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Citation	Geochemical Journal, 45(2): 109-124
Issue Date	2011-06
URL	http://hdl.handle.net/20.500.12000/37848
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Hydrothermal fluid geochemistry at the Iheya North field in the mid-Okinawa Trough: Implication for origin of methane in subseafloor fluid circulation systems

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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 NH_4 contents and alkalinity are derived from decomposition of the sedimentary organic matters.

Compositional and isotopic properties of gas species, CH_4, H_2, CO_2, and C_2H_6, strongly suggest a dominance of biogenic CH_4 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 CH_4 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 CH_4 in the deep-sea hydrothermal systems but also for those of cold seep CH_4 and for the presently uncertain hydrothermal fluid paths in the subseafloor environments. In the near future, the IODP 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

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INTRODUCTION

Hydrothermal fluid chemistry in the Okinawa Trough hydrothermal systems has been often characterized by higher concentrations of CO_2, CH_4, NH_4, I and K and higher alkalinity than those in typical sediments-free Mid
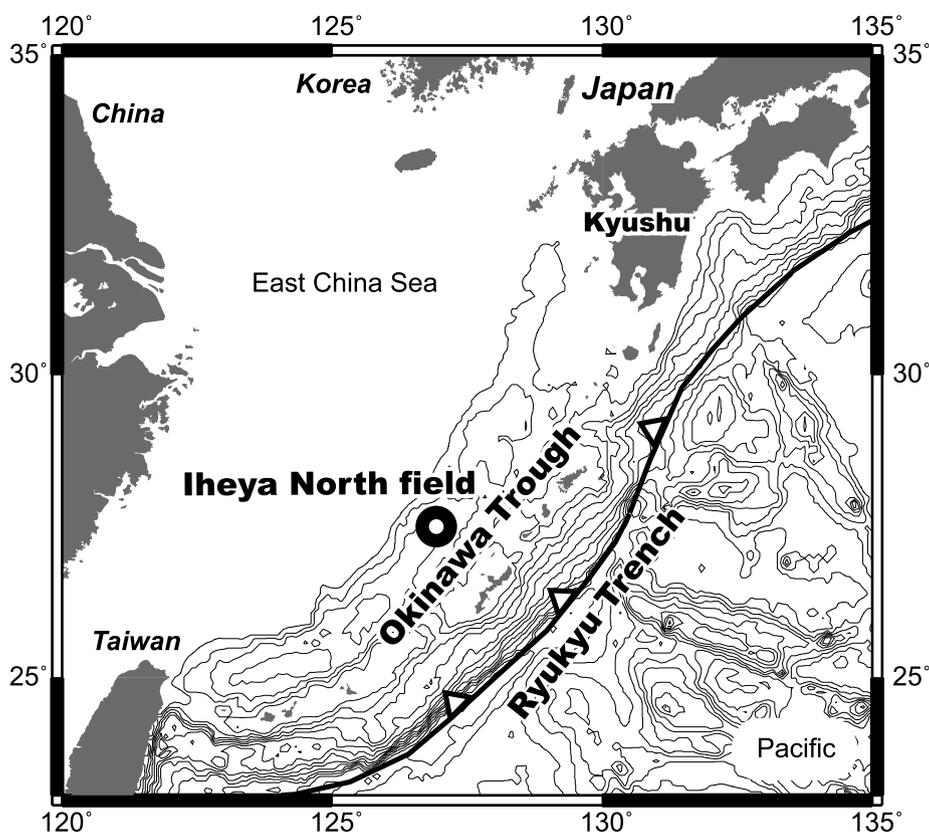
Fig. 1. Map of the Okinawa Trough with the location of the Iheya North hydrothermal field.

