PALEOCEANOGRAPHY, VOL. 15, NO. 5, PAGES 541-550, OCTOBER 2000

# An organic tracer for surface ocean radiocarbon

A. Pearson and T. I. Eglinton

Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution
Woods Hole, Massachusetts

A. P. McNichol

National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility, Department of Marine Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

**Abstract.** The $\Delta^{14}C$ of surface water dissolved inorganic carbon (DIC) in the Southern California Bight was compared to $\Delta^{14}C$ as recorded by the sterols in Santa Monica and Santa Barbara Basin sediments. All of the $C_{26}$, $C_{27}$, $C_{28}$, and $C_{29}$ sterols as well as dinosterol had $^{14}C$ concentrations equal to surface water DIC, indicating that all of the major sterols were derived from phytoplanktonic production. There is no detectable terrestrial component. Their tracer capability was confirmed by comparing the "bomb $^{14}C$"-derived change in surface water $\Delta^{14}C_{DIC}$ with the change in $\Delta^{14}C_{sterol}$. The "prebomb" $\Delta^{14}C_{DIC}$ was –82‰, and prebomb sterols averaged –75 ± 19‰. The $\Delta^{14}C$ value in 1996 was +71‰. Eighteen measurements representing eight different sterols from the sediment-water interface of both Santa Monica and Santa Barbara Basins averaged +62 ± 23‰. When three of these values were eliminated because of suspected contamination, the remaining data averaged +71 ± 12‰. The entire compound class could serve as an excellent proxy for the $^{14}C$ concentration of ocean surface waters.

## 1. Introduction

The concentration of $^{14}C$ in surface ocean dissolved inorganic carbon (DIC) varies with time [*Stuiver et al.*, 1986; *Druffel*, 1989; *Broecker et al.*, 1990]. Over glacial-interglacial timescales, it is a function of the ventilation rate and dynamics of deep water formation [*Broecker et al.*, 1990; *Edwards et al.*, 1993; *Bard et al.*, 1994; *Adkins and Boyle*, 1997]. Over decadal and centennial time scales, variations in $^{14}C$ reservoir age can reflect rapid changes in the $\Delta^{14}C$ of atmospheric $CO_2$ [*Stuiver and Braziunas*, 1995], abrupt climatic changes [e.g., *Adkins et al.*, 1998; *Hughen et al.*, 1998], and subtle changes in patterns of ocean circulation [*Guilderson and Schrag*, 1998].

Short- and long-term records of oceanic $\Delta^{14}C$ and ventilation rate have been restricted to $\Delta^{14}C$ measurements on organic materials from extreme coastal environments [*Southon et al.*, 1990; *Stuiver and Braziunas*, 1995]; on clam shells from temperate and polar coastal areas [*Mangerud and Gulliksen*, 1975; *Southon et al.*, 1990; *Weidman and Jones*, 1993], on corals from tropical surface waters [*Druffel*, 1989; *Edwards et al.*, 1993; *Guilderson and Schrag*, 1998] or the deep ocean [*Adkins et al.*, 1998], and on planktonic foraminifera from high sedimentation rate topographical highs [*Duplessy et al.*, 1989; *Bard et al.*, 1994; *Hughen et al.*, 1998]. Nearly all of these methods require preservation of calcium carbonate. In sediments where dissolution of calcite is extensive and in areas dominated by siliceous production, other means are needed to determine accurately the records of surface water $\Delta^{14}C_{DIC}$ and paleocirculation. This is especially critical for the Southern Ocean, where the ventilation rate during glacial periods and its effect on atmospheric $CO_2$ have been inferred from isotopic proxies other than carbon [e.g., *François et al.*, 1997].

The total organic carbon (TOC) in marine sediments derives from multiple sources and is isotopically heterogeneous [e.g., *Hedges and Parker*, 1976; *Eglinton et al.*, 1997]. Neither the stable carbon isotopic composition ($\delta^{13}C_{TOC}$) nor the total organic radiocarbon content ($\Delta^{14}C_{TOC}$) can be assumed exclusively to reflect surface water primary productivity. In continental shelf sediments, organic carbon includes autochthonous contributions (phytodetritus, fecal pellets, and bacterial biomass) and allochthonous components (terrestrial vascular plant remains, soil organic matter, and weathered shale and kerogen [*Hedges*, 1992]). Therefore down core measurements of $\Delta^{14}C_{TOC}$ commonly do not correspond to the known depositional ages of the sedimentary horizons [e.g., *Emery and Bray*, 1962; *Benoit et al.*, 1979; *Jones and Gagnon*, 1994]. $\Delta^{14}C_{TOC}$ is almost always more negative, or "older", than would be predicted by the sedimentation rate.

Stable isotopic ($^{13}C$) measurements of source-specific biomarker compounds [*Hayes et al.*, 1990] frequently are used to investigate the sources and transformation of carbon in the marine environment. Recently, this approach was expanded to include measurements of $^{14}C$ in individual biomarkers [*Eglinton et al.*, 1996, 1997]. Tens of micrograms of pure compounds are obtained by preparative capillary gas chromatography (PCGC), and $\Delta^{14}C$ values are measured by accelerator mass spectrometry (AMS).

The goal of the current study was to identify a specific biomarker or organic compound class suitable to use as a universal $^{14}C$ tracer of marine phytoplanktonic production and therefore of euphotic zone $\Delta^{14}C_{DIC}$. Recently, there has been renewed interest in a sterol, specifically the $C_{27}$ sterol,



Paper number 1999PA000476.
0883-8305/00/1999PA000476$12.00

cholesterol, as an isotopic tracer for marine primary production [*Schouten et al.*, 1998; *Grice et al.*, 1998]. $C_{27}$ and $C_{28}$ sterols found in sediments already have been used as marine biomass tracers [e.g., *Volkman et al.*, 1987; *McCaffrey et al.*, 1991; *Wakeham and Beier*, 1991]. Cholesterol often is the dominant sterol of zooplankton grazers [*Goad*, 1981], while $C_{28}$ sterols are common in prymnesiophytes and diatoms [*Volkman*, 1986, and references therein]. As a compound class, sterols may reflect the average isotopic composition of the entire surface mixed layer, integrating both time (averaged annual production) and space (total depth of the euphotic zone) [*Grice et al.*, 1998].

To evaluate a biomarker proxy for $\Delta^{14}C_{DIC}$, we established the following criteria: (*1*) the compound must record temporal changes in the $^{14}C$ isotopic composition of surface water DIC, (*2*) the surface water $\Delta^{14}C_{DIC}$ record should be independently verified through direct measurement(s) and/or a $CaCO_3$ proxy, and (*3*) the biomarker should be shown to preserve the surface water $\Delta^{14}C_{DIC}$ signature even in an environment in which the TOC contains a significant fraction of nonmarine organic carbon. Accordingly, we first compare the record of "bomb $^{14}C$" invasion into marine surface waters to the record of $\Delta^{14}C_{DIC}$ as preserved by planktonic foraminifera in Santa Monica Basin, California. The major sterols of Santa Monica and Santa Barbara Basin sediments are subsequently identified, and their isolation by PCGC methods is described. Then the sterol $\Delta^{14}C$ values, which represent both "prebomb" and "postbomb" sedimentary horizons, are compared to the $\Delta^{14}C_{DIC}$ records. Finally, the $^{14}C$ data are examined for biases caused by heterotrophic carbon consumption or contributions from terrestrial sources. The data are in agreement with other studies, suggesting that all of the major sterols found in these marine sediments are representative of autochthonous biomass production. The entire compound class may serve as a paleoceanographic tracer for surface ocean processes.

## 2. Methods

### 2.1. Samples

Sediment samples were collected in November 1996 (R/V *Roger Revelle*, cruise Pulse-32) from the central Santa Monica Basin (SMB) (33°44.0'N, 118°50.0' W, 905 m water depth), California. An Ocean Instruments® Multicorer was used to collect identical 10 cm diameter sediment subcores in sets of eight per deployment. The tops (0-1 cm) of two subcores from Santa Barbara Basin (SBB) (34°13.5'N, 120°03.5'W, 595 m water depth) were also collected. All samples were homogenized and freeze-dried. A 500 mL surface water sample (20 m water depth) for $\Delta^{14}C_{DIC}$ was collected according to the WOCE protocol [*McNichol and Jones*, 1991].

