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研究課題名（和文）Clumped isotope signature of abiotic methane formed via Fischer-Tropsch catalysis and its implication in identifying the pathway of natural abiotic methane  
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研究成果の概要（和文）：メタンは主要な温室効果ガスであり、地球規模のメタン循環の解明は注目されている研究テーマの一つである。本研究では、天然メタン生成・消費経路の探索に利用可能な最先端のメタン二重置換同位体分析法を構築した。  
(1) 日本海のカスハイドレート：海洋堆積物環境におけるメタン二重置換同位体効果の基本的なプロセスに注目し、メタンの起源と移動に関する基礎的な疑問に答える可能性を示した。  
(2) 当研究室では、ガス状FTT型反応によって非生物学的メタンを合成した。非生物学的メタン化における同位体比変化を制御するメカニズムを議論した。さらにその結果を天然非生物メタン貯留層で観測される同位体パターンへ応用した。

研究成果の学術的意義や社会的意義  
新しいメタン二重置換同位体分析法を適用することにより、地球規模のメタン循環や過去および将来の気候変動を制約するための有用性を実証した。また、実験室でのメタン生成実験成果は、地球や他の惑星における初期生命シグナルの探索に応用できる可能性がある。

研究成果の概要（英文）：Understanding global methane cycles is one of the hot research topics as CH<sub>4</sub> is a major greenhouse gas and an important energy resource. In this study, we have developed the most advanced methane clumped isotope analytical technique which could be used for exploring the natural CH<sub>4</sub> formation and consumption pathways. We applied this method in two types of samples:  
(1) natural gas hydrate recovered from the sediment of Japan Sea: our study sheds new light into the fundamental processes of methane clumped isotope effects in marine sediment environment and their potential to answer fundamental questions regarding the source and migration of CH<sub>4</sub> found in naturally occurring hydrate accumulations.  
(2) the laboratory synthesized abiotic CH<sub>4</sub> via gaseous Fischer-Tropsch Type reactions: we discussed the mechanisms controlling isotopic changes during abiotic methanation and further applied our observations in better understanding the observed isotope patterns in natural abiotic CH<sub>4</sub> reservoirs.

研究分野：地球科学

キーワード：メタン 同位体 カスハイドレート 非生物学的メタン

## 1. 研究開始当初の背景

Methane (CH<sub>4</sub>), one of the major greenhouse gases, plays an important role in the global carbon cycle. Constraining its sources and sinks in nature can provide valuable information to understand the climate changes and search for potential energy resource (e.g. Nisbet et al., 2014). Furthermore, 'abiotic' CH<sub>4</sub> gases presented in serpentinization systems, such as hydrothermal vents and continental geothermal seeps, are considered to support the earliest life as the carbon and energy source, although the detailed formation mechanisms have yet been unclear (Russell et al., 2010).

Naturally occurring CH<sub>4</sub> may be produced via plenty of formation pathways, including 3 major types: thermogenic, biogenic, and abiotic. However, these conventional methods, i.e., the isotopic compositions of CH<sub>4</sub>, e.g., <sup>13</sup>C/<sup>12</sup>C and D/H ratios, are not always effective in some occasions: the partial overlap of isotope signatures from different CH<sub>4</sub> sources, mixtures of CH<sub>4</sub> from two or more sources, and the alteration of isotope compositions via post-generation processes such as gas migration and microbial methanotrophy (Milkov and Etiope, 2018).

Owing to the progresses of instrumental development, analyzing the trace level rare species in CH<sub>4</sub> became possible these years (Stolper et al., 2014 and thereafter). The novel approach, named as the clumped isotope method, focusing on methane molecules substituted by two or more rare stable isotopes, e.g. <sup>13</sup>CH<sub>3</sub>D and <sup>12</sup>CH<sub>2</sub>D<sub>2</sub>, provides new possibilities to constrain natural methane formation and consumptions pathways. However, as an under constructive method, our fundamental knowledge is still unsatisfied, for instance, how to improve the analytical precision and accuracy; which mechanisms control the observed  $\Delta^{13}\text{CH}_3\text{D}$  vs.  $\Delta^{12}\text{CH}_2\text{D}_2$  patterns; how to apply this method in constraining the natural methane formation pathways, etc. In this study, we have developed the methane clumped analysis protocols using an ultra high resolution isotope ratio mass spectrometry (Thermo Scientific 253 Ultra) in Tokyo Institute of Technology. We further explored its application in two different types of methane samples: natural gas hydrate reservoirs and the laboratory synthesized abiotic methane via gaseous Fischer-Tropsch Type (FTT) reactions.

