Carbon isotope composition of bishomohopanoic acid in Miocene to recent marine sediments from the Nankai Trough (ODP Leg 190, Site 1178)

Hiroyuki Saito *,a and Noriyuki Suzuki **
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Abstract
The distribution and carbon isotope composition of 17β(H), 21β(H)-bishomohopanoic acid (ββC32-HA) were investigated in Miocene to recent marine sediments from Site 1178 of ODP Leg 190, Nankai Trough, offshore Shikoku, Japan. The concentration of ββC32-HA tends to be higher in accreted sediments, which are characterized by a large contribution of terrestrial organic matter. The δ13C values of ββC32-HA are lighter in accreted sediments than in slope sediments, indicating different sources to some degree. The constant δ13C values within the slope sediments and within the accreted sediments indicate that the sources of ββC32-HA were unchanged during the deposition of each unit. In accreted sediments, the δ13C value of ββC32-HA is similar to that in soil components, suggesting that the hopanoic acids in accreted sediments may be mainly terrestrial organic compounds derived from the oxidation products of bacteriohopanepolyols on land.

1. Introduction
Hopanoids are a class of pentacyclic triterpenoid lipids that occur mainly in bacterial membranes (Ourisson et al., 1979) and that are widely preserved in soils, sediments, and ancient rocks. It has been suggested that hopanoids are the most abundant natural products on Earth (Ourisson and Albrecht, 1992). Biohopanoids are synthesized by a wide range of bacteria and are structurally diverse, thereby showing great potential as molecular markers of bacterial populations and processes (Talbot et al., 2007; Blumenberg et al., 2009). After the death of bacteria, diagenetic processes modify the side chain structure of biohopanoids, leading to the formation of geohopanoids, including hopanols, hopanoic acids, and hopanes (Innes et al., 1997). However, little is known about the reactions involved in the conversion of a biohopanoid into the geohopanoids found in sediment.

Saturated hydrocarbons of the hopane series are one of the ultimate diagenetic products of biohopanoids, being formed during the burial diagenesis. Their application as markers of specific depositional conditions or organic matter inputs is based on empirical relationships established through many years of study, rather than a comprehensive understanding of their origins and geological fate (Farrimond et al., 2000). Hopanoic acids, which are possible precursors of hopanoid hydrocarbons, are also widely distributed in recent and immature sediments. In particular, 17β(H), 21β(H)-

*Research Division of JAPEX Earth Energy Frontier, Creative Research Institution, Hokkaido University, N21W10, Kita-ku, Sapporo 001-0021, Japan
**Department of Natural History Sciences, Graduate School of Science, Hokkaido University, N10W8, Kita-ku, Sapporo 060-0810, Japan
*Corresponding author. e-mail: hsaito@cris.hokudai.ac.jp Tel/Fax: +81-11-706-9242
bishomohopanoic acid (ββC32-HA) is ubiquitous in diverse environments, making it problematic to assign a specific source to this compound.

Previous studies have examined the carbon isotope compositions of the hopanoids with the aim of clarifying their sources. Few continuous isotope records of hopanoic acids have been reported, although several studies have examined the isotope composition of hopanoic acids in recent surface sediments and in Miocene–Pliocene sedimentary rocks (e.g., Naraoka et al., 2000; Yamamoto et al., 2005). In the present study, we report on a depth profile of the carbon isotopic composition of ββC32-HA in Miocene to recent marine sediments from the Nankai Trough.