### 2.2. Bulk Sample Analysis

Subsamples of dry mud were reserved for bulk isotopic analysis ($\Delta^{14}C_{TOC}$) and for measurement of excess $^{210}Pb$ activity to assign a calendar year chronology [*Pearson*, 2000] to the SMB core. Carbon isotopic measurements ($\Delta^{14}C_{TOC}$) were made following standard procedures at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility [*McNichol et al.*, 1994a]. Water sample $\Delta^{14}C_{DIC}$ was measured on stripped $CO_2$ (World Ocean Circulation Experiment (WOCE) protocol [*McNichol and Jones*, 1991; *McNichol et al.*, 1994b]).

### 2.3. Foraminifera

Sediments were washed with Calgon®/HOOH solution and sieved through 150 μm and 63 μm mesh sieves. Benthic foraminifera, *Uvigerina peregrina* and *Bolivina* spp., were picked from the >150 μm fraction. Planktonic foraminifera were difficult to obtain in high mass abundance for $\Delta^{14}C$; samples were picked from the >150 μm fraction and contained a mixture of *Neogloboquadrina pachyderma* (dextral (d)), *N. dutertrei*, and *pachyderma-dutertrei* (P-D) intergrade species. The $\Delta^{14}C$ values for the foraminifera (4-11 mg $CaCO_3$ prior to hydrolysis) were measured using $CO_2$ prepared according to *McNichol et al.* [1994a].

### 2.4. Lipid Analysis

For each of the horizons selected for isotopic analyses of individual lipids (SMB 0–0.75 cm, SMB 4.5–5.5 cm, and SBB 0–1 cm) the remainder of the dry sample was extracted with 93:7 $CH_2Cl_2/CH_3OH$ (Fisher GC Resolv or Burdick and Jackson GC$^2$) using a large Soxhlet apparatus. The total lipid extracts (TLE) were transesterified, and the lipids were partitioned into hexane. These extracts were separated into 10 fractions on a Biotage® Flash 40Mi pressurized chromatography system (column: 15 cm x 40 mm, $SiO_2$ gel, 32-63μm). The 4-methyl-sterols eluted in hexane/ethyl acetate (4:1) and were separated from straight-chain alcohols by removing the latter as urea adducts. Desmethyl-sterols eluted in hexane/ethyl acetate (3:1), and this fraction was used for isotopic analysis without further purification. Each alcohol fraction was acetylated using an Alltech Acetylation kit ($\delta^{13}C$ = –27.1‰, $\Delta^{14}C$ = –997‰) to produce hydrolysis-resistant derivatives necessary for isotopic analysis. The contribution of derivative carbon to the $\Delta^{14}C$ values was removed by mass balance.

### 2.5. High-Resolution Gas Chromatography (HRGC)

Routine gas chromatography (GC) was performed on an HP 5890 Series II GC equipped with dual columns and FID detectors. Capillary columns were J and W Scientific DB-5 and Chrompack CP-Sil 5CB, both 60 m x 0.32 mm x 0.25 μm (length times inner diameter (I.D.) times film thickness). Samples were run using constant flow mode with He as the carrier gas. The GC temperature program was 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).

### 2.6. Gas Chromatography Mass Spectrometry (GC/MS)

Compounds were identified using an HP 6890 GC with attached HP 5973 mass selective detector (EI, 70 eV) and/or a high-resolution mass spectrometer (VG Autospec-Q hybrid MS; EI ionization energy, 70 eV) interfaced with an HP 5890 Series II GC. J and W Scientific DB-5 columns were used, and GC conditions were as stated above. The identity of β-sitosterol also was confirmed with an authentic standard.

### 2.7. Preparative Capillary Gas Chromatography (PCGC)

Collection of individual lipids by PCGC was described in detail by *Eglinton et al.* [1996]. An HP 5890 series II GC, equipped with HP 7673 autoinjector, Gerstel CIS-2 injection system, and Gerstel preparative trapping device (PTD) is fitted with a SGE BPX-5 (95%-dimethyl-5%-phenyl-polysiloxane), ultralow bleed, "megabore" (60 m x 0.53 mm x 0.5 μm) capillary column. One percent of the effluent passes to the flame ionization detector and the remaining 99% is collected in a series of seven U-tube traps. Computer control synchronizes injection and trapping time windows, permitting collection of multiple identical runs (often > 100 consecutive injections). Six traps are programmed to collect peaks of interest, while the seventh receives the remainder of the mixture. The GC temperature program was 40°C (1 min), 20°C/min to 270°C, 2.5°C/min to 320°C (25 min). The PTD was operated at 320°C, and the U-tube traps were at room temperature; the compounds condensed in the U-tubes as solids. Minor amounts of column bleed were removed from the SBB 0-1 cm batch by eluting the trap contents through $SiO_2$ gel columns (prepared in Pasteur pipettes, then combusted at 450°C for 8 hours). The faint color was always retained on the $SiO_2$ gel. No cleanup steps were done for the SMB sterols, and the consequences are noted in the discussion.

### 2.8. Accelerator Mass Spectrometry (AMS)

The purified compounds were sealed in evacuated quartz tubes with 100 mg CuO and combusted to $CO_2$ (850°C for 5 hours). The $CO_2$ was reduced to graphite over cobalt catalyst [*Pearson et al.*, 1998]. All $^{14}C$-AMS analyses were performed using special methods [*von Reden et al.*, 1998] necessary for the accurate determination of $\Delta^{14}C$ in samples containing < 0.5 mg C. For our samples, which all have known geochronological ages, the reported $\Delta^{14}C = [f_m e^{(1950-x)\lambda} - 1] \times 1000$ [*Stuiver and Polach*, 1977], where $\lambda = 1/8267$ ($yr^{-1}$), $f_m$ is fraction modern $^{14}C$, corrected for isotopic fractionation using $\delta^{13}C$, and $x$ equals the year of deposition (determined from the $^{210}Pb$ chronology). This removes the effects of in situ $^{14}C$ decay and normalizes the $\Delta^{14}C$ data to the values each sample would have had when deposited at the sediment-water interface.

## 3. Results and Discussion

### 3.1. Bulk Samples and Foraminifera

High sedimentation rates and the absence of bioturbation in central SMB sediments allow decadal resolution of changes in the regional environment. This includes the recent increase in surface ocean $^{14}C$ concentration due to uptake of "bomb $^{14}C$" from the atmosphere. For the SMB core, $\Delta^{14}C$ values were determined for samples of bulk TOC, planktonic foraminifera, and benthic foraminifera. These values were used to compare the recent history of water mass $\Delta^{14}C_{DIC}$ with the sterol biomarker $\Delta^{14}C$ record.

Surface ocean $\Delta^{14}C_{DIC}$ reached a maximum in the middle 1970s, ~ 10 years after the maximum in atmospheric $^{14}CO_2$ concentration caused by aboveground testing of nuclear weapons [*Levin et al.*, 1985; *Levin and Kromer*, 1997].

**Table 1.** A History of Surface Water $\Delta^{14}C_{DIC}$, Mollusc Shell $\Delta^{14}C$, and Pteropod $\Delta^{14}C$ Measurements Recorded in the SCB[a]

| Year Collected | Sample Type | $\Delta^{14}C$, ‰ |
|---|---|---|
| 1920 | pteropod (*L. helicina*) | about –78 |
| Pre-1950s | mollusc ($n$ = 5 specimens) | –81 ± 5 |
| 1959 | DIC | –88 ± 10 |
| 1965 | DIC | 49 ± 8 |
| 1969 | DIC | 138 ± 15 |
| 1974 | DIC | 195 ± 4 |
| 1980 | DIC | 109 ± 8 |
| 1996 | DIC | 71 ± 3 |

[a]Except for the 1996 sample (this study), the dissolved inorganic carbon (DIC) data were summarized previously by *Williams et al.* [1992, and references therein]. The first three samples were collected off of the Scripps Institution of Oceanography Pier (32°52'N, 117°44'W); the fourth is a Geochemical Ocean Sections Study (GEOSECS) station (28°30'N, 121°29'W); the fifth is south of San Diego (31°9.9'N, 117°12'W); the sixth is from the central Santa Monica Basin (SMB). The mollusc shell data are from coastal California (33°–38°N) and were reported by *Robinson* [1981]. The pteropod value is from Santa Barbara Basin (SBB) sediment with an approximate calendar date of 1920 A.D. [*Baumgartner and Southon*, 1996].

