Age discrepancy between molecular biomarkers and calcareous foraminifera isolated from the same horizons of Northwest Pacific sediments

Masao Uchida, Yasuyuki Shibata, Ken’ichi Ohkushi, Minoru Yoneda, Kimitaka Kawamura, Masatoshi Morita

Laboratory for Molecular Biogeochemistry and Chemical Oceanography, Institute of Observational Research for Global Change (IORGC), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushimatyo, Yokosuka, Kanagwa 237-0061, Japan
AMS Facility, Environmental Chemistry Division, National Institute for Environmental Studies, Tsukuba, Japan
Faculty of Education, Ibaraki University, Mito, Japan
Institute of Low Temperature Sciences, Hokkaido University, Sapporo, Japan

Received 6 April 2004; received in revised form 13 December 2004; accepted 26 January 2005

Abstract

Recent observations show that establishment of molecular-level radiocarbon stratigraphy is increasingly critical for paleoceanographic studies, especially to enable comparable discussion about past ocean and climate changes inferred from multiple proxy records based on lipid biomarkers and calcareous foraminiferal microfossils. So far, although we have interesting evidence that there are temporal and spatial age offsets between the algal alkenone biomarker used for SST (sea surface temperature) estimates and planktonic foraminifera in regions with high sedimentation rates, less is known about such age offsets in the settings of lower sedimentation. In this study, to investigate the potential of biomarkers as an alternative dating proxy to foraminifera in a low sedimentation rate setting, we measured radiocarbon ages of 17 different lipid biomarkers [fatty acids (FAs), n-alkanes, and alkenones], bulk total organic matter (TOC), and foraminifera from two sections (12–15 cm and 21–24 cm depth) of a surface sediment core in the Northwest Pacific. The sedimentation rate, estimated from the TOC, ranged from 10.5 cm/kyr in the core top to 0.9 cm/kyr in the lower part of the core. The ages of the FAs detected at 12–15 cm depth ranged from 530 yr BP (C18) to 3250 yr BP (C28). The 14C analysis of the FAs could be divided into two groups: FAs (C16, C18) derived from marine organisms and those (C24, C26, C28) derived from terrestrial higher plants. The high molecular weight (HMW) FAs’ ages were older [2550 yr BP (C24) to 3250 yr BP (C28)] than those of the low molecular weight (LMW) FAs [530 yr BP (C18) to 1820 yr BP (C16)]. At 21–24 cm depth, the alkenone ages were 7100–7300 yr younger than those of the planktonic foraminifera. In this horizon, the alkenone 14C age (7500 yr BP) and the alkenone-estimated SST (15.3 °C) suggest that these alkenones were produced in this region during the Holocene. The alkenone 14C age was also in good agreement with those of the LMW FAs (C14, iC15, aC15, C16, and C18:1) derived from marine plankton and bacteria. Similarly, the TOC age was 5700 yr
younger than that of the planktonic foraminifera. These age differences are large compared with those estimated for the horizon at 12–15 cm depth, which was characterized by a relatively higher sedimentation rate. These trends between ages of alkenones, TOC, and planktonic foraminifera are not comparable to the results from sites with high sedimentation rates, such as the Benguela upwelling system [Mollenhauer, G., Eglinton, T.I., Ohkouchi, N., Schneider, R.R., Muller, P.J., Grootes, P.M., et al., 2003. Asynchronous alkenone and foraminifera records from the Benguela upwelling system. Geochim. Cosmochim. Acta 67, 2157–2171] or the Bermuda Rise drift deposit [Ohkouchi, N., Eglinton, T.I., Keigwin, L.D., Hayes, J.M., 2002. Spatial temporal offsets between proxy records in a sedimt drift. Science 289, 1224–1227], which are significantly different sedimentary settings from our site. The radiocarbon results from these high sedimentation rate regions suggest that the alkenones are several thousand years older than the coexisting planktonic foraminifera. On the other hand, the age offsets between alkenones and planktonic foraminifera at our site are larger than those from the other sites, and the alkenones are younger than the planktonic foraminifera. © 2005 Elsevier B.V. All rights reserved.

Keywords: Compound-specific radiocarbon analysis (CSRA); Molecular chronology; Alkenones; Fatty acid; n-alkanes; Northwest Pacific

1. Introduction

Recent advances in compound-specific radiocarbon analysis (CSRA) have been achieved by using a preparative capillary gas chromatography (PCGC) system, which makes it possible to separate target compounds in complex mixtures of marine organic matter and to recover sufficient quantities of individual organic compounds for accelerator mass-spectrometry (AMS) $^{14}$C measurements (Eglinton et al., 1996; Uchida et al., 2000). Several studies have already provided molecular-level radiocarbon data of marine-derived and terrestrial-derived organic compounds found in marine sediments (Domack et al., 1999; Eglinton et al., 1997, 2000; Pearson et al., 2000, 2001; Uchida et al., 2001). Moreover, compound-specific radiocarbon data, as well as compound-specific stable carbon isotope data, provide valuable information on the origin of sedimentary organic carbon in marine sediments and carbon cycling in the ocean.

For Late Quaternary paleoceanographic studies, planktonic foraminifera-based radiocarbon stratigraphy is believed to be the single best tool. However, it is often difficult to obtain sufficient amounts of planktonic foraminifera, even for AMS dating methods. As a result, instead of foraminifera, alternative age models based on the radiocarbon age of bulk total organic matter (TOC) are generally used (Nakatsuka et al., 1995; Harada et al., 2004). However, recent research on compound-specific radiocarbon from sediments has shown that ages of TOC in marine sediments are unreliable, because pre-aged and relict organic material such as humic detritus is often reworked in the sediments and because of the age uncertainty of organic components from marine and terrestrial sources (Eglinton et al., 1997; Pearson et al., 2000, 2001; Pearson and Eglinton, 2000; Uchida et al., 2001). Moreover, such observations lead us to suspect the critical assumption that there are no age discrepancies between foraminifera and other sediment constituents, especially molecular organic compounds (biomarkers) such as alkenones, which are widely used for paleo-sea surface temperature (SST) reconstruction. In fact, we already know that there are large age discrepancies between alkenone and foraminifera from sites with enhanced accumulation rates (e.g., basin depocenters, drift deposits, and coastal upwelling areas), which are strongly influenced by lateral advection and resuspension (Ohkouchi et al., 2002; Mollenhauer et al., 2003). To better understand climate changes inferred from sediment cores and to assess the validity of coupling paleoenvironmental information from alkenones and calcareous microfossils, independent dating of these two proxies in sedimentary records is required (Sachs et al., 2000). This investigation is important not only in light of the establishment of a chronology by using organic matter but also to allow comparable discussion of different proxy records for paleoceanographic studies. To date, such investigations have focused on sediments deposited at a high sedimentation rate, and less is known about sites with low sedimentation rates.
In this study, we focused on a site with a low sedimentation rate to examine age offsets between marine- and terrestrial-derived compounds (fatty acids, \( n \)-alkanes, and alkenones), total organic carbon, and foraminifera isolated from the same sediment horizons.

