Hydrothermal fluid geochemistry at the Iheya North field in the mid-Okinawa Trough: Implication for origin of methane in subseafloor fluid circulation systems

SHINSUKE KAWAGUCCI,1,2*, HITOSHI CHIBA,3 JUN-ICHIRO ISHIBASHI,4 TOSHIRO YAMANAKA,3 TOMOHIRO TOKI,5 YASUYUKI MURAMATSU,5 YUSUKE USHIO,2,7 AKIKO MAKABE,8 KAZUHIRO INOUE,8 NAOHIRO YOSHIDA,8 SATOSHI NAGAGAWA,9,10 TAKURO NUNOURA,9 KEN TAKAI,2,9 YUJI SANO,1† TAKU NARITA,1 GENTA TERANISHI,1 HIJIME OBATA1† and TOSHITAKA GAMO1†

1Ocean Research Institute (ORI), The University of Tokyo, 1-15-1, Minamidai, Nakano-ku, Tokyo 164-8639, Japan
2Precambrian Ecosystem Laboratory (PEL), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka 237-0061, Japan
3Faculty of Science, Okayama University, 3-1-1 Tsushima-naka, Kita, Okayama, Okayama 700-8530, Japan
4Faculty of Science, Okayama University, 3-1-1 Tsushima-naka, Kita, Okayama, Okayama 700-8530, Japan
5Faculty of Science, Kyushu University, 6-10-1, Hakozaki, Higashi, Fukuoka 812-8581, Japan
6Faculty of Science, University of the Ryukyus, 1 Senbaru, Nishihara, Okinawa 903-0215, Japan
7Faculty of Science, Gakushuin University, Nejiro 1-5-1, Toshima-ku, Tokyo 171-8588, Japan
8Department of Environmental Science and Technology, Tokyo Institute of Technology, G1-25, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan
9Subsurface Geobiology Advanced Research (SUGAR) Project, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka 237-0061, Japan
10Faculty of Fisheries Sciences, Hokkaido University, 3-1-1 Minato-cho, Hakodate 041-8611, Japan

(Received March 3, 2010; Accepted August 16, 2010)

Geochemical characteristics of hydrothermal fluids in the Iheya North hydrothermal field, mid-Okinawa Trough, was investigated. Twelve-years observation reveals temporal variation of vent fluid chemistry potentially controlled by temporally varying pattern of the phase-separation and -segregation, while the constant Element/Cl ratios among the periods and chimneys indicate the stable chemical composition of the source hydrothermal fluid prior to undergoing phase-separation. The high K contents in the estimated source fluid are typical in the arc-backarc hydrothermal systems due to the hydrothermal reaction with the K-enriched felsic rocks. The high I, B and NH4 contents and alkalinity are derived from decomposition of the sedimentary organic matters.

Compositional and isotopic properties of gas species, CH4, H2, CO2, and C2H6 strongly suggest a dominance of biogenic CH4 associated with the sedimentary organic matter. Based on the carbon mass balance calculation and the multidisciplinary investigations of the Iheya North hydrothermal system since the discovery, we hypothesized that the microbial methanogenesis occurs not only within the Central Valley where hydrothermal vents exist, but also in the spatially abundant and widespread basin-filling sediments surrounding the Iheya North Knoll, and that the microbially produced CH4 is recharged together with the source fluid into the deep hydrothermal reaction zone. This “Microbial Methanogenesis at Recharge area in hydrothermal circulation” (MMR) model would be an implication for the generation and incorporation of hydrothermal fluid CH4 in the deep-sea hydrothermal systems but also for those of cold seep CH4 and for the presently uncertain hydrothermal fluid paths in the subseafloor environments. In the near future, theIODP drilling will be conducted in the Iheya North hydrothermal system, and give an excellent opportunity to testify our MMR model.

Keywords: origin of methane, sediment-associated hydrothermal field, Iheya North hydrothermal field, Okinawa Trough, hydrothermal fluid geochemistry

INTRODUCTION

Hydrothermal fluid chemistry in the Okinawa Trough hydrothermal systems has been often characterized by higher concentrations of CO2, CH4, NH4 I and K and higher alkalinity than those in typical sediments-free Mid
Ocean Ridge (MOR) hydrothermal fluids (Sakai et al., 1990a, b; Gamo et al., 1991; Chiba et al., 1993; Nakano et al., 2001; Kishida et al., 2004; Konno et al., 2006; Inagaki et al., 2006; Hongo et al., 2007; Suzuki et al., 2008). The notable hydrothermal fluid chemistry has been linked with the tectonic settings and the existing thick terrigenous sediments of the Okinawa Trough. Philippine plate subduction along the Ryukyu trench–arc system provides K-enriched and volatiles-rich dacitic–rhyolitic magma supply in the Okinawa Trough (e.g., Sakai et al., 1990a; Gamo et al., 2006). Organics-rich terrigenous sediments burying the Okinawa Trough (Narita et al., 1990) not only supply the sedimentary chemical inputs (NH₄, I, etc.) (Gamo et al., 1991; You et al., 1994) but also promote the widespread occurrence of functionally active microbial communities and the microbiological impacts on the hydrothermal fluid circulation (Inagaki et al., 2006; Nunoura et al., 2010). In addition to the chemical aspects potentially affecting the hydrothermal fluid chemistry, relatively shallow water depths of many Okinawa Trough hydrothermal systems serve as a physical factor to induce frequent boiling (subcritical phase-separation) and subsequent phase-segregation, because the boiling temperature of seawater steeply decreases with decreasing pressure at around 100 bar (Bischoff and Rosenbauer, 1988). The phase-separation and -segregation sometimes results in quite different chemical compositions of the hydrothermal fluids among different vent sites in the same hydrothermal field although they are derived from the common source fluid (Gamo, 1995).

