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Author(s)	Toki, Tomohiro; Gamo, Toshitaka; Tsunogai, Urumu
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Origins of hydrocarbons in the Sagara oil field, Central Japan

Tomohiro Toki ^{a, 1, *}, Toshitaka Gamo ^{a, 1}, Urumu Tsunogai ^a

^a *Division of Earth and Planetary Sciences, Graduate School of Science, Hokkaido University, N10 W8,*

Kita-ku, Sapporo 060-0810, Japan.

¹ *Present address: Marine Inorganic Chemistry Group, Department of Chemical Oceanography, Ocean*

Research Institute, The University of Tokyo, 1-15-1, Minamidai, Nakano-ku, Tokyo 164-8639, Japan.

* Corresponding author. Tel.: +81 (3) 5351-6453; Fax: +81 (3) 5351-6452.

E-mail address: toki@ori.u-tokyo.ac.jp (Tomohiro Toki).

ABSTRACT

We collected free gas and in situ fluid samples up to a depth of 200.6 m from the Sagara oil field, Central Japan (34°44'N, 138°15'E), during the Sagara Drilling Program (SDP) and measured the concentrations and stable carbon isotopic compositions of CH₄ and C₂H₆ in the samples. A combination of the CH₄/C₂H₆ ratios

with the carbon isotope ratios of methane indicates that the hydrocarbon gases are predominantly of thermogenic origin at all depths. The isotope signature of hydrocarbon gases of $\delta^{13}\text{C}_{\text{CH}_4} < \delta^{13}\text{C}_{\text{C}_2\text{H}_6}$ suggests that these gases in the Sagara oil field are not generated by polymerization, but by the decomposition of organic materials.

Keywords: Sagara oil field, SDP, hydrocarbons, free gas, in situ fluid, carbon isotope, thermogenic origin, microbial origin

INTRODUCTION

The Sagara oil field, in the southern part of Shizuoka prefecture, is the only oil field on the Pacific Ocean side of the Japan Islands (Fig. 1). The region is composed of conglomerate, sandstone, mudstone, and limestone, which are considered to be forearc basin sediments on the Nankai accretionary prism, presently developing in the southward of the Sagara field (e.g. Tsuchi 1961; Ujiie 1962; Ibaraki 1986; Shiba *et al.* 1996; Shiba *et al.* 1997). This oil field is unique from many geological, geophysical,

and geochemical perspectives (e.g. Uemura & Yamada 1988; Kato 1992; Morikawa & Imanaka 1993; Morikawa *et al.* 1998; Tanaka *et al.* 1999). First, Sagara oil is light rather than ordinary oil (Kato 1992). Second, the oil reservoir is found in a shallow layer; and third, heat flow data sets suggest there is no local heat source in the adjacent area (Tanaka *et al.* 1999). The production of Sagara oil has been explained by two different processes: (1) the formation at a greater depth (Uemura & Yamada 1988) and subsequent upward migration on the basis of the carbon isotope ratio of the Sagara oil (Kato 1992); (2) formation by the action of a petroleum-degrading bacterium grown anaerobically with CO_2 and H_2 (Morikawa & Imanaka 1993), which forms alkane/alkene with carbon numbers from 14 to 30 in addition to fatty acids inside the cell (Morikawa *et al.* 1998). If the latter process does occur, the chemical and stable carbon isotopic compositions of hydrocarbon gases from the oil field should provide evidence of microbial activity (e.g. Rice & Claypool 1981; Schoell 1983; Berner & Faber 1993; Sackett *et al.* 1968). To test these hypotheses, the Sagara Drilling Program (SDP) was conducted by Hirano *et al.* (this volume) at the Sagara oil field from January 31 to March 17, 2002 to obtain drilling cores, in situ fluids, and logging data.