2. Materials and methods

2.1. Core location and modern hydrography

One multiple-core sample (26 cm long) was collected at a water depth of 1536 m on the continental slope of the Northwest Pacific (40°29′N, 142°59′E) during cruise MR00-K01 of the Japan Agency for Marine-Earth Science and Technology (JAMSTEC) R/V Mirai. The sampling location (St. 1) is shown in Fig. 1. The sediments consisted of dark olive-colored homogenous diatomaceous mud. The sections from 12–15 and 21–24 cm depths were used for the compound-specific \(^{14}C\) analysis; 1-cm-thick sections from another multiple core collected at the same time and site were used for other analyses (water content, C/N ratio, TOC, TOC\(^{13}C\), TOC\(^{14}C\), alkenone-SST, and quantification of fatty acids).

Hydrographically, the sampling region is located in a mixed water region, where two important water-mass fronts, the Kuroshio and Oyashio fronts, are juxtaposed. The Kuroshio front is the northern limit of the warm, saline Kuroshio Extension current, and the Oyashio front is the southern limit of the cold, less saline Oyashio current. This region is characterized by considerable annual and interannual variation in SST as a result of the mixing of the two currents (Kawai, 1972). In addition, this region seems to be greatly influenced by past latitudinal migrations of the two major water-mass fronts related to climate changes during the Late Quaternary (Yamane and Oba, 1999; Oba et al., 1999).

Fig. 1. Sampling location of the multiple cores, which were collected at 1536 m water depth on the continental margin in the western North Pacific. Sampling locations of terrestrial (OR3) and marine (SR72) sediments in which \( \delta^{13}C \) values of individual fatty acids were measured by Naraoka et al. (1995) and Naraoka and Ishiwatari (2000) are also shown.
2.2. Lipid analysis

About 300 g each of freeze-dried and homogenized sediment samples was extracted for CSRA by using a large Soxhlet apparatus with dichloromethane/methanol (99:1 v/v) as the solvent (Eglinton et al., 1996). The 1-cm-thick samples (3–5 g each) were extracted to obtain fatty acids, n-alkanes, and alkenone SST by using an accelerated solvent extraction method (ASE200 system, Dionex., Sunnyvale, California, USA) at 100 °C and 6.9 MPa (1000 psi) with dichloromethane/methanol (99:1 v/v) as the solvent (Uchida et al., 2004a). Then the total extracts were saponified with 0.5 M KOH/methanol for 2 h under reflux. Neutral lipids were separated by extracting with dichloromethane/n-hexane (10:1 v/v), whereas acidic lipids were extracted with dichloromethane after the remaining solution was acidified to pH<1. The neutral fraction was further separated into four subfractions by using silica gel column chromatography (Bio-Sil A, Bio-Rad, Hercules, CA, USA; 200–400 mesh, deactivated with 1% water, Kawamura, 1995). Aliphatic hydrocarbons (N-1), polynuclear aromatic hydrocarbons (N-2), ketones and aldehydes (N-3), and n-fatty alcohols plus sterols (N-4) were eluted with n-hexane, n-hexane/dichloromethane (2:1 v/v), dichloromethane, and dichloromethane/methanol (95:5 v/v), respectively. The acidic lipids were derivatized to methyl esters with 14% BF3/methanol at 100 °C for 30 min. The methyl esters were separated into three subfractions (A-1, A-2, A-3) on the silica gel column by stepwise elution. Fatty acid methyl esters (FAMEs) (A-1) were eluted with n-hexane/dichloromethane (1:2 v/v). To determine the compound concentration and yield in a series of lipid extractions, 15-methyl hexadecanoic acid and 19-methyl octadecanoic acid were used as internal and external standards, respectively.

Each FAME, alkenone, and n-alkane fraction isolated by PCGC was analyzed by gas chromatography with flame ionization detection (GC-FID) and gas chromatography/mass spectrometry (GC/MS) to determine its amount and purity. Stable carbon isotope ratios of isolated compounds were also determined by isotope ratio monitoring gas chromatography/mass spectrometry (GC/C/IRMS) on a system consisting of an HP6890 GC and a Finnigan MAT252. n-Alkane and fatty acid isotopic compositions were obtained by using a fused silica capillary column (60 m, 0.32 mm i.d.) with an on-column injector. The GC oven temperature was increased from 50 °C (hold time: 1 min) to 120 °C at a rate of 10 °C/min and from 120 °C to 320 °C at a rate of 5 °C/min (hold time: 10 min.). The standard deviations of the replicate measurements, reported individually for each peak, were generally <±0.5‰.

To minimize potential errors with respect to carbon source introduced by the addition of carbon accompanying methyl ester derivatization of fatty acids prior to chromatographic separation, we applied a correction by measuring δ13C MeOH (−29.3‰, V-PDB) of the derivative reagent (BF3/MeOH) and using the following simple isotopic balance equation:

\[ C_n^{13}C_{\text{free}} = (C_n + 1) \cdot \delta^{13}C_{\text{MeOH}} - 1 \cdot \delta^{13}C_{\text{MeOH}} \]

where δ13C MeOH is the original value and Cn represents the carbon number of the derivatized compounds.

We determined the carbon isotopic compositions of bulk-phase organic matter and total lipid extract (TLE) by combustion in a sealed quartz tube with CuO/Ag at 850 °C for 4 h. The isotope ratios are relative to the V-PDB carbonate reference material (NBS-19).

2.3. PCGC system

The PCGC system consisted of an HP6890 GC system with FID, a cooled injection system (CIS, Gerstel, Mülheim an der Ruhr, Germany), a zero-dead-volume effluent splitter, and a cryogenic preparative fraction collection device (PFC, Gerstel). The PFC device consisted of an eight-port zero-dead-volume valve in a heated interface (320 °C) and six 10-ml glass traps and a 100-l glass waste trap supported in cooled units (−5 °C), with ethylene glycol circulation by an electric cooler.

