12960, $\delta^{13}C = -45.3‰$ for carbon in the TMS group, predetermined by addition to a standard of known isotopic composition) (S. Sylva, personal communication) was mixed 1:1 with pyridine (60°C, 5 min). The contribution of derivative carbon to the $\delta^{13}C$ values was removed by mass balance. No fractionation occurs because no carbon-containing bonds are made or broken during silylation. Irregular fractionation renders acetates unacceptable derivatives for determination of compound-specific $\delta^{13}C$ by IRM-GC-MS.

2.3. High-Resolution Gas Chromatography

Routine GC analyses were performed with a HP 5890 Series II GC equipped with dual columns and flame ionization detector (FID) detectors and a Gerstel Cooled Injection System 3 (CIS-3). Capillary columns were 2 of the following (in various combinations): J&W Scientific DB-5, Chrompack CP-Sil 5CB, Restek RTX 200, all 60 m × 0.32 mm × 0.25 μm (length × inner diameter × film thickness). Samples were run by means of constant flow mode with He as the carrier gas. Temperature programs for *n*-alkane samples (in hexane) were 40°C (1 min), 4°C/min to 320°C (35 min); for FAME samples (in CH_2Cl_2), 40°C (1 min), 20°C/min to 160°C, 4°C/min to 320°C (35 min); for acetylated alcohols (in CH_2Cl_2), 40°C (1 min), 30°C/min to 120°C, 10°C/min to 260°C, 2.5°C/min to 320°C (25 min); and for ether-linked isoprenoid hydrocarbons (in hexane), 40°C (1 min), 20°C/min to 130°C, 4°C/min to 320°C (40 min). Temperature programs for alcohols in pyridine (TMS ethers for IRM-GC-MS) were 100°C (1 min), 20°C/min to 260°C, 2.5°C/min to 320°C (20 min).

2.4. GC-MS

Compound identities were confirmed either on a HP 6890 GC with attached HP 5973 mass selective detector (EI, 70eV), or on a high-resolution mass spectrometer (VG Autospec-Q hybrid MS; EI ionization energy, 70 eV) interfaced with a HP 5890 Series II GC.

Alkane, *n*-alcohol, and FAME structures were determined by examination of the mass spectra; in the case of *anteiso*- and *iso*-$C_{15:0}$ and $C_{18:1\omega7}$, authentic standards also were used. Sterols were identified as both TMS ethers and acetates. Hopanols were identified by comparing acetate-derivative mass spectra to the spectra published by McCaffrey (1990); the mass-191 ion chromatogram was also compared with the mass-191 trace published by Venkatesan et al. (1990). Alkan-1,15-diols and alkan-15-one-1-ols were identified on the basis of the previously published mass spectra of TMS ethers and acetates (e.g., de Leeuw et al., 1981; McCaffrey, 1990). C_{40} isoprenoids were identified by comparison of GC retention characteristics and individual mass spectra with the data of Hoefs et al. (1997), DeLong et al. (1998), and King et al. (1998). Example structures and nomenclature for a representative compound from each class are shown in Figure 1.

2.5. IRM-GC-MS

Compound-specific $\delta^{13}C$ values for all samples were determined in triplicate on a Finnigan Delta^{Plus} stable isotope mass spectrometer with attached Finnigan GC combustion III interface and HP 6890 GC. Samples were injected via cool on-column injection and separated on a J&W Scientific DB-5MS (60 m × 0.25 mm inner diameter × 25 μm film thickness) column equipped with a 1-m deactivated silica guard column. Isotope ratios for all peaks were calculated relative to multiple pulses of CO_2 reference gas of known isotopic composition, introduced both before and after the sample peaks of interest. The standard deviations of the replicate measurements are given individually for each peak and generally are $< \pm 0.3‰$.

2.6. PCGC

Collection of purified, individual lipids by PCGC was described in detail by Eglinton et al. (1996). A HP 5890 series II GC, equipped with HP 7673 autoinjector, Gerstel CIS-3 cooled injection system, and Gerstel preparative trapping device is fitted with a SGE BPX-5 (95% dimethyl, 5% phenyl-polysiloxane), ultralow-bleed, megabore (60 m × 0.53 mm inner diameter × 0.5 μm film thickness) capillary column. One percent of the effluent passes to the FID, and the remaining 99%

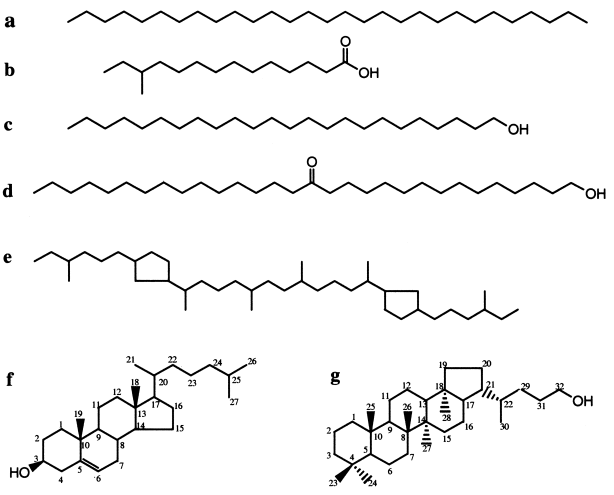

Fig. 1. Structures of and common abbreviations for representative compounds from each lipid class discussed in this work. (a) *n*-C_{29} alkane. (b) *anteiso*-$C_{15:0}$ fatty acid (*a*-$C_{15:0}$). (c) *n*-$C_{24:0}$ alcohol (C_{24}-OH). (d) C_{30}-alkan-15-one-1-ol. (e) Archaeal C_{40} isoprenoid with two pentacyclic rings ($C_{40:2cy}$). (f) cholest-5-en-3β-ol (cholesterol, $C_{27}\Delta 5$). (g) (22*R*)-17β(H),21β(H)-bishomohopan-32-ol (C_{32} hopanol).

is collected in a series of seven U-tube traps. Six traps collect compounds of interest, and the seventh receives the remainder of the mixture. This configuration was used for all FAME and alcohol samples. GC temperature programs for FAME samples (in CH_2Cl_2) were 40°C (1 min), 20°C/min to 160°C, 4°C/min to 320°C (28 min); and for alcohols (in CH_2Cl_2), 40°C (1 min), 20°C/min to 270°C, 2.5°C/min to 320°C (25 min). The preparative trapping device was operated at 320°C and the U-tube traps at room temperature for alcohol samples. FAMEs smaller than the *n*-$C_{21:0}$ FAME standard were collected with the U-tube traps chilled to 0°C to prevent volatile losses.

The *n*-alkane samples were separated with a Chrompak CP-Sil 5 CB capillary column as described in Pearson and Eglinton (2000). The U-tube traps were left at room temperature because no compounds with carbon number below *n*-C_{24} were collected. The C_{40} isoprenoid hydrocarbons and *n*-C_{30} alkane (from reduction of C_{30}-alkan-1,15-diol, fraction 9) were isolated with an Alltech 1-m multicapillary column (film thickness 0.2 μm, 900 microscopic capillaries in a bundle with overall diameter ~3 mm). The GC temperature program was 40°C (0.5 min) and 20°C/min to 280°C (7 min), at a He flow rate of 60 mL/min.

Purified compounds, especially those with carbon number $\geq$30, often had a faint yellow-orange color. The source of this color was probably column bleed that had migrated into the traps. To remove this component, samples were purified (for all $\geq C_{24}$ biomarkers reported here) by eluting with 10% ethyl acetate/hexane through SiO_2 gel columns (prepared in Pasteur pipettes, then combusted at 450°C, 8 h); *n*-alkanes and C_{40} isoprenoids were eluted with hexane only. The faint color was retained on the SiO_2 gel.

2.7. AMS

Samples were sealed in evacuated quartz tubes with 100 mg CuO, combusted to CO_2 (850°C, 5 h), and reduced to graphite over cobalt catalyst. ^{14}C-AMS analysis was performed by means of special methods for the accurate determination of Δ^{14}C in small samples (von Reden et al., 1998). For our samples, which all have known geochronological ages, the reported $\Delta^{14}C = 1000[f_m e^{(1950-x)\lambda} - 1]$ (Stuiver and Polach, 1977), where λ is 1/8267 (yr^{-1}), f_m is the fraction of modern ^{14}C corrected for isotopic fractionation by use of δ^{13}C, and x is the year of deposition (determined from the ^{210}Pb chronology). This removes the effects of in situ ^{14}C decay and normalizes the Δ^{14}C data to the values each sample would have had when deposited at the sediment–water interface.

The amount of carbon converted to graphite for ^{14}C-AMS analysis averaged 55 μg C (range, 19–172 μg C; median, 47 μg C). The FAME fraction from the SMB 0- to 0.75-cm horizon was sufficiently concentrated to allow collection of two separate PCGC batches, yielding nine samples representing eight different FAMEs. To provide an independent replicate, *a*-$C_{15:0}$ FAME was collected in both batches. Also, for several compounds (e.g., trap AS-2, $C_{16:0}$ FAME), the large quantity of recovered material was made into two separate AMS graphite targets. These identical replicates were used to assess the internal variability in Δ^{14}C results due to AMS performance. Δ^{14}C values for replicates differed by 16‰, on average (range, 9–21‰). This is slightly larger than the AMS measurement errors, which typically are about $\pm$15‰.

Δ^{14}C values determined for PCGC recovery standards also were used to evaluate the accuracy of the data. Three measurements of *n*-C_{19}-OH standard had Δ^{14}C values of −990‰, −990‰, and −988‰. This indicated that no more than 1% of any contaminant carbon was of modern origin. However, most of our analytical considerations implicated dead carbon ($\Delta^{14}C = -1000$‰) contaminants. These components are invisible in a ^{14}C-dead standard. Two measurements for $C_{21:0}$ fatty acid recovery standard yielded Δ^{14}C values of −353‰ and −366‰. These values represent 36‰ and 23‰ enrichment in ^{14}C compared with pure, combusted $C_{21:0}$ fatty acid (−389‰). There was no apparent negative Δ^{14}C bias from "dead" contaminant carbon.