Gaseous hydrocarbons and their carbon isotope composition ($\delta^{13}\text{C}$) have been used by many researchers to determine the origin of hydrocarbons and the hydrocarbons-forming processes in natural environments. The origin of hydrocarbons can be broadly divided into microbial and thermogenic. The microbial gas is formed by methane production from CO_2 and H_2 through CO_2 reduction by microbes and the thermogenic gas is due to the thermal degradation of organic matter. The hydrocarbons of microbial origin consist predominantly of methane. As much as 2% of the heavier hydrocarbons produced in this way, and the associated methane is depleted in the heavy isotope ^{13}C (with a $\delta^{13}\text{C}$ value less than -55‰) due to kinetic isotope fractionation by methanogens (Rice & Claypool 1981). In contrast, the hydrocarbon fraction of thermogenic gas consists of relatively heavier hydrocarbons, and thermogenic methane is enriched in ^{13}C (Schoell 1983). A $\delta^{13}\text{C}_{\text{CH}_4}$ value of less than -55‰ and a $\text{CH}_4/\text{C}_2\text{H}_6$ ratio of greater than 10^2 are diagnostic of gas of microbial origin, while a $\delta^{13}\text{C}_{\text{CH}_4}$ value of greater than -50‰ and a $\text{CH}_4/\text{C}_2\text{H}_6$ ratio of less than 10 indicate gas of thermogenic origin (Berner & Faber 1993).

The hydrocarbons-forming processes consist of (1) carbon-carbon bond

breakages of heavier hydrocarbons, or (2) the bond syntheses of lighter hydrocarbons.

The relative distribution of carbon isotope ratios of gaseous hydrocarbons has been used to classify these processes. During carbon-carbon bond breakages of heavier hydrocarbon molecules, a ^{12}C - ^{12}C bond is easier to break than a ^{13}C - ^{13}C bond, resulting in the orderly distribution of hydrocarbons in which methane is isotopically lightest among gaseous molecules, followed by ethane, propane, etc., due to the kinetic isotope effect (e.g. Sackett *et al.* 1968; Smith *et al.* 1971; Frank *et al.* 1974). In contrast, hydrocarbons synthesized from CO_2 and H_2 tend to show $\delta^{13}\text{C}$ values that decrease in order from CH_4 and C_2H_6 . This distribution of carbon isotope ratios among gaseous hydrocarbons is referred to as the isotopic reversal (Jenden *et al.* 1993).

In this study, we measured variations in the carbon isotope ratios of hydrocarbons and discuss their geochemical implications for the origin and formation processes of hydrocarbons in the Sagara oil field in central Japan.

MATERIALS AND METHODS

FREE GAS SAMPLING

The drilling achieved a total depth of 200.6 meters (Hirano *et al.* this volume). 23 free gas samples were collected every morning during the drilling campaign from the top of the borehole using an acrylic bag. The recovered gas samples were immediately transferred to 5-cm³ evacuated glass vials using a gas-tight syringe for measurement of the content and the isotope ratio of CH₄ (methane) and C₂H₆ (ethane).

IN SITU FLUID SAMPLING

In situ fluid samples were collected on 13 February and 19 to 21 March 2002 within the borehole using the following in situ pressure sampler from desired intervals sectioned by packers: 58 m, 90 m, 135 m, and 162 m (oil sign, respectively), and 196 m (bottom of the borehole).

The sampler consists of a valve connected with a reservoir 400 cm³ in volume. The valve of the sampler can be controlled by He pressure from the ground so that the

sampler can collect fluid samples without evaporation, degassing, and contamination during the ascent of the sampler. Gas and liquid phases were immediately isolated using the following procedures: first, the outlet of the sampler was connected to the Tygon tube, and the gas phase was transferred to a 5-cm³ evacuated glass vial. After the gas phase was obtained, the liquid phase was taken into a 100-cm³ glass vial (Ar-purged). The liquid samples were poisoned with HgCl₂ as a preservative, and the glass vial was then capped with a gray butyl rubber septum. All samples were stored in the dark and at room temperature until analysis.

