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研究課題名（和文）Insights into hydrocarbons cycling in the subsurface from isotopologue analysis

研究課題名（英文）Insights into hydrocarbons cycling in the subsurface from isotopologue analysis

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交付決定額（研究期間全体）：（直接経費）　　23,020,000円

研究成果の概要（和文）：このプロジェクトの目的は、地下における炭化水素の循環を理解することである。地下での炭化水素の生産と消費に微生物が関与していることは知られているが、そのプロセスを定量的に評価することは必ずしも容易ではない。2つの泥火山で試料を採取した： 十日町と後生掛である。
水、ガス、泥を採取し、化学分析や同位体分析、培養実験を行った。同位体をベースとした方法を用いることで、(i)新たなメカニズムを解明し、(ii)地下における炭化水素の循環に関する定量的な推定を行うことができた。全体として、新しい同位体法とユニークな地質環境の組み合わせにより、そうでなければ不明瞭なままであったプロセスを解明することができた。

研究成果の学術的意義や社会的意義
Hydrocarbons are important in several scientific areas, including climate and energy resources. In this project, we have identified and quantify hydrocarbons cycling processes in the subsurface, which will be of importance to understand the global budget of hydrocarbons in the Earth's atmosphere.

研究成果の概要（英文）：The goal of this project was to use newly developed isotope analyses to understand hydrocarbons cycling in the subsurface. While it is known microorganisms can play a role in producing and consuming hydrocarbons in the subsurface, a quantitative estimation of these processes is not always accessible. We sampled at two mud volcanoes with different characteristics: Tokamachi which is a sedimentary system, and Goshogake which is a hydrbrid magmatic/sedimentary system.
We sampled water, gases and mud to run chemical and isotope analysis, as well as culture experiments. Using isotope-based methods we were able to (i) shed light on new mechanisms and (ii) give quantitative estimates regarding the hydrocarbons cycling in the subsurface. Overall, the combination of novel isotope methods and unique geological settings allowed clarifying processes that otherwise would have remained obscure.

研究分野：Organic Geochemistry

キーワード：Hydrocarbons　Stable isotopes　Isotopologue　Subsurface life

１．研究開始当初の背景

There is considerable uncertainty regarding biotic and abiotic processes occurring in the subsurface of the Earth. Shedding light on these processes can have impacts on several scientific areas including climate, carbon and other elements cycling and astrobiology. The goal of the project is to explore the transformations of hydrocarbons in the subsurface, notably in geological settings with high abundance of hydrocarbons, namely, petroleum and natural gas reservoirs. The importance of studying hydrocarbons cycle in the subsurface relies mainly on understanding the processes responsible for their formation and destruction. Hydrocarbons are crucial entities in the Earth-life system, particularly due to their role in climate as direct or indirect climate impactors. Despite their importance, little is known about the hydrocarbons cycling in the subsurface. This is mainly due to the numerous processes involved. In this project, in order to shed light on hydrocarbons cycling in the subsurface, we planned to use genomics, thermodynamics, chemical and new isotopic approaches to shed light on hydrocarbons cycling in the subsurface. We will take advantage of mud volcanoes, i.e., structures emitting gases and water from the deep subsurface to the surface, to explore the deep subsurface carbon cycling.

２．研究の目的

The goal of this project was to use newly developed isotope analyses to understand hydrocarbons cycling in the subsurface. While it is known microorganisms can play a role in producing and consuming hydrocarbons in the subsurface, a quantitative estimation of these processes is not always accessible. We proposed to use novel methods based on isotopologues (isotopically substituted molecules) to shed light on the origin and history of hydrocarbons in the subsurface. So far, the isotope ratio (e.g. $^{13}C/^{12}C$) of organic molecules were measured as a bulk value, namely, the average of ^{13}C atoms over ^{12}C atoms was obtained. In the recent years, we have developed tools that allow the precise and sensitive measurement of doubly-subsituted (‘clumped’), as well as position-specific isotope molecules. In this project, we specifically apply position-specific ^{13}C isotope composition of propane as well as doubly-substituted isotope species of methane, to get insights into the mechanisms and fluxes related to hydrocarbons transformations in the subsurface. For the first time, these two new tools will be used in the same samples, leading to an unprecedented amount of information regarding the origins and history of hydrocarbons in the subsurface.

３．研究の方法

We focus on two mud volcanoes: Tokamachi area (Niigata prefecture) and Goshogake area (Akita prefecture). The two mud volcanoes are easily accessible, although the composition of their fluids is quite different. In Tokamachi, the gases are arising from a subsurface natural gas reservoir, and the fluids are dominated by methane. On the other hand, in Goshogake, the gases are from a magmatic and/or sedimentary origin and are dominated by CO_2. We sampled water, gas and mud extruded in these mud volcanoes. We analyzed metagenomics of microorganisms living in the water, and isotope composition of gases.