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 (NH_4, 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 CH_4 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 CH_4, including chemical synthesis from reduction of CO_2 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 CH_4 should be produced by thermal decomposition of sedimentary organic matters during high temperatures of fluid circulation (Ishibashi *et al.*, 1995). However, recent investigations have demonstrated the compositional and isotopic
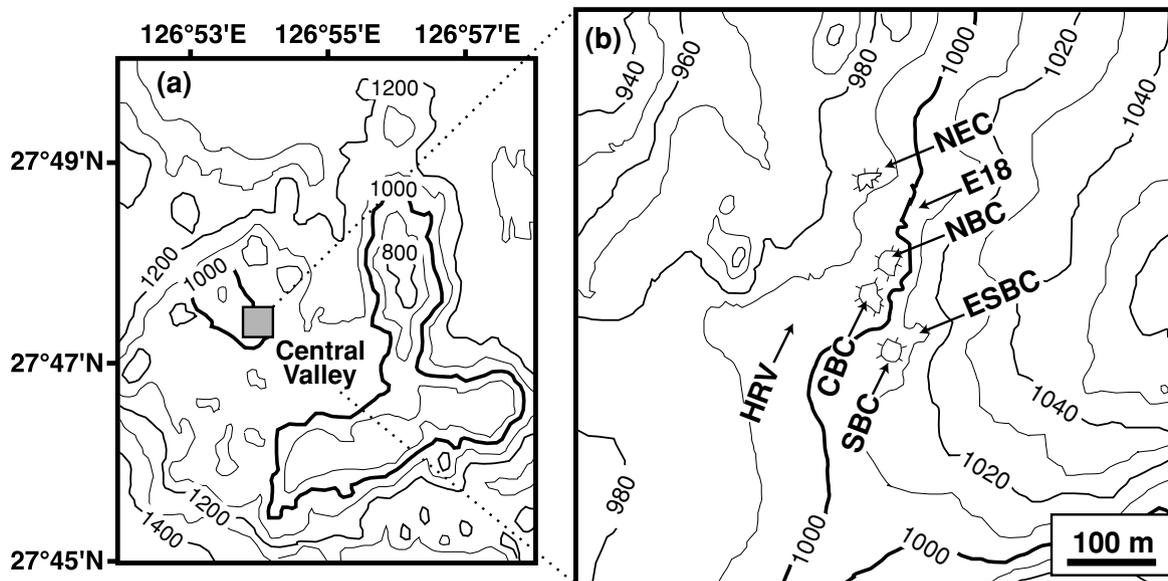
Fig. 2. Locations of the Iheya North field (a) and each vent site (b).

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 $-41\sim-36‰$ in the JADE field and 1.2~9.3 mM and $-27\sim-24‰$, 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 ($\leq122°C$) (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′50N, 126°53′80E), 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 detail location of the hydro-thermal 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 de-posits of the pumicious rocks interbedded with layered minor sediments. However, the seafloor surface around the Iheya North hydrothermal field and the Central Val-ley are covered with the pelagic sediments. It is also no-table 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 ac-companying the proximal mounds named as North Edge Chimney (NEC), Event 18 (E18), North Big Chimney (NBC), Central Big Chimney (CBC), High Radio-activity 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 μmol/kg	Mn μmol/kg	Fe mmol/kg	B mmol/kg	NH₄ μmol/kg	SO₄ mmol/kg	Alk. mmol/kg	SiO₂ mmol/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	1.74	1710	0		12.3	11.0	44.8	952
NBC (2002)	2002	304	4.8	544	432	72.3	1.225	16.1	61.4	619		1.65	2130	–6	1.73	10.13			
NBC (2000)	2000	168		405	308	63.8	1.300	15.7	67.0	602		1.65	2020	–1	1.59	10.47			
NBC (1999)	1999	311		474	367	66.6	1.270	19.2	69.7	669		1.65	2020	–1	1.59	8.86			
NBC (1997)	1997	311		511	405	73.0	1.222	18.1	65.9	631		1.78	2060	3	0.63				
ESBC (2007)	2007	288	5.0	576	459	73.0		23	81	662	<0.13			2		12.16	11.5	47.5	1034
SBC (2002)	2002	153	5.4	191	185	26.9	0.355	4.6	9.4	115		0.67	3550	–7	3.30	5.94			
SBC (2000)	2000	180		24	8	11.8	0.206	2.0	13.3			0.60	2260	–4	1.99	3.05			
SBC (1999)	1999	205		390	288	75.5	0.989	12.5	53.7	397		1.55				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	585	466	79.2	1.362	20.5	75	678		2.27	2320	–3		11.56			
HRV (1999)	1999	117		410	297	75.0	1.179	17.4	57.6	578		1.60	2520	–2	0.22	11.06			
HRV (1996)	1996	238		424	331	57.6	1.121	16.1	57.2	567		1.67			0.94	9.29			
70°C (1997)	1997	70		338	288	56.2	0.900	11.9	53.4	445		1.75	1850	15	2.78				
180°C (1996)	1996	180		238	174	37.7	0.682	12.3	41.4	456		1.52	2970	–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 (2002)	2002	177	5.1	16	40	6.9	0.109	–0.4	0.4	160		0.44				4.45			
Yonaguni IV	(1)	325	5.7	614	416	86.4		23.2		1120		3.91	14700	0	0.25	11.3			
JADE	(2)	320	4.7	550	425	72		22		110			5000	0	1.9	12.9			
Hatoma	(3)	240	5.2	381	285	54.6		17	62	483		3.3	7200		4.7	12			
Seawater				560	480	10	0.026	11	91	<0.01		0.43		29	2.5		<0.04	0.5	860