Previously reported measurements of $\Delta^{14}C_{DIC}$ from the Southern California Bight (SCB) are summarized in Table 1. The data are sufficient to make a time series plot of the evolution of surface water $^{14}C$ concentration during the twentieth century (Figure 1). A simple bimodal cubic spline was fit to the data to produce a smooth model curve. The prebomb value represents seven distinct data points with an average $\Delta^{14}C_{DIC}$ = –82‰; this value was extrapolated throughout the years 1850–1950 under the assumption that $\Delta^{14}C_{DIC}$ of surface waters remained nearly constant prior to atmospheric weapons testing. Small deviations in $\Delta^{14}C_{DIC}$ due to the Suess effect are not shown [*Suess*, 1953; *Druffel and Suess*, 1983]; the resolution of this study is not sensitive enough to detect the Suess effect. The values of $\Delta^{14}C_{DIC}$ are also assumed to be equal in SMB and SBB surface waters because the basins are adjacent and share similar water masses.

Using our $^{210}Pb$ chronology, calendar years were assigned to the sectioned horizons of the SMB core (Figure 2). The sedimentation rate is in agreement with other recent reports [*Christensen et al.*, 1994; *Hagadorn et al.*, 1995]. Then the surface water $\Delta^{14}C_{DIC}$ model was transposed onto the core chronology (Figure 2). Sedimentary horizons below 2.5 cm have calendar year dates before the time of significant change in surface water $^{14}C$ concentration. The upper three horizons were deposited during the time of elevated $\Delta^{14}C_{DIC}$. $\Delta^{14}C$ data for bulk phases and calcareous microfossils are shown in Table 2.

The values recorded by foraminifera provide an independent verification of the reconstructed surface water $\Delta^{14}C_{DIC}$ model (planktonics) and of the stability of bottom water $\Delta^{14}C_{DIC}$ (benthics) over the time interval preserved in this core. Planktonic species were picked from the upper six horizons, and the calcite $\Delta^{14}C$ values are shown in Figure 2.

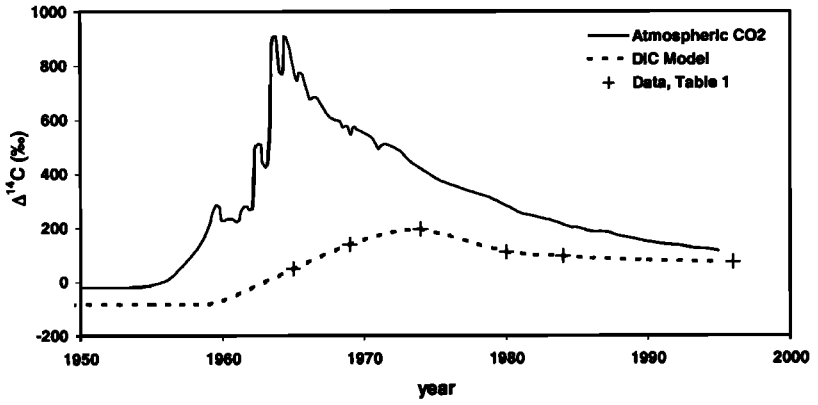


**Figure 1.** Evolution of Southern California Bight (SCB) surface water $\Delta^{14}C_{DIC}$ through the twentieth century, showing the incorporation of $^{14}CO_2$ produced by atmospheric nuclear weapons testing. Solid line represents $\Delta^{14}C_{CO2}$, dashed line represents $\Delta^{14}C_{DIC}$ model, and pluses represent $\Delta^{14}C_{DIC}$ data (Table 1).

The assemblage was dominated by *N. pachyderma* (d), although a significant percentage was comprised of *N. dutertrei* and/or *pachyderma/dutertrei* intergrade species.

Two kinds of benthic foraminifera were also picked from the samples (data in Table 2). *Bolivina* species (dominated by *B. spissa*) were the most abundant. The three horizons below 2.5 cm also contained *U. peregrina* in high abundance; however, a transition in the benthic environment apparently occurred in the middle twentieth century. No *U. peregrina* individuals were found in the upper horizons. Unlike *B. spissa*, however, *U. peregrina* is not a low-$O_2$ tolerant species and may only flourish immediately following strong bottom water flushing events [e.g., *Behl and Kennett*, 1996]. It is possible the intensity and/or frequency of these events abruptly changed and affected the benthic populations.

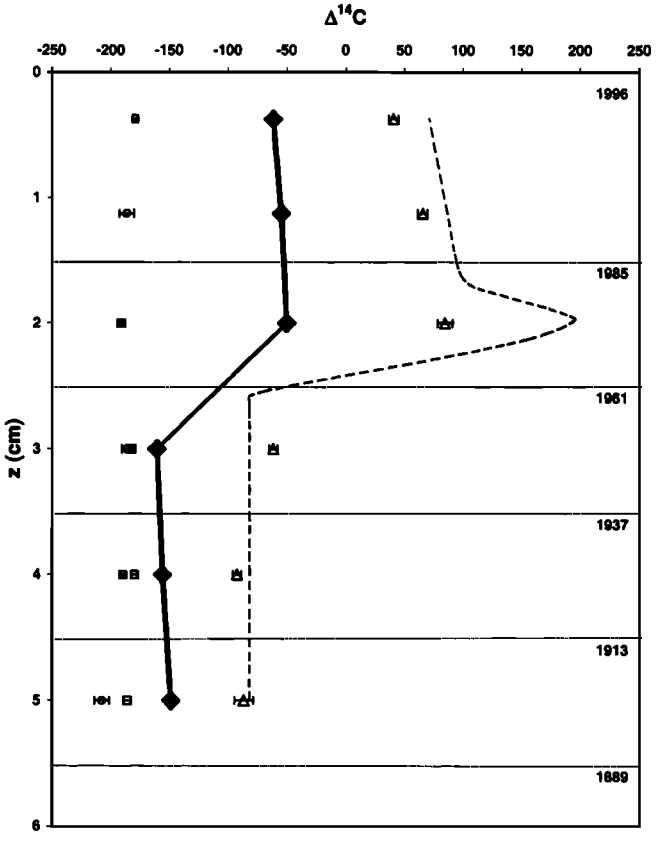


**Figure 2.** Bulk sample $\Delta^{14}C$ data for the Santa Monica Basin (SMB) core. Foraminifera are shown with open symbols (triangles are planktonics, circles are *Bolivina* spp., and squares are *U. peregrina*), TOC samples are shown with solid diamonds, and the surface water $\Delta^{14}C_{DIC}$ model is shown with a dashed line.

**Table 2.** Isotopic Data for Bulk Samples, SMB Core

| Sample | $\Delta^{14}C$, ‰ |
|---|---|
| Surface water DIC | |
| 20 m | 71 ± 3 |
| Total organic carbon | |
| 0–0.75 cm | −62 ± 3 |
| 0.75–1.5 cm | −55 ± 2 |
| 1.5–2.5 cm | −51 ± 3 |
| 2.5–3.5 cm | −161 ± 3 |
| 3.5–4.5 cm | −156 ± 2 |
| 4.5–5.5 cm | −149 ± 2 |
| Foraminifera | |
| *Neogloboquadrina* spp. | |
| 0–0.75 cm | 41 ± 4 |
| 0.75–1.5 cm | 65 ± 4 |
| 1.5–2.5 cm | 84 ± 6 |
| 2.5–3.5 cm | −62 ± 4 |
| 3.5–4.5 cm | −93 ± 4 |
| 4.5–5.5 cm | −87 ± 8 |
| *Bolivina* spp. | |
| 0–0.75 cm | −179 ± 3 |
| 0.75–1.5 cm | −187 ± 6 |
| 1.5–2.5 cm | −191 ± 4 |
| 2.5–3.5 cm | −186 ± 4 |
| 3.5–4.5 cm | −190 ± 3 |
| 4.5–5.5 cm | −208 ± 6 |
| *U. peregrina* | |
| 2.5–3.5 cm | −182 ± 3 |
| 3.5–4.5 cm | −180 ± 2 |
| 4.5–5.5 cm | −186 ± 3 |

The primary feature in Figure 2 is the appearance of excess $^{14}C$ after 1960, corresponding to the uptake of bomb-produced $^{14}CO_2$ into the surface DIC pool. This signal reaches its maximum in the 1.5–2.5 cm sediment horizon as recorded by the planktonic foraminifera, *N. pachyderma* (d) and *N. dutertrei*. However, a persistent negative offset does exist between the foraminiferal $\Delta^{14}C$ and the surface water $\Delta^{14}C_{DIC}$ model in the three postbomb sediment horizons. The mixed assemblage of planktonic foraminifera utilized for isotopic measurements may explain why the data do not perfectly match the model. No discrimination was made on the basis of growth stage or species morphology. Isotopic variation in *N. dutertrei* occurs at least partly because gametogenic *N. dutertrei* populate the $^{13}C$- and $^{14}C$-depleted waters at the base of the thermocline [*Curry and Crowley*, 1987; *Ravelo and Fairbanks*, 1992]. The gradient in $\Delta^{14}C_{DIC}$ between surface and thermocline waters became steeper following the uptake of bomb-derived $^{14}CO_2$. The isotopic composition of this planktonic foraminiferal assemblage may be biased by the presence of the deeper-dwelling *N. dutertrei* species. This would result in a negative offset in $\Delta^{14}C_{calcite}$ relative to surface water $\Delta^{14}C_{DIC}$ in the postbomb samples. Species that live in the upper 20 m (e.g., *Globigerinoides ruber*) are better tracers of surface water masses.