The injection volume was approximately 10 ml hexane per injection, which corresponds to a total amount of approximately 5 mg C. The injection port (CIS) temperature was programmed to increase from 40 °C to 350 °C (hold time: 10 min) at a rate of 12.0 °C/min. Individual compounds were separated on a 60-m megabore (0.53 mm i.d.) fused silica capillary column coated with a cross-bonded methyl silicone phase (Rtx-1, Restek; film thickness 0.5 mm). The GC oven temperature for the FAME and n-alkane fractions was programmed to increase from 50 °C...
(hold time: 1 min) to 120 °C at a rate of 10 °C/min, and then to 320 °C at a rate of 5 °C/min (hold time: 10 min.). Run time was about 60 min. Helium was used as the carrier gas, with a flow rate of 5 ml/min. A more detailed account of the methodology for separating alkenones (C_{37}, C_{38}, C_{39}) will be presented by Uchida and Shibata (in preparation).

Prior to the compound-specific 14C analysis, we investigated the reproducibility of the results by replicate injections on the PCGC system. Isolation of the target compounds was successful with >90% trapping efficiency. In addition, the reliability of isolation of the target compounds by PCGC was checked. High-resolution gas chromatograms of the FAME and alkenone (C_{37}–C_{39}) fractions for the 21–24 cm horizon are shown in Figs. 2 and 3, respectively. The gas chromatograms of the target compounds before and after PCGC isolation and those of the vent traps after the PCGC separation are also shown. For the high molecular weight (HMW) FAMEs (C_{24}, C_{26}, C_{28}) and alkenones, additional carbon from the liquid phase of the capillary column must be removed after trapping; therefore, the trapped compounds were loaded onto a silica gel column to remove the additional carbon so that pure compounds were eluted by the dichloromethane. The estimated remove the additional carbon so that pure compounds before and after PCGC separation were 0.57 and 0.56, respectively. Purification of FAMEs and alkenones after PCGC separation was successful (Figs. 2 and 3). Yields of C_{37}:2Me and C_{37}:3Me were 45.1% and 58.6%, respectively. In addition, 94 µg of C_{38}–C_{39} alkenones were collected. The 14C age of the C_{38}–C_{39} alkenones was not measured owing to sample loss during the preparation for graphitization.

2.4. Preparation of PCGC-trapped compounds as graphite targets for AMS

After PCGC isolation, the trapped components were recovered from the U-tubes by the addition of CH$_2$Cl$_2$ (1 ml) and transferred to 2-ml glass vials. An aliquot (50 µl) of each trapped component was used to determine its purity, yield, and the stable carbon isotope ratios. For combustion, each trapped compound was transferred to a quartz tube (10 cm × 6 mm o.d.) by using CH$_2$Cl$_2$, and then the solvent was removed under a stream of high purity helium (99.999%). Then, Cu, Ag, and Cu were added to the quartz tubes, and the contents were combusted at 850 °C. As a precautionary measure to remove the residual solvent from the quartz tubes, they were evacuated to 10⁻⁶ Torr while immersed in dry ice/ethanol. Graphite targets for TOC and TLE containing approximately 1 mg C were prepared by the batch preparation method (Kitagawa et al., 1993). For microscale graphitization (for making graphite from <100 µg carbon), the technique developed by the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS), Woods Hole Oceanographic Institution, was applied (Pearson et al., 1998). A detailed account of microscale radiocarbon analysis used at the AMS facility of the National Institute for Environmental Studies (NIES-TERRA) is given by Uchida et al. (2004b). Radiocarbon analysis of bulk-phase organic matter with normal amounts (~1 mg carbon) of carbon was performed at NIES-TERRA (Kume et al., 1997; Shibata et al., 1997; Tanaka et al., 2000; Yoneda et al., 2004).

To minimize potential errors with respect to carbon sources introduced by the addition of carbon accompanying methyl ester derivatization of fatty acids prior to chromatographic separation, we applied a correction by measuring $\Delta^{14}$C$_{\text{MeOH}}$ (−995‰, 41,950 ± 240 yr BP) of the derivative reagent (BF$_3$/MeOH) and using the following simple isotopic balance equation:

$$C_n \cdot \Delta^{14}$C$_{\text{free}} = (C_n + 1) \cdot \Delta^{14}$C$_{\text{ester}} - 1 \cdot \Delta^{14}$C$_{\text{MeOH}}$$

where $\Delta^{14}$C$_{\text{free}}$ is the original age without contribution of derivative carbon and $C_n$ represents the carbon number of the derivatized compounds.

2.5. Radiocarbon analysis of foraminifera

A part of each sediment sample was washed with tap water over a 63-µm screen, rinsed in distilled water, and then dried at 50 °C. Under a binocular microscope, planktonic and benthic foraminifera were hand-picked from the samples and then cleaned by soaking in 30% hydrogen peroxide solution to remove adhering contaminants. Foraminifera shells (5–10 mg) were converted to CO$_2$ by dissolution in phosphoric acid as described by Uchida et al. (2004b), Ahagon and Uchida (2004) and Ohkushi et al. (2004). The gas was purified, reduced to graphite over an iron catalyst in the presence of H$_2$, and then dated at the AMS facilities at NIES-TERRA.
Fig. 2. High-resolution gas chromatography (HRGC) chromatograms of fatty acid methyl esters (FAMEs). The upper chromatogram shows GC traces before preparative capillary gas chromatography (PCGC) isolation of compounds, and the lower chromatograms show the traces of the individual compounds after PCGC isolation. The bottom chromatogram shows vent trap after PCGC isolation of target compounds. The peak numbers in the upper chromatogram correspond to the compounds isolated by PCGC as follows: 1, C14; 2, C16; 3, C18; 4, C24; 5, C26; and 6, C28. Chromatograms of trapped compounds after PCGC separation show successful isolation of target compounds with enough purity for AMS dating. I.S peak in the chromatogram shows an internal standard.
Fig. 3. HRGC chromatograms of long-chain (C₃₇–C₃₉) methyl and ethyl ketones with two to four double bonds (alkenones). The upper chromatogram shows high-resolution gas chromatography (HRGC) chromatograms before PCGC isolation and the lower two chromatograms show GC traces after PCGC isolation. The bottom chromatogram shows vent trap after PCGC isolation of target compounds.
2.6. Dual isotopic balance model using molecular-level $^{14}$C and $^{13}$C values