2. Material and methods

Sediment samples were collected from drillcore recovered down to a depth of ca. 680 m below sea floor (mbsf) at Site 1178 of ODP Leg 190 in the Nankai Trough accretionary prism, offshore Shikoku, Japan (Fig. 1). Two fundamental lithostratigraphic units were recovered in the drillcore: slope-apron facies (Unit I) and accreted sediments (Unit II). The sediments below 200 mbsf are characterized by abundant sand–silt turbidites in accreted sediments. The samples from 200 to 400 mbsf (Subunit IIA) are rich in terrestrial organic matter (Saito and Suzuki, 2007a), being characterized by high concentrations of total organic carbon (TOC), high C/N values, high concentrations of plant-derived long-chain n-alkanes, n-alkanoic acids, and n-alkanols, and a high terrigenous to aquatic (H/L) ratio. The sediments range in age from Late Miocene to Holocene. The analytical method followed that described by Saito and Suzuki (2007b). Freeze-dried samples were extracted by ultrasonication with increasing dichloromethane (DCM)/methanol (MeOH) values (1:3 v/v 2×, 1:1 v/v 2×, and 1:0 v/v 2×). The extract was saponified with 0.5 N KOH/MeOH. The acid fraction was esterified with 12% BF3/MeOH to convert free acids to methyl ester derivatives. n-C30D62 was added to the acid fractions as an internal standard. Hopanoic acids were analyzed using gas chromatography (GC) and GC/mass spectrometry (MS) (HP6890GC and HP6890GC/HP5973MSD). Compound-specific carbon isotopic compositions of hopanoic acids were analyzed using gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS, HP6890GC/Finnigan Mat 252 IRMS), employing n-C36H74 as an external isotope standard. Carbon isotopes are given as δ values (δ13C in ‰) relative to Vienna Peedee Belemnite (VPDB) and were corrected for the addition of carbon (δ13C = −57.6‰) during the preparation of methyl ester derivatives. Instrument precision was assessed using a mixture of n-alkanes with known isotope compositions, indicating a precision within 0.7‰.

3. Results and discussion

3.1. Distribution of hopanoic acids

The C30–C34 hopanoic acids and bishomohop-17(21)-enioic acid were commonly detected in the sediment samples (Fig. 2). In all the samples, the main hopanoic acid is ββC32-HA, accounting for up to 86% of the hopanoic acids detected in this study. The dominance of this compound has also been reported in recent sediments from other regions (Buchholz et al., 1993; Innes et al., 1997, 1998; Naraoka et al., 2000). Zundel and Rohmer (1985) suggested that side chain degradation of bacteriohopanepolyols (BHPs) with periodic acid/sodium borohydride is similar to the degradation of hopanoids in sediments. In this process, hexa-, penta- and tetrafunctionalized BHPs

Fig. 1. Location of ODP Site 1178 at the Nankai Trough, offshore Shikoku, Japan.
are converted to C\text{30}, C\text{31}, and C\text{32} geohopanoids, respectively. The dominance of $\beta\beta$C\text{32}-HA in sediments from the Nankai Trough is consistent with the dominance of tetrafunctionalized BHPs, including bacterihopanetetrol and aminobacteriohopanetriol, in marine and lacustrine sediments (Farrimond et al., 2000; Talbot et al., 2007).

The concentration of $\beta\beta$C\text{32}-HA in the analyzed sediments ranges from 6.9 to 51.7 $\mu$g/gTOC (average, 26.6 $\mu$g/gTOC) (Table 1). $\beta\beta$C\text{32}-HA is relatively abundant in the sediments from 150 to 250 mbsf and below 550 mbsf (i.e., Subunits IC, IIA, and IIC; Fig. 3). Subunits IIA and IIC are dominated by turbidite layers, indicating a large contribution of terrestrial organic
This inference is supported by the characteristics of subunit IIA, including high TOC contents, high C/N ratios, high concentrations of plant-derived long chain n-alkanes, n-alkanoic acids, and n-alkanols, and high H/L ratios (Fig. 3; Saito and Suzuki, 2007a). The comparatively high concentration of hopanoic acids in the sediments from Site 1178 may be related to the relatively high input of terrestrial organic matter, as discussed above.