Prebomb values of surface water $\Delta^{14}C_{DIC}$, as recorded by the planktonic foraminifera below 2.5 cm (–80 ± 16‰; $n = 3$), are in good agreement with the average literature value of –82‰. The two species of benthic foraminifera also show the uniformity in bottom water DIC. The *B. spissa* and *U. peregrina* data record an average benthic $\Delta^{14}C_{DIC}$ of –188 ± 8‰. There is no significant trend with time in these values, as bomb $^{14}C$ has not yet penetrated below a depth of ~ 500 m in the northeastern Pacific Ocean [*NOSAMS*, 1994].

Bomb $^{14}C$ also appears in the TOC pool in the upper three sedimentary horizons (Figure 2). The critical characteristic for $\Delta^{14}C_{TOC}$ in this core, however, is that even though the timing of bomb $^{14}C$ uptake is identical to that observed for the DIC pool, the total $^{14}C$ concentration is always less than that measured in the surface waters or as recorded by planktonic foraminifera. The "preaged" fraction may be of nonmarine origin. Whether its primary source represents terrigenous carbon [e.g., *Goñi et al.*, 1998], incorporation of deep water DIC [*Rau et al.*, 1986], refractory dissolved organic carbon [e.g., *Wang et al.*, 1998], or "black carbon" [*Masiello and Druffel*, 1998], this component of TOC is not turned over quickly enough to have incorporated bomb $^{14}C$ labeled $CO_2$. Therefore the down core profile of $\Delta^{14}C_{TOC}$ cannot be used as a direct proxy for the isotopic composition of surface waters.

### 3.2. Molecular-Level $\Delta^{14}C$ Analysis

A prebomb sediment horizon (4.5–5.5 cm) and the core top (0–0.75 cm) from the SMB core were selected for compound-specific analysis of $^{14}C$ in individual sterols. These samples provide a clear contrast between the isotopic composition of photosynthetic biomarkers from prebomb and postbomb surface waters. The excellent agreement between the literature data for prebomb DIC and our planktonic foraminiferal measurements provides independent verification that $\Delta^{14}C_{DIC} = -82‰$ at the time the 4.5–5.5 cm sample was formed. The surface horizon (0–0.75 cm corresponds to ~ 10 years of deposition) can be compared to the $\Delta^{14}C_{DIC}$ sample collected at the same time as the sediment core ($\Delta^{14}C_{DIC} = +71‰$).

The SBB 0–1 cm sample was included to address an apparent contamination problem in the initial data from the SMB 0–0.75 cm sample. This SBB sample contained very fresh phytoplanktonic detritus (0–3 years [*Schimmelmann and Tegner*, 1991]). The immediate geographic proximity of SBB and SMB also means they share surface water masses with comparable DIC isotopic composition, and they probably have a similar phytoplanktonic species distribution. The SBB sterol isotopic data were expected to be similar to the values from SMB.

Partial HRGC traces of the sterol fractions are shown in Figure 3. Peaks are identified in Table 3. The 4-methyl-sterol sub-fractions, from which dinosterol was the only compound selected for isotopic analysis, are not shown. The chromatograms for all three samples are quite similar. In the surface sediment of SBB, cholesterol is the most abundant free sterol, although dinosterol was not quantified and may equal or exceed cholesterol in this environment. The absolute abundance of all sterols is also higher in SBB sediment than in SMB surface sediment (31 versus 11 μg cholesterol per gram dry weight). The absolute abundance of all sterols decreased with depth in the SMB core, although the percent TOC remained approximately constant (~ 4–5%).

Compound-specific $\delta^{13}C$ analysis of these samples by isotope ratio monitoring GC/MS [*Pearson*, 2000] suggested very strongly that each of two peaks initially identified as single compounds ($C_{29}\Delta^5$, X; and 5α-$C_{29}$, XI), in fact, represented two isomers, redesignated X(*A,B*) and XI(*C,D*) (Figure 3). However, their mass spectra were generally consistent with $C_{29}\Delta^5$ and $C_{29}$ stanol structures.

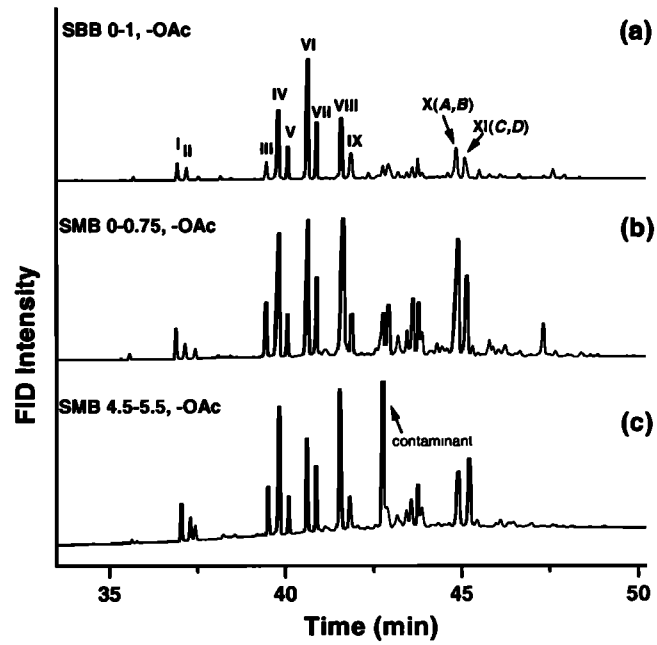


**Figure 3.** HRGC traces of the sterol fractions selected for compound-specific isotopic analysis. (a) SBB 0-1 cm, (b) SMB 0-0.75 cm, and (c) SMB 4.5-5.5 cm, all derivatized to acetates for PCGC separation and $^{14}C$ analysis. Compounds I-XI are identified in Table 3.

**Table 3.** Sterols Identified in the Chromatograms in Figures 3 and 4

| Peak | Sterol | Abbreviation |
|---|---|---|
| I | 24-nor-cholesta-5,22-dien-3β-ol | $C_{26}\Delta^{5,22}$ |
| II | 24-nor-5α-cholest-22-en-3β-ol | $C_{26}\Delta^{22}$ |
| III | 27-nor-24-methylcholesta-5,22-dien-3β-ol | $C_{27}\Delta^{5,22*}$ |
| IV | cholesta-5,22-dien-3β-ol | $C_{27}\Delta^{5,22}$ |
| V | 5α-cholest-22-en-3β-ol | $C_{27}\Delta^{22}$ |
| VI | cholest-5-en-3β-ol | $C_{27}\Delta^{5}$ (cholesterol) |
| VII | 5α-cholestan-3β-ol | $5\alpha$-$C_{27}$ |
| VIII | 24-methylcholesta-5,22-dien-3β-ol | $C_{28}\Delta^{5,22}$ |
| IX | 24-methyl-5α-cholest-22-en-3β-ol | $C_{28}\Delta^{22}$ |
| X | 24-ethylcholest-5-en-3β-ol | $C_{29}\Delta^{5}$ |
| XI | 24-ethyl-5α-cholestan-3β-ol | $5\alpha$-$C_{29}$ |
| XII[a] | 4, 23, 24-trimethyl-5α-cholest-22-en-3β-ol | dinosterol |

[a]Eluted with another fraction, not shown.