## 2. 研究の目的

(1) As a very recent technique, the laboratories succeeded in methane clumped isotope analysis are limited, which are mainly in U.S. The first purpose of this research proposal is to establish the most advanced methane clumped isotope analytical protocols in Japan.

(2) Natural gas hydrate is widely distributed in marine sediments along continental margins, as has been observed since the 1980s (Milkov, 2005). 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 these non-conventional energy resource. By applying the methane clumped isotope technique in methane samples dissociated from gas hydrate collected from the sediment of Japan Sea, we hope to explore how could this new approach be benefit in understanding the methane behaviors during production and storage in the marine sediment reservoirs.

(3) 'Abiotic' CH<sub>4</sub> has been widely observed in natural systems, such as non-sedimentary systems in deep boreholes of Precambrian shields, seafloor and continental geothermal systems like springs, volcanos, and

mud volcanos (Etiope and Whiticar, 2019). Comprehensively understanding its formation mechanisms and post-genesis behaviors would provide valuable information for exploring the origins of early life on Earth and potentially on other planets, since abiogenic  $\text{CH}_4$  is considered to play an important role in fueling the evolution of early life as the carbon and energy source which has also been observed at other rocky planets such as Mars, Enceladus, etc. However, our basic knowledge on naturally occurred abiogenic  $\text{CH}_4$  is yet insufficient. Although plenty of  $\text{CH}_4$  reservoirs have been considered as primarily abiogenic origin, the detailed formation mechanisms, the quantification or even the identification of abiogenic source in each reservoir, are still under debate (Etiope and Whiticar, 2019; Klein et al., 2019). Preliminary clumped isotope data of some natural abiogenic  $\text{CH}_4$  samples have been reported, however, the results are variable and disperse for samples collected from different serpentinization systems (Fig. 4). To better explain these observations, laboratory studies on clumped isotope signatures of methane formed from different abiogenic pathways are necessary. To achieve this goal, we have carried out a series of Nickel catalyzed FTT reactions to produce abiogenic methane and studied its clumped isotope signatures.

### 3. 研究の方法

#### (1) Gas hydrate samples.

The studied materials are recovered from 3 major areas along the eastern Japan Sea margin (Joetsu Basin, Oki Trough and Mogami Trough) using conventional drill coring and pressure coring techniques during cruises in 2014 and 2015, including 5 sampling sites in total (Fig. 1). Frozen hydrates were dissociated at ambient temperature at  $\sim 5^\circ\text{C}$  and the gas samples were collected and further purified by passing through a gas chromatograph (GC-4000, GL-Science) equipped with two 2 m Haysep Q columns (2.2 mm I.D.).

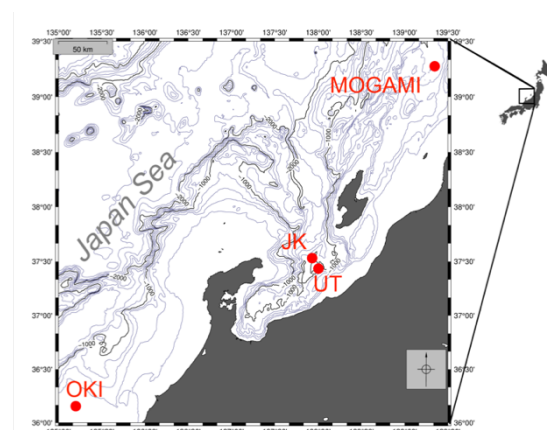


Fig 1. Sampling locations.

