

Article

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 $17\beta(\text{H})$, $21\beta(\text{H})$ -bishomohopanoic acid ($\beta\beta\text{C}_{32}\text{-HA}$) were investigated in Miocene to recent marine sediments from Site 1178 of ODP Leg 190, Nankai Trough, offshore Shikoku, Japan. The concentration of $\beta\beta\text{C}_{32}\text{-HA}$ tends to be higher in accreted sediments, which are characterized by a large contribution of terrestrial organic matter. The $\delta^{13}\text{C}$ values of $\beta\beta\text{C}_{32}\text{-HA}$ are lighter in accreted sediments than in slope sediments, indicating different sources to some degree. The constant $\delta^{13}\text{C}$ values within the slope sediments and within the accreted sediments indicate that the sources of $\beta\beta\text{C}_{32}\text{-HA}$ were unchanged during the deposition of each unit. In accreted sediments, the $\delta^{13}\text{C}$ value of $\beta\beta\text{C}_{32}\text{-HA}$ 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, $17\beta(\text{H})$, $21\beta(\text{H})$ -

*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

^aCorresponding author. e-mail: hsaito@cris.hokudai.ac.jp Tel/Fax: +81-11-706-9242

bishomohopanoic acid ($\beta\beta\text{C}_{32}\text{-HA}$) 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 $\beta\beta\text{C}_{32}\text{-HA}$ 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 \times , 1:1 v/v 2 \times , and 1:0 v/v 2 \times). The extract was saponified with 0.5 N KOH/MeOH. The acid fraction was esterified with 12% BF_3/MeOH to convert free acids to methyl ester derivatives. *n*- $\text{C}_{30}\text{D}_{62}$ was added to the acid fractions as an internal standard. Hopanoic acids were analyzed using gas chromatography (GC)

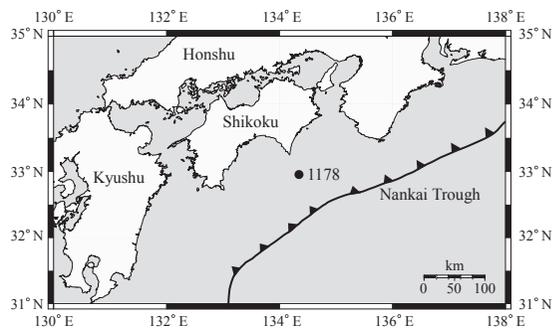


Fig. 1. Location of ODP Site 1178 at the Nankai Trough, offshore Shikoku, Japan.

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*- $\text{C}_{36}\text{H}_{74}$ as an external isotope standard. Carbon isotopes are given as δ values ($\delta^{13}\text{C}$ in ‰) relative to Vienna Peedee Belemnite (VPDB) and were corrected for the addition of carbon ($\delta^{13}\text{C} = -57.6\text{‰}$) 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 $\text{C}_{30}\text{--C}_{34}$ hopanoic acids and bishomohop-17(21)-enoic acid were commonly detected in the sediment samples (Fig. 2). In all the samples, the main hopanoic acid is $\beta\beta\text{C}_{32}\text{-HA}$, 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

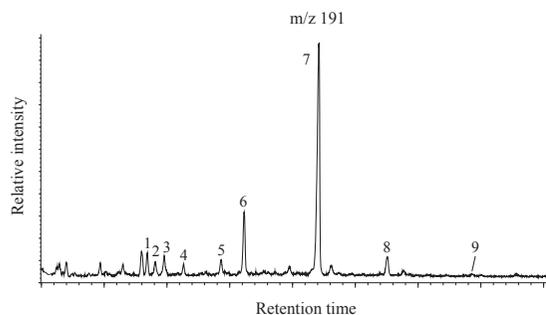


Fig. 2. An m/z 191 chromatogram showing hopanoic acids in a sample (1178A-15H, 130 mbsf) from Site 1178. 1: 17β (H), 21β (H)-hopanoic acid (S), 2: 17α (H), 21β (H)-homohopanoic acid (R), 3: 17β (H), 21β (H)-hopanoic acid (R), 4: bishomohop-17(21)-enoic acid, 5: 17α (H), 21β (H)-bishomohopanoic acid (R), 6: 17β (H), 21β (H)-homohopanoic acid (R), 7: 17β (H), 21β (H)-bishomohopanoic acid (R), 8: 17β (H), 21β (H)-trishomohopanoic acid (R), 9: 17β (H), 21β (H)-tetrahomohopanoic acid (R).