For $\Delta^{14}C$ analysis, individual sterols from the SMB 0–0.75 cm sample were collected in two separate PCGC batches. In the first run the following six compounds were collected: I+II (composite sample), VI, VII, VIII, X, and XI (subsequently lost during analysis). Sufficient sample remained to allow a second separation, and I+II (composite sample), IV, VI, and XI were selected. The repeat collections of I+II and VI provided independent replicates with which to assess the quality of the $^{14}C$ data obtained. After combustion to $CO_2$, the second collection of VI was also split into two samples of identical gas (VI a,b) to provide additional replicates.

Aliquots of each trapped compound were reanalyzed by HRGC to verify compound identity and purity. Figure 4 shows chromatograms of the sterols recovered from the first run as an example of the quality of isolation typically achieved by PCGC separation. Closely eluting isomers sometimes are collected and have entrained small amounts (< 5%) of adjacent peaks. In the case of adjacent stanol/stenol pairs, however, the resulting $^{14}C$ isotopic biases should be small.

For the prebomb SMB 4.5–5.5 cm sample the following compounds were collected: I+II, VI, VII, VIII, X, and XI, of which the I+II and VII samples subsequently were lost. To compare the SBB 0–1 cm sediment horizon to the SMB surface sediments, IV, VI, VII, VIII, X, and XI were collected from the SBB sample. Finally, dinosterol (XII) was obtained from separate lipid fractions from the two SMB horizons. Two splits were made of the dinosterol obtained from SMB 0–0.75 cm, and two $^{14}C$ measurements were obtained. All of the sterol $\Delta^{14}C$ data are given in Table 4 and shown in Figure 5.

The $\Delta^{14}C$ values for the SBB sterols ranged between +50 and +90‰; their average was +69 ± 14‰. The $\Delta^{14}C$ data for the SMB 0–0.75 cm (batch 1) samples, especially for the smaller samples from this batch, had a noticeable negative bias resulting from column bleed ($\Delta^{14}C_{bleed} = -1000‰$). The average $\Delta^{14}C$ for batch 1 was +38 ± 27‰, with three compounds (+13, +13, and +31‰) having much lower $\Delta^{14}C$ values than the remainder of the SMB and SBB postbomb sterols. The questionable quality of this batch of postbomb sterols does not affect the fundamental conclusions. The SMB 0 – 0.75 cm (batch 2) sterol data are of comparable quality to the SBB samples. The average $\Delta^{14}C$ for SMB 0–0.75 cm batch 2 sterols was +73 ± 12‰. The two measurements made on a single PCGC isolation of dinosterol (SMB 0–0.75 cm) yielded $\Delta^{14}C$ = +61 and +81‰. The entire set of 18 measurements made for postbomb sedimentary sterols has a mean value of +62 ± 23‰.

The $\Delta^{14}C$ values determined for individual sterols from the SMB prebomb sedimentary horizon (4.5–5.5 cm) ranged from –59 to –102‰. The average of the five data points was –75 ± 19‰.

The quality of the data can be evaluated in terms of specific replicates, including both (*1*) $CO_2$ splits obtained from the same sample and (*2*) identical isomers collected in different PCGC series. Isotopic differences among identical $CO_2$ splits are due to graphite preparation and AMS instrumental effects only. The identical splits of SMB postbomb cholesterol and dinosterol each differ by ~ 20‰, so ± 20‰ is taken as the estimate of the accuracy, or reproducibility, of the $^{14}C$ data. This is slightly larger than the AMS measurement precision, which averages about ± 15‰. However, the entire set of postbomb data, with the exception of the three points that are believed to be contaminated, is within about ±20‰ of the average value of about +70‰. In a sense, the entire data set replicates itself. This has implications for using sterols as a compound class, rather than individually, as paleoceanographic tracers.

### 3.3. Discussion

The sterol $\Delta^{14}C$ data are shown in Figure 5 along with the surface water $\Delta^{14}C_{DIC}$ values, $\Delta^{14}C_{DIC}$ as recorded by planktonic foraminifera, and $\Delta^{14}C_{TOC}$ for the SMB samples. As indicated, the mean and standard deviation of the prebomb and postbomb sterol data sets are shown on the right-hand side of Figure 5.

The solid line at the top of Figure 5 is the value measured for 1996 surface water DIC (+71‰), while the dashed line is the $\Delta^{14}C$ of SMB 0–0.75 cm planktonic foraminifera. Bomb $^{14}C$ incorporation into the surface sedimentary horizon is apparent, as the sterol samples all have $\Delta^{14}C$ values > 0‰. The three "outliers" from the contaminated SMB batch 1 are the samples with $\Delta^{14}C$ values lower than the planktonic foraminifera. These samples and the calcite $\Delta^{14}C$ value

(+41‰) do not agree with the measured $\Delta^{14}C_{DIC}$ as well as the majority of the individual sterol compounds do. Eliminating these three sterol samples would result in a mean $\Delta^{14}C$ exactly equal to the measured $\Delta^{14}C_{DIC}$ (+71 ± 12‰).

The $\Delta^{14}C$ value for prebomb surface water DIC (–82‰) is comparable to the value for planktonic foraminifera picked from the 4.5–5.5 cm horizon of the SMB core (–87‰). The prebomb sterols also have $\Delta^{14}C$ values significantly < 0‰, and their average is not significantly different from surface water $\Delta^{14}C_{DIC}$ at the time of their production and sedimentation. The scatter in the data is slightly larger than desirable, and it is probably due to the relatively poor AMS precision obtained for these samples.

Previous studies of sterol distributions in the water column and sediments attribute a marine origin to all but the $C_{29}$ sterols, which in many cases have been interpreted to represent input from vascular land plants [e.g., *Volkman et al.*, 1987]. Our compound-specific $^{14}C$ data show that the individual sterols in these marine sediments reflect photosynthetic $CO_2$ uptake in isotopic equilibrium with surface water DIC. There appear to be no obvious exceptions. No single sterol isomer is systematically enriched or depleted in $^{14}C$ relative to the corresponding surface water $\Delta^{14}C_{DIC}$, and no sterol fails to make the transition between prebomb and postbomb end-member isotopic composition. This result has two major implications for interpreting the sources of sterols in marine sediments.

The first implication is that there is no significant lag time between algal photosynthesis and heterotrophic consumption. Zooplankton obtain essentially all of their sterols through ingesting and modifying freshly synthesized algal biomass rather than through new biosynthesis [*Goad*, 1981; *Harvey et al.*, 1987; *Grice et al.*, 1998]. Surface water $\Delta^{14}C_{DIC}$ and, by extension, algal biomass had values > +110‰ as recently as 1980 (Figure 1), but the zooplanktonic sterols (e.g., cholesterol), do not show $^{14}C$ enrichment relative to algal sterols (e.g., $C_{28}\Delta^{5,22}$). Therefore heterotrophic consumption and subsequent sedimentation must proceed without a decadal-scale lag in the water column suspended particulate organic carbon (POC) pool. This is consistent with other observations of particle reworking and transport to sediments on time scales of weeks to months [e.g., *Deuser*, 1986]. There is also no systematic $^{14}C$ depletion, indicating that the fraction of steroidal carbon derived from preaged sources is