3.2 Carbon isotope composition of $\beta$βC$_{32}$-HA

Table 1 lists the carbon isotope composition of $\beta$βC$_{32}$-HA. No other homologues of the hopanoic acids were determined, due to their low concentrations. The $\delta^{13}$C values of $\beta$βC$_{32}$-HA in slope and accreted sediments range from $-26.2\%$ to $-24.5\%$ (average, $-25.5\%$) and from $-29.9\%$ to $-28.8\%$ (average, $-29.3\%$), respectively. The $\delta^{13}$C value is largely constant above 200 mbsf, and shows a sharp decline at the lithostratigraphic boundary between slope and accreted sediments. Below this boundary, the $\delta^{13}$C value remains constant. This pattern of $\delta^{13}$C values indicates that $\beta$βC$_{32}$-HA in slope and accreted sediments has different sources to some degree and that the sources of $\beta$βC$_{32}$-HA were largely unchanged during the period of deposition of each lithostratigraphic unit.

The $\delta^{13}$C values and possible bacterial sources of $\beta$βC$_{32}$-HA in various environments are summarized in Table 2. The $\delta^{13}$C values of $\beta$βC$_{32}$-HA derived from methanotrophs are diagnostic and are significantly depleted in $^{13}$C. Thiel et al. (2003) reported strongly $^{13}$C-depleted hopanoic acids ($-78\%$ to $-66\%$) in a microbial mat from an anoxic environment in the Black Sea, and inferred that anaerobic bacteria may be the producers of $^{13}$C-depleted hopanoids. The anaerobic oxidation of methane (AOM) at seeps is mediated by a consortia of methane-oxidizing archaea and sulfate-reducing bacteria (SRB) (e.g., Hinrichs et al., 1999). $^{13}$C-depleted hopanoids have been not reported in SRB, although Blumenberg et al. (2006) confirmed the presence of hopanoids in SRB (Desulfovibrio spp.). Other anaerobic bacteria are potential sources of $^{13}$C-depleted hopanoids in methane seep deposits.

In the present study, such a $^{13}$C-depleted $\beta$βC$_{32}$-HA was not found, indicating no contribution of aerobic or anaerobic methanotrophic bacteria. Although the

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**Table 2. Carbon isotope compositions and possible bacterial sources of 17$\beta$(H), 21$\beta$(H)-bishomohopanoic acid in various environments**