As one of the most fundamental questions to the Okinawa Trough hydrothermal fluids, it has been discussed how and where the abundant CH₄ is generated and supplied into the hydrothermal fluids (Chiba et al., 1993; Ishibashi et al., 1995; Konno et al., 2006). At hydrothermal systems, there are a variety of possible contributors to the CH₄, including chemical synthesis from reduction of CO₂ during hydrothermal circulation (e.g., McCollom and Seewald, 2007), thermal decomposition of organic matter (e.g., Giggenbach, 1997), and microbial hydrogenotrophic and fermentative methanogenesis (e.g., Valentine et al., 2004b). In the early study of the Okinawa Trough hydrothermal fluids in the JADE field of the Izena Cauldron, it was suggested that the abundant CH₄ should be produced by thermal decomposition of sedimentary organic matter during high temperatures of fluid circulation (Ishibashi et al., 1995). However, recent investigations have demonstrated the compositional and isotopic
variation of hydrothermal fluid CH$_4$ among the Okinawa Trough hydrothermal fields (e.g., concentrations and $\delta^{13}$C values of CH$_4$ are respectively 7.6 mM and $-41$ to $-36\%e$ in the JADE field and 1.2 to 9.3 mM and $-27$ to $-24\%e$ in the Yonaguni Knoll IV filed) (Ishibashi et al., 1995; Konno et al., 2006). These results, especially the $\delta^{13}$C values, suggest that the generation and incorporation of CH$_4$ in the hydrothermal fluids could differ among each hydrothermal field in the Okinawa Trough. In addition to the conventional thermogenic origin of CH$_4$, microbial methanogenesis is now recognized to be operative in the elevated temperature range of the hydrothermally active subseafloor environments ($\leq 122^\circ$C) (Parkes et al., 2007; Takai et al., 2008a). Indeed, it has been pointed out that the microbial methanogenesis serves as a source of abundant CH$_4$ in the hydrothermal fluids of other sediments-covered hydrothermal systems (Pearson et al., 2005; Cruse and Seewald, 2006).

In this study, the compositional and isotopic characteristics of hydrothermal fluids in the Iheya North hydrothermal field, mid-Okinawa Trough, was investigated. Twelve-years observation revealed temporal variation of vent fluid chemistry potentially controlled by temporally varying pattern of the phase-separation and -segregation. In 2007, the detail gas chemistry was also characterized to clarify the generation and incorporation processes of hydrothermal fluid CH$_4$ in the Iheya North field. Based on the results in this study and other geophysical and microbiological investigations of the Iheya North hydrothermal system, we hypothesize a model for generation and incorporation of abundant CH$_4$ in the Okinawa Trough hydrothermal systems including the Iheya North field.

**Observation**

**Geography and geology**

A hydrothermal activity was discovered in 1995 by a deep-sea camera survey (Momma et al., 1996) in the Iheya North Knoll (27°47′50″N, 126°53′80″E), which was located about 150 km NNW of the Okinawa Island (Fig. 1). Since the discovery, more than 40 dives by DSVs and ROVs have been conducted, and detailed location of the hydrothermal activities and events at the seafloor has been well characterized. In the middle of the Iheya North Knoll, there is a valley, called as the “Central Valley” (Fig. 2a), representing the subseafloor structure with the relatively strong subbottom seismic reflectors (up to 300 m below seafloor surface). Based on the geophysical investigation and seafloor observation, it is now interpreted that the Central Valley is buried with abundant volcanic flow deposits of the pumicious rocks interbedded with layered minor sediments. However, the seafloor surface around the Iheya North hydrothermal field and the Central Valley are covered with the pelagic sediments. It is also notable that several faults with a north-south (N-S) trend are observed around the hydrothermal vent sites. Indeed, major hydrothermal vent chimneys (mounds) stand along one of the N-S faults (Fig. 2b).

The Iheya North hydrothermal field is located in the western cove of the Central Valley of the Iheya North Knoll (Fig. 2a). Totally, nine hydrothermal vent sites accompanying the proximal mounds named as North Edge Chimney (NEC), Event 18 (E18), North Big Chimney (NBC), Central Big Chimney (CBC), High Radioactivity Vent (HRV), Ese South Big Chimney (ESBC),...
Table 1. Measured maximum temperatures and estimated endmember compositions from Iheya North Knoll

| Venting site | Sampling year | Temp. °C | pH | Cl mmol/kg | Na mmol/kg | K mmol/kg | Li mmol/kg | Ca mmol/kg | Sr mmol/kg | Mn mmol/kg | Fe µmol/kg | B µmol/kg | NH₄ µmol/kg | SO₄ µmol/kg | Alk µmol/kg | SiO₂ µmol/kg | Al µmol/kg | I µmol/kg | Br µmol/kg |
|--------------|---------------|---------|----|------------|------------|-----------|------------|-----------|----------|-----------|------------|-----------|------------|------------|-------------|-------------|-------------|-----------|----------|------------|
| NBC (2007)   | 2007          | 309     | 5.0| 557       | 407        | 72.4      | 21.9       | 73        | 658      | <0.16     | 1710       | 0         | 12.3       | 11.0       | 44.8        | 952         |
| NBC (2002)   | 2002          | 304     | 4.8| 544       | 432        | 72.3      | 1.225      | 19.2      | 697      | 669       | 1.65       | 21.30     | -6         | 1.73       | 16.47       |
| NBC (2000)   | 2000          | 168     | 4.5| 308       | 63.8       | 1.300     | 15.7       | 67.0      | 602      | 1.65      | 21.30     | -6         | 1.73       | 10.47      |
| NBC (1999)   | 1999          | 311     | 4.6| 474       | 367        | 66.6      | 1.270      | 19.2      | 697      | 669       | 1.65       | 20.20     | -1         | 1.59       | 8.86        |
| NBC (1997)   | 1997          | 311     | 5.1| 405       | 73.0       | 1.222     | 18.1       | 659      | 631      | 1.78      | 20.00     | 3         | 0.63       |            |             |
| ESBIC (2007) | 2007          | 388     | 5.0| 576       | 499        | 73.0      | 23         | 81        | 662      | <0.13     | 2         | 12.16     | 11.5       | 47.5       | 10.34       |
| SBC (2002)   | 2002          | 153     | 5.4| 191       | 185        | 26.9      | 0.355      | 4.6       | 9.4      | 0.67      | 5.94       |            |            |            |             |
| SBC (2000)   | 2000          | 180     | 5.4| 24        | 8          | 11.8      | 0.206      | 2.0       | 13.3     | 1.15      | 3.50       | -7         | 3.30       | 3.05       |             |
| SBC (1999)   | 1999          | 205     | 5.0| 590       | 288        | 75.5      | 0.989      | 12.5      | 53.7     | 397       | 1.55       | 22.00     | -4         | 1.59       | 7.87        |
| CBC (2002)   | 2002          | 86      | 5.3| 449       | 363        | 66.8      | 1.132      | 17        | 60.5     | 532       | 1.95       |            |            |            | 11.57       |
| HRV (2002)   | 2002          | 189     | 5.0| 565       | 466        | 79.2      | 1.362      | 20.5      | 75       | 678       | 2.27       |            |            |            | 11.56       |
| HRV (1999)   | 1999          | 117     | 4.1| 410       | 297        | 75.0      | 1.179      | 17.4      | 57.6     | 578       | 1.60       | 21.20     | -3         | 0.22       | 11.06       |
| HRV (1996)   | 1996          | 238     | 4.2| 424       | 331        | 57.6      | 1.121      | 16.1      | 57.2     | 567       | 1.67       | 25.20     | -2         | 0.94       | 9.29        |
| 70°C (1997)  | 1997          | 70      | 3.3| 288       | 56.2       | 9.000     | 11.9       | 53.4     | 445      | 1.75     | 18.50     | 15         | 2.78       |            |             |
| HRV (1993)   | 1993          | 180     | 5.0| 238       | 174        | 37.7      | 0.082      | 12.3      | 41.4     | 456       | 1.52       | 29.70     | -3         | 1.67       | 6.90        |
| NEC (2002)   | 2002          | 177     | 5.1| 521       | 469        | 71.8      | 1.28       | 18.7     | 69.8     | 633       | 1.87       |            |            |            | 9.83        |
| NEC (2012)   | 2012          | 177     | 5.1| 16        | 40         | 6.9       | 0.109      | -0.4      | 0.4      | 160       | 0.44       |            |            |            | 4.45        |