3. RESULTS

3.1. Sediment Core Chronology

Suboxic bottom waters in SMB and SBB result in the deposition of laminated sediments. The absence of bioturbation allows decadal resolution of the changes in sedimentary ^{14}C concentrations. Details of the Δ^{14}C values obtained for bulk total organic carbon (TOC), planktonic foraminifera, and benthic foraminifera in the central SMB were reported in Pearson et al. (2000). Benthic foraminiferal data established that the Δ^{14}C of bottom water dissolved inorganic carbon (DIC) has remained nearly constant during the last century, whereas surface ocean $\Delta^{14}C_{DIC}$ varied. The latter reached a maximum in the middle 1970s, about 10 yr after the maximum in atmospheric $^{14}CO_2$ concentration caused by atmospheric testing of nuclear weapons.

Calendar dates based on excess ^{210}Pb activity were assigned to the horizons of the SMB core. This chronology agreed with previously published rates of sediment accumulation (Huh et al., 1987; Christensen et al., 1994) and laminae counts based on X-ray stratigraphy (Hagadorn et al., 1995). Bomb ^{14}C was present between 0 and 2.5 cm. The calendar years assigned to the 1.5- to 2.5-cm horizon (1961–1985) also correctly placed the maximum bomb ^{14}C entrainment in this interval. The Δ^{14}C of TOC had a constant value of $\sim$ −155‰ before 1960 (beneath 2.5 cm). Although the entire core represents very little time in comparison to the half-life of ^{14}C (5730 yr), minor decay corrections were applied to all reported Δ^{14}C values by use of the ^{210}Pb chronology.

The 0- to 1-cm core top obtained from SBB is equivalent to 0- to 3-yr sedimentation, consistent with the report of Schimmelmann and Tegner (1991).

3.2. ORGANIC GEOCHEMICAL ANALYSIS

The organic fractions selected for isotopic analysis are described below. The following figures represent the samples obtained from SMB surface sediment (0–0.75 cm), unless otherwise noted. A brief description of each sample is given, and the individual compounds isolated for Δ^{14}C measurement are indicated.

3.2.1. Sediment Horizons for Compound-Specific Isotopic Analysis

The primary goal of this work was to compare $\Delta^{14}C$ values for identical or related biomarkers extracted from both postbomb and prebomb sedimentary horizons. Depending on initial concentrations of the biomarkers and other analytical considerations, the selection of horizons varied. Because *n*-alkanes were present in very low concentrations, the core was divided into postbomb (0–2.5 cm) and prebomb material (2.5–7.5 cm) to assure enough carbon in each sample. For fatty acids and sterols, a single prebomb sediment horizon (4.5–5.5 cm) and the surface horizon (0–0.75 cm) were chosen. The remaining *n*-alcohol, ketol, diol, and hopanol data were obtained from the 0.75- to 1.5-cm (postbomb) and 5.5- to 8.5-cm (prebomb) horizons. The prebomb archaeal lipid data are from the SMB 5.5- to 8.5-cm horizon; low abundance and reaction yields for the archaeal lipids did not allow ^{14}C measurements for a SMB postbomb horizon, so $\Delta^{14}C$ data for SBB 0- to 1-cm archaeal lipids are reported instead.

3.2.2. *n*-Alkanes

The total aliphatic hydrocarbon fraction from SMB 0- to 2.5-cm (postbomb) sediment was described previously by Pearson and Eglinton (2000). The total mixture was characterized by the presence of an abundant unresolved complex mixture that obscured the *n*-alkanes. Purification by urea adduction with subsequent removal of linear alkenes by elution through $AgNO_3$ yielded a sample for isotopic analysis that contained a homologous series of *n*-alkanes. Similar results were obtained for the prebomb (2.5–7.5 cm) aliphatic hydrocarbon fraction. In both surface and deeper sediments, the *n*-alkanes were present at concentrations of less than 1 μg per gram of dry weight (gdw), less abundant than the other classes of lipids analyzed in the rest of this study. In both horizons, there was a strong odd over even predominance, and *n*-C_{29} was the most abundant compound.

3.2.3. Fatty Acids

Figure 2a shows the fatty acids (as FAMEs) from the SMB 0- to 0.75-cm sample, after the ketones and polyunsaturated fatty acids were removed from the original fraction. Fatty acids were the most abundant SMB biomarkers studied in SMB sediments (Fig. 2b), with concentrations of 5 to 40 μg/gdw in the surface horizon, decreasing to 1 to 10 μg/gdw at 4.5 to 5.5 cm. The mixtures were dominated by the common planktonic and bacterial lipid, palmitic acid ($C_{16:0}$), and also show strong $C_{14:0}$ and $C_{18:0}$ peaks. In both the surface and deep horizons, the $C_{14:0}$ and $C_{18:0}$ concentrations are not enriched relative to $C_{16:0}$. The surface horizon also showed a strong contribution of fatty acids characteristic of bacterial sources, especially the monounsaturated $C_{16:1\omega7}$ and $C_{18:1\omega7}$ isomers; these compounds were much less abundant at depth. Branched-chain (*iso*- and *anteiso*-) $C_{15:0}$—and to a lesser extent, $C_{13:0}$ and $C_{17:0}$, fatty acids typical of gram-positive bacteria (Kaneda, 1991)—also were present in both samples, and their relative concentrations did not vary greatly with depth in the sediment.

High-molecular-weight fatty acids ($>C_{20}$) occurred in both horizons as homologous series with even over odd predominance. These compounds were relatively enriched in extracts from the 4.5- to 5.5-cm horizon when compared with the 0- to 0.75-cm horizon, in contrast to the planktonic and bacterial fatty acids. The two series otherwise are identical in even–odd preference and distribution (maximum at $C_{24:0}$).

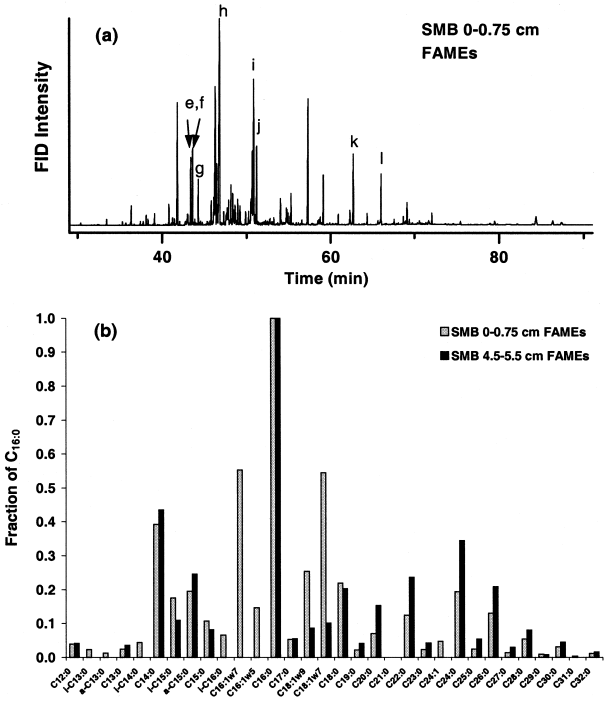

Fig. 2. (a) FAME fraction from the SMB 0- to 0.75-cm horizon; letters identify compounds collected by PCGC for ^{14}C-AMS analysis (Table 1). (b) Abundance of fatty acids (as FAMEs) relative to $C_{16:0}$.

3.2.4. Alcohols

Figures 3 and 4 show representative chromatograms of the alcohol fractions used in this study. Urea adduction was used to split fraction 7 into straight-chain components (*n*-alcohols and ketols; Fig. 3a) and branched-chain and cyclic structures (4-methylsterols and hopanols; Fig. 3b). The absolute abundance of all alcohols decreased at depth, with approximately 1 to 20 μg/gdw in the surface sediments and 0.1 to 10 μg/gdw below 5 cm. Concentrations of these alcohols relative to C_{24}-OH are shown in Figure 3c.

The *n*-alcohols are characterized by high even–odd predominance with a maximum at C_{24} for the postbomb 0.75- to 1.5-cm sample, but with a maximum at C_{22} for the prebomb 5.5- to 8.5-cm sample. Qualitative evaluation of the additional SMB 0- to 0.75-cm and 4.5- to 5.5-cm horizons suggested this was a general trend, with C_{24} more abundant toward the sediment–water interface and C_{22} enriched at depth. The relative concentrations of zooplanktonic (Sargent et al., 1977) *n*-alcohols (C_{16}, C_{18}) did not change with respect to C_{24} between the two horizons. C_{30}-alkan-15-one-1-ol and the C_{31} and C_{32} hopanols (hopan-31-ol and hopan-32-ol) are relatively more concentrated in the deeper horizon, in contrast to the C_{30} hopanol (hopan-29-ol) and especially tetrahymanol (gammaceran-3β-ol), which are more abundant in the near-surface horizons.

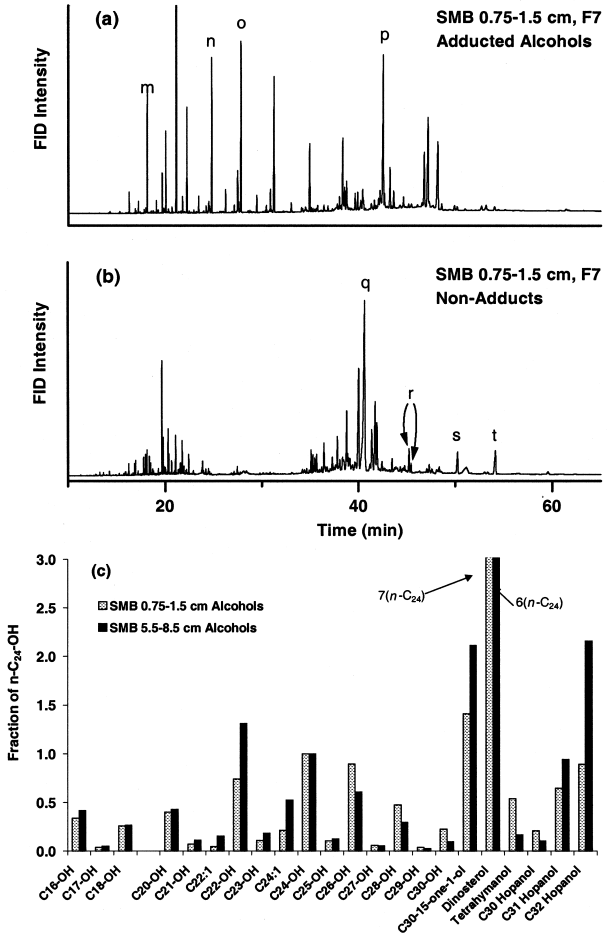

Fig. 3. Alcohols from the SMB 0.75- to 1.5-cm horizon. (a) Linear alcohol and (b) nonadducted fractions obtained after urea adduction of fraction 7 alcohols. Letters identify compounds collected by PCGC for ^{14}C-AMS analysis (Table 1). (c) Relative abundance of *n*-alcohols, C_{30}-alkan-15-one-1-ol, dinosterol, and hopanols in SMB sediments.

