Reconstruction of sedimentary environment in early Pleistocene using biomarkers from methane-oxidizing archaea.

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The outcrops in Segami area, Yokohama, have been recognized as ancient cold seep sediments based on the identification of chemoautotroph bivalve fossils (*Lucinoma spectabilis*; Majima et al., 1996) and the carbon isotopic compositions of carbonates (Tate and Majima, 1998). A 107 m-long boring core named core-E was recovered at 14m away from the lower outcrop. Based on nanno fossil record (Fujioka, 2003), sediments in the core-E were estimated to be deposited from 170 to 145 ka, which can be correlated to the upper Ofuna and the lower Koshiba Formations in Kazusa Group. Authigenic carbonates appeared in the core had a pattern of dolomite, high-Mg calcite, and aragonite (from bottom to top) with gradually decreasing their carbon isotopic compositions.

In this study we analyzed biomarkers in 19 intervals from the core-E to reconstruct the distribution of microbes associated with anaerobic oxidation of methane (AOM). Microbes associated with AOM have been known to form consortium with anaerobic methane-oxidizing archaea and sulfate reducing bacteria (e.g. Boetius et al., 2000). The membrane lipids of archaea have several unique features; For example, they have ether linkages between hydrocarbon chains and a glycerol molecule, and hydrocarbon chains are isoprenoids rather than alkyl lipids.

We observed a large amount of biomarkers derived from the archaea and the sulfate reducing bacteria in the interval with ^{13}C-depleted authigenic carbonate. We found crocetane and PMI characteristic for AOM. The carbon isotopic compositions of the PMI range from -103 to -120 per mil. Archaeol, *sn*-2-hydroxyarchaeol, and biphytanes were more abundant than the isoprenoids like crocetane and PMI. The relative abundance of four biphytanes (acyclic:0R, monocyclic:1R, dicyclic:2R, tricyclic:3R) was in a descending order of 1R, 0R, 2R, and 3R, suggesting them to be derived from the methane-oxidizing archaea. Because in our samples the biphytane1R had the lightest carbon isotopic composition among the four, it could have been synthesized mostly by the methane-oxidizing archaea.

In the dolomite layers, total abundance of the archaea biomarkers was less abundant. The relative abundance of biphytanes was in a descending order of 0R, 3R, 2R, and 1R. In the dolomite layers, the carbon isotopic compositions of PMI (-45 to -55 per mil), phytane (-37 to-61 per mil), squalane (-24 to -27 per mil), and archaeol (-64 per mil) were substantially heavier than those in the aragonite and calcite layers. It suggested planktonic archaea synthesized most of these molecules. Furthermore, we suspect that they also synthesized PMI, although the PMI has been thought to be a characteristic biomarker of AOM (e.g. Bian, 1994).

Based on these results, we recognized the molecular features characteristic for the AOM are; (1) biphytane1R is more abundant than 3R, (2) lower carbon isotopic composition of PMI (-100 per mil or lower), (3) high abundance of archaeol, and (4) frequently co-occurrence of certain DAGEs. Since lipids from planktonic archaea are potentially preserved in cold seep sediments, compound-specific carbon isotopic analysis is required for identifying AOM.

Reference

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