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Carbon isotope signatures of bacterial 28-norhopanoic acids in Miocene–Pliocene diatomaceous and phosphatic sediments

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Abstract

A series of C_{29}–C_{31} 28-norhopanoic acids occur in Neogene marine sediments of the Onnagawa, Funakawa and Tentokuji Formations, northeastern Japan, and in the Monterey Formation of California, USA. The 28-norhopanoic acids exist mainly as free acids but are partly bound to kerogen and the polar fraction of the solvent extract via an ester bond. The ^{13}C depletions of C_{29} and C_{31} 28-norhopanoic acids compared with those of C_{30} and C_{32} regular hopanoic acids indicate that these 28-demethylated and regular hopanoic acids are derived from different precursor organisms. The Upper Onnagawa Formation contains abundant 28-norhopanoic acids and is characterized by the occurrence of *Calyptogena* sp. (Bivalvia), which lives in a specific chemoautrophic ecosystem that utilizes chemical substrates from hydrothermal vents or cold seeps. The depletion of 28-norhopanoic acids in ^{13}C compared with kerogen suggests that the 28-norhopanoic acids have been derived from bacteria that utilized ^{13}C-depleted CO_2 as their carbon source.

Keywords: 28-Norhopanoic acids; Hopanoic acids; Hopanoids; Carbon isotope; Cold seeps; Bacteria

1. Introduction

Hopanoids are biosynthesized principally by prokaryotic organisms and are widely distributed in the geological record (Ourisson et al., 1979; Rohmer et al., 1992). Although biogenic hopanoids have a C_{30} pentacyclic nucleus derived from squalene, demethylated C_{27}–C_{29} hopanoids occur in geological samples.

C-28 demethylated hopanoids includes 28,30-dinorhopane (DNH), 25,28,30-trisnorhopane (TNH), other 28-norhopanes, 28,30-dinorhop-17(18)-ene, 28,30-dinorneohop-13(18)-ene and 28-norhopanoic acids (28-NHAs). DNH occurs in marine sediments and crude oils of late Proterozoic to Pleistocene age (e.g., Seifert et al., 1978; Grantham et al., 1980; Rullkötter et al., 1982b; Moldowan et al., 1984;

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Summons and Powell, 1992) and nonmarine sediments (Hendrix et al., 1995). Recently, a series of 28-norhopanes (C_{26} and C_{28}–C_{34}), including DNH, were identified in Jurassic oils and rock extracts from the West Greenland and North Sea oil fields (Nytoft et al., 2000). TNH always occurs in samples that contain DNH and has possibly been formed by the microbial demethylation of DNH at C-10 (Bjorøy and Rullkötter, 1980; Volkman et al., 1983). 28,30-Dinorhop-17(18)-ene was tentatively identified in a Pleistocene sediment that also contained abundant DNH (Rullkötter et al., 1982b), suggesting a genetic linkage between these two compounds (Rullkötter et al., 1982a; Volkman et al., 1983; Moldowan et al., 1984). 28,30-Dinorneohop-13(18)-ene was reported in Cretaceous black shales (Sinninghe Damsté, 1997). A tentative identification was made of C_{30}–C_{33} homologues of 28-NHAs in Pliocene to Quaternary anoxic sediments of the California margin by Simoneit and Mazurek (1981) who speculated that the biogenic precursors of the extended 28-NHAs provided the source of DNH.

An early application of compound-specific isotope analysis has indicated that DNH is depleted in ^{13}C by ~9‰ compared with whole oil, regular hopanes and phytoplankton-derived lipids from the Miocene Monterey Formation, which suggests that DNH may derive from chemoautotrophs that utilize ^{13}C-depleted substrates (Schoell et al., 1992). Schouten et al. (1997) demonstrated large variation in DNH $\delta^{13}C$ values that exceeded the variation range of phytoplankton-derived lipids. These authors suggested that DNH may be derived from an organism or organisms that assimilate pore water CO_2 that has been isotopically modified by sulfate reduction and methanogenesis. Nytoft et al. (2000) demonstrated that there was little isotopic difference between the 28-norhopanes and regular hopanes in a Jurassic oil and shale sample and provided no evidence to indicate different origins for the 28-norhopanes and regular hopanes. These authors suggested that the complete series of 28-norhopanes and regular hopanes could form from the same precursors, but that when an extremely high content of DNH was present, some of it may have had a different origin.

In this article, we report the gas chromatography–mass spectrometric (GC–MS) characterization of 28-NHAs, their occurrence and their specific stable carbon isotopic composition, and discuss their genetic relationship to regular hopanoic acids and 28-norhopanes.

2. Samples and analytical methods

2.1. Samples

A total of 18 marine diatomaceous–argillaceous mudstone samples were collected from the middle Miocene to Pliocene (12–3 Ma) Onnagawa, Funakawa and Tentokuji Formations that occur in the Yashima area of the Akita oil-producing Neogene basin, northern Honshu, Japan (Fig. 1). Detailed descriptions of these samples have been given by Yamamoto and Watanabe (1994, 1995). The maturity of the samples ranges from <0.3% Ro in the Tentokuji and Funakawa Formations to 0.3–0.4% Ro in the Onnagawa Formation (Yamamoto and Watanabe, 1994). The redox condition of the benthic water changed from oxic to anoxic during deposition of the Lower Onnagawa Formation (12–10 Ma) and gradually altered from anoxic to oxic during deposition of the overlying formations (10–3 Ma; Yamamoto and Watanabe, 1994). A marine phosphate sample M1 (15.3–14.4 Ma) was provided from the Miocene Monterey Formation, Naples Beach, California, USA (Ingle, 1981). The Onnagawa Formation and the Monterey Formation are age equivalents on the northwest and northeast Pacific margins (Iijima, 1994). The rock samples were crushed and milled to a particle size of 30 μm.

2.2. Methods

2.2.1. Solvent extraction

The analytical procedure used is outlined in Fig. 2. The sample (~20–30 g) was extracted two or three times with benzene/methanol (7:3, vol/vol) for 15 h using a Tecator Soxtec system HT2. Elemental sulfur was removed during the extraction by adding elemental copper to the boiling flask. The solvent extract was condensed by rotary evaporation and dried under a stream of nitrogen.

2.2.2. Sequential extraction

The bound lipids were liberated and extracted from sample 927-3 according to the modified method of