(1) Suzuki et al., 2008 (Lion vent).
(2) Sakai et al., 1990a, b.
(3) Kishida et al., 2004.
Sampling and sample treatment

The first sampling of the hydrothermal fluid was carried out by DSV “Shinkai 2000” in 1996. Then, the fluid samples have been collected from various hydrothermal chimney sites by Shinkai 2000 and ROV “Hyper Dolphin” (Table 1). The fluid sampling was conducted by using ORI-pump sampler (Sakai et al., 1990b), plastic bags with peristaltic pump, and a gas-tight sampler WHATS II (Saegusa et al., 2006). The temperature of each vent fluid was monitored during the sampling using a Pt resistant temperature probe equipped at the intake of sampling systems. The fluid samples were filtered by 0.2 or 0.45 µm pore-size filters in order to remove particles prior to subsampling for each of the chemical analyses. The samples for onshore cation analyses were acidified by nitric or hydrochloric acids down to at pH < 2.

In 2007, we obtained the fluid samples for gas analyses by WHATS II. After the recovery of WHATS II onboard, the fluids in stainless-steel gas-tight bottles (150 mL) were immediately opened to a vacuum line (ca. 1500 mL) to recover the gas components. Reagent-grade solid sulfamic acid (HOSO₂NH₂) was added to the fluid in the vacuum line to extract CO₂. After degassing for 10 min, the gas phase was collected into 50 mL stainless bottles for the subsequent gas analyses. At the same time, all of the degassed liquid phase was filtered (using a 0.45 µm pore-size filter) and collected for the magnesium measurements. In addition to the gas chemical analyses of natural fluid samples, an onboard incubation experiment was carried out to assess the microbial H₂ consumption in the diffusing hydrothermal fluid in terms of the compositional and isotopic composition of H₂. The diffusing fluid was taken from a dense *Paralvinella* colony at NBC into three bottles by WHATS II, then the bottles were incubated onboard under room temperature (25°C) (Table 2).

**Analyses**

The major cation concentrations (Mg, Na, K, Li, Ca, Sr, Fe, and Mn) in the fluid samples were measured by inductively coupled plasma (ICP) emission spectrophotometry. The analytical precision was estimated to be within 5% for each component. The alkalinity and pH and the concentrations of SiO₂ and NH₄ were analyzed onboard. The pH and alkalinity were determined using a pH meter by potentiometric titration with 0.1 M HCl. The SiO₂ and NH₄ concentrations were measured by spectrophotometries of silicofluoride complex and phenol blue, respectively. The analytical precisions were estimated to be within 0.5% for pH, 5% for alkalinity, and 7% for SiO₂ and NH₄. Parts of the results of these analyses have been reported elsewhere (Nakagawa et al., 2005). Dissolved B concentration was determined using a colorimetric technique involving a curcumin complex with a precision of 3%. Dissolved I and Br concentrations were determined by ICP-MS with standard deviations less than 5% (Muramatsu et al., 2007). The Al concentration was determined with the fluorometric method using Lumogallion (Obata et al., 2000) after diluting the samples with seawater of open ocean.

The concentrations of CO₂, CH₄, H₂S, and C₂H₄ were determined by GC-TCD with 10% errors. The H₂ concentration and its stable isotope ratio were determined by using a continuous-flow isotope ratio mass spectrometer (CF-IRMS: Kawagucci et al., 2010a). Carbon and hydrogen isotope ratios of CH₄ were also determined by a CF-IRMS (Popp et al., 1995; Umezawa et al., 2009) while Dual-Inlet IRMS technique was used for carbon isotope analysis of CO₂. Stable hydrogen and carbon isotope ratios are represented by the generally-used linear δ-notation in per-mil scales against the standards of VSMOW and PDB, respectively. The δ³⁴S in this study was measured by a conventional noble gas mass spectrometer (Sano and Wakita, 1988; Sano et al., 2008).
RESULTS AND DISCUSSION

Major geochemistry

The major chemical composition of vent fluid demonstrated linear correlations against Mg concentration for each of the chimney sites, while the correlation pattern was different among the sampling years. Estimated endmember compositions using Mg-Element diagrams, represented by y-intercepts of least squares fits forcing lines to go through the ambient seawater composition (Von Damm et al., 1985), were listed in Table 1. The major chemical composition differed among the vents and among the years (Fig. 3). These results indicated that the vent fluid of each chimney site would be generated by two-endmember mixing between the vent fluid and the infiltrated seawater, but the chemical composition of endmember hydrothermal fluid and the mixing pattern would change temporally. The endmember Cl concentrations were ranged between 16-585 mmol/kg (cf., [Cl]\textsubscript{seawater} = 560 mmol/kg) (Table 1), representing the significant phase-separation-controlled variation of hydrothermal fluid chemistry (Nakagawa et al., 2005).