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

South Big Chimney (SBC), "180°C vent" (~100 m south from SBC), and "70°C vent" (~100 m south from ESBC) from north to south are recognized (Fig. 2b). Among these mounds, a hydrothermal vent at NBC has had the highest temperature (maximum measured temperature of 311°C, near the boiling point (315°C: Bischoff and Rosenbauer, 1988) at seafloor pressure (100 bar)) and the highest flow-rate of hydrothermal emission (~1 m/sec estimated based on video image observation) for more than 10 years, indicating that the NBC stands on the main hydrothermal flow or passage. The eight mounds of the nine (except for the HRV) are aligned in the N-S direction with the NBC at the center (Fig. 2b). With increasing distance from the NBC, the hydrothermal mounds have lower temperatures and lower flow-rates of hydrothermal emissions. The present hydrothermal vents and the diffusing flows are observed within 400 m in the N-S direction and 500 m in the east-west (E-W) direction. The west side of the hydrothermal field is the pumicious volcanic rock and the southern or eastern side is covered with the sediments.

The sedimentation in the Iheya North Knoll and the surrounding basin is a key for hydrothermal fluid chemistry of the Iheya North field. The sediments in the mid-Okinawa Trough are primarily supplied laterally from the East China Sea, largely originated from the Yangtze River (Narita *et al.*, 1990). The sedimentation rate is still controversial in different area of the Okinawa Trough but is estimated to be 1–2 m ka^{-1} in the mid Okinawa Trough (Tsugaru *et al.*, 1991). The sediment cores obtained from the basin around the Iheya North Knoll during JAMSTEC KR01-09 cruise were frequently intervened by pumice layers and showed an average organic carbon content of the subseafloor sediments (>1 mbsf) at 0.001% (w/w).

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 subsumpling 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 ($HOSO_2NH_2$) was added to the fluid in the vacuum line to extract CO_2. 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 chemistry analyses of natural fluid samples, an onboard incubation experient was carried out to assess the microbial H_2 consumption in the diffusing hydrothermal fluid in terms of the compositional and isotopic composition of H_2. 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 SiO_2 and NH_4 were analyzed onboard. The pH and alkalinity were determined using a pH meter by potentiometric titration with 0.1 M HCl. The SiO_2 and NH_4 concentrations were measured by spectrophotometries of silicomolybdate complex and phenol blue, respectively. The analytical precisions were estimated to be within 0.5% for pH, 5% for alkalinity, and 7% for SiO_2 and NH_4. 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 CO_2, CH_4, H_2S, and C_2H_6 were determined by GC-TCD with 10% errors. The H_2 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 CH_4 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 CO_2. 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 $^3He/^4He$ ratio was measured by a conventional noble gas mass spectrometer (Sano and Wakita, 1988; Sano *et al.*, 2008).