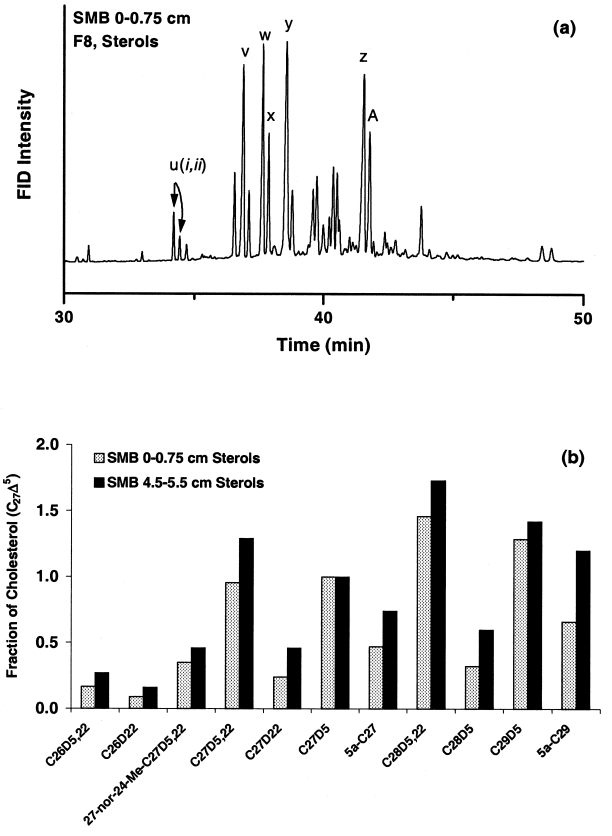

Fig. 4. (a) 4-Desmethyl-sterols (fraction 8) from the SMB 0- to 0.75-cm horizon; letters identify compounds collected by PCGC for ^{14}C-AMS analysis (Table 1). (b) Relative abundance of sterols in SMB sediments.

A partial gas chromatogram of the SMB 0- to 0.75-cm 4-desmethyl-sterols (fraction 8) is shown in Figure 4a. The sterol distributions in the SMB sediment horizons and the SBB 0- to 1-cm sample were described in Pearson et al. (2000). Figure 4b shows the concentrations of the major sterols in the SMB samples relative to cholesterol. For both horizons, $C_{28}\Delta^{5,22}$, $C_{29}\Delta^{5}$, and dinosterol were more abundant than cholesterol, and $C_{27}\Delta^{5,22}$ and 5α-C_{29} exceeded cholesterol in the deeper SMB horizon only. Concentrations ranged from ~2 to 20 μg/gdw at the sediment–water interface and from 0.5 to 5 μg/gdw at 4.5 to 5.5 cm. The stanol/stenol ratios for isomeric pairs (e.g., 5α-C_{27}/$C_{27}\Delta^{5}$) also increased in the deeper horizon. The concentrations of sterols in SBB 0- to 1-cm sediment were three times greater than for SMB 0 to 0.75 cm; cholesterol was the most abundant.

3.2.5. Diols and Archaeal Ether Lipids

The polar lipid fraction containing ether-linked lipids of *Archaea* is shown in Figure 5. The chromatogram in Figure 5a shows this material after HI cleavage of the ether linkages and reduction by use of $LiAlH_4$. Chromatograms from both the SMB prebomb and postbomb samples were similar. A regular series of alkanes, probably derived from the reduction of linear midchain diols, also is observed. These compounds have very high even–odd predominance, and although the maximum occurs at *n*-C_{30}, the distribution is weighted toward lower carbon numbers. Above C_{30}, there is only a small amount of C_{32}, and the concentration of C_{34} is less than the concentration of C_{20}.

Four biphytanes (C_{40} isoprenoids) derived from the membrane lipids of *Archaea* were observed in both samples. The concentrations of these lipids relative to C_{30}-1,15-diol (reduced to *n*-C_{30} alkane) are shown in Figure 5b. The C_{40} isoprenoids are present in low concentrations (~1 μg/gdw) relative to other sedimentary biomarkers such as the sterols and fatty acids. However, their concentration is enriched relative to C_{30}-1,15-diol in the deeper horizon, perhaps reflecting enhanced preservation.

The abundance of archaeal lipids in the SMB 0- to 0.75-cm horizon was not high enough for compound-specific ^{14}C analysis, but enough material was obtained from the prebomb SMB 5.5- to 8.5-cm horizon. Archaeal lipids from the SBB 0- to 1-cm horizon were analyzed for the postbomb isotopic comparison. The distribution of archaeal lipids was identical in the SBB sample, but the absolute concentration was ten times higher than in SMB.

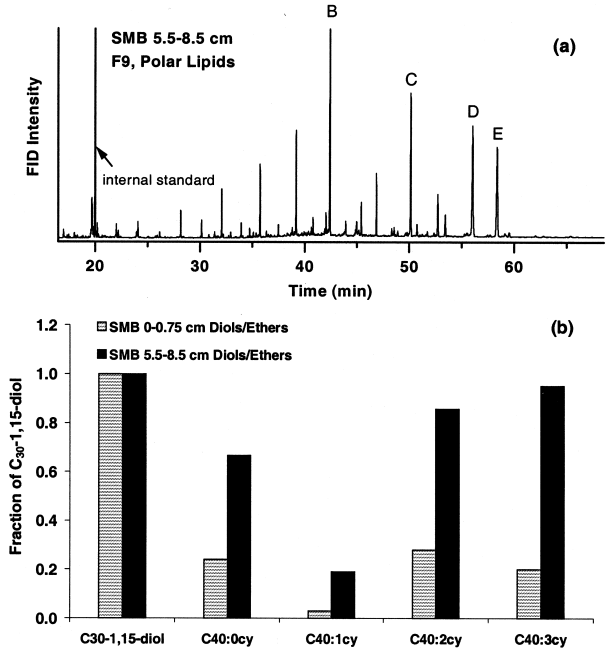

Fig. 5. Total diols and archaeal ether-linked isoprenoid lipids. (a) Hydrocarbon fraction generated by HI cleavage and $LiAlH_4$ reduction of the SMB 5.5- to 8.5-cm polar lipid fraction; letters identify compounds collected by PCGC for ^{14}C-AMS analysis (Table 1). (b) Relative abundance of C_{30}-alkan-1,15-diol and C_{40} isoprenoid lipids of *Archaea* in SMB sediment.

3.3. $\Delta^{14}C$ Data

The $\Delta^{14}C$ data for SMB and SBB individual biomarker lipids are presented in Table 1. The data are organized by organic compound class and divided into postbomb and prebomb samples. This highlights the changes in biomarker $\Delta^{14}C$ values due to the uptake of bomb ^{14}C. In the cases where identical compounds were recovered from both prebomb and postbomb sedimentary horizons, the difference in $\Delta^{14}C$ between each prebomb/postbomb pair is reported in the right-hand column as $\Delta(\Delta^{14}C)$.

The following sections are organized by organic compound class and describe the general characteristics of the $\Delta^{14}C$ data. These features can be summarized as follows: most lipids from SMB postbomb sediment have $\Delta^{14}C$ values similar to the $\Delta^{14}C$ of surface-water DIC; and the lipids with $\Delta^{14}C$ values that vary from this pattern belong to distinct compound classes. (For the temporal evolution of SMB surface water $\Delta^{14}C_{DIC}$, see Pearson et al. (2000).)

3.3.1. n-Alkanes

The *n*-alkanes represent the only lipid class for which the $\Delta^{14}C$ values of homologous compounds varied greatly. A complete treatment of the data was given in Pearson and Eglinton (2000). The prebomb, odd-chain *n*-alkanes had $\Delta^{14}C$ values between −223‰ (*n*-C_{27}) and −122‰ (*n*-C_{29}), whereas the postbomb, odd-chain *n*-alkanes had an even larger $\Delta^{14}C$ range, −243‰ (*n*-C_{27}) to +30‰ (*n*-C_{29}). The composite sample of even-numbered (*n*-$C_{24+26+28+30}$) alkanes from postbomb sediment was more ^{14}C depleted (−741‰) than the equivalent sample from prebomb sediment (−617‰).

3.3.2. Fatty Acids

The $\Delta^{14}C$ value for palmitic acid ($C_{16:0}$) from prebomb sediment (−76 ± 14‰) agrees within measurement error with the composite estimate of prebomb surface-water $\Delta^{14}C_{DIC}$ (−82‰). The $\Delta^{14}C$ values for $C_{16:0}$ and $C_{18:0}$ (+86 ± 11‰ and +83 ± 14‰, respectively) from the surface, postbomb sediment are slightly ^{14}C enriched relative to 1996 surface-water $\Delta^{14}C_{DIC}$ (+71‰). However, because this sedimentary horizon integrates ~5- to 10-yr material and $\Delta^{14}C_{DIC}$ in this region was > +80‰ as recently as 1990, these values also are consistent with the ^{14}C concentration of surface-water DIC. The $\Delta^{14}C$ value of *cis*-vaccenic acid ($C_{18:1\omega7}$) from postbomb sediment (+64 ± 11‰) also is not significantly different from +71‰. In both horizons, therefore, the ^{14}C concentrations of C_{16} and C_{18} fatty acids reflect carbon originating from the euphotic zone.

