Distribution of acyclic and cyclic biphytanediols in recent marine sediments from IODP Site C0001, Nankai Trough

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Abstract

The distribution of acyclic and cyclic biphytanediols, which are the putative breakdown products of glycerol dialkyl glycerol tetraethers (GDGTs), was investigated for recent marine sediments from Nankai Trough, offshore Kii Peninsula. The most abundant diol is tricyclic biphytanediol of which relative abundance is in the range from 32 to 46%. The carbon skeleton of the detected tricyclic biphytanediol is the same as would be expected from crenarchaeol and has two cyclopentane rings and one

cyclohexane ring. Based on the molecular structure of crenarchaeol, the tricyclic biphytanediol is considered to be derived not only from crenarchaeol but also from other unknown sources. The ring distributions of biphytanediols are different from those of biphytanes obtained from intact polar lipids by chemical treatment, suggesting that biphytanediols are not solely the diagenetic products of in situ GDGTs.

1. Introduction

Glycerol dialkyl glycerol tetraethers (GDGTs) containing various dibiphytanyl chains are recognized as characteristic markers of numerous archaea (Koga and Mori, 2005). GDGTs have been reported in various environmental samples from extreme environments such as hot springs and hydrothermal vents (e.g. Ward et al., 1985), but as well in non-thermophilic marine and lacustrine environments (e.g. Sinninghe Damsté et al., 2002). Biphytanediols and biphytanic diacids, putative breakdown products of GDGTs, have been detected in several environments, as for example in water column and marine sediments (Hoefs et al., 1997; Schouten et al. 1998, 2000; Schefuss et al., 2001), hydrothermally influenced sediments (Schouten et al., 2003), and AOM-dominated cold seep sediments and limestone (Pancost et al., 2001; Birgel et al., 2008). Although diols and diacids have not yet been identified in organisms and the distribution patterns and $\delta^{13}C$ values of the diols and diacids are different from those of GDGT-derived biphytanes within the same samples (Schouten et al., 1998; Birgel et al., 2008), the biphytane carbon skeleton is found exclusively in archaea (De Rosa et al., 1988; Fuhrman et al. 1993). It therefore has been proposed that these compounds are biosynthesized by archaea (Schouten et al., 1998; Birgel et al., 2008). In the present study, we report a depth profile of acyclic and cyclic biphytanediols in recent marine

sediments from Nankai Trough and discuss the putative source of these archaeal biomarkers.

2. Material and methods

The sediment samples were collected from the seafloor of slope apron in the Nankai Trough, offshore Kii peninsula during Expedition 315 of the Integrated Ocean Drilling Program (IODP) in 2007 which was the second drilling expedition of the Nankai Trough Seismogenic Zone Experiment (NanTroSEIZE) (Fig. 1). The sediments were extracted using Dionex^{TM} accelerated solvent extraction (ASE) with increasing dichloromethane (DCM)/methanol values (1:0 v/v twice, 1:1 v/v twice and 0:1 twice) at high temperature (100ºC) and high pressure (1000psi). The extract was saponified with 0.5N KOH/methanol. The neutral fraction was separated into four fractions with silica gel column chromatography (95% activated). The alcohol fraction was eluted with ethyl acetate/methanol (1:1 v/v) and treated with bis (trimethylsilyl) trifluoroacetamide (BSTFA) to derivatize functional group prior to analysis using gas chromatography (GC) and GC/mass spectrometry (MS). For analysis of biphytanes from GDGTs, two samples were treated using the method of Oba et al. (2006). The extract was separated into 10 fractions. The neutral and intact polar lipid fraction was subjected to ether cleavage via HI treatment at 100ºC for 2h and reduction of the iodides with $LiAlH_4$ at 100ºC for 2h. The analytical methods employed in the present study have been previously described (Saito and Suzuki, 2007). GC was performed using a Hewlett Packard 6890 instrument equipped with a fused silica capillary column (DB-5HT, 30 m x 0.25 mm i.d.). The oven temperature was 70 ºC (2 min) and was programmed from 70 ºC to 130 ºC at 20 ºC/min, 130 ºC to 320 ºC at 4 ºC/min and was held at 320 ºC for 20

min. GC/MS was carried out using a Hewlett Packard 6890 instrument equipped with the same capillary column and linked to a HP5973 mass selective detector (MSD). The oven temperature conditions were the same as those for GC analysis. Acyclic and cyclic biphytane diols and the produced biphytanes were assigned on the basis of mass spectra and retention time in comparison with the literature. The acid fraction was esterified with BF_3/methanol and analyzed by GC/MS using the same conditions described by Birgel et al. (2008). The each of the sample was analyzed only once due to the limited amount of the sample. The measurement error for the contribution estimates of biphytanediols and biphytanes is estimated to be less than 5 % based on the empirical experience.

