Carbon and hydrogen isotopic compositions of archaeal lipids in deeper part of methane hydrate bearing sediment

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Introduction

Significant contribution of microbially mediated methanogenesis in marine sediment is suggested by isotopic compositions of methane, methane/ethane ratio, phylogenetic analysis etc. However, it is still unclear where methanogen distributes in sediment column and what metabolic pathway it utilizes. Archaeal lipid biomarkers and their isotopic composition could provide information about archaeal activity in deep sediment where incubation is difficult to be conducted. In this study, we discussed archaeal activity in deeper part of methane hydrate-bearing sediment (50-300 mbsf), using distribution of archaeal lipid biomarkers and their carbon and hydrogen isotopic compositions.

Materials & experimental methods

Sediments in this study were collected at Site U1328 (total depth: 300 mbsf) during IODP exp 311 in northern Cascadia margin, gas hydrate zone. Lipid was extracted from dried sediment by organic solvents. Hydrocarbon and alcohol fractions were separated from neutral lipid using silica gel chromatography. An aliquot of alcohol fractions was silylated and the another aliquot was treated with HI to extract alkyl chains from archaeal ether lipids. Quantification and qualification of hydrocarbons, silylated alcohols and hydrocarbons derived from ether lipids were conducted using gas chromatograph and gas chromatograph/mass spectrometer. Carbon and hydrogen isotopic compositions of these compounds were analyzed by gas chromatograph/isotope mass spectrometer.

Results & discussion

All sediment used in this study contained crocetene, 2,6,10,15,19-pentamethylicosane(PMI), archaeol, acyclic biphytane diol (BPD [0], number means number of pentane ring in alkyl chain), BPD [3], phytane (phy.) derived from archaeol and biphytanes (BP [0]-BP [3]) derived from glycerol dialkyl glycerol tetraethers (GDGTs) known as archaeal biomarkers. Concentration of crocetene and PMI in hydrocarbon fraction were 5 ug/gC_{org} in maximum, whereas maximum concentrations of BPD [0] and BP [0] were relatively high (49.6 ug/gC_{org}, 458 ug/gC_{org}, respectively). Distribution pattern of the biomarkers tended to increase between 100 mbsf and 200 mbsf. Especially, BP [0]-BP[3] derived from GDGTs were maximum at 173 mbsf. There were positive correlations between concentration of the biomarkers and TOC content (e.g. correlation coefficient of BPD [0] and BP [0] is r^2=0.65 and r^2=0.93, respectively), suggesting that archaeal activity strongly depend on the TOC content. Carbon and hydrogen isotopic compositions of archaeal biomarkers at 142 mbsf showed two distinctive compositional ranges. One group consisted of BP[0], BP [2] and BP [3] and ranged in $d^{13}C$ from -22.1 to -19.4 permil and in dD from -280 to -222 permil. Carbon isotopic composition of crocetene in same depth showed similar value of -23.9 permil. The another group consisted of phy. and BP [1] and showed in $d^{13}C$ of -42.8 and -40.8 permil and in dD of -204 and -172 permil. Carbon isotopic composition of PMI at 249 mbsf was -46.7 permil and closed to the value of this group. Given $d^{13}C$ values of the former group were similar to the value of sedimentary organic matter (-21.5 permil), these biomarkers are derived from heterotrophic archaea that utilizes sedimentary organic matter as its carbon source. Another group could be derived from chemoautotrophic archaea based on their carbon isotopic signatures. Hydrogen isotopic composition is identical with that of methane (-160 permil, Pohlman, 2006) and carbon isotope fractionation during methanogenesis of CO_2 reduction is reported 23-60 permil (e.g. Valentine et al, 2004). Assumed that the fractionation during lipid synthesis is similar to that during methanogenesis (e.g. Summons et al, 1998), the latter group of biomarkers could be derived from methanogen. We will also discuss about carbon and hydrogen isotopic compositions of the biomarkers in other sediment depth.