The branched-chain fatty acids, *i*-$C_{15:0}$ and *a*-$C_{15:0}$, as well as the linear $C_{15:0}$, derive primarily from bacterial sources (e.g., Perry et al., 1979). Only one prebomb $\Delta^{14}C$ value is available, −113 ± 14‰ for *a*-$C_{15:0}$. This number is significantly less than the prebomb surface-water $\Delta^{14}C_{DIC}$ (−82‰). The same effect is observed for the postbomb C_{15} fatty acids: $\Delta^{14}C$ values for *i*-$C_{15:0}$, *a*-$C_{15:0}$, and $C_{15:0}$ range between +32‰ and +44‰. The average value, +35‰, although still containing bomb ^{14}C, also is lower than contemporary surface-water DIC (+71‰).

Data for the long-chain fatty acids from both prebomb and postbomb sedimentary horizons show that $C_{26:0}$ is more ^{14}C depleted than $C_{24:0}$. The measured values (+62‰ and −69‰) for $C_{24:0}$ agree within measurement errors with the estimated $\Delta^{14}C_{DIC}$ end members, +71‰ and −82‰. However, the $\Delta^{14}C$ values measured for $C_{26:0}$ (+14‰ and −108‰) are ^{14}C depleted relative to $\Delta^{14}C_{DIC}$ and therefore contain a portion of preaged carbon.

3.3.3. n-Alcohols, C_{30}-alkan-15-one-1-ol, and C_{30}-alkan-1,15-diol

The SMB 0.75- to 1.5-cm horizon approximately corresponds to the years 1985 to 1990, and SMB surface-water $\Delta^{14}C_{DIC}$ during this time was higher than the present-day +71‰. A reasonable estimate for the range of $\Delta^{14}C_{DIC}$ during this time, made on the basis of a linear decrease from a value of +109‰ in 1980 (Williams et al., 1992), is ~ +95‰ in 1985 to ~ +83‰ in 1990. The $\Delta^{14}C$ values for C_{22} and C_{24} alcohols (+85 ± 11‰, +88 ± 10‰) fall within this range. The single value for C_{16}-OH is slightly lower (+69 ± 10‰) than the predicted range of surface-water $\Delta^{14}C_{DIC}$, but it is still very modern. The prebomb $\Delta^{14}C$ values for C_{22} and C_{24} alcohols (−41 ± 13‰ and −59 ± 15‰) are somewhat ^{14}C enriched compared with prebomb SMB surface-water DIC (−82‰).

Two $\Delta^{14}C$ values were obtained for C_{30}-alkan-15-one-1-ol in postbomb sediments. Some of this compound eluted and was recovered with the SMB 0- to 0.75-cm desmethyl-sterol lipid fraction ($\Delta^{14}C$ = +58 ± 18‰), whereas a second sample was obtained from the SMB 0.75- to 1.5-cm alcohol fraction ($\Delta^{14}C$ = +72 ± 11‰). The first value is potentially contaminated with a small amount of column bleed (no clean-up was

Table 1. Summary of compound-specific $\Delta^{14}C$ and $\delta^{13}C$ data; the $\delta^{13}C$ values are based on *irm*-GC-MS measurements unless otherwise indicated

		Postbomb			Prebomb			
Biomarker		Horizon (cm)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	Horizon (cm)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	$\Delta(\Delta^{14}C)$
n-Alkanes								
n-$C_{24+26+28+30}$	a	0–2.5	−30.0 ± 0.5	−741 ± 16	2.5–7.5	−30.5 ± 0.5	−617 ± 11	*−124*
n-C_{27}	b	0–2.5	−30.5 ± 0.1	−243 ± 20	2.5–7.5	−30.7 ± 0.1	−223 ± 17	*−20*
n-C_{29}	c	0–2.5	−31.3 ± 0.2	+30 ± 17	2.5–7.5	−31.9 ± 0.1	−122 ± 7	+151
n-C_{31}	d	0–2.5	−32.0 ± 0.1	−113 ± 19	2.5–7.5	−33.0 ± 0.1	−170 ± 15	+57
FAMEs								
i-$C_{15:0}$	e	0–0.75	−23.2 ± 0.1	+33 ± 15	4.5–5.5	−25.9 ± 0.2	—	—
a-$C_{15:0}$	f	0–0.75	−24.1 ± 0.2	+32 ± 12[a]	4.5–5.5	−30.6 ± 0.6, −24.6[b]	−113 ± 14	+145
$C_{15:0}$	g	0–0.75	−24.0 ± 0.2	+44 ± 13	4.5–5.5	−26.5 ± 0.6	—	—
$C_{16:0}$	h	0–0.75	−25.0 ± 0.3	+86 ± 11[a]	4.5–5.5	−26.3 ± 0.2	−76 ± 14	+162
$C_{18:1\omega7}$	i	0–0.75	−23.2 ± 0.3, −27.2[b]	+64 ± 11	4.5–5.5	−26.4 ± 0.2	—	—
$C_{18:0}$	j	0–0.75	−24.1 ± 0.2	+83 ± 14	4.5–5.5	−26.3 ± 0.5	—	—
$C_{24:0}$	k	0–0.75	−26.4 ± 0.2	+62 ± 14	4.5–5.5	−26.3 ± 0.2	−69 ± 15	+131
$C_{26:0}$	l	0–0.75	−26.8 ± 0.4	+14 ± 13	4.5–5.5	−26.7 ± 0.2	−108 ± 19	+122
n-Alcohols								
C_{16}-OH	m	0.75–1.5	−27.6 ± 0.5	+69 ± 10	5.5–8.5	—	—	—
C_{22}-OH	n	0.75–1.5	−28.2 ± 0.3	+85 ± 11	5.5–8.5	−29.6 ± 0.5	−41 ± 13	+126
C_{24}-OH	o	0.75–1.5	−28.7 ± 0.3	+88 ± 10	5.5–8.5	−29.0 ± 0.5	−59 ± 15	+147
C_{30}-alkan-15-one-1-ol	p	0–0.75, 0.75–1.5	−31.6 ± 0.3	+58 ± 18, +72 ± 11	3.5–4.5	−30.9 ± 0.3	−95 ± 17	+153, +167
Sterols/hopanols								
Dinosterol	q	0–0.75	−23.4 ± 0.1, −26.6[b]	+71 ± 14[a]	4.5–5.5	−24.4 ± 0.2	−88 ± 14	+159
Tetrahymanol/C_{30} hopanol	r	0.75–1.5	−24.5[b]	+47 ± 12	—			—
C_{31} hopanol	s	—	—	—	5.5–8.5	−24.0[b]	−96 ± 15	—
C_{32} hopanol	t	0.75–1.5	−24.9[b]	+16 ± 11	5.5–8.5	−26.1[b]	−134 ± 18	+150
$C_{26}\Delta^{5,22}+\Delta^{22}$	u	0–0.75	−27.6 ± 0.8	+62 ± 19	4.5–5.5	−26.9 ± 1.4	—	—
$C_{27}\Delta^{5,22}$	v	0–0.75, 0–1[c]	−24.9 ± 0.1, −24.3 ± 0.1[c]	+71 ± 10, +50 ± 11[c]	4.5–5.5	−25.4 ± 0.2	—	—
$C_{27}\Delta^{5}$	w	0–0.75, 0–1[c]	−24.9 ± 0.2, − 23.9 ± 0.2[c]	+72 ± 10[a], +70 ± 10[c]	4.5–5.5	−23.8 ± 0.1	−64 ± 23	+136, +134
5α-$C_{27}\Delta^{0}$	x	0–1[c]	−24.7 ± 0.2[c]	+61 ± 10[c]				
$C_{28}\Delta^{5,22}$	y	0–0.75, 0–1[c]	−26.6 ± 0.2, −25.9 ± 0.1[c]	+58 ± 11, +71 ± 14[c]	4.5–5.5	−25.2 ± 0.1	−61 ± 15	+119, +132
$C_{29}\Delta^{5}$	z	0–0.75, 0–1[c]	−25.5 ± 0.2, −24.4 ± 0.2[c]	— +72 ± 10[c]	4.5–5.5	−25.3 ± 0.1	−59 ± 20	+131
5α-$C_{29}\Delta^{0}$	A	0–0.75, 0–1[c]	−25.5 ± 0.2, −25.4 ± 0.2[c]	+90 ± 15, +93 ± 19[c]	3.5–4.5 4.5–5.5	−25.3 ± 0.1	−102 ± 20, −73 ± 9	+177, +166
Diols and archaeal lipids								
n-C_{30} (diol)	B	—	—	—	5.5–8.5	−33.5 ± 0.4	−101 ± 20	—
$C_{40:0cy}$	C	—	—	—	5.5–8.5	−20.8 ± 0.4	−123 ± 35	—
$C_{40:2cy}$	D	0–1[c]	−22.1 ± 0.4[c]	−101 ± 21[c]	5.5–8.5	−20.3 ± 0.4	−141 ± 24	+40
$C_{40:3cy}$	E	0–1[c]	−22.5 ± 0.4[c]	−100 ± 25[c]	5.5–8.5	−20.5 ± 0.4	−121 ± 21	+21

[a] Average of two $\Delta^{14}C$ values.
[b] $\delta^{13}C$ determined by off-line irMS on splits of CO_2.
[c] Samples from SBB 0–1-cm sediment.

performed), but the second measurement represents a sample that was isolated and measured under optimal PCGC preparative and AMS analytical conditions. The surface-water $\Delta^{14}C_{DIC}$ values at the time of sediment deposition, +71‰ for SMB 0 to 0.75 cm and +83 to +95‰ for SMB 0.75 to 1.5 cm, are slightly higher than the measured $\Delta^{14}C$ values for this lipid, but insignificantly different when the measurement errors are considered.

Two $\Delta^{14}C$ values also were obtained for C_{30}-alkan-15-one-1-ol and C_{30}-alkan-1,15-diol in prebomb sediments. One is a measurement obtained from a methods development sample (SMB 3.5–4.5 cm). This alkan-15-one-1-ol did not receive a column bleed clean-up step, so the measured $\Delta^{14}C = -95 \pm 17$‰ is considered a minimum value, but it is within measurement error of prebomb surface-water $\Delta^{14}C_{DIC}$ (−82‰). The other prebomb data point is the one sample of *n*-C_{30} alkane isolated with the archaeal ether lipids (SMB 5.5–8.5 cm; $\Delta^{14}C = -101 \pm 20$‰). This compound is believed to derive from the reduction of C_{30}-alkan-1,15-diol with $LiAlH_4$. This sample also is slightly ^{14}C depleted relative to prebomb surface water. Again, these differences may be insignificant, considering the large error bars associated with the measurements.