Many of the vent fluids in the Iheya North field were Cl-depleted (Fig. 3a). The NBC vent fluids had relatively stable Cl contents and were close to that of the ambient seawater (Fig. 3a), while the Cl contents in the vent fluids became lower at chimney sites with increasing distance from the NBC site (Fig. 2b). This distribution pattern of the Cl-depleted hydrothermal fluids in a field was also observed in the Yonaguni Knoll IV field (Suzuki et al., 2005). Hence, it is hypothesized that the subseafloor boiling (subcritical phase-separation) of hydrothermal fluid would induce the different mobility of different phases, and the vapor phase may further migrate to the exterior chimney sites. This may explain that the more Cl-depleted hydrothermal fluids are found at the exterior chimney sites and the Cl-enriched or -moderate fluids are distributed around the hydrothermal activity center, the NBC site. The more Cl-enriched (brine) fluids may reside in hydrothermal reaction zone (Von Damm et al., 2005).

Other major components (K, Na, Ca, and so on) of the endmember fluids were correlated well with the Cl concentration (Fig. 4, Table 1), also supporting the boiling-controlled hydrothermal fluid chemistry. In addition, the almost constant Element/Cl ratio (Table 1) provided an estimated chemical composition of the source hydrothermal fluid that was the primary hydrothermal fluid prior to undergoing phase-separation and -segregation (Butterfield et al., 1994). The estimated endmember source fluid in the Iheya North field had high K, Li, B, I and NH\textsubscript{3} contents and alkalinity relative to those in the typical MOR fields. In particular, the high K contents were an outstanding feature of the hydrothermal fluids in the Okinawa Trough (Kishida et al., 2004; Sakai et al., 1990b;
It has been pointed out that the high K contents in the hydrothermal fluids are typical in the arc-backarc hydrothermal systems due to the hydrothermal reaction with the K-enriched felsic rocks (Sakai et al., 1990b; Suzuki et al., 2008) although the sedimentary organic matters may serve as the other K source in the fluids (Seewald et al., 1994). The high I, B and NH₄ contents and alkalinity are common features in the sediment-associated hydrothermal fluids (Gamo et al., 1991; Lilley et al., 1993; You et al., 1994). These chemical components are supplied from the sedimentary organic matters through thermal and/or biological degradation processes. The major chemical composition and its variation of the Iheya North hydrothermal fluids are consistent with the physical and chemical impacts of the host rocks, the sediments and the shallow water depth that was previously pointed to in the similar hydrothermal systems in the Okinawa Trough and in the sediments-associated settings.

**Gas geochemistry**

Gas composition Results of gas analyses are listed in Table 2. Low Mg concentrations of high temperature fluid samples (ID #713-W4 and #712-W4) allowed us to regard the observed gas compositions as the nearly endmember compositions. The high CO₂ contents of 227 and 187 mmol/kg respectively in the NBC and ESBC fluids were notable. The δ¹³C values of CO₂ were −10.1‰ and −9.7‰ (Table 2, Fig. 5). Considering the stable carbon isotopic composition ranges of the ¹³C-depleted and enriched magmatic CO₂ (−9.3~0‰: Blank et al., 1993; Takai et al., 2008b) and of the typical ¹³C-depleted thermogenic CO₂ (−25~−20‰: Seewald et al., 1994), the extraordinary high concentration of CO₂ in the Iheya North field would be largely derived from the magmatic CO₂.
input (Ishibashi et al., 1995; Lupton et al., 2008; Toki et al., 2008) rather than the thermogenic CO₂ as previously suggested although the quantitative input of thermogenic CO₂ was not yet excluded. The helium isotope ratios ([³⁷He/⁴He]/[³⁷He/⁴He] atm) of high temperatures vent fluids were 7.15 and 7.07, indicating the potential mantle-derived helium input (Lupton and Craig, 1975). A significant difference of H₂ concentration between the NBC (229 µmol/kg) and ESBC (25 µmol/kg) fluids was observed (Table 2). However, the difference is very difficult to explain only by the fluid boiling and the preferential partition of insoluble gas components such as H₂, CH₄ and He in the Cl-depleted fluids (Chiodini et al., 2001; Takai et al., 2008b) because the CH₄ concentrations were relatively similar between the NBC and ESBC fluids (Table 2). Possible explanations are the microbial H₂ consumption (H₂ depletion) and/or the additional CH₄ input with little H₂ in the subseafloor environments around ESBC site after the phase-separation and -partition process. Since the δD values of the NBC and ESBC fluids (describe below) are almost identical (Table 1), the microbial H₂ consumption seems to be not significant. On the contrary, the additional CH₄ input is more likely as the liquid CO₂ pools enriched with both CH₄ and H₂S are probably widespread in the Okinawa Trough hydrothermal systems (Sakai et al., 1990b; Konno et al., 2006; Inagaki et al., 2006; Nunoura et al., 2010) and would serve as the CH₄ (CO₂ and H₂S) sources. Thus, it is still just a speculation but may be possible that the ESBC hydrothermal fluid is additionally enriched with the gas components such as CO₂, H₂S and CH₄ by encountering the liquid CO₂ pools somewhere in the subseafloor environments around ESBC site.

Microbial modification of stable isotope ratio of H₂. The stable isotope ratios of H₂ (δD) in the obtained high-temperature fluids are around −430‰ (Table 2). It is known that the δD value in high-temperature hydrothermal fluid is dominated by the hydrogen isotope equilibrium between H₂ and H₂O (Proskurowski et al., 2006) that induces temperature-dependent fractionation between deuterium and hydrogen (Horibe and Craig, 1995) as following reactions:

\[
\begin{align*}
\text{H}_2 & \leftrightarrow 2\text{H}^+ + 2\text{e}^- \\
\text{H}_2\text{O} & \leftrightarrow \text{H}^+ + \text{OH}^- \\
\text{HD} + \text{H}_2\text{O} & \leftrightarrow \text{H}_2 + \text{HDO}.
\end{align*}
\]

(1)

The relationship between the observed δD values and the measured maximum temperature during the sampling was analyzed (Fig. 6) in order to examine the isotopic equilibrium between H₂ and H₂O at the venting fluid tem-
perature. The δD values (−430‰ and −428‰) were comparable with −405‰ corresponding to an equilibrated δD value based on the calculation from the isotope fractionation factor (Horibe and Craig, 1995) assuming δD = +40‰ (hydrothermal δD = +5‰; Shanks III et al., 1995) in the case when the fluid temperature is 300°C. This indicates that the δD values in the high temperature fluids in the Iheya North field were dominated by the equilibrium at the temperature of hydrothermal endmember.