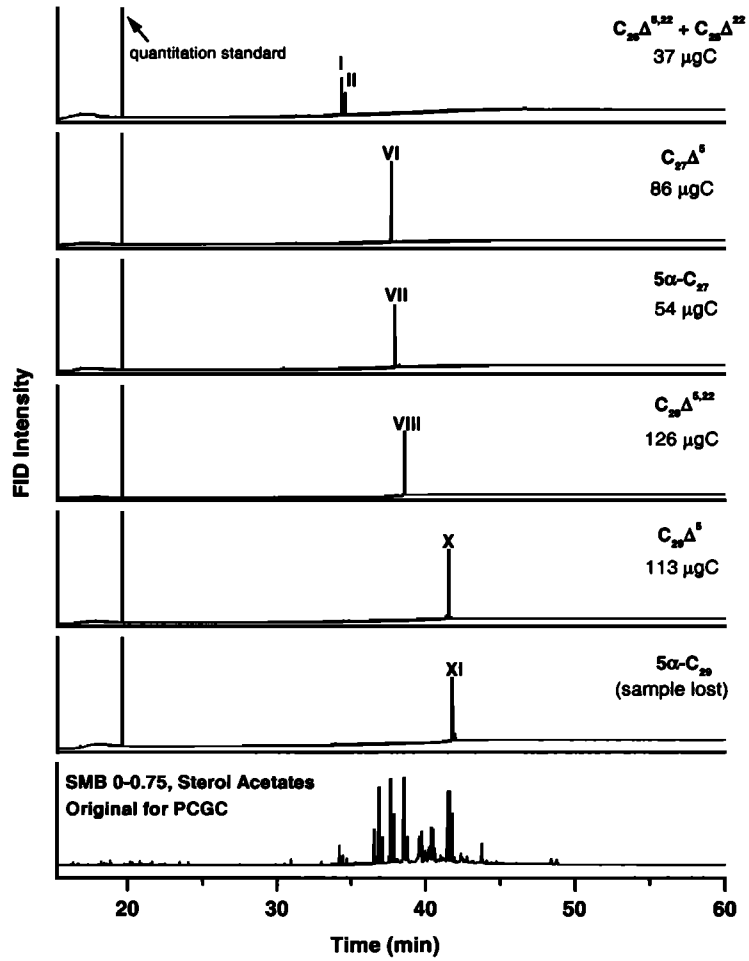


**Figure 4.** Purified compounds from the SMB 0–0.75 cm 4-desmethyl-sterol fraction. The original mixture is shown at the bottom. Re-analyzed aliquots of individual PCGC trap contents are shown above. Sterol peaks are labeled as in Figure 3, and recovered quantities (as $CO_2$) of the pure compounds are given.

negligible. For example, uptake of refractory DOC by bacteria and subsequent zooplanktonic ingestion of this bacterial carbon does not affect the sterol $^{14}C$ signal. All of the sedimentary sterols apparently are derived directly from photoautotrophic biomass production and carry a surface mixed layer $\Delta^{14}C_{DIC}$ signal.

Second, the data suggest that preaged terrestrial carbon contributes insignificantly to the sterol lipid class. The $C_{29}$ sterols have been used as indicators of the terrestrial organic carbon contribution to marine sediments [e.g., *Huang and Meinschein,* 1976]. However, on the basis of the similarity between $\Delta^{14}C$ values determined for the $C_{29}$ sterols and for the algal $C_{26}$-$C_{28}$ sterols, we find no clear evidence of a quantitatively significant terrestrial component. By coincidence, the terrestrial residence time and surface ocean reservoir could be equal in the prebomb interval (–80‰ ≈ 670 radiocarbon years), but the presence of bomb radiocarbon in the core top sterols seems to rule out this possibility. Statistical analyses of Peru Margin sediments [*McCaffrey et al.,* 1991] support the generality of this interpretation. In that environment the four biomarkers most strongly correlated with phytoplanktonic sources were phytol and the $C_{27}\Delta^5$, $C_{28}\Delta^{5,22}$, and $C_{29}\Delta^5$ sterols.

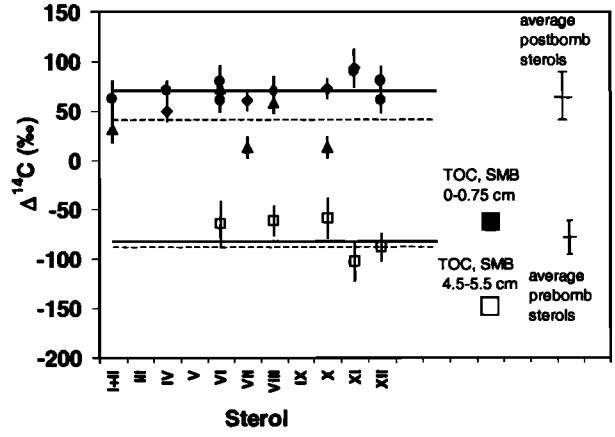


**Figure 5.** $\Delta^{14}C$ data for sterol biomarkers, showing agreement of prebomb and postbomb compound-specific $\Delta^{14}C$ data with the record of surface water $\Delta^{14}C_{DIC}$. Surface water $\Delta^{14}C_{DIC}$ measurements are shown as solid lines; dashed lines represent planktonic foraminifera. Open squares, SMB 4.5–5.5 cm (prebomb) sterols; triangles, SMB 0–0.75 cm (postbomb batch 1) sterols; circles, SMB 0–0.75 cm (postbomb batch 2) sterols; diamonds, SBB 0–1 cm sterols; large squares, TOC. The average and standard deviations of the $\Delta^{14}C$ values for prebomb and postbomb sterols are shown at the far right.

**Table 4.** Isotopic Data for Individual Sterols from SMB and SBB Sediments

| | Sterol | Amount, μg C | $\Delta^{14}C$, ‰ |
|---|---|---|---|
| | *SBB 0–1 cm*[a] | | |
| IV | $C_{27}\Delta^{5,22}$ | 44 | 50 ± 11 |
| VI | $C_{27}\Delta^5$ | 73 | 70 ± 10 |
| VII | 5α- $C_{27}$ | 38 | 61 ± 10 |
| VIII | $C_{28}\Delta^{5,22}$ | 29 | 71 ± 14 |
| X | $C_{29}\Delta^5$ | 38 | 72 ± 10 |
| XI | 5α-$C_{29}$ | 24 | 93 ± 19 |
| | *SMB 0–0.75 cm*[b] *(First batch)* | | |
| I,II | $C_{26}\Delta^{5,22}$+$C_{26}\Delta^{22}$ | 37 | 31 ± 13 |
| VI | $C_{27}\Delta^5$ | 86 | 73 ± 10 |
| VII | 5α-$C_{27}$ | 54 | 13 ± 11 |
| VIII | $C_{28}\Delta^{5,22}$ | 126 | 58 ± 11 |
| X | $C_{29}\Delta^5$ | 113 | 13 ± 11 |
| XI | 5α-$C_{29}$ | (lost) | |
| | *SMB 0–0.75 cm*[c] *(Second batch)* | | |
| I,II | $C_{26}\Delta^{5,22}$+$C_{26}\Delta^{22}$ | 46 | 62 ± 19 |
| IV | $C_{27}\Delta^{5,22}$ | 113 | 71 ± 10 |
| VI | $C_{27}\Delta^5$ (a,b) | 50, 74 | 80 ± 16; 61 ± 12 |
| XI | 5α-$C_{29}$ | 96 | 90 ± 15 |
| XII | dinosterol(a,b) | 48, 85 | 61 ± 13; 81 ± 14 |
| | *SMB 4.5–5.5 cm*[d] | | |
| I,II | $C_{26}\Delta^{5,22}$+$C_{26}\Delta^{22}$ | (lost) | |
| VI | $C_{27}\Delta^5$ | 39 | -64 ± 23 |
| VII | 5α-$C_{27}$ | (lost) | |
| VIII | $C_{28}\Delta^{5,22}$ | 63 | -61 ± 15 |
| X | $C_{29}\Delta^5$ | 48 | -59 ± 20 |
| XI | 5α-$C_{29}$ | 37 | -102 ± 20 |
| XII | dinosterol | 98 | -88 ± 14 |

[a]Batch average $\Delta^{14}C$ is 69 ± 14‰.
[b]Batch average $\Delta^{14}C$ is 38 ± 27‰.
[c]Batch average $\Delta^{14}C$ is 73 ± 12‰.
[d]Batch average $\Delta^{14}C$ is –75 ± 19‰.

The $\delta^{13}C$ values obtained for SMB and SBB sterols [*Pearson,* 2000] also support this conclusion. For the SMB 0–0.75 cm fraction, $\delta^{13}C$ ranged between –26.7‰ ($C_{26}\Delta^{5,22}$) and –24.9‰ ($C_{27}\Delta^5$). The SMB 4.5–5.5 cm sample had $\delta^{13}C$ values between –25.9‰ (5α-$C_{27}$) and –23.8‰ ($C_{27}\Delta^5$). The SBB sterols were similar to the SMB 0–0.75 cm data (–25.9‰ for $C_{28}\Delta^{5,22}$ to –23.9‰ for $C_{27}\Delta^5$). There is no isotopic depletion in the $C_{29}$ compounds as would be expected from a significant terrestrial $C_3$ plant contribution.