The dual isotopic balance model is used to constrain source contributions from terrestrial vascular plants, marine organisms, relict, and refractory organic carbon (e.g., kerogen), in relation to the origins of TOC (Pearson and Eglinton, 2000; Drenzek et al., 2003). Measurement of both $^{13}$C and $^{14}$C in bulk organic matter and its constituents allows three simultaneous equations to be written:

$$F_T + F_M + F_F = 1$$  \(3\)

$$\Delta^{14}C_{Bulk} = F_T \cdot \Delta^{14}C_T + F_M \cdot \Delta^{14}C_M + F_F \cdot \Delta^{14}C_F$$  \(4\)

$$\delta^{13}C_{Bulk} = F_T \cdot \delta^{13}C_T + F_M \cdot \delta^{13}C_M + F_F \cdot \delta^{13}C_F$$  \(5\)

where $F$ is the fractional abundance and the subscripts T, M, F, and Bulk indicate terrestrial (vascular plant), marine, fossil, and bulk OC, respectively. For the calculations performed here, a 1–2‰ TOC-to-$^{13}$C offset for marine organic carbon was systematically used.

2.7. Alkenone $U_{37}^K$ records

The alkenone thermometer, which has been used to calculate SST, is based on the unsaturation ratios of the C$_{37}$ alkenones, primarily the $U_{37}^K$ index. The $U_{37}^K$ index is defined as the ratio $(C_{37:2})/(C_{37:2}+C_{37:3})$, where $(C_{37:2})$ and $(C_{37:3})$ are the concentrations of methyl ketones with two and three double bonds, respectively. The $U_{37}^K$ index has been shown to have a linear relationship with the temperature of the water in which the alkenone producer lived (Brassell et al., 1986; Prahl and Wakeham, 1987; Prahl et al., 1988).

3. Results

3.1. Bulk parameters, stable carbon isotopes of TOC, and $U_{37}^K$

Down-core profiles of the TOC content, C/N ratio, $^{13}$C values of TOC, and water content are shown in Fig. 4. TOC ranged from approximately 2.5% to 1.0%, with higher values at the top of the core, and C/N ratios were between 7.4 and 9.5, with lower values...
13C values of TOC ranged between $-21.8\%$ and $-21.0\%$, with lighter values at the core bottom.

TOC 14C ages of 11 samples from the core were measured (Fig. 5). The TOC 14C ages of the upper 6 cm were constant, indicating that it is a mixing layer. The age of the bottom layer of the core sample, measured on bulk TOC, was approximately 12 000 yr BP. The sedimentation rates were estimated from the TOC 14C ages and varied drastically, from 10.5 cm/kyr (6–12 cm depth) to 2.8 cm/kyr (12–21 cm depth), to 0.9 cm/kyr (21–26 cm depth). These sedimentation rates were used to calculate the fluxes of fatty acids and alkenones. From these sedimentation rates, the 12–15 cm horizon corresponds to a time interval of 1070 yr and the 21–24 cm horizon corresponds to 3330 yr.

3.2. Down-core abundance profiles of fatty acids (FAs)

A typical chromatogram of straight-chain saturated C_{12}–C_{34} fatty acids (FAs) from the 21–24 cm horizon is shown in a top chromatogram of Fig. 2. The saturated fatty acids showed a bimodal pattern with maxima at C\textsubscript{16} and C\textsubscript{26} and even-carbon-number predominance. Monounsaturated fatty acids (C\textsubscript{16:1} and C\textsubscript{18:1}) and branched fatty acids (iC\textsubscript{15:0}, aIC\textsubscript{15:0}), which are derived from phytoplankton and bacteria, respectively (Perry et al., 1979; Reiten et al., 1994), were also detected in the sediments. In addition, it is known that benthos produces massive amounts of wax esters with long chain monounsaturated fatty acids (Kattner et al., 1989; Hagen et al., 1993). A similar chromatogram was previously obtained from the 12–15 cm horizon (Uchida et al., 2001). Saturated FAs in organisms are synthesized through the elongation of acetyl-CoA (e.g., Hitchcock and Nichols, 1971). Exogenous FAs may also be incorporated into phospholipids (Kattner and Hagen, 1995; Graeve et al., 1997). Marine benthos organisms contain higher C\textsubscript{18:1}FA than other marine organisms (Graeve et al., 1997). Down-core profiles of total FAs (C\textsubscript{14}–C\textsubscript{32}), iC\textsubscript{15} and anteisoC\textsubscript{15} FAs, C\textsubscript{16}FA, C\textsubscript{18}FA, C\textsubscript{24}FA, and C\textsubscript{26}FA concentrations and their fluxes are shown in Fig. 6. All concentrations gradually decreased down-core. In some layers, the decrease was drastic. The total FA flux was relatively high (3.8–5.8 \mu g cm\textsuperscript{-2} kyr\textsuperscript{-1}) above approximately 12 cm and low (0.3–2.1 \mu g cm\textsuperscript{-2} kyr\textsuperscript{-1}) below that depth; it was 3.8 \mu g cm\textsuperscript{-2} kyr\textsuperscript{-1} at the core top and 0.5 \mu g cm\textsuperscript{-2} kyr\textsuperscript{-1} at the bottom. Drastic changes in other fluxes were also observed to occur between 12 and 13 cm depth. The fluxes of isoC\textsubscript{15} and anteisoC\textsubscript{15} FAs, C\textsubscript{16}FA, and C\textsubscript{18}FA, which are derived from marine sources, were similar to those of the total FA flux.

3.3. Down-core profiles of alkenone abundance and alkenone-based SST

Down-core profiles of alkenone-based SST based on U\textsubscript{37}K, alkenone abundance, and alkenone flux are shown in Fig. 7. The SST varied between 13.5 °C (core bottom) and 15–17 °C (10–20 cm). The SST at the core top was 14.5 °C, which corresponds to the present-day SST for June (12 °C) to July (17.0 °C). Estimated alkenone-based SSTs from a nearby site (41°07.10’ N, 142°24.20’ E) range from ~17 °C during the Holocene to ~8 °C during the last glacial maximum (Harada et al., 2004). Alkenone abundances ranged between 0.1 and 1.4 \mu g/g dry sediments and displayed a bimodal pattern, with maxima at 4–6 and 15–20 cm depth. The large variation in abundance...
Fig. 6. Down-core profiles of total fatty acids (C14–C32), iC15 and aiC15, C16, C18, C24, and C26 fatty acids and their down-core flux profiles.