3. Results and Discussion

One acyclic biphytanediol and three cyclic biphytanediols with 1-3 cycloalkane rings were found in all the samples down to 190 meter below seafloor (Fig. 2), whereas no biphytanic diacids were found. Their total concentrations show little variation with depth except for the deepest sample (Fig. 3A). The concentrations range from 54.3 to 167.7 μg/gTOC with 89.9 μg/gTOC on average. Qualitative distributions of four biphytanediols except for 2 samples from 5 and 28.4 mbsf are remarkably similar to be tricyclic > acyclic > bicyclic > monocyclic biphytanediols (Fig. 3B). In the samples from 5 and 28.4 mbsf, monocyclic biphytanediol concentration is relatively high. The most abundant diol is tricyclic biphytanediol, of which relative abundance is in the range from 32 to 46%. The carbon skeleton of the detected tricyclic biphytanediol is the

same as would be expected from crenarchaeol and has two cyclopentane rings and one cyclohexane ring (Schouten et al., 1998).

The GDGT-derived biphytanes from intact polar lipid fraction are used as biomarker for living archaeal cells (Oba et al. 2006). Their ring distributions are in the relationship of acyclic > tricyclic > bicyclic > monocyclic. The distribution of rings in biphytanediols is different from those in the GDGT-derived biphytanes (Table 1), suggesting that biphytanediols are not solely the diagenetic products of in situ GDGTs. In addition, if the tricyclic biphytanediol is only derived from cleavage of crenarchaeol which has bicyclic biphytane moiety and tricyclic biphytane moiety in equal amounts (Sinninghe Damsté et al., 2002), the amount of bicyclic biphytanediol has to be equal to or more than that of tricyclic biphytanediol. Actually, the concentrations of bicyclic biphytanediol in sediments from Site C0001 are less than half of tricyclic biphytanediol, suggesting that all tricyclic biphytanediols can not be derived from crenarchaeol. Tricyclic biphytanediol with one cyclohexane ring is considered to be derived not only from crenarchaeol but also from other unknown sources. It has been proposed that biphytanediols can be biosynthesized by planktonic marine archaea (Schouten et al., 1998). Several studies have identified sedimentary archaea thriving in deep subsurface sediments (Biddle et al., 2006; Lipp and Hinrichs; 2009). A mixed input of both planktonic and sedimentary archaea are most likely the major sources of biphytanediol preserved in the sediments. According to Oba et al. (2006), biphytanes derived from IPL-GDGTs are considered to be mainly derived from in situ living archaeal cells. The different sources of biphytanediols and biphytanes could be responsible for their different compositional distributions in deep sediments from the Nankai Trough. Sequential alteration and degradation of various C_{40} moieties in

GDGTs during diagenesis also can be another important factor for the compositional discrepancy between biphytanediols and GDGT-derived biphytanes. Further researches on biphytanes and biphytanediols in various types of geological samples, cultured archaea, and degraded archaeal lipids would shed light on the potential source and fate of acyclic and cyclic biphytanediols in deep subsurface sediments.

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Figure and table captions

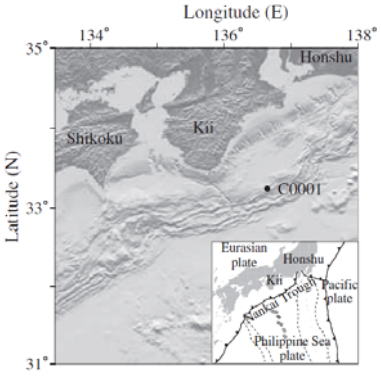

Fig. 1. Location of IODP Site C0001 in southwestern Japan (after Moore et al., 2009).