#### (2) Laboratory synthesized abiogenic samples.

A series of nickel catalyzed FTT reactions ( $n = 26$ ) with different reaction times ranging from 20 mins to 45 hrs have been conducted using a designed vacuum glass line. A  $\text{CO}/\text{H}_2$  mixture gas ( $\text{CO}/\text{H}_2 = 1/4$ ; Air Liquide Japan G.K.) was introduced into the closed reaction vessel for conducting FTT reaction at the initial pressure of  $0.73 \pm 0.3$  bar and the temperature of  $335 \pm 5^\circ\text{C}$ . After reaction, residual gas was successively passed through a water-U-trap and a methane-U-trap filled with silica gel, both of which were immersed into the liquid nitrogen. Methane was then trapped and purified by GC for further isotope analysis.

#### (3) Methane clumped isotope analytical protocols.

The abundance of singly and doubly substituted methane isotopologues, including  $^{13}\text{CH}_4$ ,  $^{12}\text{CH}_3\text{D}$ ,  $^{13}\text{CH}_3\text{D}$  and  $^{12}\text{CH}_2\text{D}_2$ , were analyzed by a commercial version of Thermo 253 Ultra IRMS (Ultra) installed at Earth-Life Science Institute in Tokyo Institute of Technology in 2018. Nine faraday cups are equipped in Ultra and eight of them are moveable. The mass resolving powers (MRP, 5%, 95% edge definition) can reach  $\sim 50,000$  with a narrow source slit (HR+ aperture mode, slit width:  $5\ \mu\text{m}$ ) to ensure the full separation of target peaks ( $[^{13}\text{CH}_4^+]$ ,  $[^{12}\text{CH}_3\text{D}^+]$ ,  $[^{13}\text{CH}_3\text{D}^+]$ ,  $[^{12}\text{CH}_2\text{D}_2^+]$ ) and adducts ( $[^{12}\text{CH}_5^+]$ ,  $[^{13}\text{CH}_5^+]$ ,  $[^{12}\text{CH}_4\text{D}^+]$ ). The detailed analytical protocols have been reported in Zhang et al. (2021).

#### 4. 研究成果

##### (1) Clumped isotope signatures of gas hydrate samples: implications for methane clumped isotope effect, source apportionments and global hydrate reservoirs.

We have examined the potential influences of various post-generation processes in clumped isotopes in gas hydrates recovered from marine sediments and explored how this relatively new approach may be applied to natural hydrocarbon systems. All analyzed hydrate samples recovered from the Japan Sea sediment presented near-intra-species-equilibrium results, corresponding to apparent temperatures ranging from ~15 to ~170 °C (Fig. 2a). With bulk stable isotopes and other geochemical parameters, we discussed the mechanisms contributing to the observed clumped isotope signatures, and concluded that they were primarily the result of mixing between a (near-)equilibrated thermogenic methane end-member formed at  $165 \pm 15$  °C and a biogenic one equilibrated at 1-2 °C. The intra-species equilibrium signatures of thermogenic source were probably inherited from the thermal-cracking process which occurred in deep sediment, while the near-equilibrium values in biogenic end-member were most likely attributed to the combination effects of slow methanogenesis and bond re-ordering catalyzed by AOM. Other processes, such as gas migration, hydrate formation and dissociation, presented insignificant contribution to the overall clumped isotope signatures.

Using the methane clumped isotope approach, our study quantitatively deciphers end-member information for naturally occurring methane gases, which are usually comprised of two or more sources and cannot be accurately determined by traditional isotope approaches (Fig. 2). In addition, the source temperatures estimated from clumped isotope may provide a direct and independent way to reconstruct the geothermal gradient history when the thermogenic methane was formed in the marine sedimentary system. The accurate source apportionment and formation mechanisms reconstruction can also improve our knowledge on the role of gas hydrates in the present and past global carbon cycle.

##### (2) Clumped isotope signatures of laboratory synthesized methane via nickel-catalyzed Fischer-Tropsch reactions: implications for abiotic methane formation in nature.