The lower temperature fluids obtained from the animal colonies showed significantly lower δD values (<−635‰) than those in high temperature fluids (−430‰). Because a negligible δD change was expected at a mixing between hydrothermal fluid and ambient seawater due to little H2 content in deep-sea seawater (<0.1 mmol/kg; Moore et al., 2009), the lower δD values should result from some processes other than the mixing. The isotope exchange reaction (xn 1) after the fluid cooling can make a δD value decreasing from that of the high temperature fluid, because of decreasing the equilibrated δD value with decreasing temperature (Fig. 6) due to larger isotope fractionation factor at lower temperature (Horibe and Craig, 1995). As opposed to the abiotic isotope exchange reaction rate drastically decreases at lower temperatures (e.g., Campbell et al., 2009), microbial H2 metabolisms are known to catalyze the isotope exchanging (Vignais, 2005) even at temperatures as low as 30°C (Romanek et al., 2003; Valentine et al., 2004a). The lower δD values in the low temperature fluid than those in the high temperature fluid were observed in other hydrothermal fields and considered as results from subsurface microbial H2-consuming or -producing activities (Kawagucci et al., 2010a). Microbial H2-metabolisms in the low temperature hydrothermal environment can account for the variation of δD values in the Iheya North fluids. In fact, the methane fermentation experiment using the Paraglobopulla colony water indicated that δD values shifted to the equilibrated δD value at 25°C during the incubation (Fig. 6, Table 2). Although a quantitative relation between the δD charge and the microbial H2 metabolisms has been poorly understood, the microbial δD change may be consistent with the previous microbiological characterization (Nakagawa et al., 2005), pointing to the abundant hydrogenotrophic and hydrogenogenic metabolisms in the microbial communities in the Iheya North hydrothermal field.

Methane

Biogenic methane The CH4 concentrations in the high-temperature fluids were ~3 mmol/kg (Table 2). The high mean level of CH4 contents are common in the sediment-associated hydrothermal fluids (Lilley et al., 1993; Pearson et al., 2005; Cruse and Seewald, 2006; McCollom, 2008) including Okinawa Trough hydrothermal fluids (Chiba et al., 1993; Ishibashi et al., 1995; Konno et al., 2006). The abundant hydrothermal fluid CH4 has been considered to be a thermogenic origin (via thermal degradation of sedimentary organic matters) (Ishibashi et al., 1995; Lilley et al., 1993) and to be in some cases a biogenic origin (via microbial methanogenesis) (Cruse and Seewald, 2006). The observed δ13CCH4 values in the Iheya North fluids were −54.0‰ and −51.0‰. These values are among the most δ13C-depleted values so far observed in the hydrothermal fluids (Fig. 5). A trace amount of ethane (<1 µmol/kg) was detected in a hydrothermal fluid, resulting in a C2/C1 ratio of >3.7 × 10^5. Concentration of H2 (<200 µmol/kg) is not so high relative to those in other felsic-rock based fields (e.g., Takai et al., 2008b) and results in a H2/CH4 ratio lower than 0.07. While H2/CH4 ratios in sediment-free fields are typically higher than 1, those in sediment-associated fields are lower than 1 (Kawagucci et al., 2010b). In addition, the stable hydrogen isotope ratio of CH4 (δDCH4) was −132‰, comparable with those so far
observed in both sediment-starved and -associated hydrothermal systems (~125–96‰; Welhan and Craig, 1983; Proskurowski et al., 2006) (Fig. 7).

The abiotic CH4 input is estimated to be quite low based on the CH4 contents in the hydrothermal fluids obtained from typical sediments-starved, arc-backarc (felsic-rock based) hydrothermal systems in the Suiyo Seamount (Toki et al., 2004b) and in the Lau Basin (Takai et al., 2008b). Thus, it is obvious that the Iheya North hydrothermal fluid CH4 should be derived from the thermogenic or the biogenic process or the both processes. The δ13CCH4 values (<–51‰) are lower than the δ34S values of so-called “thermogenic CH4” (~50–20‰; Whiticar, 1999) and than the values of the experimentally produced CH4 (δ13CCH4 = –24–21‰) from the in situ experiments of CH4 generation in sedimentary organic carbons (~–17‰) at 325°C and 500 bar (Seewald et al., 1994). Thus, the stable carbon isotopic composition of the Iheya North fluid CH4 cannot be attained only by the thermogenic source of CH4. Rather, the more predominant contribution of the 13C-depleted CH4 to the hydrothermal fluid CH4 should be predicted. Based on several experiments of carbon isotopic fractionations by hydrogenotrophic and aceticlastic methanogens, the kinetic isotopic effects have been estimated to be ~10 to ~50‰ for the hydrogenotrophic methanogens (e.g., House et al., 2003; Valentine et al., 2004b; Penning et al., 2005; Takai et al., 2008a) and approx. ~20‰ for the aceticlastic methanogens (e.g., Gelwicks et al., 1994). In the case of the Okinawa Trough, the δ13CCH4 values of the organic carbons and the derivative acetate and CO2 in the sediments are all assumed to be ~30–20‰ due to the primitive origins of marine planktonic and terrestrial plant productions, while the δ13C value of seawater bicarbonate is ~0‰. Thus, to yield the Iheya North fluid CH4 of which δ13CCH4 is totally lower than ~51‰, most of the hydrothermal fluid CH4 should be derived from the hydrogenotrophic methanogenesis using CO2 derived from sedimentary organic carbons.

The high C1/C2 ratio of >3.7 × 103 also supports the generation of source CH4 by the microbial methanogenesis. When the C1/C2 ratios of biogenic gases and thermogenic gases are respectively assumed to be 104 (Vogel et al., 1982; Belch and Daniels, 1988) and 102 (Cruse and Seewald, 2006; McCollom, 2008), the C1/C2 ratio of >3.7 × 103 in the Iheya North fluid CH4 indicates that more than 97% of CH4 is provided from microbial methanogenesis. Furthermore, the relatively low H2 concentration (<200 μmol/kg) may be a signature that the thermogenic gases (CH4, CO2 and H2) via the thermal degradation of organic matters are much less incorporated into the Iheya North hydrothermal fluids because the H2 concentrations are sometime more than 1 mmol/kg in the sediments-covered hydrothermal systems (Cruse and Seewald, 2006; McCollom, 2008). The hydrothermal experiment using the in situ sediments of the Guaymas Basin has also estimated that more than 1 mmol/kg of H2 can be produced via the hydrothermal degradation of the sedimentary organic matters (Seewald et al., 1994).