Fig. 7. Down-core profile of alkenone SST and alkenone abundances and fluxes. The SST of the core top was 14.5 °C, which corresponds to the present-day SST from June (12 °C) to July (17.0 °C). The arrow shows a decrease in the SST of −4.4 °C, from an analysis of a warm-water planktonic foraminifera assemblage, took place between the interglacial and glacial periods at the study site (Oba et al., 1999; Yamane and Oba, 1999).
likely reflects the variation in sedimentation rate. The highest alkenone flux was observed at 4–6 cm depth. On the other hand, the maximum fluxes of total FAs (C\textsubscript{14}–C\textsubscript{32}), iC\textsubscript{15} and anteisoC\textsubscript{15} FAs, C\textsubscript{16}FA, C\textsubscript{18}FA, C\textsubscript{24}FA, and C\textsubscript{26}FA were also observed at the upper layer of 12 cm depth.

Table 1

AMS radiocarbon ages of fatty acids, alkenones, n-alkanes, foraminiferas, and TOC in the Northwest Pacific sediments

<table>
<thead>
<tr>
<th>Target compounds</th>
<th>Inferred source</th>
<th>$\delta^{13}C$\textsuperscript{a} (%)</th>
<th>Yields\textsuperscript{b} (µgC)</th>
<th>$\Delta^{14}C$\textsuperscript{c} (%)</th>
<th>$^{14}$C age\textsuperscript{d} ± error (yrs BP)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sediment layers of 12 to 15 cm</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fatty acids s methyl ester (FAMEs)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{16}</td>
<td>Plankton</td>
<td>−25.1</td>
<td>265</td>
<td>−198</td>
<td>1830 ± 130</td>
</tr>
<tr>
<td>C\textsubscript{18}</td>
<td>Plankton/benthos</td>
<td>−27.1</td>
<td>220</td>
<td>−62</td>
<td>530 ± 60</td>
</tr>
<tr>
<td>C\textsubscript{24}</td>
<td>Plant wax</td>
<td>−30.6</td>
<td>158</td>
<td>−266</td>
<td>2550 ± 70</td>
</tr>
<tr>
<td>C\textsubscript{26}</td>
<td>Plant wax</td>
<td>−28.2</td>
<td>262</td>
<td>−296</td>
<td>2900 ± 210</td>
</tr>
<tr>
<td>C\textsubscript{28}</td>
<td>Plant wax</td>
<td>−31.8</td>
<td>233</td>
<td>−328</td>
<td>3250 ± 370</td>
</tr>
<tr>
<td>TOC</td>
<td></td>
<td>−20.9</td>
<td></td>
<td></td>
<td>2260 ± 70</td>
</tr>
<tr>
<td>Benthic foram. (mix)e,f</td>
<td></td>
<td>−1.2</td>
<td></td>
<td></td>
<td>2520 ± 40</td>
</tr>
<tr>
<td><strong>Sediment layers of 21 to 24 cm</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fatty acids as methyl ester (FAMEs)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{14}</td>
<td>Plankton</td>
<td>−24.3</td>
<td>211</td>
<td>−579</td>
<td>7120 ± 10</td>
</tr>
<tr>
<td>C\textsubscript{16}</td>
<td>Plankton</td>
<td>−23.6</td>
<td>372</td>
<td>−589</td>
<td>7330 ± 100</td>
</tr>
<tr>
<td>C\textsubscript{18}</td>
<td>Plankton/benthos</td>
<td>−23.2</td>
<td>290</td>
<td>−309</td>
<td>3050 ± 140</td>
</tr>
<tr>
<td>i and ai C\textsubscript{15}</td>
<td>Bacteria</td>
<td>−25.4</td>
<td>70</td>
<td>−621</td>
<td>8000 ± 110</td>
</tr>
<tr>
<td>C\textsubscript{18:1}</td>
<td>Bacteria/plankton</td>
<td>−25.9</td>
<td>265</td>
<td>−580</td>
<td>7120 ± 110</td>
</tr>
<tr>
<td>C\textsubscript{24}</td>
<td>Plant wax</td>
<td>−34.5</td>
<td>153</td>
<td>−747</td>
<td>11 200 ± 140</td>
</tr>
<tr>
<td>C\textsubscript{26}</td>
<td>Plant wax</td>
<td>−33.2</td>
<td>207</td>
<td>−742</td>
<td>11 200 ± 140</td>
</tr>
<tr>
<td>C\textsubscript{28}</td>
<td>Plant wax</td>
<td>−32.6</td>
<td>172</td>
<td>−778</td>
<td>12 100 ± 140</td>
</tr>
<tr>
<td>Alkenos (C\textsubscript{37–39})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{37}</td>
<td>Coccolithforia</td>
<td>−25.1</td>
<td>103</td>
<td>−608</td>
<td>7520 ± 110</td>
</tr>
<tr>
<td>C\textsubscript{38}, C\textsubscript{39}</td>
<td>Coccolithforia</td>
<td>na</td>
<td>103</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>n–Alkanes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{24}, 26, 28</td>
<td>Plant wax</td>
<td>na</td>
<td>46</td>
<td>−791</td>
<td>12 570 ± 440</td>
</tr>
<tr>
<td>C\textsubscript{25}</td>
<td>Plant wax</td>
<td>na</td>
<td>89</td>
<td>−770</td>
<td>11 790 ± 290</td>
</tr>
<tr>
<td>C\textsubscript{27}</td>
<td>Plant wax</td>
<td>na</td>
<td>117</td>
<td>−787</td>
<td>11 690 ± 300</td>
</tr>
<tr>
<td>C\textsubscript{28}</td>
<td>Plant wax</td>
<td>na</td>
<td>122</td>
<td>−772</td>
<td>11 870 ± 310</td>
</tr>
<tr>
<td>C\textsubscript{24}, 26, 28</td>
<td>Plant wax</td>
<td>na</td>
<td>87</td>
<td>−838</td>
<td>14 630 ± 390</td>
</tr>
<tr>
<td>Total lipid extract (TLE)</td>
<td></td>
<td>−23.4</td>
<td>−678</td>
<td></td>
<td>9110 ± 90</td>
</tr>
<tr>
<td>TOC</td>
<td></td>
<td>−21.6</td>
<td>−678</td>
<td></td>
<td>9100 ± 60</td>
</tr>
<tr>
<td>Benthic foram. (mix)e,f</td>
<td></td>
<td>−1.15</td>
<td>−861</td>
<td>15 830 ± 100</td>
<td></td>
</tr>
<tr>
<td>Benthic foram. 1 (specific)e,g</td>
<td></td>
<td>−1.26</td>
<td>−857</td>
<td>15 650 ± 120</td>
<td></td>
</tr>
<tr>
<td>Benthic foram. 2 (specific)e,g</td>
<td></td>
<td>−1.32</td>
<td>−863</td>
<td>15 590 ± 130</td>
<td></td>
</tr>
<tr>
<td>Planktonic foram. (mix)e,h</td>
<td>0.06</td>
<td>−839</td>
<td>14 640 ± 90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Planktonic foram. (specific)e,i</td>
<td>−0.08</td>
<td>−842</td>
<td>14 810 ± 20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