As described before, we have studied the clumped isotope signatures of abiotic methane synthesized via Fischer-Tropsch type (FTT) reactions ( $\text{CO}/\text{H}_2=1/4$ ; Nickel; ~ 335 °C) using a 253 Ultra IRMS at Tokyo Tech. During experiment, the concentration of methane increased fast and approached 100% yield at about 1 hr, indicating almost all of the CO has been transformed into  $\text{CH}_4$  during the Ni-FTT experiments. Our results exhibit a dramatically disequilibrium pattern in  $\Delta^{12}\text{CH}_2\text{D}_2$  (~-45‰) while the  $\Delta^{13}\text{CH}_3\text{D}$  values present near-equilibrium values (+1.4‰) at the beginning of experiment. With reaction proceeding,

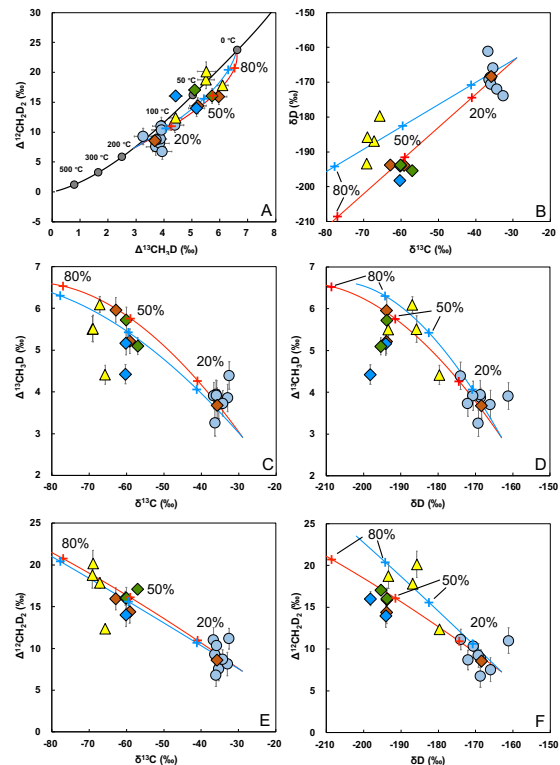


Fig 2. Mixing model for thermogenic and biogenic end-members.

$\Delta^{13}\text{CH}_3\text{D}$  decreased gradually and approached the lowest value ( $\sim 1.7\text{‰}$ ) at 100% CO conversion rate; inconsistently, the trend of  $\Delta^{12}\text{CH}_2\text{D}_2$  was not significant. Decreased  $\Delta^{13}\text{CH}_3\text{D}$  values are likely controlled by the kinetic isotope effect, while disequilibrated  $\Delta^{12}\text{CH}_2\text{D}_2$  values are mainly determined by the

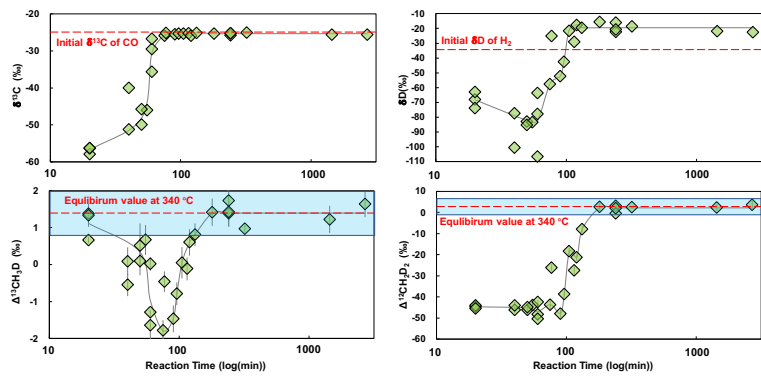


Fig 3. Changes of methane isotopic signatures with reaction time.

combinatory effect (D from different H pools caused by different reversibility of hydrogenation steps on the catalyst surface) (Cao et al., 2019). After then, both clumped values increased to equilibrium with a  $\Delta^{12}\text{CH}_2\text{D}_2$  vs.  $\Delta^{13}\text{CH}_3\text{D}$  slope around a unit due to bond reordering catalyzed by Ni.