ANALYTICAL METHOD

The concentrations and stable carbon isotopic compositions of CH₄ and C₂H₆ were measured using a continuous-flow gas chromatography isotope-ratio mass spectrometry (GC/IRMS) system (Tsunogai *et al.* 2002). The gas samples were injected into the analytical system using a gas-tight syringe through a silicon rubber septum. The liquid samples were introduced to a He-sparging bottle, and the stripped hydrocarbon

gases were captured on a Porapak-Q trap at a liquid N₂ temperature prior to introduction into the system. The extracted gases were then carried into the system by He carrier gas at a flow rate of 100 ml/min.

The system consists of three functional units: (1) pre-concentration of CH₄ and C₂H₆ gases; (2) subsequent chromatographic separation of the CH₄ and C₂H₆ from the remaining non condensed gases in a GC oven; and (3) quantification of the ¹³C/¹²C ratio using the isotope-ratio mass spectrometer.

The pre-concentration trap is immersed in liquid N₂ to collect the hydrocarbon gases. The pre-concentrated hydrocarbon gases are then cryo-focused in the front of the capillary column in liquid O₂. The GC oven is mounted with a PoraPLOT-Q analytical capillary column (Chrompack) for final separation under the column oven temperatures ranging +30 to +120°C. The separated CH₄ and C₂H₆ are converted to CO₂ by combustion at a temperature of 960°C (Thermo Finnigan Combustion-II). The isotope-ratio mass spectrometer (Thermo Finnigan MAT 252) with a commercial open split interface (Thermo Finnigan Gas Bench) is employed to couple sample and reference CO₂ flows via two open splits.

The hydrocarbon content in the sample is determined by comparing the $^{44}\text{CO}_2$ output with that of a working standard gas, which is made from a NIST RM 8560 (IAEA NGS2) standard. The precision of the concentration determination was better than 6.5%.

The isotope ratio of the hydrocarbons is analyzed with the isotope-ratio mass spectrometer in conjunction with ISODAT software. The carbon isotope ratios are reported relative to the PeeDee Belemnite (PDB) and are reported using the per mil notation, where:

$$\delta^{13}\text{C} = \{((^{13}\text{C}/^{12}\text{C})_{\text{sample}}/(^{13}\text{C}/^{12}\text{C})_{\text{PDB}}) - 1\} \times 1,000.$$

The precision of the isotopic analysis for CH_4 and C_2H_6 was estimated to be 0.3%.

RESULTS

The concentrations and $\delta^{13}\text{C}$ values of CH_4 and C_2H_6 are shown in Tables 1, 2,

and 3. The methane and ethane concentration in the free gas samples showed significant variation with depth (Table 1), particularly at 123.6 meters, where the methane and ethane concentration decreases dramatically down to 74 ppm and 7.6 ppm, respectively, as shown in Table 1. At this depth, the drilling pipe was broken by accident during the drilling expedition, which may have caused this decrease in hydrocarbon concentrations. The concentration of methane and ethane in the liquid samples also showed significant variations (Table 2). This variation suggests that the hydrocarbon gases are present under the cap rock layers, and the gases could not permeate the cap rocks themselves due to lithological and/or physicochemical factors.

The $\text{CH}_4/\text{C}_2\text{H}_6$ ratios, however, are relatively constant with depth: (Tables 1, 2, and 3) (9.8 ± 2.7 for the free gas, 9.4 ± 4.5 in the gas phase of the in-situ fluid sample, and 7.5 ± 1.8 in the liquid phase of the in-situ fluid sample where the error is given at a 1σ level). This suggests that the hydrocarbons are chemically homogenous.

The $\delta^{13}\text{C}_{\text{CH}_4}$ values are relatively constant with depth, as shown in Tables 1, 2, and 3 ($-40.6 \pm 2.4\text{‰}$ for the free gas, $-39.6 \pm 1.0\text{‰}$ in the gas phase of the in-situ fluid sample, and $-37.8 \pm 1.6\text{‰}$ in the liquid phase of the in-situ fluid sample). The $\delta^{13}\text{C}_{\text{C}_2\text{H}_6}$

values show no significant variation with depth, as shown in Tables 1, 2, and 3 ($-28.5 \pm 1.2\text{‰}$ for the free gas, $-28.5 \pm 0.4\text{‰}$ in the gas phase of the in-situ fluid sample, and $-27.8 \pm 0.6\text{‰}$ in the liquid phase of the in-situ fluid sample). The isotopic distribution suggests that isotopically homogenous characteristics of the hydrocarbons exist in the Sagara oil field.

