Anhydrobacteriohopanetetrol in Deep Subsurface Sediments From Nankai Trough and Gulf of Mexico

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ABSTRACT

32,35-Anhydrobacteriohopanetetrol (anhydroBHT) is the most abundant hopanol in sediments from ODP Leg 190, Nankai Trough and IODP Exp. 308, Gulf of Mexico. Dehydration and cyclization of polyfunctionalized hopanol side chain have been proposed as the major process for the formation of anhydroBHT. The concentrations of anhydroBHT in these sediments are considerably higher than bacteriohopanetetrol which is common and abundant hopanol in many of eubacteria. AnhydroBHT is the diagenetic product rather than the intact constituent of living cell. Higher concentration of anhydroBHT in the sediments corresponds well to a terrestrial contribution, suggesting its genetic relationship with the contribution of terrestrial organic matter.

Keywords: 32, 35-Anhydrobacteriohopanetetrol, Bacteriohopanetetrol, Sedimentary hopanoids, Nankai Trough, Gulf of Mexico

INTRODUCTION

A large fraction of prokaryotic biomass is assumed to be in oceanic and terrestrial subsurface biosphere [1]. The presence of a subsurface biosphere is especially expected in areas where fluid circulation provides energy and carbon sources necessary for the survival of microbes. For example, at Site 1299 on the continental margin of Peru, ODP Leg 201, high cell concentrations occur in two subsurface sulfate-methane interfaces, which were formed by SO_4^{2-} introduction at depth and upward diffusion from ancient brine along the Peru Shelf [2]. Nankai Trough and Gulf of Mexico are known as the areas of active subsurface fluid circulation. Nankai Trough is located at the subduction zone between the Shikoku Basin and the southwest Japan arc. Many fractures and faults are developed within the accretionary prism of Nankai Trough, providing conduits for fluids. In the Gulf of Mexico, high overpressure due to high sedimentation rate induces an active fluid flow.

Bacteriohopanepolyols (BHPs), such as bacteriohopanetetrol (BHT), are a group of pentacyclic triterpenoids biosynthesized by a variety of bacteria as cell membrane constituents [3]. BHPs are rapidly transformed to diagenetic products after the death of bacteria. They, therefore, can be potential life markers of some eubacteria which contains BHPs in their cell membranes [4]. On the other hand, recent studies showed that 32,35-anhydrobacteriohopanetetrol (anhydroBHT) is major hopanol in sediments from various depositional environments [5–7]. AnhydroBHT has a furan ring in its side chain and has not been detected yet in any microorganisms. Dehydration and cyclization of polyfunctionalized hopanol side chain has been proposed as the major process for the formation of anhydroBHT [8], which

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is closely related to the fate of BHPs in sediments. In the present study, the possible origin of anhydroBHT in sediments from Nankai Trough (ODP Leg 190) and Gulf of Mexico (IODP Exp. 308) was investigated.

MATERIALS AND METHODS

Sediment samples were collected from the borehole at Site 1178 in the Nankai Trough during of the ODP Leg 190 in 2000 (Fig. 1) The drilling at Site 1178 penetrated both slope sediments and accreted sediments to a depth of ca. 680 meter below seafloor (mbsf). The sediments are characterized by predominantly abundant sand and silt turbidites in the accreted sediments below 200 mbsf. The geological age of the sediments ranges from late Miocene to Holocene (Fig. 2). We also used the sample collected from Gulf of Mexico. Drilling was conducted in two different depositional environments during Exp. 308 of the IODP in 2005 (Fig. 1). Brazos-Trinity (BT) Basin #4 is a classic area for analysis of ponded turbidite depositional environments [9]. Site U1319 is located on the southern flank of the basin where turbidite deposits are more condensed relative to Site 1321, which is in the center of the basin. Ursa Basin mainly consists of continental slope sediments. Site U1324 is the westernmost site drilled in the Ursa Basin during Exp. 308. Schematic geologic columns of boreholes at both sites in the Gulf of Mexico are shown in Fig. 3. Subunits IB, ID and IF at Site U1324 are composed of tilted, contorted and faulted beds. These intervals have been remobilized downslope and they are thus interpreted as mass transport depositions [9]. The relatively mild deformation observed in these subunits indicates that they

