

Origin of residual hydrocarbon gases within fossil methane-seep carbonates: original vs. secondary gases

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Authigenic carbonates precipitated via anaerobic oxidation of methane at methane seeps are regarded as recorders of geochemistry of seep fluid and gas. A few studies have reported that methane and heavier gaseous hydrocarbons were extracted from modern and fossil methane-seep carbonates. While such residual gases within methane-seep carbonates are promising to know the origin of methane and fluid at ancient seeps, it is also likely that the residual gases were secondary entrapped within the carbonates during their burial and thermal maturation, rather than originally contained in the ancient seep fluid. This study extracted gaseous hydrocarbons from Neogene methane-seep carbonates in Japan. Whether the extracted gases could be explained only by the secondary processes was examined based on the molecular and stable carbon isotopic compositions of them. The examined seep carbonates were collected from the Serravallian Bessho Formation, central Japan (Anazawa/Akanuda site) and the Tortonian or Messinian Nodani Formation, central Japan (Nakanomata site). Methane, ethane, and propane were successfully liberated from the carbonates by acid digestion of powdered samples. It was revealed that the molecular and isotopic compositions of the liberated hydrocarbons cannot be classified using the conventional schemes (e.g., Bernard et al., 1976; Berner and Faber, 1996). Regardless of the $\delta^{13}\text{C}$ values of the methane ranging between -67.2% and -38.1% (vs. VPDB), the methane to ethane+propane ratios ($C_1/(C_2 + C_3)$) of the liberated hydrocarbons were consistently low (2–30). The $\delta^{13}\text{C}$ values of the ethane and propane showed anomalous values as low as -83.7% , and were lower than the coexisting methane, i.e., $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2$ at Anazawa/Akanuda and $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2 > \delta^{13}\text{C}_3$ at Nakanomata. These features contradict conventional thermogenic hydrocarbons. The anomalously ^{13}C -depleted hydrocarbons most likely originated from secondary thermal cracking of strongly ^{13}C -depleted organic compounds preserved within the seep carbonates ($\delta^{13}\text{C} < -100\%$). The “reverse” isotopic trends could be explained by mixing of two-component gases: normal thermogenic hydrocarbons that were generated from sedimentary kerogens and migrated through the host sediments of the carbonates; and strongly ^{13}C -depleted hydrocarbons with relatively higher ethane and propane contents generated by secondary thermal cracking of the organic matter within the carbonates. The variation in the isotopic trend of the residual gases between the study sites could be related to the mixing ratio or molecular composition of the secondary thermogenic hydrocarbons. However, the slightly elevated $C_1/(C_2 + C_3)$ ratios (~ 30) and isotopic trends observed at Nakanomata suggest mixing of biogenic methane in addition to the two thermogenic components. There is a significant positive correlation between the $\delta^{13}\text{C}$ values of the methane and the carbonate. This correlation implies that the methane extracted from the Nakanomata carbonate at least partly originated from the ancient seep fluid and was preserved within the carbonate cements, which were precipitated from bicarbonate ions produced by the oxidation of the biogenic methane.

Keywords: Carbonate, Carbon isotope ratio, Cold seep, Ethane, Methane, Propane