<table>
<thead>
<tr>
<th>Sediment sample</th>
<th>Environment</th>
<th>Location</th>
<th>Age</th>
<th>$\delta^{13}$C</th>
<th>Possible bacterial source (reference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northwestern Pacific Ocean</td>
<td>Marine</td>
<td>Pacific Ocean</td>
<td>Recent</td>
<td>$-24$ to $-19$</td>
<td>Heterotrophs in water column and/or sediment (Naraoka et al., 2000)</td>
</tr>
<tr>
<td>Northwestern Pacific Ocean</td>
<td>Marine</td>
<td>Riverine and bay</td>
<td>Pacific Ocean</td>
<td>$-31$ to $-30$</td>
<td>Bacteria in soil (Naraoka et al., 2000)</td>
</tr>
<tr>
<td>Omagawa Fm.</td>
<td>Marine</td>
<td>Japan</td>
<td>Miocene</td>
<td>$-24$ to $-21$</td>
<td>Primary producers or heterotrophs living in sea surface water (Yamamoto et al., 2005)</td>
</tr>
<tr>
<td>Tentokuji Fm., Funakawa Fm.</td>
<td>Marine</td>
<td>Japan</td>
<td>Pliocene</td>
<td>$-30$ to $-24$</td>
<td>Various bacteria including bacteria living on isotopically modified pore water CO$_2$ (Yamamoto et al., 2005)</td>
</tr>
<tr>
<td>Santa Monica Basin</td>
<td>Marine (with anoxic bottom water)</td>
<td>USA</td>
<td>Recent</td>
<td>$-45$ to $-30$</td>
<td>Chemolithotrophs (Gong and Hollander, 1997)</td>
</tr>
<tr>
<td>Santa Monica Basin</td>
<td>Marine (with oxic bottom water)</td>
<td>USA</td>
<td>Recent</td>
<td>$-42$ to $-34$</td>
<td>Chemolithotrophs (Gong and Hollander, 1997)</td>
</tr>
<tr>
<td>Guaymas Basin</td>
<td>Marine (hydrothermally active site)</td>
<td>USA</td>
<td>Recent</td>
<td>$-47$ to $-40$</td>
<td>Methanotrophs (Schouten et al., 2003)</td>
</tr>
<tr>
<td>Lake Clarkia</td>
<td>Lacustrine</td>
<td>USA</td>
<td>Miocene</td>
<td>$-55$ to $-38$</td>
<td>Methanotrophs (Huang et al., 1996)</td>
</tr>
<tr>
<td>Microbial mat</td>
<td>Marine (methane seep)</td>
<td>Black Sea</td>
<td>Recent</td>
<td>$-78$ to $-66$</td>
<td>Bacteria involved in the anaerobic cycling of methane carbon (Thiel et al., 2003)</td>
</tr>
<tr>
<td>Pietralunga</td>
<td>Marine (methane seep)</td>
<td>Italy</td>
<td>Miocene</td>
<td>$-72$</td>
<td>Aerobic methanotrophs (Birgel and Peckmann, 2008)</td>
</tr>
<tr>
<td>Marmorito</td>
<td>Marine (methane seep)</td>
<td>Italy</td>
<td>Miocene</td>
<td>$-75$</td>
<td>Aerobic methanotrophs (Birgel and Peckmann, 2008)</td>
</tr>
<tr>
<td>Tepee Buttes</td>
<td>Marine (methane seep)</td>
<td>USA</td>
<td>Campanian</td>
<td>$-43$</td>
<td>Various bacteria including methanotroph (Birgel and Peckmann, 2008)</td>
</tr>
</tbody>
</table>
isotopic compositions of individual hopanoids may provide clues to their sources, the mixing of different sources with different isotope compositions may yield a wide range of $\delta^{13}C$ values; consequently, it is difficult to identify the sources of hopanoids based solely on their isotope compositions.

In accreted sediments with abundant terrestrial organic matter, the $\delta^{13}C$ value of $\beta\beta C_{32}$-HA is similar to that in soil components ($-31\%$ to $-30\%$) (Naraoka et al., 2000). Because some eukaryotes (e.g., ferns and lichens) do not have extended carbon skeletons ($>C30$) but synthesize hopanoids (Rohmer et al., 1984), the extended hopanoids in soil components are considered to be derived from bacteria in soil. It is therefore suggested that the hopanoic acids in accreted sediments are mainly terrestrial organic compounds derived from the oxidation products of bacteriohopanepolyols on land.

Summary

1. $17\beta(H), 21\beta(H)$-bishomohopanoic acid ($\beta\beta C_{32}$-HA) are the most abundant hopanoic acid found in sediments from Site 1178 of ODP Leg 190, Nankai Trough. The concentration of $\beta\beta C_{32}$-HA are higher in accreted sediments, which are characterized by a large contribution of terrestrial organic matter.

2. The $\delta^{13}C$ values of $\beta\beta C_{32}$-HA in slope and accreted sediments range from $-26.2\%$ to $-24.5\%$ and from $-29.9\%$ to $-28.8\%$, respectively, indicating different sources to some degree. The constant $\delta^{13}C$ values within each lithostratigraphic unit indicate that the sources of $\beta\beta C_{32}$-HA were largely unchanged during the period of deposition of each unit.

3. The $\delta^{13}C$ value of $\beta\beta C_{32}$-HA in accreted sediments is similar to those in soil components, suggesting the hopanoic acids in accreted sediments are mainly terrestrial organic compounds derived from the oxidation products of bacteriohopanepolyols on land.

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References