3.3.4. Sterols

The 4-desmethyl-sterol data were presented extensively in Pearson et al. (2000). Three PCGC batches (two from SMB

0–0.75 cm and one from SBB 0–1 cm) were obtained from surface sediments. Statistical analysis showed that the results from the first SMB batch were significantly different ($p < 0.05$) from the other two batches, probably due to the use of a new PCGC column exhibiting greater column bleed; this series subsequently was eliminated. Average $\Delta^{14}C$ values for the sterols in these sediments (SMB, +73 ± 12‰; SBB, +69 ± 14‰) are identical to the measured 1996 surface-water $\Delta^{14}C_{DIC}$ (+71‰) and reflect marine phytoplanktonic and zooplanktonic production. All of the individual compounds are insignificantly different from surface-water $\Delta^{14}C_{DIC}$, with the possible exception of 5α-C_{29}, which is slightly ^{14}C enriched (+90‰ and +93‰ in SMB and SBB, respectively) relative to the other structures.

For the 5 sterols studied in SMB prebomb sediment, the data ranged from −59‰ to −102‰ and averaged −75 ± 19‰. This average is close to the estimated prebomb surface-water $\Delta^{14}C_{DIC}$ (−82‰). The sterols in both pre and postbomb sedimentary horizons consistently reproduce the $\Delta^{14}C$ of surface-water DIC.

3.3.5. Hopanols

Analytically, the hopanols were difficult to obtain by PCGC. Separation of tetrahymanol and C_{30} hopanol was not possible because the two compounds partially coeluted. The high boiling points of these compounds also resulted in problems with low recoveries. $\Delta^{14}C$ data of sufficient quality were obtained for hopanols from the SMB 0.75- to 1.5-cm and SMB 5.5- to 8.5-cm sediment horizons. Clean-up procedures to remove column bleed were performed for both sets of samples.

The SMB 0.75- to 1.5-cm tetrahymanol plus C_{30} hopanol ($\Delta^{14}C = +47 \pm 12$‰) and C_{32} hopanol ($\Delta^{14}C = +16 \pm 11$‰) samples have positive $\Delta^{14}C$ values reflecting bomb ^{14}C incorporation. However, these values are significantly lower than the predicted $\Delta^{14}C_{DIC}$ for this horizon (~ +83 to +95‰). ^{14}C depletion also was observed for the C_{32} hopanol (−134 ± 18‰) and C_{31} hopanol ($\Delta^{14}C = -96 \pm 15$‰) samples from prebomb sediments, although the latter is only slightly ^{14}C depleted relative to prebomb surface-water DIC (−82‰).

3.3.6. Archaeal Lipids

The archaeal lipids isolated for $\Delta^{14}C$ analysis were the acyclic $C_{40:0}$ isoprenoid and the isomers containing 2 and 3 cyclopentane rings ($C_{40:2cy}$ and $C_{40:3cy}$; for structures, see Schouten et al., 2000). All three compounds obtained from the SMB prebomb (5.5–8.5 cm) sediment horizon exhibited $\Delta^{14}C$ values (−121‰ to −141‰) that were equivalent within measurement error. There was not enough material to collect these lipids from SMB surface sediments. However, $\Delta^{14}C$ values were obtained for $C_{40:2cy}$ and $C_{40:3cy}$ extracted from the SBB 0- to 1-cm horizon. These two C_{40} compounds yielded equivalent $\Delta^{14}C$ values, −100‰ and −101‰.

The large error bars associated with these difficult measurements make both data sets statistically equal in ^{14}C concentration. The $\Delta^{14}C$ values for the SBB 0- to 1-cm samples also show that the archaeal isoprenoids are the only lipid class presented here that contains no bomb ^{14}C. Because bomb ^{14}C has penetrated the water column in the Northeast Pacific Ocean to a depth of >200 m, the carbon in these lipids originates from an environment removed from the influence of surface-water processes.

4. DISCUSSION

4.1. Carbon Isotope Distributions

The arrangement of the compound-specific isotopic data in Table 1 can be used to examine patterns within the entire data set. The individual $\Delta^{14}C$ values are shown in Figure 6. This distribution by organic compound class allows discrimination among the different biologic sources and/or biosynthetic pathways of carbon incorporation for these lipids. The $\Delta^{14}C$ axis serves as an index of the end-member $\Delta^{14}C$ values and especially of the relative amount of bomb ^{14}C contained within each sample.

The solid line near the top of Figure 6 is the $\Delta^{14}C$ value we measured for SMB surface-water DIC in 1996 (+71‰). The solid symbols all represent compounds isolated from sedimentary horizons deposited between 1965 and the present (0–2.5 cm). One distinct characteristic of the data is that most of these lipids, including fatty acids, linear alcohols, and isoprenoid alcohols, have $\Delta^{14}C$ values > 0‰ in the postbomb sedimentary horizons. (The archaeal and *n*-alkane data are the only exceptions.) The presence of bomb ^{14}C indicates that these lipids are all derived from contemporary biomass production. These lipid classes, shown on the left-hand side of Figure 6, cluster around the $\Delta^{14}C_{DIC} = +71$‰ line. The same uniformity in $\Delta^{14}C$ values is observed for the lipids from prebomb sediments (deeper than 2.5 cm). The sterols, hopanols, linear alcohols, and fatty acids generally fall within ±25‰ of prebomb $\Delta^{14}C_{DIC}$ (−82‰, dashed line).

The other two lipid classes studied, *n*-alkanes and archaeal ether-linked isoprenoids, did not follow the general pattern of $\Delta^{14}C_{prebomb} \sim -80$‰ and $\Delta^{14}C_{postbomb} \sim +70$‰. The *n*-alkanes clearly behaved differently from the other biomarker classes with respect to mechanisms of bomb ^{14}C incorporation. The $\Delta^{14}C$ values for two of the *n*-alkane samples were more ^{14}C depleted in the postbomb sediment. This signals that at least one component of the *n*-alkane series does not contain bomb $^{14}CO_2$. Also, the proportion of this component is higher in the SMB 0- to 2.5-cm horizon than it is in the prebomb sediment, possibly due to a higher influx of anthropogenic petroleum sources (Pearson and Eglinton, 2000).

In contrast, the archaeal lipids appear to have experienced little or no change in ^{14}C concentration over time. Within the uncertainties caused by comparing the data between samples from different locations (SMB and SBB), the prebomb and postbomb $\Delta^{14}C$ values remain essentially constant. Specifically, there is no bomb ^{14}C component to the SBB surface sedimentary (0–1 cm) archaeal lipids. These values are in sharp contrast to the bomb ^{14}C uptake within SBB and SMB fatty acids and sterols.

It is not surprising that the main feature that distinguishes the surface sedimentary lipids from the lipids of deeper horizons is the presence of bomb ^{14}C. What is surprising, perhaps, is the uniformity of this change in ^{14}C concentration for most of the biomarkers analyzed. Only the *n*-alkane and archaeal lipid classes are distinguished by their unusual rate of change in $\Delta^{14}C$, or their $\Delta(\Delta^{14}C)$. This $\Delta(\Delta^{14}C)$ parameter can be added,

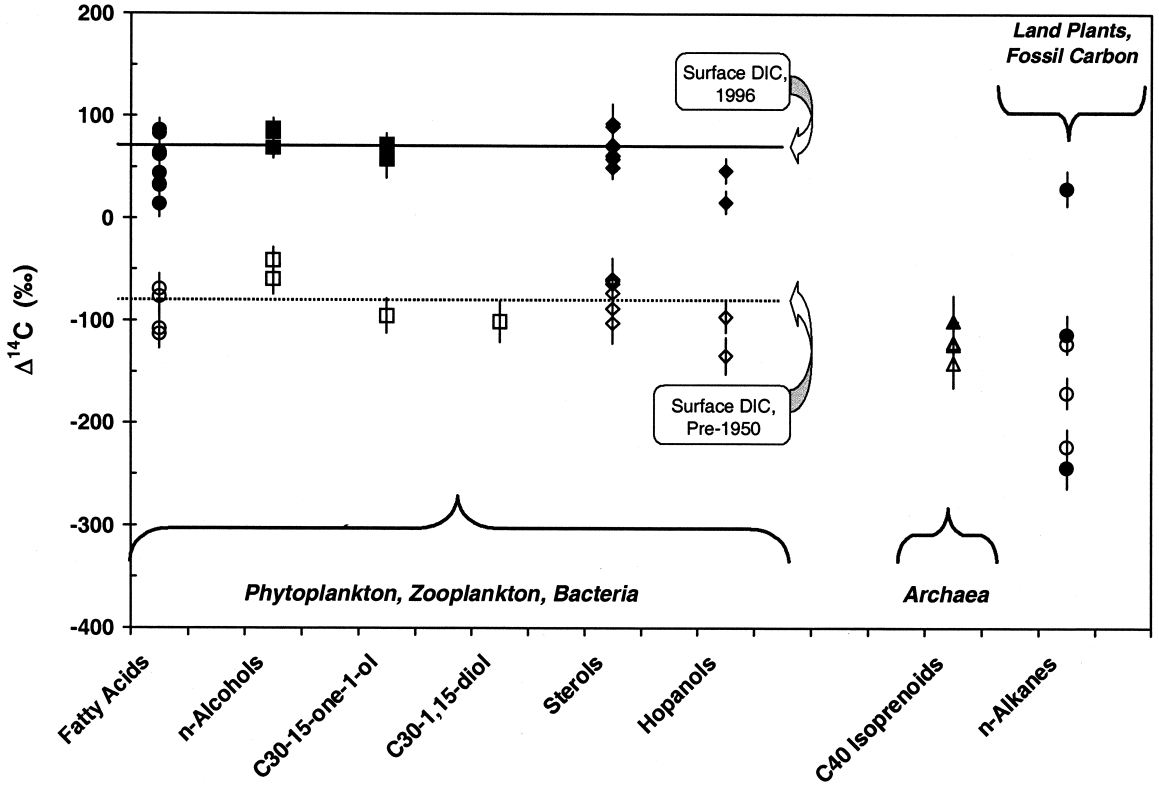

Fig. 6. Δ^{14}C distribution for SMB biomarkers. Data are shown from postbomb sediment (0–2.5-cm horizons) (solid symbols) and prebomb sediment (2.5–7.5-cm horizons) (open symbols).

along with the compound-specific δ^{13}C data, to produce a three-dimensional distribution of the carbon isotopic data (Fig. 7).