The carbon and hydrogen isotope composition of hydrocarbons and CO_2 were determined by conventional isotope ratio mass spectrometry. The clumped (= multi-substituted) isotopes of methane were measured using a high-resolution mass spectrometer recently installed at Tokyo Tech (Zhang et al. 2021). The position-specific 13C isotope composition of propane samples was measured using the recently developed method from our group (Gilbert et al., 2016). Briefly, the propane molecule is broken into fragments (mostly CH4, C2H4 and C2H6) each of which originating from different position of the original propane. From the fragments isotope composition, the isotope composition of each position in the original propane can be determined (Gilbert et al. 2016).

４．研究成果

The bulk ^{13}C isotope composition of methane from the two fields show different histories: in Tokamachi, methane appears to be from thermogenic origin (breakdown of organic molecules), while in Goshogake, methane seems to be formed either from thermogenic processes or from abiotic ones. Since the amount of hydrocarbons in Goshogake mud volcanoes is quite low or even under the detection limit, we focused on Tokamachi mud volcanoes which show abundant hydrocarbons. The 13C-position-specific isotope composition of propane (i.e., the relative amount of $CH_3\mathbf{^{13}C}H_2CH_3$ vs $\mathbf{^{13}C}H_3CH_2CH_3$) show a strong ^{13}C-enrichment in the central position of propane. In a previous study, we have shown that this is due to bacterial degradation of propane in the subsurface (Gilbert et al. 2019). While our results from Tokamachi agree qualitatively with that of bacterial culture experiments, quantitatively, the fractionation factors (i.e., the relative rate of propane isotope species degradation) are not the same. This can be explained by the involvement of not only bacteria but also archaea degrading propane which show lower isotope fractionation factors compared with bacteria (Gilbert et al. in prep). By a simple mass-balance model, we can show that in Tokamachi, the rate of propane biodegradation in the subsaurface is 90% done by archaea and 10% by bacteria. This is emphasizing the advantage of using such tools to understand the biological cycling in the subsurface.

To go further, using mutiply-subsituted methane isotopologues in combination with position-specific isotope composition of propane, we were able to (i) quantify the amount of

methane produced from the degradation of other hydrocarbons in Tokamachi mud volcano in Niigata pref. (Zhang et al. in prep). This is of crucial importance because there currently is no estimate for this process; (ii) quantify the amount of archaea- vs bacteria biodegradation (Jajalla et al,. in prep), which is a first in the world and (iii) shed light on the nature of fluids emitted from Goshogake mud volcano (Akita pref.) and show that this mud volano was indeed a hydrob system between geothermal and sedimentary mud volano (Mazzini et al.; prep.).

Overall, our project led to new and refined information that would not have been accessible with conventional isotope method, which makes this project a great success.

５．主な発表論文等

〔雑誌論文〕　計3件（うち査読付論文　3件／うち国際共著　3件／うちオープンアクセス　2件）

１．著者名 Gilbert Alexis、Nakagawa Mayuko、Taguchi Koudai、Zhang Naizhong、Nishida Akifumi、Yoshida Naohiro	４．巻 10
２．論文標題 Hydrocarbon Cycling in the Tokamachi Mud Volcano (Japan): Insights from Isotopologue and Metataxonomic Analyses	５．発行年 2022年
３．雑誌名 Microorganisms	６．最初と最後の頁 1417～1417
掲載論文のDOI（デジタルオブジェクト識別子） 10.3390/microorganisms10071417	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

１．著者名 Bekaert D. V., Nakagawa,M. et al.	４．巻 118
２．論文標題 High 3He/4He in central Panama reveals a distal connection to the Galapagos plume	５．発行年 2021年
３．雑誌名 Proceedings of the National Academy of Sciences	６．最初と最後の頁 e2110997118
掲載論文のDOI（デジタルオブジェクト識別子） 10.1073/pnas.2110997118	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

１．著者名 Fullerton Katherine M., Nakagawa M. et al.	４．巻 14
２．論文標題 Effect of tectonic processes on biosphere-geosphere feedbacks across a convergent margin	５．発行年 2021年
３．雑誌名 Nature Geoscience	６．最初と最後の頁 301-306
掲載論文のDOI（デジタルオブジェクト識別子） 10.1038/s41561-021-00725-0	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

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１．発表者名 Alexis Gilbert
２．発表標題 Deciphering Hydrocarbons’ Sources and Sinks through Isotopologue measurements
３．学会等名 GRC Organic Geochemistry（招待講演）（国際学会）
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１．発表者名
Alexis Gilbert

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2022年

１．発表者名
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３．学会等名
GOLDSCHMIDT（国際学会）

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１．発表者名
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３．学会等名 GOLDSCHMIDT（招待講演）（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

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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