Table 2. Gas composition of hydrothermal fluids and incubations

Sample ID	Location	Temp. °C	Mg mmol/kg	CO₂ conc. mmol/kg	CO₂ δ13C ‰	CH₄ conc. mmol/kg	CH₄ δ13C ‰	CH₄ δD ‰	H₂ conc. μmol/kg	H₂ δD ‰	C₂H₆ μmol/kg	C₁/C₂ mol/mol	H₂S mmol/kg	³He/⁴He R/Ratm	Note
#713-W4	ESBC	288	4.41	187	-10.1	2.6	-51	n.a.	25	-428	n.d.	n.d.	2.6	7.15	vigorous vent
#712-W4	NBC	309	0.23	227	-9.7	3.7	-54.0	-132	229	-430	(<1)	>3700	4.5	7.07	top vent
#696-W3	NBC	30.2	52.84	15.4	-9.3	0.5	-52.8	-120			n.d.	n.d.	0.2	6.94	Polychaete colony
#702-W2	NBC	4.7	53.72	3.5	n.a.	0.03	n.a.	n.a.	0.3	-664	n.d.	n.d.	n.d.	n.a.	Bathymodious colony
#711-W1	NBC	10	51.73	2.7	-6.5	0.071	-53.9	-133	8	-635	n.d.	n.d.	n.d.	6.37	Paralvinella colony 0 hour
#711-W2	NBC	(25)	53.55	3.3	-6.1	0.069	-53.7	n.a.	14	-694	n.d.	n.d.	n.d.	6.23	Paralvinella colony 5 hour
#711-W4	NBC	(25)	53.75	2.7	-6.7	0.044	-53.7	n.a.	5	-736	n.d.	n.d.	n.d.	5.82	Paralvinella colony 48 hour
Yonaguni IV		328		22-329	~-8.0	1.2-13.5	~-27-~-25		800-5500							Konno et al. (2006)
JADE		320		209.0	~-5.0	7.600	-41-~-36		50		1-3	(>1000)			6.1-6.5	Ishibashi et al. (1995) (Kawagucci et al. (2010b))
Endeavour		368		11.6-18.2		1.8-3.4	-55-~-48	~-100	160-420	-387-~-332		449-539				Lilley et al. (1993)
Guaymas		298		40	-8.3	54	-43.3	-101	3000	-379	444	122				McCollom (2008)
Middle Valley		281		8.4	-23.8	20.3	-54.3	~-110	2600	-424-~-416	232	88				McCollom (2008)

Data of H₂ isotope ratio at Endeavour, Guaymas, and Middle Valley are from Proskurowski et al. (2006).
n.a.: not analyzed, n.d.: not detected.

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 indicate 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., $[Cl]_{seawater}$ = 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.*, 2008). 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 NH₄ 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;
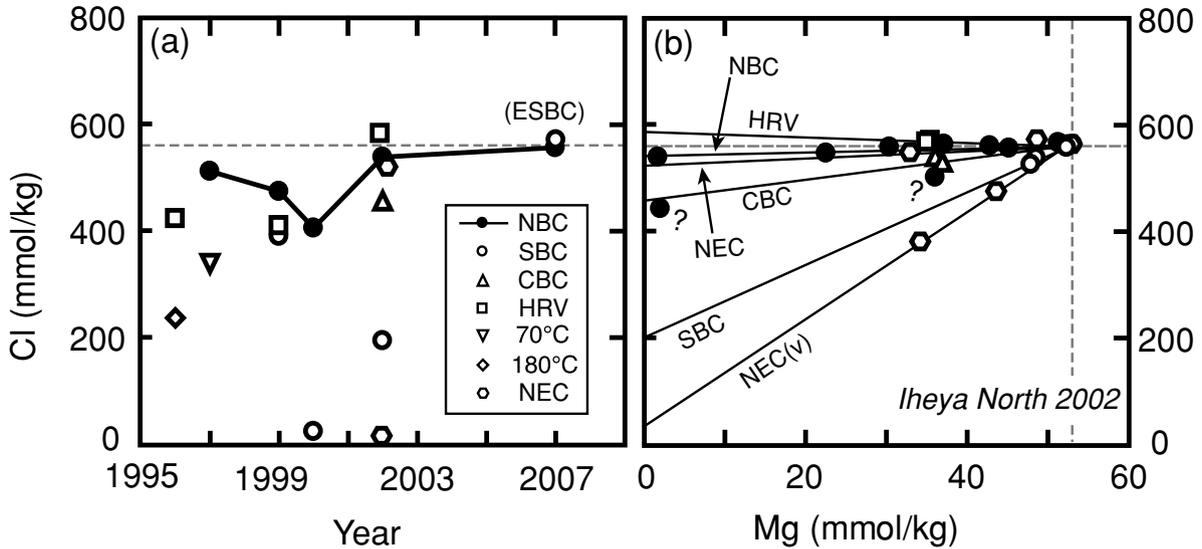
Fig. 3. (a) Estimated endmember-Cl concentrations of each vent and year and (b) measured Mg and Cl concentrations in 2002. Solid lines are least-square regressions for each vent passing through the seawater composition, while those with "NEC" and "NEC(v)" respectively represent the regressions of some normal samples and the other anomalously vapor-enriched samples obtained from the NEC site. Dashed lines represent seawater values.