The $\Delta(\Delta^{14}C)$ values ranged between +119‰ and +194‰ for all fatty acids, *n*-alcohols, sterols, and hopanols (Table 1). The average of these differences was $+147 \pm 21$‰. In comparison, the estimated change in Δ^{14}C of surface-water DIC over the same time interval was +153‰. In Figure 7, the horizontal plane through $\Delta(\Delta^{14}C) = +150$‰ represents the incorporation of bomb ^{14}C into surface-water DIC. All compounds except archaeal isoprenoids and *n*-alkanes fall within ±30‰ of this plane. The value for C_{30}-alkan-15-one-1-ol (compound "p") lies outside of the oval shape drawn to indicate this cluster, only because its δ^{13}C value is much more negative than the other alcohols and fatty acids.

Therefore, this first-order approximation indicates that all of the measured fatty acids, linear alcohols, sterols, and hopanols are predominantly marine in origin. The carbon in these molecules reflects the production of photosynthetic biomass in the surface waters of SMB and SBB. The individual compounds within these lipid classes include products derived directly from photoautotrophs (e.g., dinosterol), lipids of herbivorous zooplankton (e.g., $C_{27}\Delta^5$, cholesterol), lipids of heterotrophic bacteria (e.g., the C_{31} hopanol), and products representing mixed sources (e.g., $C_{16:0}$ fatty acid). The relatively close agreement of bacterial lipid Δ^{14}C data with the Δ^{14}C of phytoplanktonic carbon also indicates the deep SMB is a dominantly heterotrophic environment.

In Figure 7, the sharp contrasts between biomarker alcohols and acids, the archaeal lipids (compounds D and E), and the *n*-alkanes (compounds a, b, c, and d) are apparent. The archaeal lipids and alkanes must represent carbon fixation processes not directly linked to the isotopic composition of marine surface waters. The archaeal compounds are ^{13}C enriched relative to other classes (e.g., fatty acids) and are unchanged in ^{14}C concentration over time. In contrast, the alkanes are relatively ^{13}C depleted and vary widely in their ^{14}C concentration over time.

4.2. Sources of Lipid Biomarkers

4.2.1. n-Alkanes

Although petroleum must contribute a fraction of the hydrocarbons to SMB sediments, the high carbon preference index values of the *n*-alkane distributions suggest this material is minor with respect to the fraction originating from terrestrial sources. The wide range of measured Δ^{14}C values agrees with these expectations. The even-numbered homologues ($\Delta^{14}C = -617$‰ and −741‰) are predominantly petroleum derived ($\Delta^{14}C_{fossil} = -1000$‰). These compounds also are more ^{13}C enriched than are the odd-chain homologues. This ^{13}C enrichment is consistent with a dominant petroleum source (Wilhelms et al., 1994) and with the known heavy isotopic composition of the nearby Monterey Formation (Schouten, 1995).

The odd carbon number alkanes, although also containing fossil components, contain a higher proportion of material from modern plant waxes. The fraction derived from modern terres-

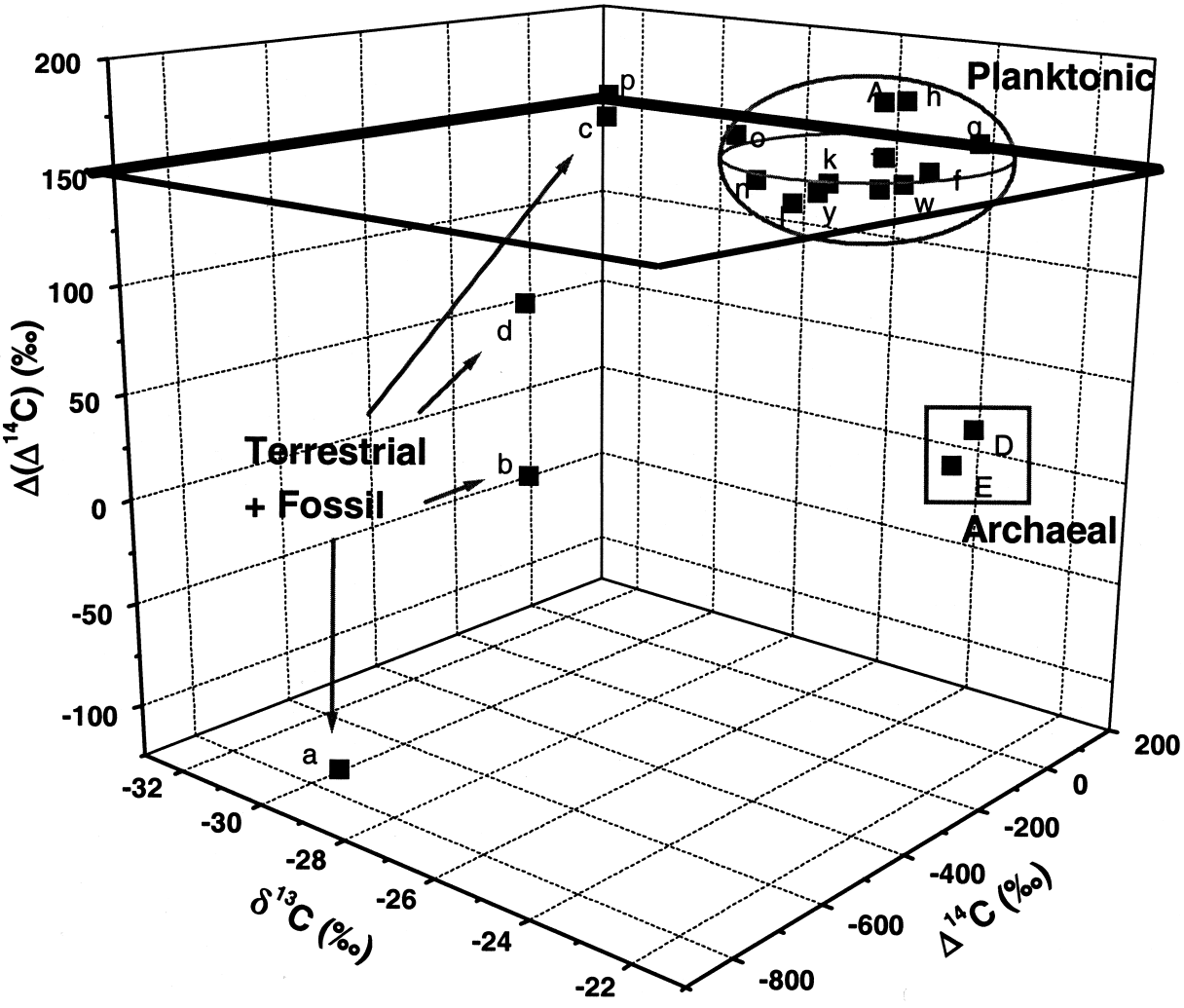

Fig. 7. Three-dimensional $\{\delta^{13}C, \Delta^{14}C, \Delta(\Delta^{14}C)\}$ distribution in carbon isotope space of the postbomb sediment (0–2.5 cm) data presented in Figure 6. The x- and y-axes are used to distribute the data by raw $\delta^{13}C$ and $\Delta^{14}C$, respectively. The z-axis shows the change in $\Delta^{14}C$ relative to the prebomb horizon: $\Delta(\Delta^{14}C) = \Delta^{14}C_{postbomb} - \Delta^{14}C_{prebomb}$. The horizontal plane at $\Delta(\Delta^{14}C) = +150‰$ represents the change in SMB surface-water $\Delta^{14}C_{DIC}$ over the same time interval. All of the analyzed lipids except *n*-alkanes and archaeal isoprenoids fall within ±30‰ of this plane.

trial sources varies, resulting in the range of $\Delta^{14}C$ values observed for *n*-C_{27}, C_{29}, and C_{31}. For a more complete discussion, see Pearson and Eglinton (2000).

4.2.2. Fatty Acids

The fatty acid isotopic data suggest a mixture of biosynthetic sources for these compounds, consistent with the concentration data and other biogeochemical considerations. In both the surface and deep horizons, $C_{14:0}$, $C_{16:0}$, and $C_{18:0}$ have similar $\Delta^{14}C$ (and $\delta^{13}C$) signatures. Their concentrations also remain constant relative to each other. Together, this evidence indicates either a common origin or unvarying relative contributions from multiple sources. $C_{16:0}$ and $C_{14:0}$ are the most common fatty acids of diatoms (Volkman et al., 1980), the dominant primary producers in the Southern California Bight. $C_{18:0}$ is found in green algae and zooplankton (Wakeham and Beier, 1991, and references therein). Therefore, the $C_{14:0}$, $C_{16:0}$, and $C_{18:0}$ fatty acids may reflect large contributions from (eukaryotic) planktonic species. The $\Delta^{14}C$ values for $C_{16:0}$ and $C_{18:0}$ all are consistent with a euphotic zone planktonic source.