DISCUSSION

A combination of the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio with the carbon isotope ratio of methane can be used to classify the gases into various source types, microbial or thermogenic. Carbon isotope ratios of CH_4 compared to the $\text{CH}_4/\text{C}_2\text{H}_6$ ratios of the core samples are shown in Fig. 2, together with data in the Nankai Trough (Berner & Faber 1993). The data in the Nankai Trough can be explained by the mixing of methane of microbial origin and that of thermogenic origin, based on the cross-correlation of molecular composition and methane carbon isotope ratios (Berner & Faber 1993). All the gases from the Sagara oil field indicate a clear thermogenic signature: $\delta^{13}\text{C}(\text{CH}_4)$ and a

$\text{CH}_4/\text{C}_2\text{H}_6$ ratio of -36 and -46‰ and 4 to 16 , respectively (Tables 1, 2, and 3). This result suggests that microbial activity is negligible in the Sagara oil field.

Hydrocarbons formation by polymerization of methane precursors would show a pattern of isotopic reversal, with $\delta^{13}\text{C}_{\text{CH}_4} > \delta^{13}\text{C}_{\text{C}_2\text{H}_6}$ (Des Marais *et al.* 1981; Sherwood Lollar *et al.* 2002; Du *et al.* 2003). Differences between $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{C}_2\text{H}_6}$ in the samples are depicted in Tables 1, 2, and 3. The isotope compositions of methane are significantly lighter than those of ethane. This observed isotope pattern for hydrocarbon gases ($\delta^{13}\text{C}_{\text{CH}_4} < \delta^{13}\text{C}_{\text{C}_2\text{H}_6}$) can be explained by a kinetic isotope fractionation where the ^{12}C - ^{12}C bonds of source organic matter are preferentially cracked, leading to the formation of ^{13}C -depleted gas hydrocarbons, with methane being the isotopically lightest compound (Andresen *et al.* 1995; Behar *et al.* 1997; Berner & Faber 1997; Tang *et al.*, 2000). The isotopic distribution obtained in this study suggests that the hydrocarbon gases in the Sagara oil field are not generated by polymerization, but by the decomposition of organic matter. The thermocatalytic decarboxylation ($\text{R-CO}_2\text{H} \rightarrow \text{R-H} + \text{CO}_2$) of organic acid functional groups occurs in diverse environments with high temperatures ($> 50^\circ\text{C}$), such as oil fields, geothermal fields,

sediment-rich hydrothermal systems (e.g. Welhan & Lupton 1987), and accretionary prisms at depths of 1,000 meters below the seafloor (Gamo *et al.* 1993; Berner & Faber 1993; Fig. 2).

Our molecular and isotopic analysis of hydrocarbons in the free gas and in situ fluid from the Sagara oil field suggest that the formation process of the hydrocarbons appears to be organic matter decomposition. Furthermore, the isotopic compositions of CH_4 and C_2H_6 are consistently depleted with regard to ^{13}C compared to the composition of the Sagara oil itself (-24.5‰PDB ; Kato 1992). Thus, the thermal decomposition of organic matter, including Sagara oil, to produce methane and ethane appears to be the most important source for these hydrocarbons.

CONCLUSIONS

We measured the concentration ratios of $\text{CH}_4/\text{C}_2\text{H}_6$ and the carbon isotope ratios for gas samples from the Sagara oil field. The results show that the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio is 4 to 16 and that the $\delta^{13}\text{C}(\text{CH}_4)$ is between -36 and -46‰ , suggesting that the

hydrocarbons are of thermogenic origin. Based on the isotope signature of hydrocarbon gases of $\delta^{13}\text{C}_{\text{CH}_4} < \delta^{13}\text{C}_{\text{C}_2\text{H}_6}$, we conclude that the formation process for hydrocarbon gases involves a thermocatalytic breakdown of organic carbon compounds and is not associated with hydrocarbons synthesis.