Suzuki *et al.*, 2008) (Fig. 4). 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 NH_4 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 CO_2 contents of 227 and 187 mmol/kg respectively in the NBC and ESBC fluids were notable. The $\delta^{13}C$ values of CO_2 were –10.1‰ and –9.7‰ (Table 2, Fig. 5). Considering the stable carbon isotopic composition ranges of the ^{13}C-depleted and
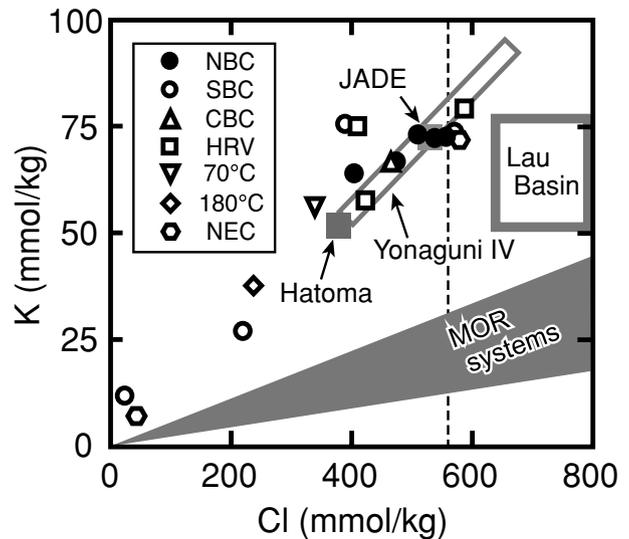

Fig. 4. Estimated endmember Cl and -K concentrations. Data areas for JADE, Hatoma, Yonaguni IV, and Lau Basin hydrothermal fluids were respectively from Sakai et al. (1990b), Kishida et al. (2004), Suzuki et al. (2008), and Fouquet et al. (1991). A dashed vertical line indicates seawater Cl content.

-enriched magmatic CO_2 (–9.3~0‰: Blank *et al.*, 1993; Takai *et al.*, 2008b) and of the typical ^{13}C-depleted thermogenic CO_2 (–25~–20‰: Seewald *et al.*, 1994), the extraordinary high concentration of CO_2 in the Iheya North field would be largely derived from the magmatic CO_2
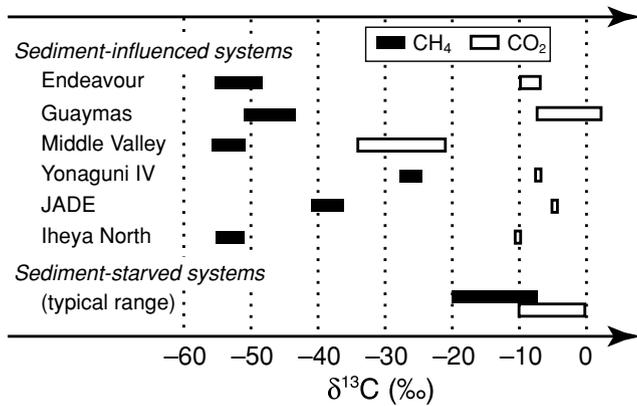
Fig. 5. Stable carbon isotope composition of CH_4 and CO_2 in hydrothermal fluids. The composition in the Yonaguni IV, JADE, and Iheya North are respectively from Konno et al. (2006), Ishibashi et al. (1995), and this study. The other data is from McCollom (2008) and therein.
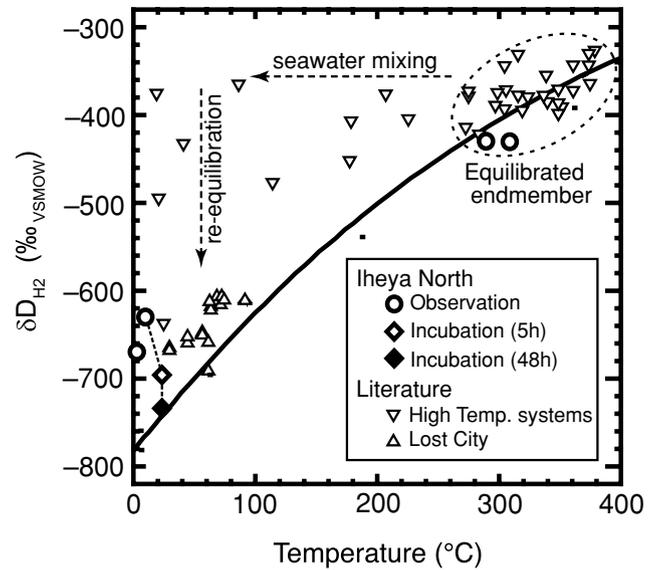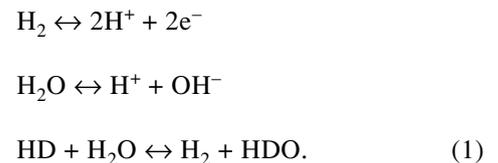