The utility of a marine photosynthetic biomarker proxy for $\Delta^{14}C_{DIC}$ lies in the universal nature of its application. Any marine sediment sample containing sufficient quantities of these compounds could potentially yield a record of surface water $^{14}C$ reservoir age. This finding could open problematic geographical regions such as the Southern Ocean to new investigations of paleocirculation. It is also independent of biologically determined "vital effects" or variations in calcification depth that may affect the foraminiferal isotopic signal. The $^{14}C$ isotopic variation for algal biomarkers is limited to the gradient in $\Delta^{14}C_{DIC}$ observed within the euphotic zone, to seasonal variations in growth patterns, and to changes in the extent of upwelling or other circulation changes.

Since the sterol $^{14}C$ data correspond so well to the $\Delta^{14}C_{DIC}$ record, it is possible that in certain environments, the entire sterol lipid class could be used as a surface water isotopic tracer. This could eliminate the time-consuming nature of compound-specific PCGC isolations by requiring only wet-chemical separations. Combining all the sterols also would effectively reduce the sample size requirement. This would be an advantage when dealing with more highly degraded, deeper core horizons in which diagenetic degradation has reduced the sterol concentrations. It would also reduce the sample preparation time and make this approach more accessible to laboratories lacking the expensive PCGC machinery.

## 4. Conclusions

Values of $\Delta^{14}C$ for eight different sterols isolated from Santa Monica and Santa Barbara Basin sediments showed that these lipids preserved the record of $\Delta^{14}C_{DIC}$ at the time of biomass production. The data showed the sterols accurately tracked a temporal change in surface water isotopic composition. In this case, they recorded the increase in mixed layer $^{14}C$ concentration caused by uptake of $^{14}CO_2$ generated during atmospheric nuclear weapons tests.

The rapid translation of the change in $\Delta^{14}C_{DIC}$ into the sedimentary record indicated that heterotrophic processing and export of euphotic zone primary production proceeded very rapidly (< 10 years), without a long residence time within the suspended POC pool. The agreement of $\Delta^{14}C_{sterol}$ and $\Delta^{14}C_{DIC}$ values also confirmed that recently produced phytoplanktonic carbon was the major food source for heterotrophic consumers.

The $\Delta^{14}C$ data for the $C_{29}$ sterols in these sediments were very similar to the data for algal and zooplanktonic ($C_{26}$-$C_{28}$) sterols. No significant fraction of the $C_{29}$ isomers appeared to be of terrestrial origin. This is consistent with several studies that have shown a widespread occurrence of $C_{29}$ sterols in marine organisms and questioned their use as a tracer of terrestrial inputs.

**Acknowledgments.** The authors wish to thank the NOSAMS facility staff for AMS analytical support, C. Johnson, L. Houghton, and E. Franks for $\delta^{13}C$ analyses, and B. Benitez-Nelson for general laboratory assistance. SIO and the crew of the R/V *Roger Revelle* generously donated their time for 2 days of sample collection in SMB and SBB. B. Popp and S. Schouten are thanked for their helpful reviews. This work was supported by NSF grants OCE-9415568, OCE-9809624, and OCE-9708478 to T.I.E. and by the NOSAMS-NSF cooperative agreement. A.P. was also supported by an MIT Ida Green fellowship and an EPA graduate fellowship. WHOI contribution number 10246.

## References

Adkins, J. F., and E. A. Boyle, Changing atmospheric $\Delta^{14}C$ and the record of deep water paleoventilation ages, *Paleoceanography, 12*, 337-344, 1997.

Adkins, J. F., H. Cheng, E. A. Boyle, E. R. M. Druffel, and R. L. Edwards, Deep-sea coral evidence for rapid change in ventilation of the deep North Atlantic 15,400 years ago, *Science, 280*, 725-728, 1998.

Bard, E., M. Arnold, J. Mangerud, M. Paterne, L. Labeyrie, J. Duprat, M.-A. Mélières, E. Sønstegaard, and J.-C. Duplessy, The North Atlantic atmosphere-sea surface $^{14}C$ gradient during the Younger Dryas climatic event, *Earth Planet. Sci. Lett., 126*, 275-287, 1994.

Baumgartner, T. R., and J. Southon, A 1500-year radiocarbon record of near-surface ocean reservoir ages obtained from the varved sediments of the Santa Barbara Basin, California, *Eos Trans. AGU, 77*(46), Fall Meet. Suppl., F298, 1996.

Behl, R. J., and J. P. Kennett, Brief interstadial events in the Santa Barbara basin, NE Pacific, during the past 60 kyr, *Nature, 379*, 243-246, 1996.

Benoit, G. J., K. K. Turekian, and L. K. Benninger, Radiocarbon dating of a core from Long Island Sound, *Estuarine Coastal Mar. Sci., 9*, 171-180, 1979.

Broecker, W. S., T.-H. Peng, S. Trumbore, G. Bonani, and W. Wolfli, The glacial distribution of radiocarbon in the glacial ocean, *Global Biogeochem. Cycles, 4*, 103-117, 1990.

Christensen, C. J., D. S. Gorsline, D. E. Hammond, and S. P. Lund, Non-annual laminations and expansion of anoxic basin-floor conditions in Santa Monica Basin, California Borderland, over the past four centuries, *Mar. Geol., 116*, 399-418, 1994.

Curry, W. B., and T. J. Crowley, The $\delta^{13}C$ of equatorial Atlantic surface waters: Implications for ice age $pCO_2$ levels, *Paleoceanography, 2*, 489-517, 1987.

Deuser, W. G., Seasonal and interannual variations in deep water particle fluxes in the Sargasso Sea and their relation to surface hydrography, *Deep Sea Res., 33*, 225-246, 1986.

Druffel, E. R. M., Decade timescale variability of ventilation in the North Atlantic: High-precision measurements of bomb radiocarbon in banded corals, *J. Geophys. Res., 94*(C3), 3271-3285, 1989.

Druffel, E. M., and H. E. Suess, On the radiocarbon record in banded corals: Exchange parameters and net transport of $^{14}CO_2$ between atmosphere and surface ocean, *J. Geophys. Res., 88*(C2), 1271-1280, 1983.

Duplessy, J.-C., M. Arnold, E. Bard, A. Juillet-Leclerc, N. Kallel, and L. Labeyrie, AMS $^{14}C$ study of transient events and of the ventilation rate of the Pacific intermediate water during the last deglaciation, *Radiocarbon, 31*, 493-502, 1989.

Edwards, R. L., J. W. Beck, G. S. Burr, D. J. Donahue, J. M. A. Chappell, A. L. Bloom, E. R. M. Druffel, and F. W. Taylor, A large drop in atmospheric $^{14}C/^{12}C$ and reduced melting in the Younger Dryas documented with $^{230}Th$ of corals, *Science, 260*, 962-968, 1993.

Eglinton, T. I., L. I. Aluwihare, J. E. Bauer, E. R. M. Druffel, and A. P. McNichol, Gas chromatographic isolation of individual compounds from complex matrices for radiocarbon dating, *Anal. Chem., 68*, 904-912, 1996.

Eglinton, T. I., B. C. Benitez-Nelson, A. Pearson, A. P. McNichol, J. E. Bauer, and E. R. M. Druffel, Variability in radiocarbon ages of individual organic compounds from marine sediments, *Science, 277*, 796-799, 1997.

Emery, K. O., and E. E. Bray, Radiocarbon dating of California Basin sediments, *Am. Assoc. Petrol. Geol. Bull., 46*, 1839-1856, 1962.

François, R., M. A. Altabet, E.-F. Yu, D. M. Sigman, M. P. Bacon, M. Frank, G. Bohrmann, G. Bareille, and L. D. Labeyrie, Contribution of Southern Ocean surface-water stratification to low atmospheric $CO_2$ concentrations during the last glacial period, *Nature, 389*, 929-935, 1997.

Goad, L. J., Sterol biosynthesis and metabolism in marine invertebrates, *Pure Appl. Chem., 51*, 837-852, 1981.

Goñi, M. A., K. C. Ruttenberg, and T. I. Eglinton, A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico, *Geochim. Cosmochim. Acta, 62*, 3055-3075, 1998.

Grice, K., W. C. M. Klein Breteler, S. Schouten, V. Grossi, J. W. de Leew, and J. S. Sinninghe Damsté, Effects of zooplankton herbivory on biomarker proxy records, *Paleoceanography, 13*, 686-693, 1998.

Guilderson, T. P., and D. P. Schrag, Abrupt shift in subsurface temperatures in the tropical Pacific associated with changes in El Niño, *Science, 281*, 240-243, 1998.

Hagadorn, J. W., L. D. Stott, A. Sinha, and M. Rincon, Geochemical and sedimentologic variations in inter-annually laminated sediments from Santa Monica Basin, *Mar. Geol., 125*, 111-131, 1995.