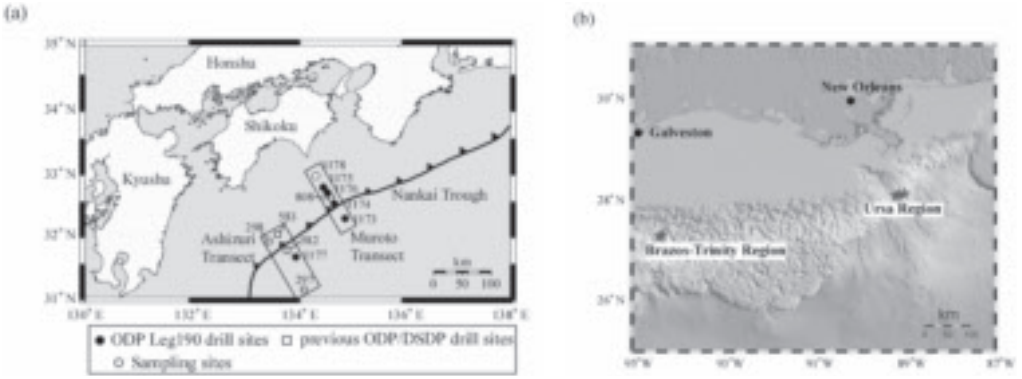

Fig. 1 Location map of (a) ODP Leg 190 in Nankai Trough, and (b) IODP Exp. 308 in Gulf of Mexico [9].

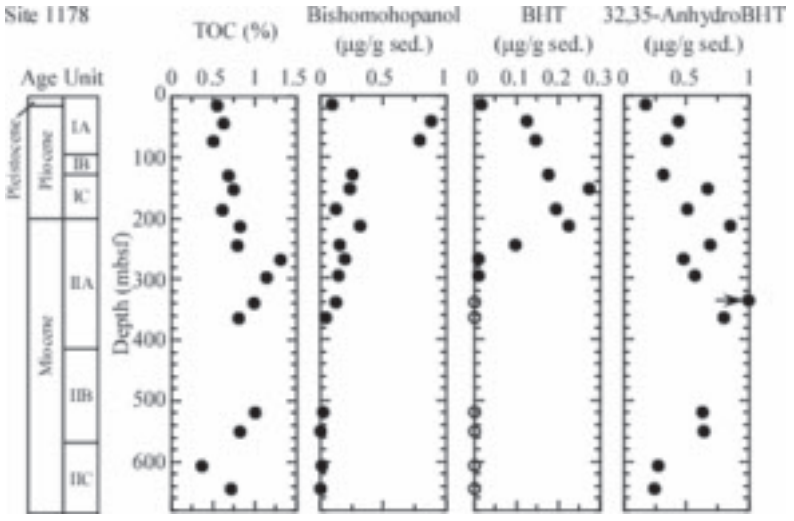

Fig. 2 Depth profiles of TOC, bishomohopanol, BHT and anhydroBHT in sediments from Nankai Trough, Site 1178. (solid circles = detected, open circles = not detected)

have remained relatively intact during transport and probably have not moved significant distances from the location of their original deposition [9]. Therefore, the mass transport depositions at Site U1324 do not seriously affect the distribution of sedimentary organic matter. In the present study, the sediment samples from ODP Leg 190, Site 1178 and IODP Exp. 308, Sites U1319 and U1324 were used for hopanol analyses.

The analytical methods employed in the present study have been described elsewhere [4]. A brief outline of analytical procedure is given here. The sediment samples were freeze-dried, then extracted with dichloromethane/methanol. Total extract was saponified with 0.5N KOH/methanol solution. The neutral fraction was subjected to silica gel chromatography to obtain an alcohol fraction. The alcohol fraction was silylated with bis (trimethylsilyl) trifluoroacetamide (BSTFA) prior to analysis. Derivatized hopanols were analyzed using gas chromatography (GC) and GC/mass spectrometry (GC/MS). 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.). 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). Hopanoids were identified from mass spectra (m/z 50–750) for the samples and comparison with published mass spectra. Concentrations of each compound were determined from peak area comparison with those of internal standards (n-$C_{36}H_{74}$ and n-$C_{40}H_{82}$). The response factor of individual compounds relative to the standard was assumed to be 1.0.