na: not analyzed. Compounds with asterisks in the table are also treated under silicagel column chromatography in order to remove influences of column bleed.

\textsuperscript{a} Isotope ratio is relative to the V-PDB standard material and is corrected by measuring isotope ratio of derivative reagent (MeOH; −29.3\%).
\textsuperscript{b} Determined after PCGC isolation.
\textsuperscript{c} Radiocarbon concentration corrected for the presence of derivative carbon (MeOH; −995\%).
\textsuperscript{d} Radiocarbon age (yrs BP) reported using the Libby half-life of 5568 years.
\textsuperscript{e} Collected in the layer for compound-specific $^{14}$C analysis.
\textsuperscript{f} Uvigerina akitaensis and Globobulimina auriculata.
\textsuperscript{g} 1, Uvigerina akitaensis; 2, Nonionellina labradorica.
\textsuperscript{h} Neogloboquadrina pachyderma and Globigerina bulloides.
\textsuperscript{i} Neogloboquadrina pachyderma.
3.4. \(^{14}\text{C}\) ages of FAs, alkenones, n-alkanes, and foraminifera

The two sections from 12 to 15 cm and 21 to 24 cm depth were used for compound-specific \(^{14}\text{C}\) analysis of n-alkanes, alkenones, and fatty acids (FAs) and for the \(^{14}\text{C}\) analysis of planktonic and benthic foraminifera. However, the \(^{14}\text{C}\) age of planktonic foraminifera was reported only for the 21–24 cm horizon because the quantity of planktonic foraminifera in the 12–15 cm horizon was insufficient for the AMS analysis. The results of \(^{14}\text{C}\) age are shown in Table 1 and Fig. 8. The compound-specific \(^{14}\text{C}\) ages of 10 fatty acids were determined as fatty acid methyl esters (FAMES). These fatty acids represent marine organisms (C\(_{14}\), C\(_{16}\), C\(_{18}\), and C\(_{18:1}\) FAs), bacterial (iso- and anteiso-C\(_{15}\) FAs), and terrestrial carbon sources (C\(_{24}\), C\(_{26}\), and C\(_{28}\) FAs).

3.4.1. 12–15 cm horizon

The FAs detected in the 12–15 cm horizon of the core ranged from 530 yr BP (C\(_{18}\)) to 3250 yr BP (C\(_{28}\)) in age. The \(^{14}\text{C}\) ages of FAs were divided into two groups: low molecular weight (LMW) FAs (C\(_{16}\), C\(_{18}\)) derived from marine organisms and high molecular weight (HMW) FAs (C\(_{24}\), C\(_{26}\), C\(_{28}\)) derived from terrestrial higher plants. The HMW FAs, which ranged in age from 2550 yr BP (C\(_{24}\)) to 3250 yr BP (C\(_{28}\)), were older than the LMW FAs [530 yr BP (C\(_{18}\)] to 1820 yr BP (C\(_{16}\)]. Benthic foraminifera and TOC

Fig. 8. Radiocarbon ages of several sample types: fatty acids, alkenones, n-alkanes, TOC, and TLE, and planktonic and benthic foraminifera isolated from the 12–15 cm (1(a), 1(b)) and 21–24 cm (2(a), 2(b)) horizons in the sediment core.
were dated at 2520 yr BP and 2260 yr BP, respectively. Although planktonic foraminifera were not dated, the radiocarbon age of planktonic foraminifera is usually 900–1600 yr younger than that of benthic foraminifera in this region (Ahagon et al., 2003; Ahagon and Uchida, 2004). Thus, the estimated age of planktonic foraminifera in this section was around 920 yr BP to 1620 yr BP. The estimated planktonic foraminiferal age was thus similar to the measured ages of LMW FAs, implying that there is only a small or no age offset between planktonic foraminifera and LMW FAs. In addition, the estimated age of the planktonic foraminifera was 600–2300 yr younger than LMW FAs and TOC.

3.4.2. 21–24 cm horizon

The 14C ages of compounds in the 21–24 cm horizon could also be divided into two groups: those with ages of approximately 7120–8000 yr BP (LMW FAs and alkenones, except for C18 FA) and those with ages of 11 500–12 500 yr BP (HMW FAs and n-alkanes). Exceptionally, mixed n-alkanes (C24, C26, C28) yielded the oldest ages (14,630 yr BP) among the biomarkers in this section. 14C ages of planktonic and benthic foraminifera were significantly different from those of biomarkers, which are inferred to be derived from marine sources. The ages of planktonic foraminifera were 14,640–14,810 yr BP, and those of benthic foraminifera were 15,590–15,830 yr BP. Age offsets between planktonic and benthic foraminifera were 950–1020 yr, which is consistent with the age offset between those foraminifera during the deglaciation in this region (Ahagon et al., 2003; Ohkushi et al., 2004). The 14C ages of algal lipids, “C37 alkenones,” in the 21–24 cm horizon, were 7100–7300 yr younger than those of planktonic foraminifera. The alkenone 14C age was also in good agreement with those of the LMW FAs except for C18 FA in the same horizon. If the alkenone 14C age in the 12–15 cm horizon was similar to that of the LMW FAs of the same horizon, then the age offset between alkenone and foraminifera would be very small. These results are not comparable to those from sites with very high sedimentation rates such as the Benguela upwelling system (Mollenhauer et al., 2003) and the Bermuda Rise drift deposit (Ohkouchi et al., 2002), but the latter are significantly different sedimentary settings from our site. The radiocarbon results from regions with high sedimentation rates suggest that alkenone ages are typically several thousand years older than the ages of planktonic foraminifera from the same sediments.