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Figure legends

Fig. 1 Location map of the Sagara oil field

Fig. 2 Plot of $\delta^{13}\text{C}_{\text{CH}_4}$ vs. $\text{CH}_4/\text{C}_2\text{H}_6$ ratio of free gas samples (solid diamond), gas phase in fluid samples (open diamond), and liquid phase in fluid samples (open circle), together with those of gases from Nankai Trough (cross; Berner and Faber, 1993).

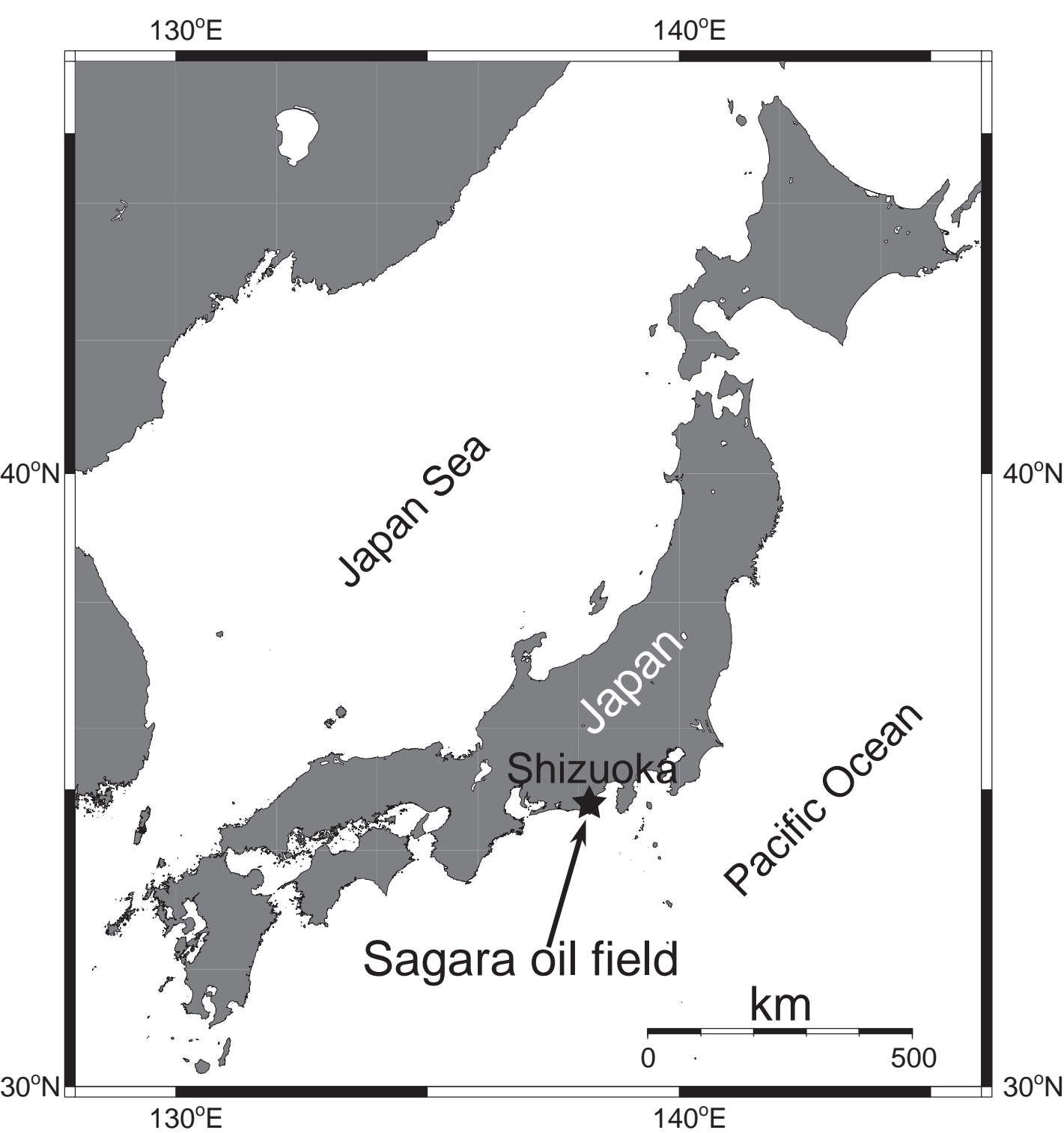


Fig. 1

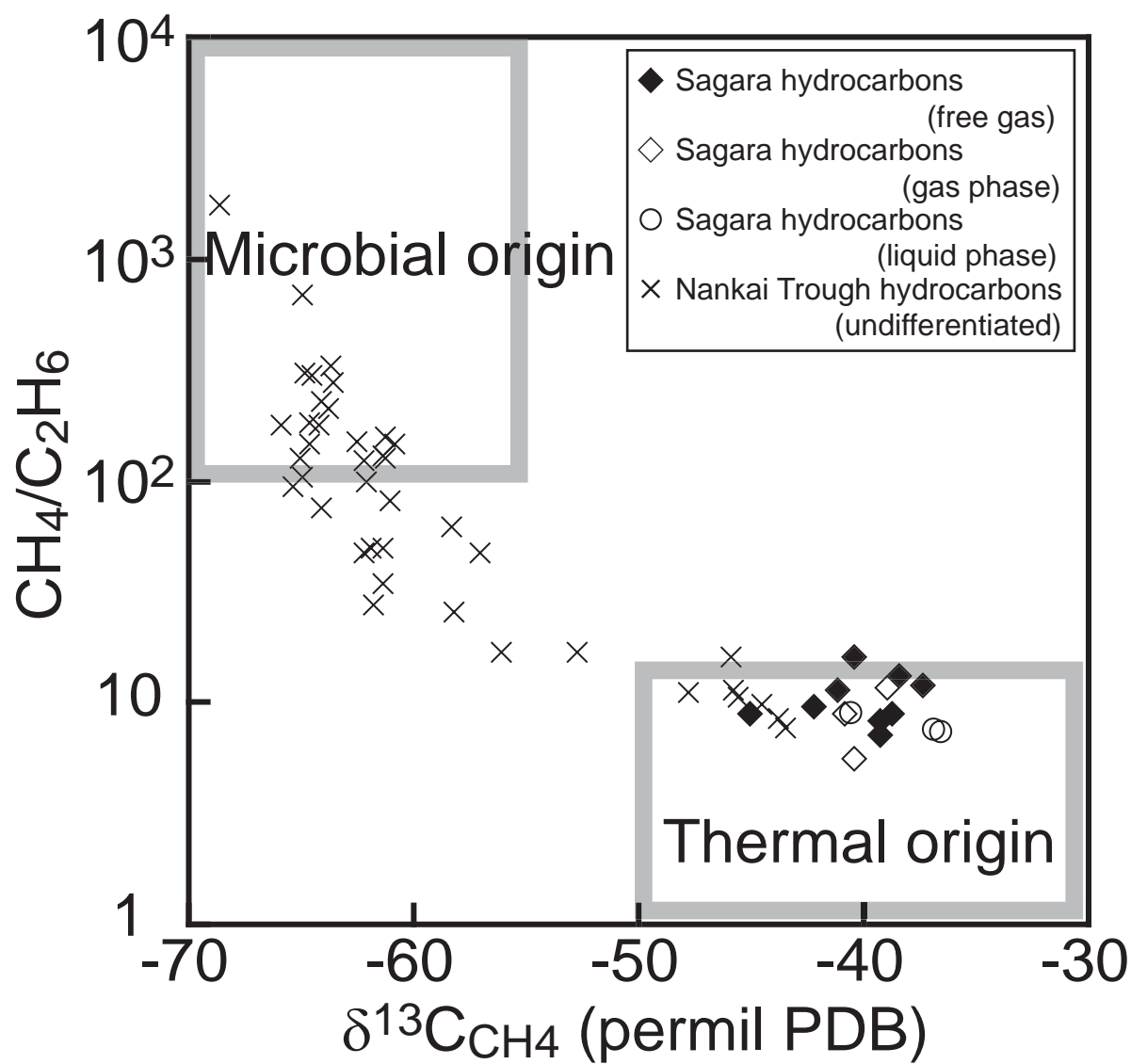


Fig. 2

Table 1 Content and isotopic composition of methane and ethane, respectively, and content ratio of methane to ethane in free gas samples

Depth m	CH ₄ %	$\delta^{13}\text{C}(\text{CH}_4)$ permil PDB	C ₂ H ₆ %	$\delta^{13}\text{C}(\text{C}_2\text{H}_6)$ permil PDB	CH ₄ / C ₂ H ₆
60.3	12	-44.4	0.80	-30.1	14