Harvey, R. H., G. Eglinton, S. C. M. O'Hara, and E. D. S. Corner, Biotransformation and assimilation of dietary lipids by *Calanus* feeding on a dinoflagellate, *Geochim. Cosmochim. Acta, 51*, 3031-3040, 1987.

Hayes, J. M., K. H. Freeman, B. N. Popp, and C. H. Hoham, Compound-specific isotopic analyses: A novel tool for reconstruction of ancient biogeochemical processes, *Org. Geochem., 16*, 1115-1128, 1990.

Hedges, J. I., Global biogeochemical cycles: Progress and problems, *Mar. Chem., 39*, 67-93, 1992.

Hedges, J. I., and P. L. Parker, Land-derived organic matter in surface sediments from the Gulf of Mexico, *Geochim. Cosmochim. Acta, 40*, 1019-1029, 1976.

Huang, W.-Y., and W. G. Meinschein, Sterols as source indicators of organic materials in sediments, *Geochim. Cosmochim. Acta, 40*, 323-330, 1976.

Hughen, K. A., J. T. Overpeck, S. J. Lehman, M. Kashgarian, J. Southon, L. C. Peterson, R. Alley, and D. M. Sigman, Deglacial changes in ocean circulation from an extended radiocarbon calibration, *Nature, 391*, 65-68, 1998.

Jones, G.A., and A. R. Gagnon, Radiocarbon chronology of Black Sea sediments, *Deep-Sea Res., 41*, 531-557, 1994.

Levin, I., and B. Kromer, Twenty years of atmospheric $^{14}CO_2$ observations at Schauinsland, *Radiocarbon, 39*, 205-218, 1997.

Levin, I., B. Kromer, H. Schoch-Fischer, M. Bruns, M. Münnich, D. Berdau, J. C. Vogel, and K. O. Münnich, 25 years of tropospheric $^{14}C$ observations in central Europe, *Radiocarbon, 27*, 1-19, 1985.

Mangerud, J., and S. Gulliksen, Apparent radiocarbon ages of recent marine shells from Norway, Spitsbergen, and Arctic Canada, *Quat. Res., 5*, 263-273, 1975.

Masiello, C. A., and E. R. M. Druffel, Black carbon in deep-sea sediments, *Science, 280*, 1911-1913, 1998.

McCaffrey, M. A., J. W. Farrington, and D. J. Repeta, The organic geochemistry of Peru margin surface sediments, II, Paleoenvironmental implications of hydrocarbon and alcohol profiles, *Geochim. Cosmochim. Acta, 55*, 483-498, 1991.

McNichol, A. P., and G. A. Jones, Measuring $^{14}C$ in seawater $\Sigma CO_2$ by accelerator mass spectrometry, WHP operations and methods, *1991 WOCE Operations Manual*, part 3.1.2, *Requirements for WHP Data Reporting*, edited by T. Joyce, C. Corry, and M. Stalcup, *WHPO Publ. 90-1*, 71 pp., Woods Hole, Massachusetts, 1991.

McNichol, A. P., E. A. Osborne, A. R. Gagnon, B. Fry, and G. A. Jones, TIC, TOC, DIC, DOC, PIC, POC–Unique aspects in the preparation of oceanographic samples for $^{14}C$-AMS, *Nucl. Instr. Meth. Phys. Res., Sect. B92*, 162-165, 1994a.

McNichol, A. P., G. A. Jones, D. L. Hutton, and A. R. Gagnon, The rapid preparation of seawater $\Sigma CO_2$ for radiocarbon analysis at the National Ocean Sciences AMS facility, *Radiocarbon, 36*, 237-246, 1994b.

National Ocean Sciences Accelerator Mass Spectrometry Facility, Radiocarbon results, *WOCE Rep. 3, WOCE Transect P17C, WOCE Data Rep. 94-093*, Woods Hole, Massachusetts, 1994.

Pearson, A., Biogeochemical applications of compound-specific radiocarbon analysis, Ph.D. thesis, Woods Hole Oceanographic Institution/Massachusetts Institute of Technology, Woods Hole, Massachusetts, 2000.

Pearson, A., A. P. McNichol, R. J. Schneider, and K. F. von Reden, Microscale AMS $^{14}C$ measurement at NOSAMS, *Radiocarbon, 40*, 61-76, 1998.

Rau, G. H., D. M. Karl, and R. S. Carney, Does inorganic carbon assimilation cause $^{14}C$ depletion in deep-sea organisms?, *Deep Sea Res., 33*, 349-357, 1986.

Ravelo, C., and R. G. Fairbanks, Oxygen isotope composition of multiple species of planktonic foraminifera: Recorders of the modern photic zone temperature gradient, *Paleoceanography, 7*, 815-831, 1992.

Robinson, S. W., Natural and man-made radiocarbon as a tracer for coastal upwelling processes, *Coastal Estuarine Sci., 1*, 298-302, 1981.

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

Schouten, S., W. C. M. Klein Breteler, P. Blokker, N. Schogt, W. I. C. Rijpstra, K. Grice, M. Baas, and J. S. Sinninghe Damsté, Biosynthetic effects on the stable carbon isotopic compositions of algal lipids: Implications for deciphering the carbon isotopic biomarker record, *Geochim. Cosmochim Acta., 62*, 1397-1406, 1998.

Southon, J. R., D. E. Nelson, and J. S. Vogel, A record of past ocean-atmosphere radiocarbon differences from the Northeast Pacific, *Paleoceanography, 5*, 197-206, 1990.

Stuiver, M., and T. F. Braziunas, Modeling atmospheric $^{14}C$ influences and $^{14}C$ ages of marine samples to 10,000 BC, *Radiocarbon, 35*, 137-189, 1995.

Stuiver, M., and H. A. Polach, Discussion: Reporting of $^{14}C$ data, *Radiocarbon, 19*, 355-363, 1977.

Stuiver, M., G. W. Pearson, and T. F. Braziunas, Radiocarbon age calibration of marine samples back to 9000 cal yr BP, *Radiocarbon, 28*, 980-1021, 1986.

Suess, H. E., Natural radiocarbon and the rate of exchange of $CO_2$ between the atmosphere and the sea, *Proceedings of the Conference on Nuclear Processes in Geological Settings*, pp. 52-56, Univ. of Chicago Press, Chicago, Ill., 1953.

Volkman, J. K., A review of sterol markers for marine and terrigenous organic matter, *Org. Geochem., 9*, 83-99, 1986.

Volkman, J. K., J. W. Farrington, and R. B. Gagosian, Marine and terrigenous lipids in coastal sediments from the Peru upwelling region at 15°S: Sterols and triterpene alcohols, *Org. Geochem., 11*, 463-477, 1987.

von Reden, K. F., R. J. Schneider, A. P. McNichol, and A. Pearson, $^{14}C$ AMS measurements of < 100 μg samples with a high-current system, *Radiocarbon, 40*, 247-253, 1998.

Wang, X.-C., E. R. M. Druffel, S. Griffin, C. Lee, and M. Kashgarian, Radiocarbon studies of organic compound classes in plankton and sediment of the northeastern Pacific Ocean, *Geochim. Cosmochim. Acta, 62*, 1365-1378, 1998.

Wakeham, S. G., and J. A. Beier, Fatty acid and sterol biomarkers as indicators of particulate matter source and alteration processes in the Black Sea, *Deep Sea Res., 38*, S943-S968, 1991.

Weidman, C. R., and G. A. Jones, A shell-derived time history of bomb $^{14}C$ on Georges Bank and its Labrador Sea implications, *J. Geophys. Res., 98*, 14,577-14,588, 1993.

Williams, P. M., K. J. Robertson, A. Soutar, S. M. Griffin, and E. R. M. Druffel, Isotopic signatures ($^{14}C$, $^{13}C$, $^{15}N$) as tracers of sources and cycling of soluble and particulate organic matter in the Santa Monica Basin, California, *Prog. Oceanogr., 30*, 253-290, 1992.

T. I. Eglinton and A. Pearson, Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Mail Stop 4, Woods Hole, MA 02543. (teglinton@whoi.edu; apearson@whoi.edu)

A. P. McNichol, NOSAMS Facility, Department of Marine Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA 02543. (amcnichol@whoi.edu)

(Received November 8, 1999;
revised June 14, 2000;
accepted June 20, 2000.)