To discuss the age difference between biomarkers and foraminifera isolated from the same horizons, we have to evaluate what the age variations between individual biomarkers mean. The 14C content of FAs in sediments, as well as the δ13C value, depends on the isotopic composition of the carbon source in which the FAs were biosynthesized. Therefore, the difference in 14C content (and, therefore, the radiocarbon age) of individual FAs depends on differences in the primary producers, that is, terrestrial or marine carbon fixers, under different conditions. The age difference between the two groups can be explained by differences in their carbon source: marine or terrestrial organisms. However, for the LMW FAs, the 14C ages of the C16 and C18 FAs in the two horizons were largely different from those of the other FAs. The C16 and C18 FAs of both horizons reflect various sources with different 14C ages, and they were not derived from homologous compounds. The C16 and C18 FAs are the most abundant FAs in sediments because these FAs are among the major lipid components of phytoplankton, especially the Bacillariophyceae (diatoms) and Prymnesiophyceae (coccolithophorids) (Reiten et al., 1994).

4. Discussion

Age offsets between lipid biomarkers and foraminifera observed from the section with the lower sedimentation rate were larger than those estimated from the section with the higher sedimentation rate. Moreover, the age offsets between alkenones and foraminifera at our site were much larger in the 21–24 cm horizon, where alkenones were systematically 7100–7300 yr younger than planktonic foraminifera. In the 12–15 cm horizon, the age offset between alkenone and foraminifera could not be determined because of sample loss during preparation for the AMS analysis. However, the alkenone 14C age in the 21–24 cm horizon was in good agreement with those of the LMW FAs except for C18 FA in the same horizon. If the alkenone 14C age in the 12–15 cm horizon was similar to that of the LMW FAs of the same horizon, then the age offset between alkenone and foraminifera would be very small. These results are not comparable to those from sites with very high sedimentation rates such as the Benguela upwelling system (Mollenhauer et al., 2003) and the Bermuda Rise drift deposit (Ohkouchi et al., 2002), but the latter are significantly different sedimentary settings from our site. The radiocarbon results from regions with high sedimentation rates suggest that alkenone ages are typically several thousand years older than the ages of planktonic foraminifera from the same sediments.
The $^{14}$C ages of TOC and TLE in the 21–24 cm horizon were much younger than those of the compounds ($C_{24}$, $C_{26}$, and $C_{28}$ FAs) derived from terrestrial organic matter, which were dated from 11,200 yr BP ($C_{24}$) to 12,100 yr BP ($C_{28}$). Similarly, the ages of long-chain $n$-alkanes ($C_{25}$, $C_{27}$, $C_{29}$, $C_{31}$) ranged from 11,870 yr BP to 12,570 yr BP. Recent studies on the fate of terrestrial organic matter preserved in marine sediments provide the key to our understanding and interpretation of the marine sedimentary record (Hedges and Keil, 1995; Hedges et al., 1997). The age differences found between the $C_{16}$ and $C_{28}$ FAs in the two layers (13–15 cm and 21–24 cm) were too large, even taking into account the ages of the analyzed sections, which were 1420 yr and 7080 yr, respectively. If the ages of the $C_{16}$ FAs in the two horizons are assumed to be the actual sedimentary ages, then the $C_{28}$ FAs from terrestrial plant and fossil sources must have different $^{14}$C origins, that is, the $C_{28}$ FAs in the 21–24 cm horizon have a much more depleted $^{14}$C content than those in the 12–15 cm horizon. On the other hand, the $C_{24}$ FA and $C_{26}$ FA fluxes were largest in the 18–20 cm horizon, implying that terrestrial organic matter input to the sediment was significantly higher in that horizon. Variability in the constituents of terrestrial organic matter may explain the large age differences because terrestrial organic matter contains pre-aged and relict organic material such as humic detritus, which is often reworked (Eglinton et al., 1997). This variability would result in age uncertainty in organic components from marine and terrestrial sources.

$^{13}$C values of $C_{28}$ FAs were approximately similar in both horizons, as were $^{13}$C values of TOC. According to the dual isotopic balance model using the $^{13}$C and $^{14}$C data, as shown in formulas (3)–(5), we constrained source contributions from terrestrial vascular plants, marine organisms, and relict organic carbon (e.g., kerogen) with respect to the origins of the TOC (Pearson and Eglinton, 2000; Drenzek et al., 2003). According to our calculations, the relative source contributions of fossil carbon in the 12–15 cm and 21–24 cm were 4%–5% and 22%–25%, respectively. Although we need to consider the parameters used in this model further, this result indicates that fossil carbon was a significant constituent of TOC, suggesting that a significant amount of the $^{14}$C content in HMW FAs was pre-aged or fossil ($^{14}$C dead) carbon.

Because the study site was located on the continental slope off the Japanese islands, the supply of terrigenous organic matters would have been significant. During the Holocene warm period, the enhanced precipitation related to the intensified summer monsoon would have been an important mechanism of the transport of terrestrial-derived organic matter to the offshore sediment. Runoff containing organic matter from the continental margin is plausible. The molecular distribution of fatty acids in this study is very close to that of deep-sea sediments in the North Pacific (Gagosian et al., 1981; Kawamura, 1995). Terrestrial organic matter would have experienced long residence times in reservoirs such as soil, river, and lake sediments. Naraoka et al. (1995) reported $^{13}$C values of HMW FAs ($C_{20}$–$C_{30}$) of sediments from the Otsuchi River (OR3) and pelagic sediments (SR72). Our study site is located between the OR3 and SR72 sites (Fig. 1). The $^{13}$C values of HMW FAs from OR3 and SR72 ranged from $-32\%$ to $-35\%$ and from $-26\%$ to $-31\%$, respectively. The $^{13}$C values of HMW FAs ($C_{24}$–$C_{28}$) at our site ($-32.6\%$ to $-34.5\%$) were similar to those of the OR3 sediments, suggesting that terrigenous organic matter inputs increase with enhanced runoff.

The fate of terrestrial organic matter in the ocean, especially the nature of terrestrial organic carbon degradation, fractionation, and preservation in marine sediments, is still poorly understood (Hedges and Keil, 1995; Hedges et al., 1997). In addition, the transport of terrigenous organic matter to marine sediments via the atmosphere is not likely, because the distribution pattern of FAs from marine aerosol samples in the western Pacific Ocean is not similar to that of marine sediment, suggesting that only minor portions of HMW FAs were contributed by the fallout of aerosol particles into the sea (Kawamura, 1995).