Table 1. Concentration and carbon isotope composition of 17β (H), 21β (H)-bishomohopanoic acid in sediments from Site 1178

Core, section, interval (cm)	Depth (mbsf)	Bishomohopanoic acid ($\mu\text{g/gTOC}$)	(‰)
190-1178A-			
3H-2, 100-115	13.9-15.4	6.9	-26.0
6H-2, 115-130	42.4-43.9	22.4	-25.5
9X-7, 91-106	73.6-74.8	12.3	-25.9
15X-5, 115-130	129.2-130.7	13.7	-26.2
18X-2, 6-22	152.8-153.7	15.8	-24.7
21X-5, 29-44	186.4-187.9	44.6	-24.5
24X-4, 120-135	213.2-214.7	45.9	-28.9
27X-5, 10-25	243.8-245.3	51.7	-29.5
30X-1, 70-86	266.6-268.1	20.9	-29.9
33X-1, 75-90	295.5-297.0	28.7	-29.4
37X-4, 75-90	338.5-340.0	13.6	-29.1
40X-2, 34-51	364.4-365.9	21.9	-29.2
190-1178B-			
15R-3, 20-35	518.6-520.1	17.5	-29.1
18R-5, 25-38	550.4-550.8	39.3	-29.7
24R-3, 76-91	605.1-606.6	36.6	-28.8
28R-3, 66-81	643.7-645.0	33.6	-29.7

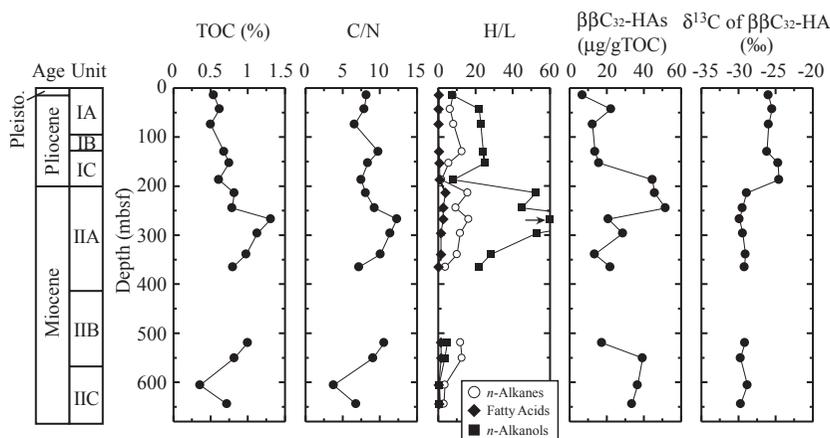


Fig. 3. Depth profiles of TOC, C/N ratio, terrigenous to aquatic lipid ratio for n -alkanes (H/L_{AK}), fatty acids (H/L_{FA}), and n -alkanols (H/L_{OH}), and the concentration and carbon isotopic composition of 17β (H), 21β (H)-bishomohopanoic acid in sediments from Site 1178. $H/L_{AK} = (C_{27}+C_{29}+C_{31})/(C_{15}+C_{17}+C_{19})$; $H/L_{FA,OH} = (C_{24}+C_{26}+C_{28})/(C_{14}+C_{16}+C_{18})$.

are converted to C_{30} , C_{31} , and C_{32} geohopanooids, respectively. The dominance of $\beta\beta C_{32}$ -HA in sediments from the Nankai Trough is consistent with the dominance of tetrafunctionalized BHPs, including bacterihopanetetrol and aminobacterihopanetriol, in marine and lacustrine sediments (Farrimond et al., 2000; Talbot et al., 2007).