Our experimental observations presented inconsistent pattern with reported clumped isotope signatures from natural ‘abiotic’ methane reservoirs (Fig. 4), especially to those collected from low temperature reservoirs ( $T < 150^\circ\text{C}$ ). The natural ‘abiotic’ methane can be either around, upper, or below the equilibrium line, while the magnitude in disequilibrium is much lower than

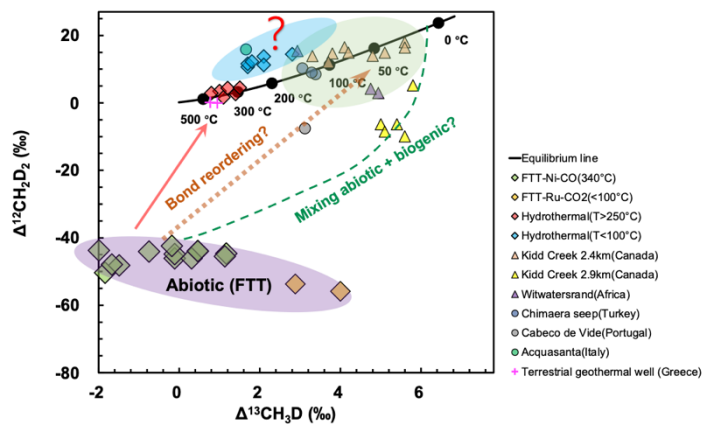


Fig 4. Comparison of clumped isotopes in lab synthetic abiotic  $\text{CH}_4$  with natural ‘abiotic’ samples.

methane produced during our FTT synthesis. This may indicate other abiotic formation pathways, such as hydrothermal reactions, electrocatalytic reactions, radiolysis, may contribute to the natural abiotic reservoirs. Alternatively, these natural ‘abiotic’ methane reservoirs may contribute by the microbial activity. Another possibility could be the post-generation processes which might have occurred in these serpentinization systems which altered the initial disequilibrium patterns during methane production. To find the best answer, further laboratory experiments combined with geological/geochemical observations on natural abiotic methane reservoirs are required in the following studies.

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5. 主な発表論文等

〔雑誌論文〕 計1件（うち査読付論文 1件/うち国際共著 1件/うちオープンアクセス 0件）

1. 著者名 Zhang Naizhong, Snyder Glen T., Lin Mang, Nakagawa Mayuko, Gilbert Alexis, Yoshida Naohiro, Matsumoto Ryo, Sekine Yasuhito	4. 巻 315
2. 論文標題 Doubly substituted isotopologues of methane hydrate (13CH3D and 12CH2D2): Implications for methane clumped isotope effects, source apportionments and global hydrate reservoirs	5. 発行年 2021年
3. 雑誌名 Geochimica et Cosmochimica Acta	6. 最初と最後の頁 127 ~ 151
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.gca.2021.08.027	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

〔学会発表〕 計5件（うち招待講演 0件/うち国際学会 4件）

1. 発表者名 Zhang N., Y. Sekine, M. Nakagawa, N. Yoshida
2. 発表標題 Clumped isotope signatures of abiotic methane formed via Fischer-Tropsch catalysis and its implication
3. 学会等名 Goldschmidt 2020: Virtual（国際学会）
4. 発表年 2020年

1. 発表者名 Zhang N., Y. Sekine, M. Nakagawa, N. Yoshida
2. 発表標題 Clumped isotope signatures of abiotic methane formed via Fischer-Tropsch catalysis and its implication
3. 学会等名 JpGU-AGU Joint Meeting 2020: Virtual（国際学会）
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3. 学会等名 第4回水惑星学全体会議
4. 発表年 2021年

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3. 学会等名 Goldschmidt 2021 (国際学会)
4. 発表年 2021年

1. 発表者名 Naizhong Zhang, Yasuhito Sekine, Keita Yamada, Mayuko Nakagawa and Naohiro Yoshida
2. 発表標題 Clumped isotope signatures of abiotic methane formed via nickel-catalyzed Fischer-Tropsch synthesis and their implications
3. 学会等名 AGU 2021 (国際学会)
4. 発表年 2021年

〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
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7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関
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