Bacterial biomass may, however, represent an additional source of these fatty acids. Bacteria are thought to contribute $C_{16:0}$ and $C_{18:0}$ to marine sediments (e.g., Perry et al., 1979). A bacterial contribution is even more likely for the monounsaturated isomers, $C_{16:1\omega7}$ and $C_{18:1\omega7}$, which are products of anaerobic fatty acid biosynthesis. The higher concentrations of these fatty acids in the SMB 0- to 0.75-cm sample may be due to the presence of live bacterial mats at the sediment–water interface. Concentrations of adenosine triphosphate (ATP) suggest that living bacteria account for ~10 to 40% of TOC in the upper 5 to 10 mm but decrease exponentially with depth in SMB sediments (Craven and Jahnke, 1992). Filaments attributed to *Beggiatoa* (and/or *Thioploca*) spp. were visible when our core was collected, and the major lipids of these bacteria

are $C_{16:0}$, $C_{16:1\omega7}$, and $C_{18:1\omega7}$ (McCaffrey, 1990). The sulfide-oxidizing *Beggiatoa* grow both autotrophically and heterotrophically, depending on the environment (e.g., Hagen and Nelson, 1996). Here the value for $C_{18:1\omega7}$ suggests they are heterotrophs utilizing fresh carbon from phytoplanktonic detritus, because the measured $\Delta^{14}C$ for this compound ($+64 \pm 11‰$) is not significantly different from surface-water $\Delta^{14}C_{DIC}$ ($+71‰$).

The branched-chain fatty acids, *i*-$C_{15:0}$ and *a*-$C_{15:0}$, as well as the linear $C_{15:0}$, are abundant in sulfate-reducing bacteria (Boon et al., 1977; Parkes and Taylor, 1983) and in gram-positive bacteria (Kaneda, 1991). The concentrations of these compounds increase relative to the straight-chain acids at increasing depth in SMB sediment. They may be more resistant to degradation or may represent bacterial species living throughout the core. High concentrations of *a*-$C_{15:0}$, especially, also were found in a previous study of SMB sediment (Gong and Hollander, 1997).

Our $\Delta^{14}C$ data suggest that a fraction of these fatty acids in both prebomb and postbomb sediments is not derived from bacterial heterotrophy. Postbomb $\Delta^{14}C$ values are near $+35‰$, compared with surface-water DIC $+71‰$; the single prebomb value for *a*-$C_{15:0}$ is $-113‰$, compared with DIC $-82‰$. One explanation is that the bacteria responsible for producing these compounds contain some carbon derived from chemoautotrophic incorporation of bottom-water DIC ($\sim -190‰$, Pearson et al., 2000). Mass balance suggests that 10 to 30% of the C_{15} fatty acid carbon in SMB sediments could derive from bacterial autotrophy, if the source of the ^{14}C-depleted carbon is bottom-water DIC.

Bacteria require either branched-chain or unsaturated lipids to regulate membrane fluidity. The biosynthetic pathways leading to these two fatty acid classes are different, and bacteria regulate one or the other, but not both (Kaneda, 1991). The $\Delta^{14}C$ data for SMB bacterial fatty acids apparently trace these separate groups of organisms and indicate they are different metabolically. Species that produce $C_{18:1\omega7}$ apparently consume photosynthetically derived carbon. The species that produce the C_{15} branched-chain fatty acids may include some heterotrophic sulfate reducers but appear also to include other groups of bacteria that have partial or obligate chemoautotrophic metabolism.

A terrestrial source often is assigned to the long-chain ($>C_{20:0}$) fatty acids (e.g., Cranwell, 1974). However, long-chain acids have been found in bacteria (Schweizer, 1988) or could come from the reduction of monounsaturated acids (e.g., $C_{24:1}$) common in zooplankton (Sargent, 1976). Haddad et al. (1992) suggested that fatty acids $>C_{20:0}$ are poor substrates for heterotrophic organisms and are not utilized as rapidly as fatty acids of lower carbon number, contributing to their enhanced preservation at depth in the sediment (e.g., Colombo et al., 1997).

Our $\Delta^{14}C$ data for SMB $C_{24:0}$ and $C_{26:0}$ fatty acids from both prebomb and postbomb sedimentary horizons show that $C_{26:0}$ is more ^{14}C depleted than $C_{24:0}$. The $\Delta^{14}C$ values for $C_{24:0}$ are not significantly different from surface-water $\Delta^{14}C_{DIC}$, indicating a marine planktonic or heterotrophic bacterial source. The values for $C_{26:0}$ are systematically more negative, however. This could occur because of a higher contribution of preaged terrestrial carbon to the $C_{26:0}$ isolates. However, the *n*-alkane data show that the terrestrial lipids arriving in the SMB environment are "fresh" products of continental plants and have $\Delta^{14}C$ values more positive than the marine carbon end members (Pearson and Eglinton, 2000). Unless there is a great offset between the ^{14}C concentrations of terrestrially sourced long-chain alkanes and fatty acids, another explanation is required for the low $\Delta^{14}C$ values of $C_{26:0}$ in these samples. One possibility is that the $C_{26:0}$ samples were slightly contaminated, because (unlike other lipids in this work having $>$ 24 carbon atoms) they were not subjected to the column bleed clean-up step before analysis. The higher-boiling $C_{26:0}$ elutes in a region of the chromatogram where thermal degradation of the column stationary phase is observed, but $C_{24:0}$ elutes before this temperature and on a flat baseline.

4.2.3. Sterols

Numerous studies of sterols in the marine environment attribute a planktonic source to these biomarkers (reviewed in Volkman, 1986). However, the C_{29} sterols are an exception, as they sometimes are considered to reflect vascular plant input (e.g., Huang and Meinschein, 1976). Our compound-specific ^{14}C data show that all of the sterols isolated from SMB and SBB surface sediments reflect CO_2 fixation in isotopic equilibrium with the ^{14}C concentration of surface-water DIC.

The sterols isolated from these samples include structures (e.g., $C_{28}\Delta^{5,22}$) commonly linked to photosynthetic organisms such as diatoms, as well as structures associated with zooplanktonic sources (e.g., $C_{27}\Delta^{5}$, cholesterol). The similar isotopic values for both classes of biomarkers indicate that the zooplankton obtain their sterols by ingesting and modifying freshly synthesized algal biomass. Also, we see little evidence of a quantitatively significant terrestrial contribution to the C_{29} sterols. Although the high $\Delta^{14}C$ values ($\sim +90‰$) for α-C_{29} stanol could reflect a minor land plant contribution, the $\delta^{13}C$ values for this compound do not show ^{13}C depletion ($\delta^{13}C$ near $-30‰$; Lockheart et al., 1996) as would be consistent with a measurable amount of C_3 plant carbon. For a more complete discussion of the sterol data, see Pearson et al. (2000).

4.2.4. Hopanols

In SMB sediments, tetrahymanol and the C_{30}, C_{31}, and C_{32} hopanols all are abundant in the surface horizon. The C_{30} hopanol and especially tetrahymanol nearly disappear at depth, consistent with the work of Venkatesan et al. (1990). This may be the result of a faster degradation rate for these compounds.

The $\Delta^{14}C$ values for the individual hopanols, especially C_{32} hopanol, were significantly depleted relative to SMB surface-water DIC. This may suggest that a fraction of the hopanoid carbon originates from chemoautotrophic bacterial biomass production. Although oxygen is not required for hopanoid synthesis, all known hopanoid producers are aerobic bacteria (Ourisson et al., 1987). This discounts the possibility of in situ hopanol biosynthesis below the sediment–water interface of the suboxic SMB. The hopanols found in deeper SMB sediments probably derive from degradation of the precursor molecule, C_{35} bacteriohopanetetrol, formed by bacteria in oxic regions of the water column (Rohmer et al., 1984). Tetrahymanol is produced by freshwater protozoa of the genus *Tetrahymena* (Mal-

lory et al., 1963). However, because of the common occurrence of tetrahymanol in marine sediments, a ubiquitous marine prokaryotic source is postulated for this compound (ten Haven et al., 1989).

In general, the hopanols in SMB sediment present a pattern of ^{14}C concentrations similar to the values obtained for the C_{15} bacterial fatty acids. Hopanoids have been found in cyanobacteria, purple nonsulfur bacteria, and gram-negative and gram-positive heterotrophs and autotrophs (Ourisson et al., 1987). They have not been found in the filamentous sulfur bacteria, however (McCaffrey, 1990), so are not expected to reflect the ^{14}C concentration of the SMB *Beggiatoa* population. Isotopic mass balance can be used to estimate what fraction of the hopanols might originate from chemoautotrophic utilization of bottom-water DIC. A calculation made in the same manner as for the C_{15} fatty acids suggests that bottom-water DIC ($\sim -190‰$) could account for 25 to 50% of the carbon in C_{32} hopanol, a larger fraction than for the C_{15} fatty acids.

The fatty acid and hopanol data together appear to distinguish two different groups of prokaryotes. $\Delta^{14}C$ data for the linear fatty acids, including monounsaturated C_{16} and C_{18} compounds, may trace heterotrophic bacteria (in addition to phytoplankton). Their $\Delta^{14}C$ values reflect carbon in equilibrium with the $\Delta^{14}C$ of surface-water DIC. The branched-chain fatty acids and the hopanols appear to contain a chemoautotrophic or other ^{14}C-depleted component and may trace contributions from bacterial groups, including some ammonium or sulfide oxidizing autotrophs.

4.2.5. *n*-Alcohols

Long-chain *n*-alcohols in marine sediments usually are attributed to terrestrial sources, including both higher plants and freshwater algae. However, in the marine environment, C_{22} and $C_{22:1}$ can be the dominant alcohol of the wax esters of copepods (Sargent et al., 1977), and by analogy, C_{24} and $C_{24:1}$ may have similar origins. C_{22} *n*-alkanol is often abundant in deeper sediments (e.g., Johns et al., 1978). The most abundant *n*-alcohols in SMB sediment are C_{22} and C_{24}. In our samples, the relative concentrations of short-chain alcohols derived from zooplanktonic wax esters (C_{16}, C_{18}; Sargent et al., 1977) also do not change with respect to the longer chain alcohols (except C_{22}). Therefore, the concentration data suggest that *n*-alcohols in SMB sediment may be dominated by marine zooplanktonic sources.

The $\Delta^{14}C$ data for postbomb C_{22} and C_{24} (+85‰, +88‰) are similar to the $\Delta^{14}C$ of SMB surface-water DIC, suggesting a predominant marine origin. It is somewhat difficult to tell if there is a terrestrial component to these samples, however, as terrestrial biomass also has a positive $\Delta^{14}C$ value. The $\Delta^{14}C$ value of atmospheric CO_2 was $> +200‰$ during this time. If the $\Delta^{14}C$ of any freshwater algal or modern terrestrial plant component also had $\Delta^{14}C > +200‰$, then only a small fraction ($\sim$10%) of C_{22} and C_{24} could originate from terrestrial sources.