RESULTS AND DISCUSSION

The structure of anhydroBHT was initially as-

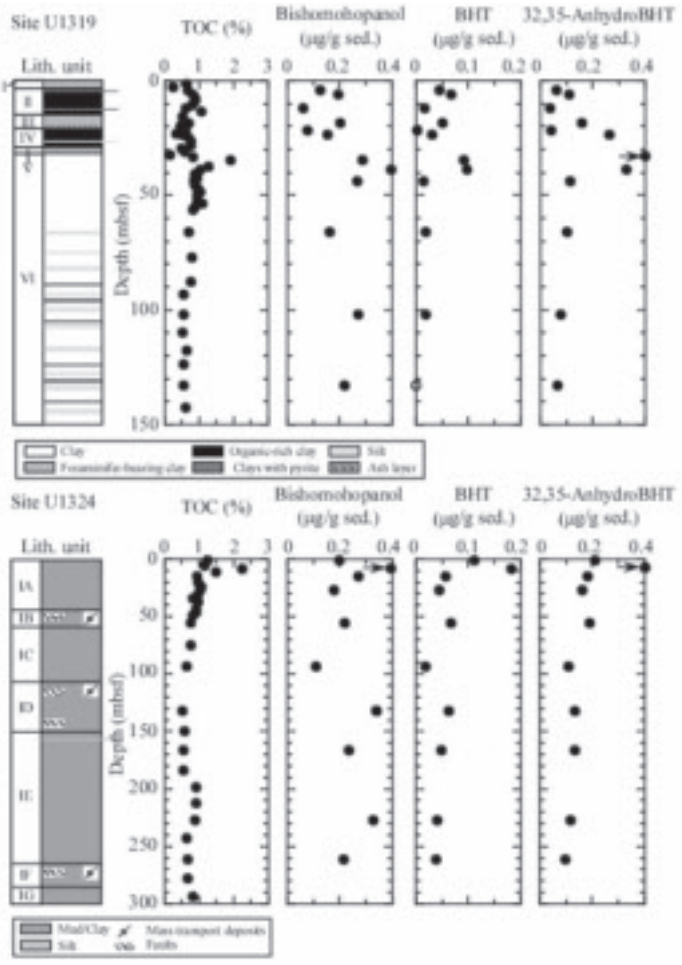

Fig. 3 Depth profiles of TOC, bishomohopanol, BHT and anhydroBHT in sediments from Sites U1319 and U1324, Gulf of Mexico. The sample description is given in more detail by [9]. (Solid circles = detected, open circles = not detected)

signed as a C_{35} hopane keto-diol from the mass spectra [5]. However, recent studies using 1D and 2D ^{1}H NMR spectroscopy have confirmed the correct structure [10–11]. The anhydroBHT has been reported in various types of marine and non-marine sediments [7]. It has been also found in sedimentary rocks of Jurassic age [11–12] and in marine deep subsurface sediments down to more than 500 m depth [6–7]. The biological sources of anhydroBHT, however, remain to be elucidated. The pathways involved in its formation are proposed as shown in Fig. 4: (1) cyclization of the polyfunctionalized side chains of the commonly occurring BHPs, biologically mediated by bacteria and/or due to acid catalyzed diagenetic transformation [8]; (2) via a hypothetical intermediates in the biosynthetic pathway of BHPs and ribosylhopane. Ribosylhopane, having a similar structure to anhydroBHT, has not been found in organisms. Adenosylhopane and the related lactone derivative found in cultured organisms [13–14] have been proposed as biosynthetic intermediates of anhydroBHT [10]. Adenosylhopane could be associated with either biosynthetic or diagenetic formation of anhydroBHT via the reductive removal of the adenine group in adenosylhopane [10]. However, intermediates within the living cell would be quickly transformed by biosynthetic reaction, and the residence time where intermediates remain non-active may be very short. The concentrations of anhydroBHT in the sediments from the Nankai Trough and the Gulf of Mexico are considerably higher than BHT which is common and abundant BHP in bacteria, suggesting that anhydroBHT is the diagenetic product rather than the intact constituent of living cell.