Fig. 6. Relationship between the δD_{H2} values and the fluid temperature at the sampling. Open circles represent the observed data in this study. Open and solid diamonds represent the results of 5 and 48 hours incubations, respectively. Open normal and inversed triangles indicate the previous data obtained from the high temperatures of hydrothermal fluids in the MOR hydrothermal systems (inversed) and the fluids from the Lost City hydrothermal field (normal) reported by Proskurowski et al. (2006) and Kawagucci et al. (2010a). The δD_{H2} values at the isotope equilibrium between H_2 and H_2O, calculated from the temperature-dependent isotope fractionation factor (Horibe and Craig, 1995) assuming δD_{H2O} = +0‰, are also shown as a curve. Fluid cooling and the subsequent isotope equilibrium reaction respectively shift the plot to the left and down.

input (Ishibashi et al., 1995; Lupton et al., 2008; Toki et al., 2008) rather than the thermogenic CO_2 as previously suggested although the quantitative input of thermogenic CO_2 was not yet excluded. The helium isotope ratios ($[^3He/^4He]/[^3He/^4He]_{atm}$) 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 H_2 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 H_2, CH_4 and He in the Cl-depleted fluids (Chiodini et al., 2001; Takai et al., 2008b) because the CH_4 concentrations were relatively similar between the NBC and ESBC fluids (Table 2). Possible explanations are the microbial H_2 consumption (H_2 depletion) and/or the additional CH_4 input with little H_2 in the subseafloor environments around ESBC site after the phase-separation and -partition process. Since the δD_{H2} values of the NBC and ESBC fluids (describe below) are almost identical (Table 1), the microbial H_2 consumption seems to be not significant. On the contrary, the additional CH_4 input is more likely as the liquid CO_2 pools enriched with both CH_4 and H_2S 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 CH_4 (CO_2 and H_2S) 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 CO_2, H_2S and CH_4 by encountering the liquid CO_2 pools somewhere in the subseafloor environments around ESBC site.

Microbial modification of stable isotope ratio of H_2 The stable isotope ratios of H_2 (δD_{H2}) in the obtained high-temperature fluids were around –430‰ (Table 2). It is known that the δD_{H2} value in high-temperature hydrothermal fluid is dominated by the hydrogen isotope equilibrium between H_2 and H_2O (Proskurowski et al., 2006) that induces temperature-dependent fractionation between deuterium and hydrogen (Horibe and Craig, 1995) as following reactions:

$$H_2 \leftrightarrow 2H^+ + 2e^-$$

$$H_2O \leftrightarrow H^+ + OH^-$$

$$HD + H_2O \leftrightarrow H_2 + HDO. \tag{1}$$

The relationship between the observed δD_{H2} values and the measured maximum temperature during the sampling was analyzed (Fig. 6) in order to examine the isotopic equilibrium between H_2 and H_2O at the venting fluid tem-