As mentioned above, we observed similar ages between alkenones and marine-derived LMW FAs in the same horizon. This similarity implies that both biomarkers were derived from the same carbon source (e.g., dissolved inorganic carbon in surface water). If the alkenone age is the actual age of the extracted sediment layer, the alkenone $^{14}$C age (7500 yr BP) corresponds to its estimated alkenone SST (15.3 °C).
The 15.3 °C temperature is consistent with Early Holocene values for alkenone SST estimated from another site further east (40°00′N, 165°04′E) in the same Oyashio–Kuroshio transition area as our studied site (Harada et al., 2004). These SSTs ranged between 15.7 °C (4.8 kyr BP) and 16.2 °C (10.8 kyr BP). The down-core profile of alkenone SSTs is shown in Fig. 7; they ranged from 13.5 °C to 16.5 °C; the profile can be divided into alkenone SSTs of about 14.5 °C above 10 cm and those of 15.6 °C between 10 and 21 cm depth. The alkenone SSTs likely reflect the Holocene SST variation in this region, because the planktonic foraminiferal δ18O values suggest that SST decreased by 4.4 °C from the Holocene to the last glacial in the same mixed water-mass region about 180 km south of our study site (Yamane and Oba, 1999). During the Holocene, there were apparently some fluctuations in SST. The increase in alkenone SSTs between 19 and 21 cm (ca. 6580 yr BP) probably corresponds to the climate transition from Early to Middle Holocene. Fujii and Fuji (1967) reported that, in the Japanese islands, the Middle Holocene, from approximately 7000 to 5000 yr BP, was warmer than the Early Holocene, based on a pollen analysis. In our study, the SST changes estimated from the alkenone 14C ages indicate that a warm period occurred from 7000 to 6000 yr BP, which is consistent with pollen-reconstructed local climate records in the Japanese islands (Fujii and Fuji, 1967). The SST fluctuations during the Holocene may be attributed to the hydrographic characteristics of the study site, which is located in a mixed water-mass region between the Kuroshio and Oyashio fronts (Kawai, 1972). The large temperature rise was likely caused by the northward migration of the mixed water mass. In addition, planktonic foraminiferal δ18O values also suggest that this region was affected by the warm water mass derived from the Kuroshio Current during the Holocene (Yamane and Oba, 1999; Oba et al., 1999).

From the ages of the biomarkers and TOC, we concluded that marine-derived biomarkers, including alkenones and LMW FAs except for C18 FA, seem to have settled under similar sedimentary conditions. On the other hand, we have only a limited data set by which to explain the cause of the age discrepancy between marine-derived biomarkers and planktonic foraminifera. The age offsets between marine-derived biomarkers and planktonic foraminifera appear to be larger in the horizon with the lower sedimentation rate. In that horizon, glacial foraminifera and Holocene biomarkers apparently coexisted. However, the sedimentary environment apparently changed after the early Holocene. Carbonate dissolution intensified in this region after the Early Holocene, and no planktonic foraminifera are found in the upper part of the core. Thus, the effect of upward mixing of glacial foraminiferal specimens as a result of bioturbation may be amplified by the reduced sedimentation rates in the horizon. In contrast, marine-origin biomarkers in the section may dilute glacial relict components as a result of enhanced export flux during the Holocene. Alternatively, part of the sedimentary horizon in the lower part of the core may have been lost by sedimentary processes such as erosion by turbidity currents or entrainment by contour currents, although we found no evidence of a short-term hiatus in this study.

5. Conclusions

In this study, we report age offsets between marine- and terrestrial-derived compounds (fatty acids, n-alkanes, and alkenones), total organic carbon, and foraminifera isolated from the same horizons in Northwest Pacific sediments accumulated at a relatively low sedimentation rate and highly influenced by bioturbation. We demonstrated that compound-specific 14C data for alkenones and some FAs (C16:1, C14, iC15, aC15) can be used as a sedimentary chronology tool, especially when calcareous fossils are absent, and as reliable marine organic carbon tracers. However, some processes generating a wide range of 14C ages in the same horizon, for example, for C18 FA, were apparent. Although our data are too limited to establish a molecular-level chronology, we show that organic constituents of coeval sediments have a variety of age controls. In regard to 14C stratigraphy in paleoceanographic studies, our results show extremely large age offsets between different classes of sedimentary constituents (TOC, alkenones, foraminifera), which can be attributed to sedimentation processes and recycling associated with secondary biological processes such as benthos and microbial intake in the sediment. Further work is necessary to clarify these processes. However, our results provide useful information about age controls to prevent incorrect inter-
interpretation of alkenone-based proxy data and to understand low sedimentation rate settings similar to that of our study site. Moreover, we showed that it is possible to obtain sedimentary ages of organic constituents by using specific compounds (fatty acids, alkenones, n-alkanes). The $^{14}$C ages of LMW FAs, except for those from $C_{18}$ FA, were in good agreement with those of alkenones, suggesting that LMW FAs may be used to estimate real age of alkenone produced in water column. In addition, our data show that using alkenone-based $^{14}$C dating of sediment cores enables one to obtain more realistic alkenone SST information with clearly higher age precision.

In this study, we did not obtain enough data to allow us to determine whether the ages of the alkenones or some of the compounds derived from marine organisms represented the actual sedimentary age of the horizon from which they were extracted. In addition, we need to obtain compound-specific $^{14}$C and $^{13}$C from more horizons of marine sediments with higher time resolution to reveal the fate and transfer process of terrigenous organic matter. The model based on the dual $\Delta^{14}$C and $\delta^{13}$C data also provides useful information to determine the marine or terrestrial origin of total organic matter preserved in sediment.

Acknowledgements

We are grateful to J. M. Hayes, A. P. McNichol, A. Pearson, and other members of the National Ocean Science AMS facility, the Woods Hole Oceanographic Institution (WHOI), for giving M.U., one of the authors, the opportunity to learn the technique of microscale $^{14}$C analysis. We also thank Y. Kumamoto and the officers and crew of the R/V Mirai, MR00-K01 cruise and members of Marine Works Japan Ltd. for collecting samples. This study is part of the “Study on the past marine environmental changes” sponsored by the Japan Agency for Marine-Earth Science and Technology (JAMSTEC) (MIO publication no. 35).

References