The stable isotopic compositions of hydrogen and carbon in the CH4 can be affected not only at the time of the generation but also during the transportation in the hydrothermal fluids. The Δδ13CCH4 value of the hydrothermal fluid CH4 is potentially controlled by the carbon isotope equilibrium through the following chemical equilibrium:

\[
\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O.}
\]

If full carbon isotope equilibrium of CH4 with CO2 (Δδ13CCH4 = –10‰) at the vent fluid temperature of 310°C is assumed, a δ34S value in the Iheya North fluid CH4 should be higher than ~–40‰ (Horita, 2001). This assumption is clearly inconsistent with the observed δ34S value of lower than ~51‰. Such disequilibrium in carbon isotopes has been observed in other sediment-associated hydrothermal systems (e.g., Cruse and Seewald, 2006; McCollom, 2008). Abiotic methane production through the rxn. 2 is thermodynamically unfavorable in the case of the Iheya North hydrothermal system due especially to the relatively low H2 concentration (McCollom, 2008). Thus the carbon isotope equilibrium between CH4 and CO2 would be negligible during the hydrothermal circulation after the CH4 generation and incorporation. In addition, it has been suggested in the Yonaguni Knoll IV hydrothermal fluids that the phase-separation and segregation processes have little effect (at most 3%) on the stable carbon isotope fractionation of CH4 (e.g., Konno et al., 2006). Thus, the δ13CCH4 values of the Iheya North hydrothermal fluid CH4 would represent the stable isotopic information at the time of generation of CH4 sources.

The ΔD value of CH4 (ΔDCH4) initially reflects the ΔD values of substrate (H2O and Org-H) and the kinetic isotope fractionations on abiotic and biotic methanogenesis (e.g., Sugimoto and Wada, 1995; Valentine et al., 2004b), potentially representing a wide range of ΔDCH4 values (Fig. 7; e.g., Schoell, 1980). However, all the ΔDCH4 values determined so far in the hydrothermal fluids including the Iheya North fluids have fallen into a narrow range (~130–96‰; Welhan and Craig, 1983; Proskurowski et al., 2006) regardless of the types of hydrothermal systems. This observation points that a common process dominates to control the ΔDCH4 values of the hydrothermal fluid CH4. The hydrogen isotope equilibrium between H2O–H2–CH4 in the high temperatures fluids would be the most likely process. The isotope systematics could be described by two of the isotopic equilibria between H2O–H2 and H2–CH4, as seen in the ΔD value via the rxn. 1
and a following isotope equilibrium reaction:

\[
\text{CH}_4 + \text{HD} \leftrightarrow \text{CH}_3\text{D} + \text{HH}
\]  

(3)

If it is assumed that (or since) the isotopic equilibria proceed faster between H\textsubscript{2}–H\textsubscript{2}O than between CH\textsubscript{4}–H\textsubscript{2} (complex reactions in detail) in the high temperatures hydrothermal fluids, the δ\textsubscript{DCH\textsubscript{4}} values of the hydrothermal fluid CH\textsubscript{4} can be calculated using the thermally equilibrated δ\textsubscript{DCH\textsubscript{4}} values according to rxn. 3. Indeed, all the known δ\textsubscript{DCH\textsubscript{4}} range of hydrothermal fluid CH\textsubscript{4} is comparable to the thermal isotopic equilibrium range calculated from the fluid temperatures and the temperature-dependent isotope fractionation factors on the CH\textsubscript{4}–H\textsubscript{2} and H\textsubscript{2}–H\textsubscript{2}O equilibriums (Horibe and Craig, 1995) assuming δ\textsubscript{DCH\textsubscript{4}} = +0‰ (Shank et al., 1995) (Fig. 7). This result suggests that the δ\textsubscript{DCH\textsubscript{4}} values of the hydrothermal fluid may be controlled by the hydrogen isotope equilibrium between H\textsubscript{2}O–H\textsubscript{2}–CH\textsubscript{4}. Given that the hydrogen isotope equilibrium between CH\textsubscript{4} and H\textsubscript{2} at around 300°C needs a time longer than ten hours even at the experimental condition using a Ni–Thoria catalyst which effectively activates the rxn. 2 (Horibe and Craig, 1995), the equilibrium under subseafloor hydrothermal environment should take a time longer than ten hours. In contrast, hydrothermal fluid upwelling velocity (1 m/sec; Schultz and Elderfield, 1999) and generally-regarded reaction zone depth (sub-kilometers to several kilometers) provides an estimated fluid residence time at fluid discharging stage as short as an hour. The significantly longer time for establishing the isotope equilibrium than the time for fluid upwelling suggests that the isotope equilibrium occurred more likely at deep reaction zone rather than the fluid discharging stage. Apparent consistency of δ\textsubscript{DCH\textsubscript{4}} values between a part of the proposed thermogenic range (School, 1980) and the observed hydrothermal range (Fig. 7) was probably circumstantial because of similar δ\textsubscript{DCH\textsubscript{4}} values observed even in sediment-starved hydrothermal systems (Logatchev and EPR21°N: Welhan and Craig, 1983; Proskurovski et al., 2006). However, a difference among the observed hydrothermal δ\textsubscript{DCH\textsubscript{4}} values is small (~34‰) but significant (analytical errors of ~10‰) so that the other factors controlling the δ\textsubscript{DCH\textsubscript{4}} values than the isotopic equilibriums at endmember hydrothermal temperatures might be involved for hydrothermal δ\textsubscript{DCH\textsubscript{4}} values. In any cases, the use of δ\textsubscript{DCH\textsubscript{4}} value to the discussion about the origin of hydrothermal methane may bring misunderstanding in this time. In other words, the deviation between the observed hydrothermal δ\textsubscript{DCH\textsubscript{4}} values and the biogenic δ\textsubscript{DCH\textsubscript{4}} range reported previously (Fig. 7: Schoell, 1980; Sugimoto and Wada, 1995; Valentine et al., 2004b) does not prove biogenic origin of methane in the Iheya North hydrothermal field.