perature. The δD_{H2} values (–430‰ and –428‰) were comparable with –405‰ corresponding to an equilibrated δD_{H2} value based on the calculation from the isotope fractionation factor (Horibe and Craig, 1995) assuming $\delta D_{H2O} = +0‰$ (hydrothermal $\delta D_{H2O} = +0 \pm 5‰$: Shanks III *et al.*, 1995) in the case when the fluid temperature is 300°C. This indicates that the δD_{H2} 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_{H2} values (<–635‰) than those in high temperature fluids (–430‰). Because a negligible δD_{H2} change was expected at a mixing between hydrothermal fluid and ambient seawater due to little H_2 content in deep-sea seawater (<0.1 nmol/kg: Moore *et al.*, 2009), the lower δD_{H2} values should result from some processes other than the mixing. The isotope exchange reaction (rxn. 1) after the fluid cooling can make a δD_{H2} value decreasing from that of the high temperature fluid, because of decreasing the equilibrated δD_{H2} value with decreasing temperature (Fig. 6) due to larger isotope fractionation factor at lower temperature (Horibe and Craig, 1995). As opposed that the abiotic isotope exchange reaction rate drastically decreases at lower temperatures (e.g., Campbell *et al.*, 2009), microbial H_2 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_{H2} values in the low temperature fluid than those in the high temperature fluid were observed in other hydrothermal fields and considered as results from subseafloor microbial H_2-consuming or -producing activities (Kawagucci *et al.*, 2010a). Microbial H_2-metabolisms in the low temperature hydrothermal environment can account for the variation of δD_{H2} values in the Iheya North fluids. In fact, the onboard incubation experiment using the *Paralvinella* colony water indicated that δD_{H2} values shifted to the equilibrated δD_{H2} value at 25°C during the incubation (Fig. 6, Table 2). Although a quantitative relation between the δD_{H2} change and the microbial H_2 metabolisms has been poorly understood, the microbial δD_{H2} 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 CH_4 concentrations in the high-temperature fluids were ~3 mmol/kg (Table 2). The mili-molar level of CH_4 contents are common in the sediments-associated hydrothermal fluids (Lilley *et al.*, 1993; Pearson *et al.*, 2005; Cruse and Seewald, 2006;
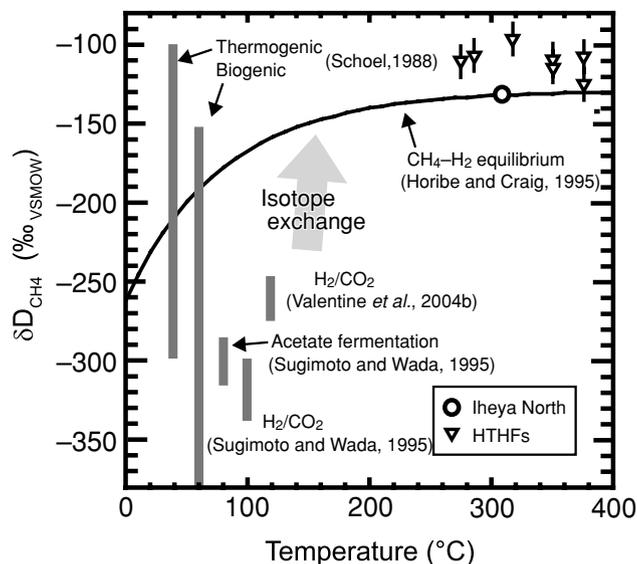

Fig. 7. Relationship between the δD_{CH4} values and the fluid temperature at the sampling. An open circle indicates the data in this study. Open triangles represent the previous data obtained from the high temperatures of hydrothermal fluids in the MOR hydrothermal systems by Proskurowski et al. (2006). The δD_{CH4} values at the isotope equilibrium between CH_4 and H_2, calculated from the temperature-dependent isotope fractionation factors (Horibe and Craig, 1995) assuming the isotope equilibrium between H_2 and H_2O at $\delta D_{H2O} = 0‰$ (shown in Fig. 6), are also shown as a curve. Gray bars represent reported ranges of δD_{CH4} values as thermogenic and biogenic methane by Schoell (1988), Sugimoto and Wada (1995), and Valentine et al. (2004b).

McCollom, 2008) including Okinawa Trough hydrothermal fluids (Chiba *et al.*, 1993; Ishibashi *et al.*, 1995; Konno *et al.*, 2006). The abundant hydrothermal fluid CH_4 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 $\delta^{13}C_{CH4}$ values in the Iheya North fluids were –54.0‰ and –51.0‰. These values are among the most $\delta^{13}C$-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 C_1/C_2 ratio of >3.7 × 10³. Concentration of H_2 (<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 H_2/CH_4 ratio lower than 0.07. While H_2/CH_4 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 CH_4 (δD_{CH4}) was –132‰, comparable with those so far

observed in both sediment-starved and -associated hydrothermal systems ($-125 \sim -96‰$: Welhan and Craig, 1983; Proskurowski *et al.*, 2006) (Fig. 7).

