

Origin of methane at ancient methane seeps inferred from organic geochemical signatures in seep carbonates

YUSUKE MIYAJIMA

Abstract

Knowing the origin of methane at submarine methane seeps (cold seeps) can provide valuable insights into the depth origin and migration process of the seep fluids as well as into the subsurface fluid circulation. The origin of methane at ancient seeps has been estimated indirectly based on geological backgrounds and carbon isotopic compositions of carbonates that formed via the anaerobic oxidation of methane (AOM). In this study, two approaches were attempted to estimate the origin of methane at ancient seeps: 1) carbon isotope analysis of lipid biomarkers for anaerobic methane-oxidizing archaea (ANME) and 2) analysis of the carbon isotopic and molecular compositions of residual gases within the methane-seep carbonates. A modern methane-seep carbonate rock obtained from the seafloor at a seep site offshore Joetsu, Niigata Prefecture, central Japan was examined to estimate the carbon isotope fractionation between methane and ANME biomarkers. For ancient seep carbonates, Miocene to

Pleistocene methane-seep carbonate rocks collected at 11 sites in the Japan Sea region were examined.

The early-diagenetic, AOM-derived carbonate phases show various $\delta^{13}\text{C}$ values ranging between -64.7‰ and -4.7‰ (vs. VPDB). This result does not tell us which is plausible thermogenic ($>-50\text{‰}$) or biogenic ($<-50\text{‰}$) origin for the methane.

Pentamethylcosane (PMI) extracted from the modern methane-seep carbonate has a $\delta^{13}\text{C}$ value of -80‰ , which shows an offset of 44‰ from the seep methane (-36‰) at this site. The ANME biomarkers PMI and crocetane were extracted from the ancient carbonates, with $\delta^{13}\text{C}$ values ranging between -137‰ and -93‰ . The estimated offset of $\delta^{13}\text{C}$ (44‰) indicates that the methane at the ancient seep had $\delta^{13}\text{C}$ values mostly lower than -50‰ and are biogenic in origin, assuming that the $\delta^{13}\text{C}$ values of the ANME biomarkers are controlled by those of the source methane and isotopic fractionations during biosynthesis. The relationship of the $\delta^{13}\text{C}$ values between methane and ANME biomarkers was assessed by regression analysis based on data taken at modern seeps in other regions of the world. The obtained regression formulae were used to constrain the $\delta^{13}\text{C}$ values of methane at the ancient seeps with 95% prediction intervals, which provided the similar results as estimated from the $\delta^{13}\text{C}$ offset. It can be concluded that the methane contained in the seep fluids at the ancient seeps in the study

area is mainly biogenic in origin and was produced in the shallow subsurface. Migration and seepage of thermogenic methane from the deep subsurface were probably minor before Pleistocene in the study area.

Methane and heavier hydrocarbons were extracted by acid digestion of powdered samples of the AOM-derived carbonate phases. The methane content tends to increase with increasing age of the carbonate. The extracted methane has $\delta^{13}\text{C}$ values of -69.6‰ to -26.9‰ and methane to (ethane+propane) ratios of 2 to 518, and therefore both thermogenic and biogenic origins are possible. Methane was also released by heating and crushing of chipped samples of the Miocene seep carbonates at the Nakanomata 1 site. These methods produced a little amount of methane as compared with acid digestion and high amounts of carbon dioxide. The $\delta^{13}\text{C}$ values were measured for the methane and carbon dioxide liberated by the crushing. The methane shows $\delta^{13}\text{C}$ values from -55.1‰ to -49.9‰ , while the carbon dioxide exhibits values ranging between -26.8‰ and -25.2‰ . The obtained $\delta^{13}\text{C}$ values can be explained by methane oxidation. The results suggest a reasonable scenario of the origin of methane at Nakanomata 1 as follows: 1) biogenic methane was originally contained in the Miocene seep fluids; 2) isotopic fractionation during AOM enriched the methane in ^{13}C ; and 3) the ^{13}C -enriched methane was trapped within the seep carbonate mainly as intracrystal inclusions. This

scenario is also supported by a positive significant correlation of the $\delta^{13}\text{C}$ values between the methane and its host carbonate. The $\delta^{13}\text{C}$ values typically increase with increasing carbon number in thermogenic and biogenic hydrocarbons. In contrast, the $\delta^{13}\text{C}$ values of the methane, ethane, and propane liberated from the examined carbonates by acid digestion showed “reverse” isotopic trends. This “reverse” isotopic trends found in the liberated hydrocarbons indicate that ethane and propane with unusually low $\delta^{13}\text{C}$ values ($<-40\text{‰}$) were mixed with normal thermogenic or biogenic gases. The unusually ^{13}C -depleted ethane and propane could have originated from secondary thermal cracking of ^{13}C -depleted organic compounds within the seep carbonates. They were extracted even from the samples of low maturity. The line of evidence indicates that the residual gases within the seep carbonates can contain incidental gases as well as original ones. The isotopic trend of the unusually ^{13}C -depleted ethane and propane was different between low and high maturities. This result suggests that the mixing ratio to the normal gases and the molecular ratio of the secondary-generated gases both depend on thermal maturity.

It is probable that the carbon isotopic compositions of the ANME biomarkers preserved within the methane-seep carbonates are less affected by thermal maturation, with respect to the petrographic textures and oxygen isotopic compositions of the

carbonates. However, in some samples of high maturity, the ANME biomarkers were not preserved probably due to thermal break down. Residual gases within the seep carbonates could be affected seriously by incidental gases even in the samples of low maturity. Therefore, the residual gases should be examined using multiple extraction methods and with other signatures such as the isotopic compositions of the carbonates and the biomarkers.