Based on the compositional and isotopic properties of the hydrothermal fluid CH\textsubscript{4} and other gas components in the Iheya North field, it is very likely that most CH\textsubscript{4} should be produced by microbial methanogenesis prior to the high temperatures hydrothermal reaction probably utilizing H\textsubscript{2} and CO\textsubscript{2} which are provided from the sedimentary organic matters by functions of co-existing fermentative microorganisms. This generation model of hydrothermal fluid CH\textsubscript{4} in the Iheya North field would be completely different from the case in another Okinawa Trough hydrothermal system, the Yonaguni Knoll IV field (Konno et al., 2006). In the Yonaguni Knoll IV field, the CH\textsubscript{4} concentrations in the fluids are similar with those in the Iheya North field while the higher H\textsubscript{2} concentrations (>1 mmol/kg) and more 13C-enriched CH\textsubscript{4} (δ\textsubscript{13C} = -27~ -24‰) are found than in the Iheya North field (Konno et al., 2006). As already discussed above, these compositional and isotopic properties of the hydrothermal gas components in the Yonaguni Knoll IV field suggest that the hydrothermal fluid CH\textsubscript{4} would be derived from the thermal degradation of the sedimentary organic matters by the high temperatures hydrothermal fluid flow in the sediments. It is still uncertain why the two Okinawa Trough hydrothermal fields have different generation and incorporation mechanisms of the hydrothermal fluid CH\textsubscript{4}. However, it would be important to know where the CH\textsubscript{4} generation and incorporation occur in the hydrothermal circulation processes.

**Microbial methanogenesis at recharge zone**

The potentially significant contribution of microbial methanogenesis to the hydrothermal fluid CH\textsubscript{4} has been suggested also at two sediment-covered systems, the Middle Valley field (Cruse and Seewald, 2006) and the Guaymas Basin field (Pearson et al., 2005). These studies have also presumed that the generation and incorporation of microbially produced CH\textsubscript{4} should occur at the time prior to the hydrothermal reaction and the fluid discharging stages in the whole fluid circulation, that is the recharging stage of source fluids (Pearson et al., 2005; Cruse and Seewald, 2006). However, since the identification of practical location of hydrothermal fluid recharging paths is quite difficult without any of the geophysical surveys for the subseafloor sedimentary and crustal structures, the direct geochemical and microbiological evidences have been not yet obtained in any of the hydrothermal systems. In the Iheya North field, more than 40 DSV and ROV seafloor observations have been conducted and the seafloor structures are relatively well elucidated. In addition, several coring expeditions and geophysical surveys (e.g., heat flow distribution and seismic reflection analyses) have been conducted for proposing a future drilling expedition by Integrated Ocean Drilling Program (IODP). Thus, the potential fluid recharge areas hosting the hydrogenotrophic methanogenesis have been hypothesized to be either in the valley-filling deposits of the Iheya North hydrothermal field.
the Central Valley in the Iheya North Knoll or in the basin-filling sediments around the Iheya North Knoll (IODP 601-Full3 proposal: http://www.iodp.org/600/). In lights of compositional and isotopic characteristics of gaseous carbons in the Iheya North hydrothermal fluids and the carbon mass balance between the hydrothermal fluids and the organic carbon potential in the Central Valley of the Iheya North Knoll, we try to draw an implication of the hydrothermal recharging area for the Iheya North field.

First, we estimate the CH4 emitting flux ($F_{CH4}$) by the discharging hydrothermal fluids using a following equation:

$$F_{CH4} = \text{[Conc.]} \times \text{[Area]} \times \text{[Vel.]} \times \text{[N vent]} \times \text{[L/H]}$$

where $\text{[Conc.]}$, $\text{[Area]}$, $\text{[Vel.]}$, $\text{[N vent]}$, and $\text{[L/H]}$ represent the endmember concentration of CH4, the average area of orifice of a vent, the average flow velocity of a venting fluid, the numbers of vent orifices, and the contribution factor for the CH4 flux between discharging hydrothermal fluids and high temperatures fluids, respectively. The $\text{[Conc.]}$ is determined to be 3 [mmol/L]. The $\text{[Area]}$ is estimated by the seafloor observation (~2 cm in radius of a vent orifice) to be 12 [cm²]. The $\text{[Vel.]}$ is set to be 1 [m/sec] by the seafloor observation, which is equivalent to the velocity previously reported for other hydrothermal vents (Schultz and Elderfield, 1999). The high temperatures hydrothermal fluid vent sites are found at the NBC (two), ESBC, SBC and CBC, and thus the $\text{[N vent]}$ is 5. The discharging hydrothermal fluids are recognized to convect more than one order of magnitude greater than the high temperature fluids (Elderfield and Schultz, 1996). Since numerous discharging flow sites are found in the Iheya North field, the [L/H] for the Iheya North field should be >20. These estimations lead to $F_{CH4}$ of 1.14 × 10³ [mol/year].

Second, the organic carbon potential of the valley-filling deposits in the Central Valley ($C_{pot}$) is calculated by a following presumptive equation:

$$C_{pot} = \text{[Vol.]} \times \text{[Density]} \times \text{[TOC]} \times 1/12$$

where the $\text{[Vol.]}$ is the total valley-filling deposit volume, the $\text{[Density]}$ is a density of the deposit and the $\text{[TOC]}$ is a total organic carbon content of deposit. The $\text{[Vol.]}$ is calculated from the apparent seafloor area of the Central Valley as 2000 m × 2000 m (Fig. 2a) and the deposit depth of 300 m with an assumption of a reverse cone shape of valley-filling deposit. It is calculated to be 3.14 × 10⁸ [m³]. The $\text{[Density]}$ and $\text{[TOC]}$ are determined for the pumiceous deposit obtained from the Central Valley and are 2 [g/cm³] and ~1 × 10⁻⁵ [g/g], respectively. These values lead to $C_{pot}$ of 5.23 × 10⁸ [mol-CH₄].

The calculated $C_{pot}$ value corresponds to maintain the $F_{CH4}$ for ~46 years. This value is highly improbable as following reasons. It is 15 years since the Iheya North field is discovered in 1995 (Momma et al., 1996) and the hydrothermal activity still continues. The enormous hydrothermal mound structures and the prosperous vent-endemic animal colonies at the time of discovery suggested that the hydrothermal activity had continued for several tens years before the discovery. In addition, the calculation is based on impractical assumptions: the whole organic carbons in the valley-filling deposits convert to CH4 without any conversion to CO₂ and other inorganic and organic carbons and the whole produced CH4 is entrained by hydrothermal fluids without any loss during the transportation. These impractical assumptions bring a difference between the $C_{pot}$ and actually produced methane from valley-filling organic carbon, which we should compare to the $F_{CH4}$, and the difference means that the term to maintain the $F_{CH4}$ (~46 years) should be overestimated. It seems unlikely, therefore, that the hydrothermal fluid CH4 in the Iheya North field is derived from the microbial methanogenesis associated with the organic carbons in the valley-filling deposits in the Central Valley of the Iheya North Knoll.

