

Doubly substituted isotopologues of methane hydrate ($^{13}\text{CH}_3\text{D}$ and $^{12}\text{CH}_2\text{D}_2$): implication for sources and history

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Natural gas hydrates have been widely discovered along continental margins since 1980s. A comprehensive understanding of physical-chemical-biological processes associated with gas hydrate formation and decomposition, as well as their methane sources, will provide valuable information to better assess the opportunity and risk of this new energy resource. Traditional methods for identifying gas hydrate sources include ‘ $\delta^{13}\text{C}$ vs. δD space’ (Whiticar plot) and ‘ $\delta^{13}\text{C}$ vs. $\text{C}_1/(\text{C}_2+\text{C}_3)$ space’ (Bernard plot). However, obvious defects exist, such as partly overlapping of isotopic signatures for different CH_4 sources, difficulty in constraining CH_4 generated from two or more sources, and suffering from post-generation processes like gas migration and microbial methanotrophy (Milkov and Etiope, 2018). These limitations promoted scientific communities to develop additional constraints for better interpreting methane sources and histories.

Methane clumped isotope signatures are defined as abundances of multiply substituted mass-18 isotopologues ($^{13}\text{CH}_3\text{D}$ and $^{12}\text{CH}_2\text{D}_2$) relative to the stochastic distribution of each isotope in the same sample (Stolper et al., 2014; Young et al., 2017; Douglas et al., 2017), which can either record formation/equilibration temperatures or kinetic isotope processes leading to disequilibrium. In this study, clumped isotope signatures of gas hydrate samples recovered from 5 different locations in the Japan Sea were analyzed using an ultra high resolution IRMS established in Tokyo Institute of Technology.

Most of these samples presented reasonable and accordant $\Delta^{13}\text{CH}_3\text{D}$ and $\Delta^{12}\text{CH}_2\text{D}_2$ temperatures, ranging from ~ 15 to ~ 170 °C. These near-equilibrium clumped isotope signatures were primarily attributed to the mixing effect of equilibrium thermogenic source formed at high temperatures and near-equilibrium biogenic source contributed by anaerobic oxidation

of methane, while the influence from other processes, such as gas migration/diffusion, hydrate formation and decomposition, is insignificant. Combining clumped isotope results with other traditional approaches, the accurate source end-member information of these gas hydrates has been documented as well.

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References: Stolper et al., 2014, *GCA*; Douglas et al., 2017, *Organic Geochemistry*; Young et al., 2017, *GCA*; Milkov and Etiope, 2018, *Organic Geochemistry*