Terrestrial material may be relatively enriched in the alkanols from prebomb sediments, however. The $\Delta^{14}C$ values for C_{22} and C_{24} ($-41‰$ and $-59‰$) are not consistent with an exclusive source from fresh terrestrial biomass, which would have $\Delta^{14}C$ equal to the prebomb atmosphere ($\sim 0‰$). However, these numbers are significantly ^{14}C enriched compared with prebomb SMB surface-water DIC ($-82‰$). As much as 50% of the C_{22} and 30% of the C_{24} could come from terrestrial input. It is unlikely that C_{22} would have a more modern ^{14}C signature than C_{24}, however, if terrestrial higher plants were the primary source. Long-chain alkanols (i.e., C_{24}, C_{26}, C_{28}) commonly are sourced to higher plants (Cranwell, 1981; Yunker et al., 1995). However, the longer-chain compounds are not present at higher relative concentrations in the deeper sediment and C_{24} alcohol is not ^{14}C enriched relative to C_{22}. Together, the $\Delta^{14}C$ data are consistent with a primarily marine zooplanktonic origin for all of these compounds, with a partial contribution from terrestrial vascular or terrestrial aquatic sources.

4.2.6. *C_{30}-alkan-15-one-1-ol and C_{30}-alkan-1,15-diol*

The $\Delta^{14}C$ data for SMB C_{30}-alkan-15-one-1-ol and C_{30}-alkan-1,15-diol are consistent with a phytoplanktonic origin for this compound, although they show some ^{14}C depletion. The +65‰ average value for C_{30}-alkan-15-one-1-ol in surface sediments is insignificantly different from surface-water DIC (+71‰), whereas prebomb sediment values of $-95‰$ and $-101‰$ (C_{30}-ketol and C_{30}-diol, respectively) may be significantly depleted relative to prebomb surface waters ($-82‰$). Given the current known sources for these compounds, it is difficult to suggest an alternate source of ^{14}C-depleted carbon to account for this offset.

Alkan-15-one-1-ols and alkan-1,15-diols have sources in the microalgae (references in Volkman et al., 1998). The main algal species in which these compounds are found are members of the *Eustigmatophyceae* and *Chlorophyceae* (Gelin et al., 1997). These groups usually are not a major fraction of the marine planktonic population, however, but they may still account for the presence of these compounds in marine sediments. *Eustigmatophyceae* produce algaenans (references in Gelin et al., 1999). Physical association of C_{30}-alkan-15-one-1-ol with these complex aliphatic biopolymers could help explain its relatively high concentration and apparent resistance to degradation in SMB sediment.

Compound-specific $\delta^{13}C$ data for C_{30}-alkan-1,15-diols from Black Sea sediments ($\delta^{13}C \sim -32‰$) are very similar to $\delta^{13}C$ measurements obtained for pyrolysis products of aliphatic biopolymers from the same sediments (T. I. Eglinton, unpublished data). These data suggest that in the Black Sea, the source(s) of the diols are related to the biosynthesis of algaenans. The SMB C_{30}-alkyl-diols and C_{30}-alkan-15-one-1-ols ($\delta^{13}C \sim -32‰$) show similar ^{13}C depletion. This suggests that the *Eustigmatophyceae*, if they are the source of both the algaenans and these compounds, have a larger photosynthetic isotope fractionation than observed for other planktonic species. The *Eustigmatophyceae* also are implicated as sources of $C_{22\ to\ 28}$ *n*-alkanols in aquatic environments (Volkman et al., 1999). The $\delta^{13}C$ values observed for C_{22} to C_{28} alcohols in SMB sediments (-28 to $-32‰$) may reflect a contribution from these organisms because they are too ^{13}C depleted to be explained by marine zooplanktonic sources alone.

4.2.7. *Archaeal Lipids*

Quantitative 16S rRNA hybridization experiments show that *Archaea* comprise a high fraction of total planktonic prokary-

otic biomass in the oceans. The group I *Archaea* (pelagic *Crenarchaeota*) are abundant below the euphotic zone (Fuhrman and Davis, 1997; Massana et al., 1997), and at depths >500 m their abundance approaches that of *Bacteria* (Karner et al., 2001). The core membrane lipids of these organisms are believed to be isoprenoid glycerol dialkyl glycerol tetraethers (GDGTs), of which two specific structures dominate in the open ocean environment: GDGT I, containing two $C_{40:0}$ isoprenoids, and GDGT VIII, containing one each of the $C_{40:2cy}$ and $C_{40:3cy}$ isoprenoids (Schouten et al., 2000). The compounds $C_{40:2cy}$ and $C_{40:3cy}$, in particular, appear to have no source other than GDGT VIII, which suggests that these lipids are specific markers for the pelagic *Crenarchaeota*. Cleaving the ether bonds in our SMB and SBB samples produced mixtures of C_{40} isoprenoids in which $C_{40:2cy}$ and $C_{40:3cy}$ were present in a 1:1 ratio, indicating the original source was GDGT VIII. In contrast, the relative amount of $C_{40:0}$, probably derived from GDGT I, was variable. This concentration distribution is consistent with other observations for water column suspended particulate matter (King et al., 1998) and recent sediments (Hoefs et al., 1997).

In modern environments, the range of δ^{13}C values measured for these compounds is very limited (−20.1 to −23.4‰, averaging −21.4 ± 0.9‰; Hoefs et al., 1997; Schouten et al., 1998; and our data). These values represent significant ^{13}C enrichment relative to our SMB bacterial lipids (δ^{13}C, −25 ± 2‰). A consistently heavy isotopic composition that exhibits little variability suggests that these organisms have unusual metabolism. Proposed explanations include autotrophic growth utilizing bicarbonate, rather than CO_2, or heterotrophic growth based primarily on ^{13}C-enriched organic substrates (Hoefs et al., 1997).

The low concentrations of these lipids in our samples prevented measurement of their Δ^{14}C in the SMB 0- to 0.75-cm horizon. However, Δ^{14}C values were measured for the SBB 0- to 1-cm and SMB 5.5- to 8.5-cm horizons. Both sets of compounds were ^{14}C depleted relative to surface-water values at the time of their formation. In the surface horizon, there was no detectable bomb ^{14}C component, and when measurement errors were included, the Δ^{14}C values for the surface (postbomb) samples were insignificantly different from the prebomb samples. In contrast, all of the bacterial fatty acids and hopanols from surface sediments (SMB 0–0.75 cm and SBB 0–1 cm) contained bomb ^{14}C. The minimum values were +32‰ for *a*-$C_{15:0}$ and +16‰ for C_{32} hopanol. The positive Δ^{14}C values imply that the organisms producing these lipids are heterotrophs that consume carbon primarily derived from the decaying biomass of phytoplankton ($\Delta^{14}C = +71$‰). However, the archaeal lipids (~ −100‰) were 170‰ depleted relative to surface-water DIC and the lipids of primary producers. In addition, there was no change in the ^{14}C concentration of the carbon source for these *Archaea* over time (Fig. 7). The Δ^{14}C value for SBB DIC at 587 m currently is −107‰ (A. Pearson, unpublished data), which is very close to the ^{14}C concentration of the archaeal lipids.

These results are consistent with the first hypothesis, that the pelagic *Crenarchaeota* are chemoautotrophs and fix their biomass from deep water column DIC, beneath the depth of significant bomb ^{14}C penetration. A newly identified pathway of autotrophic growth, the 3-hydroxypropionate cycle, has enzymes that are specific for bicarbonate, rather than CO_2, fixation (Strauss and Fuchs, 1993). This pathway has been found in the cultured *Crenarchaeota*, *Acidianus infernus*, *Sulfolobus metallicus*, and *Metallosphaera sedula* (Menendez et al., 1999). Our measurements of relatively heavy δ^{13}C values and the absence of any bomb ^{14}C component together suggest that the pelagic *Crenarchaeota* may express this pathway as well.

4. CONCLUSIONS

In this study, compound-specific Δ^{14}C measurements were presented for 31 different lipid biomarkers extracted from sediments of SMB and SBB, California. Supporting data also were obtained in the form of compound-specific δ^{13}C values. The major conclusions of this work are summarized as follows:

(i) The most valuable tracer property was the change in ^{14}C concentration observed for the individual biomarker compounds over time. The positive Δ^{14}C values measured in surface (postbomb) sediments reflected the transfer of bomb ^{14}C from the atmosphere into surface-water DIC, its uptake into the biomass of phytoplanktonic primary producers, and subsequent consumption of their detritus by heterotrophic consumers (zooplankton and bacteria). The $\Delta(\Delta^{14}C)$ parameter allowed easy identification of all biomarkers for which the rate of ^{14}C uptake equaled the rate of bomb ^{14}C incorporation into surface-water DIC.

(ii) The results indicated that the majority of the lipids we isolated from SMB sediment represent carbon fixed into biomass in the marine euphotic zone. The Δ^{14}C values for the fatty acids, *n*-alcohols, hopanols, C_{30}-ketols and diols, and sterols all were in agreement with the Δ^{14}C of surface-water DIC. Contributions from chemoautotrophic bacterial or modern terrestrial sources represented minor or insignificant fractions of the lipids in these compound classes.

(iii) Two lipid classes represented major exceptions to the general pattern of bomb ^{14}C incorporation. These were the *n*-alkanes, which were found to reflect the contributions of both modern terrestrial plant waxes and fossil sources; and the isoprenoid ether-linked lipids of *Archaea*, which yielded isotopic values inconsistent with any of the other marine-sourced lipids studied here. The archaeal data recorded no change in ^{14}C concentration over time, indicating that the carbon source for these organisms remained isolated from the atmosphere. Autotrophic biomass production in the deep water column, utilizing a fixation pathway specific for bicarbonate, could explain the ^{14}C data as well as the isotopically heavy δ^{13}C values measured for these lipids.

This work demonstrated the utility of compound-specific ^{14}C analysis. Here we used these methods both to identify the origins of lipid biomarkers and as a tool to investigate biogeochemical processes. The compound-specific ^{14}C approach has numerous future applications, and this work sets the stage for more focused studies that utilize the unique tracer properties that ^{14}C offers.

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