67	0.86	-42.1	0.075	-29.6	11
70	3.2	-39.1	0.33	-28.1	9.6
74.8	35	-41.2	2.7	-29.0	13
87.3	13	-45.0	1.8	-29.7	7.2
92.2	50	-42.2	3.1	-29.2	16
99.8	14	-38.1	1.2	-28.0	12
107.1	13	-38.5	1.5	-27.9	9.0
101.3	21	-39.2	2.3	-28.4	9.0
110.1	18	-39.0	2.2	-27.8	8.3
119.85	1.2	-38.1	0.14	-27.4	8.9
123.6	0.0074	-41.5	0.00076	-26.2	9.8
126.65	0.029	-39.3	0.0038	-27.9	7.8
136.65	19	-38.3	4.0	-28.8	4.9
141.1	2.3	-40.4	0.42	-28.4	5.5
149.35	4.7	-43.3	0.46	-26.2	10
156.45	21	-37.4	2.6	-27.3	8.1
164	1.7	-43.7	0.21	-30.3	8.0
171.75	23	-38.7	3.0	-28.2	7.8
185	4.7	-40.6	0.40	-28.5	12
191.6	0.61	-45.1	0.067	-31.0	9.1
197.7	6.8	-39.5	0.61	-28.5	11
200.6	6.2	-39.2	0.52	-28.7	12
Average		-40.6		-28.5	9.8
σ		2.4		1.2	2.7

Table 2 Content and isotopic composition of methane and ethane, respectively, and content ratio of methane to ethane in gas phase of fluid samples