Considering the carbon mass balance of the hydrothermal fluid CH4, it seems more likely that the microbial methanogenesis associated with the organic carbons should occur not only in the Central Valley, but also in the spatially abundant and widespread basin-filling sediments surrounding the Iheya North Knoll, and the microbially produced CH4 would be recharged together with the source fluid into the hydrothermal reaction and discharging stages of circulation. This “Microbial Methanogenesis at Recharge area in hydrothermal circulation” (MMR) model in the Iheya North field is hypothesized based on the hydrothermal gas chemistry. Nevertheless, this MMR model is not conflict with other chemical components such as high I, B and NH₄ contents and alkalinity because these were considered as results from decomposition of sedimentary organic matter (Gamo et al., 1991; Lilley et al., 1993; You et al., 1994) possibly independent from thermal or biological processes. The MMR model is also consistent with the interpretation of the $\delta^{13}C_{CH4}$ values in hydrothermal fluids that the CH4 produced at the recharge zone had initially shown $\delta^{13}C_{CH4}$ value within biogenic range (~35‰–250‰; Sugimoto and Wada, 1995; Valentine et al., 2004b) and the hydrogen isotope exchanges among H₂O–H₂–CH4 at high temperature reaction zone made the $\delta^{13}C_{CH4}$ value to the equilibrated value of ~130‰ (Fig. 7).

**Implication**

The MMR model in the Iheya North field may also
provide an important implication for the generation and incorporation of hydrothermal fluid CH₄ in other deep-sea hydrothermal systems in the Okinawa Trough (e.g., the JADE field of the Izena Hole) (Ishibashi et al., 1995) and in the Juan de Fuca Ridge and the Guaymas Basin (Lilley et al., 1993; Pearson et al., 2005; Cruse and Seewald, 2006; McCollom, 2008). For instance, the Endeavour field is known to occur in the sediments-starved axial valley in the Juan de Fuca Ridge (Delaney et al., 1992) while the hydrothermal fluids represent the sediment-influenced characteristics (Lilley et al., 1993; Cruse and Seewald, 2010). The compositional and isotopic characteristics of gas components, high CH₄ concentrations (1.8–3.4 mmol/kg), high C₁/C₂ ratios (449–539), highly ¹³C-depleted CH₄ (−55.0—48.4‰) and moderate H₂ concentrations (0.16–0.42 mmol/kg), are very comparable to those in the Iheya North field. However, Lilley et al. (1993) suggested that most of the hydrothermal fluid CH₄ in the Endeavour field would be thermogenic origin of the buried sedimentary organic matters. If the microbial methanogenesis via the sedimentary organic carbons is possible in the sediments at the ridge flank region located within several kilometers from the spreading axis, as in our MMR model, the generation and incorporation of hydrothermal fluid CH₄ may be more strongly associated with the venting CH₄ at the Endeavour field. Our MMR model would be not only an implication for the generation and incorporation of hydrothermal fluid CH₄ in the deep-sea hydrothermal systems but also for those of cold seep CH₄ (e.g., Toki et al., 2004) and for the presently uncertain hydrothermal fluid paths in the subseaﬂoor environments (e.g., Wheat et al., 2003). In the near future, the IODP drilling will be conducted in the Iheya North hydrothermal system. It will give an excellent opportunity to testify our MMR model.

Acknowledgments—Authors are grateful to the ofﬁcers, crews, and scientist group, as well as the Shinkai 2000 and Hyper Dolphin operating teams for their valuable collaboration. Authors also thank Drs. Pinti, Prol-Ledesma, and Koschinsky for their kind efforts to edit and review our manuscript. This research was supported by a Ministry of Education, Culture, Sports, Science and Technology (MEXT) Grant-in-Aid for Scientiﬁc Research (Nos. 16204045, 19253006, and 17101001), the Trans-crustal Advection and In-situ reaction of Global subseaﬂoor Aquifer (TAIGA) project, and the Japan Society for the Promotion of Science (JSPS) Fellows (No. 18.4415). S.K. was supported by Research Fellowships for Young Scientists from JSPS (DC).

REFERENCES


perature activation of organic matter and minerals during burial has the potential to sustain the deep biosphere over geological timescales. Org. Geochem. 38, 845–852.

Pearson, A., Seewald, J. S. and Eglington, T. I. (2005) Bacterial incorporation of relict carbon in the hydrothermal environ-

Penning, H., Pluge, C. M., Galand, P. E. and Conrad, R. (2005) Variation of carbon isotope fractionation in hydrogenotrophic methanogenic microbial cultures and en-
virontment samples at different energy status. Global Change Biol. 11, 2103–2113.


Proskurovski, G., Lilley, M. D., Kelley, D. S. and Olson, E. J. (2006) Low temperature volatile production at the Lost City Hydrothermal Field, evidence from a hydrogen stable iso-


Schoell, M. (1980) The hydrogen and carbon isotopic compo-


Seewald, J. S., Seyfried, W. E. and Shanks, W. C. (1994) Varia-
tions in the chemical and stable-isotope composition of carbon and sulfur species during organic-rich sediment alteration—an experimental and theoretical study of hydro-

Shanks, W. C., III, Bohlke, J. K. and Seal, R. R., II (1995) Sta-
ble isotopes in mid-ocean ridge hydrothermal systems; in-
teractions between fluids, minerals, and organisms. Seaﬂoor Hydrothermal Systems; Physical, Chemical, Biological, and Geologic Interactions (Humphris, S. E., Zierenberg, R. A., Mullineaux, L. S. and Thomson, R. E., eds.), 194–221, American Geophysical Union.


Umezawa, T., Aoki, S., Nakazawa, T. and Morimoto, S. (2009) A high-precision measurement system for carbon and hy-
drogen isotopic ratios of atmospheric methane and its ap-

Low-temperature formation of hydrocarbon gases in San-Francisco Bay sediment (California, USA). Chem. Geol. 37, 289–298.