The silylated BHPs detected in the present study comprise trishomohopanediol, BHT and anhydroBHT. In Nankai Trough, the concentration of BHT increases with depth in the upper 200 m, then decreases to be below the detection limit at 340 mbsf. While that of anhydroBHT increases with depth in the uppermost 400 m. Such an increase is especially apparent in Subunit IIA characterized by abundant turbidite layers. Mudstones from the Subunit IIA are correspondingly characterized by high TOC content, high C/N ratio, high concentrations of plant-derived long chain *n*-alkanes, *n*-alkanoic acids and *n*-alkanols, a high terrigenous to aquatic (H/L) ratio and abundant turbidite layers, revealing it to be rich in terrestrial organic matter [15]. Higher concentration of anhydroBHT in the Subunit IIA strongly suggests its genetic relationship with the contribution of terrestrial organic matter. BHT is the most plausible precursor of anhydroBHT as discussed above. Significant amount of BHT was detected in sediments down to 200 mbsf (Figs. 2 and 3). If the dehydration and cyclization of side chain in BHT effectively proceed in water saturated sediments, the formation of anhydroBHT can of course occur within sediments. However, the formation of anhydroBHT in sediments after the deposition is not necessarily a major process, since the concentration of anhydroBHT is generally much higher than BHT as shown in Figs. 2 and 3.

The concentration of anhydroBHT is constant throughout the hole at Site U1319 except for high concentrations at 23.7, 34.5 and 39.0 mbsf (Fig. 3). The concentrations of bishomohopanol and BHT are also high at 34.5 and 39.0 mbsf but not at 23.7 mbsf. Lithostratigraphic Unit IV from 23.5 to 29.5 mbsf, characterized by clay with very fine sand laminae, records the pulse of turbidite input to the BT basin [9]. The spike of anhydroBHT at 23.7 mbsf, therefore, suggests the contribution of terrestrial material. BHT decreases with depth and is below the detection limit at 133 mbsf. At Site U1324, the depth profile of anhydroBHT is similar to that of BHT. High concentration of anhydroBHT in sediment at

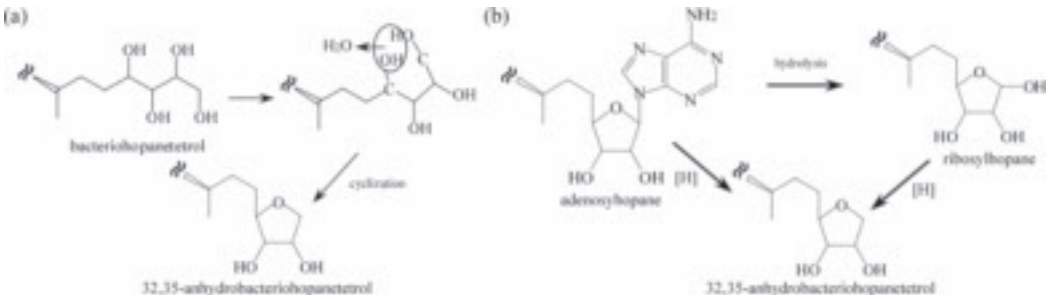

Fig. 4 Proposed synthetic pathway of 32,35-anhydrobacteriohopantetrol. (a) Cyclization of polyfunctionalized hopanoid side chain by diagenetic transformation or microbial mediation [8]. (b) Reductive removal of the adenine of adenosylhopane or reduction of the acetalfunction of ribosylhopane [10].

8.3 mbsf with high TOC of 2.24% may be due to the high contribution of terrigenous organic matter associated with the abrupt deposition of terrestrial sediments rich in coaly particles.

The anhydroBHT seems to be comparatively stable in sediments, since its concentration is significantly high in sediments at depth deeper than 400 mbsf at Site 1178 (Fig. 2). The formation of anhydroBHT requires only one reaction, dehydration within the side chain or the reductive removal of the adenine group, suggesting its formation during the very early stage of diagenesis. If the anhydroBHT is mainly generated in soil on land, this compound could be utilized as a parameter useful to reconstruct the terrestrial environment in the past. However, we do not have sufficient information about when, where and how the process to form anhydroBHT would take place after the death of bacteria, or how stable anhydroBHT would be against biodegradation and physical and chemical degradation during diagenesis. Further research on BHPs in cultured organisms, soils and various types of sediments would reveal the origin, diagenetic fate and geochemical significance of anhydroBHT in the sedimentary environments.

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