Depth m	CH ₄ %	$\delta^{13}\text{C}(\text{CH}_4)$ permil PDB	C ₂ H ₆ %	$\delta^{13}\text{C}(\text{C}_2\text{H}_6)$ permil PDB	CH ₄ / C ₂ H ₆
58.25	32	-40.9	3.5	-28.9	9.0
90	5.6	-39.2	0.49	-28.2	12
135	16	-38.9	2.9	-28.0	5.5
162	1.0	-38.4	0.19	-28.2	5.1
195.5	23	-40.5	1.5	-29.0	16
Average		-39.6		-28.5	9.4
σ		1.0		0.4	4.5

Table 3 Concentration and isotopic composition of methane and ethane, respectively, and concentration ratio of methane to ethane in liquid phase of fluid samples

Depth m	CH ₄ mmol/kg	$\delta^{13}\text{C}(\text{CH}_4)$ permil PDB	C ₂ H ₆ mmol/kg	$\delta^{13}\text{C}(\text{C}_2\text{H}_6)$ permil PDB	CH ₄ / C ₂ H ₆
58.25	3.4	-40.5	0.38	-28.2	9.0
90	2.5	-37.1	0.33	-27.3	7.5
135	4.8	-36.9	0.65	-27.7	7.4
162	0.27	-38.0	0.058	-28.7	4.7
195.5	3.7	-36.5	0.040	-27.3	9.1
Average		-37.8		-27.8	7.5
σ		1.6		0.6	1.8