The concentration of $\beta\beta C_{32}$ -HA in the analyzed sediments ranges from 6.9 to 51.7 $\mu\text{g/gTOC}$ (average, 26.6 $\mu\text{g/gTOC}$) (Table 1). $\beta\beta C_{32}$ -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

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

Sediment sample	Environment	Location	Age	$\delta^{13}C$	Possible bacterial source (reference)
Northwestern Pacific Ocean	Marine	Pacific Ocean	Recent	-24 ~ -19	Heterotrophs in water column and/or sediment (Naraoka et al., 2000)
Northwestern Pacific Ocean	Riverrine and bay	Pacific Ocean	Recent	-31 ~ -30	Bacteria in soil (Naraoka et al., 2000)
Onnagawa Fm.	Marine	Japan	Miocene	-24 ~ -21	Primary producers or heterotrophs living in sea surface water (Yamamoto et al. 2005)
Tentokuji Fm., Funakawa Fm.	Marine	Japan	Pliocene	-30 ~ -24	Various bacteria including bacteria living on isotopically modified pore water CO_2 (Yamamoto et al., 2005)
Santa Monica Basin	Marine (with anoxic bottom water)	USA	Recent	-45 ~ -30	Chemoautotrophs (Gong and Hollander, 1997)
Santa Monica Basin	Marine (with oxic bottom water)	USA	Recent	-42 ~ -34	Chemoautotrophs (Gong and Hollander, 1997)
Guaymas Basin	Marine (hydrothermally active site)	USA	Recent	-47 ~ -40	Methanotrophs (Schouten et al., 2003)
Lake Clarkia	Lacustrine	USA	Miocene	-55 ~ -38	Methanotrophs (Huang et al., 1996)
Microbial mat	Marine (methane seep)	Black Sea	Recent	-78 ~ -66	Bacteria involved in the anaerobic cycling of methane carbon (Thiel et al., 2003)
Pietralunga	Marine (methane seep)	Italy	Miocene	-72	Aerobic methanotrophs (Birgel and Peckmann, 2008)
Marmorito	Marine (methane seep)	Italy	Miocene	-75	Aerobic methanotrophs (Birgel and Peckmann, 2008)
Tepee Buttes	Marine (methane seep)	USA	Campanian	-43	Various bacteria including methanotroph (Birgel and Peckmann, 2008)

matter. 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 $\beta\beta C_{32}$ -HA

Table 1 lists the carbon isotope composition of $\beta\beta C_{32}$ -HA. No other homologues of the hopanoic acids were determined, due to their low concentrations. The $\delta^{13}C$ values of $\beta\beta C_{32}$ -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 $\beta\beta C_{32}$ -HA in slope and accreted sediments has different

sources to some degree and that the sources of $\beta\beta C_{32}$ -HA were largely unchanged during the period of deposition of each lithostratigraphic unit.

The $\delta^{13}C$ values and possible bacterial sources of $\beta\beta C_{32}$ -HA in various environments are summarized in Table 2. The $\delta^{13}C$ values of $\beta\beta C_{32}$ -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 $\beta\beta C_{32}$ -HA was not found, indicating no contribution of aerobic or anaerobic methanotrophic bacteria. Although the

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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ value of $\beta\beta\text{C}_{32}\text{-HA}$ 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 ($>\text{C}_{30}$) 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. $17\beta(\text{H})$, $21\beta(\text{H})$ -bishomohopanoic acid ($\beta\beta\text{C}_{32}\text{-HA}$) are the most abundant hopanoic acid found in sediments from Site 1178 of ODP Leg 190, Nankai Trough. The concentration of $\beta\beta\text{C}_{32}\text{-HA}$ are higher in accreted sediments, which are characterized by a large contribution of terrestrial organic matter.
2. The $\delta^{13}\text{C}$ values of $\beta\beta\text{C}_{32}\text{-HA}$ 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 $\delta^{13}\text{C}$ values within each lithostratigraphic unit indicate that the sources of $\beta\beta\text{C}_{32}\text{-HA}$ were largely unchanged during the period of deposition of each unit.
3. The $\delta^{13}\text{C}$ value of $\beta\beta\text{C}_{32}\text{-HA}$ 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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