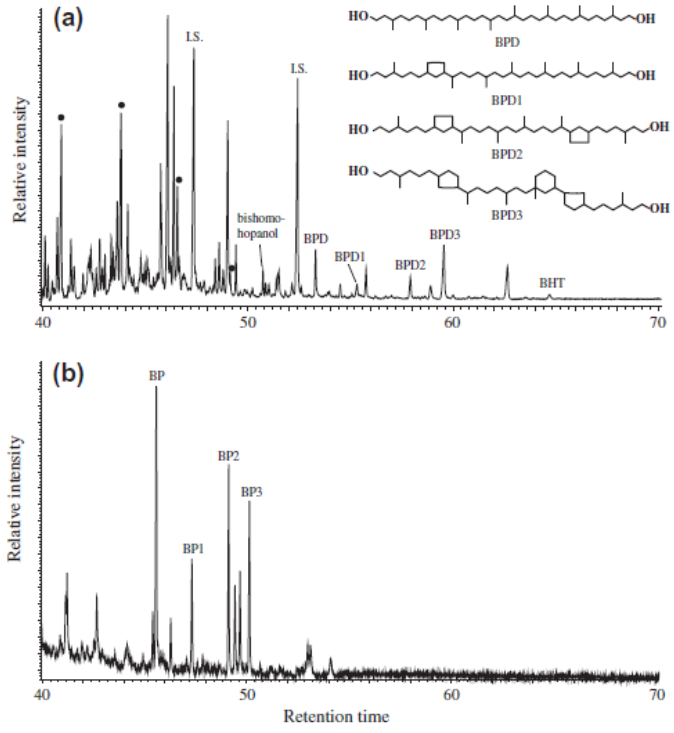

Fig. 2. Partial total ion chromatograms showing distribution of biphytanediols from alcohol fraction (a) and GDGT-derived biphytanes from polar lipid fraction (b) in sample of 1E2H6 (10.7mbsf) from Site C0001. Solid circles: n-alkanols, BPD: acyclic biphytanediol, BPD1: cyclic biphytanediol, BPD2: bicyclic biphytanediol, BPD3:

tricyclic biphytanediol, BHT: bacteriohopanetetrol, BP: acyclic biphytane, BP1: monocyclic biphytane, BP2: bicyclic biphytane, BP3: tricyclic biphytane.

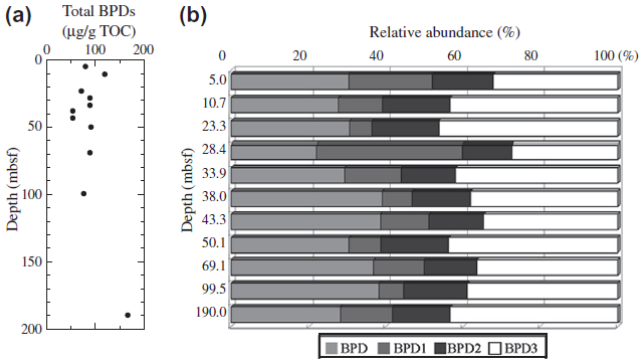

Fig. 3. Depth profiles of total biphytanediols (a) and relative abundances of bipyhtanediols (b) in sediments from Site C0001.

Table 1. Relative abundances of biphytanediols and biphytanes.

Sample			BPD and BP composition			
			acyclic (%)	monocyclic (%)	bicyclic (%)	tricyclic (%)
1E2H1	5.0 mbsf	BPDs	30.3	21.8	15.7	32.2
1E2H6	10.7 mbsf	BPDs	27.9	11.3	17.6	43.3
		BPs*	33.9	13.0	25.9	27.3
		BPs**	36.7	14.2	24.5	24.6
1E4H1	23.3 mbsf	BPDs	30.6	5.8	17.4	46.2
1E4H5	28.4 mbsf	BPDs	22.1	37.8	12.8	27.3
1E5H1	33.9 mbsf	BPDs	29.3	14.7	14.1	41.9
1E5H5	38.0 mbsf	BPDs	39.1	7.7	15.1	38.0
1E6H1	43.3 mbsf	BPDs	38.5	12.7	14.1	34.6
1E6H7	50.1 mbsf	BPDs	30.5	8.0	17.9	43.6
1E8H8	69.1 mbsf	BPDs	36.8	13.0	13.9	36.4
1E12H1	99.5 mbsf	BPDs	38.2	6.3	16.7	38.8
1F10H1	190.0 mbsf	BPDs	28.2	13.5	15.1	43.2
		BPs*	34.0	9.5	24.2	32.3
		BPs**	44.9	14.2	19.8	21.0

*,** GDGT-derived biphytanes from neutral and intact polar lipid fraction, respectively.