The abiotic CH_4 input is estimated to be quite low based on the CH_4 contents in the hydrothermal fluids obtained from typical sediments-starved, arc-backarc (felsic-rock based) hydrothermals systems in the Suiyo Seamount (Toki *et al.*, 2008) and in the Lau Basin (Takai *et al.*, 2008b). Thus, it is obvious that the Iheya North hydrothermal fluid CH_4 should be derived from the thermogenic or the biogenic process or the both processes. The $\delta^{13}C_{CH4}$ values ($<-51‰$) are lower than the $\delta^{13}C_{CH4}$ value range of so-called "thermogenic CH_4" ($-50 \sim -20‰$: Whiticar, 1999) and than the values of the experimentally produced CH_4 ($\delta^{13}C_{CH4} = -24 \sim -21‰$) from the *in situ* Guaymas Basin sediments ($\delta^{13}C_{organic} = -17‰$) at 325°C and 500 bar (Seewald *et al.*, 1994). Thus, the stable carbon isotopic composition of the Iheya North fluid CH_4 cannot be attained only by the thermogenic source of CH_4. Rather, the more predominant contribution of the ^{13}C-depleted CH_4 to the hydrothermal fluid CH_4 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 $\delta^{13}C$ values of the organic carbons and the derivative acetate and CO_2 in the sediments are all assumed to be $-30 \sim -20‰$ due to the primitive origins of marine planktonic and terrestrial plant productions, while the $\delta^{13}C$ value of seawater bicarbonate is $\sim 0‰$. Thus, to yield the Iheya North fluid CH_4 of which $\delta^{13}C_{CH4}$ is totally lower than $-51‰$, most of the hydrothermal fluid CH_4 should be derived from the hydrogenotrophic methanogenesis using CO_2 derived from sedimentary organic carbons.

The high C_1/C_2 ratio of $>3.7 \times 10^3$ also supports the generation of source CH_4 via the microbial methanogenesis. When the C_1/C_2 ratios of biogenic gases and thermogenic gases are respectively assumed to be 10^4 (Vogel *et al.*, 1982; Belay and Daniels, 1988) and 10^2 (Cruse and Seewald, 2006; McCollom, 2008), the C_1/C_2 ratio of $>3.7 \times 10^3$ in the Iheya North fluid CH_4 indicates that more than 97% of CH_4 are provided from microbial methanogenesis. Furthermore, the relatively low H_2 concentration (<200 μmol/kg) may be a signature that the thermogenic gases (CH_4, CO_2 and H_2) via the thermal degradation of organic matters are much less incorporated into the Iheya North hydrothermal fluids because the H_2 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 H_2 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 CH_4 can be affected not only at the time of the generation but also during the transportation in the hydrothermal fluids. The $\delta^{13}C_{CH4}$ value of the hydrothermal fluid CH_4 is potentially controlled by the carbon isotope equilibrium through the following chemical equilibrium:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O. \quad (2)$$
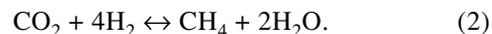
If full carbon isotope equilibrium of CH_4 with CO_2 ($\delta^{13}C_{CO2} = -10‰$) at the vent fluid temperature of 310°C is assumed, a $\delta^{13}C_{CH4}$ value in the Iheya North fluid should be higher than $-40‰$ (Horita, 2001). This assumption is clearly inconsistent with the observed $\delta^{13}C_{CH4}$ 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 H_2 concentration (McCollom, 2008). Thus the carbon isotope equilibrium between CH_4 and CO_2 would be negligible during the hydrothermal circulation after the CH_4 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 CH_4 (e.g., Konno *et al.*, 2006). Thus, the $\delta^{13}C_{CH4}$ values of the Iheya North hydrothermal fluid CH_4 would represent the stable isotopic information at the time of generation of CH_4 sources.

The δD value of CH_4 (δD_{CH4}) initially reflects the δD values of substrate (H_2O 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 δD_{CH4} values (Fig. 7: e.g., Schoell, 1980). However, all the δD_{CH4} values determined so far in the hydrothermal fluids including the Iheya North fluids have fallen into a narrow range ($-130 \sim -96‰$: 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 δD_{CH4} values of the hydrothermal fluid CH_4. The hydrogen isotope equilibrium between H_2O–H_2–CH_4 in the high temperatures fluids would be the most likely process. The isotope systematics could be described by two of the isotopic equilibria between H_2O–H_2 and H_2–CH_4, as seen in the δD_{H2} value via the rxn. 1

and a following isotope equilibrium reaction:

$$CH_4 + HD \leftrightarrow CH_3D + HH. \qquad (3)$$

If it is assumed that (or since) the isotopic equilibria proceed faster between H_2–H_2O than between CH_4–H_2 (complex reactions in detail) in the high temperatures hydrothermal fluids, the δD_{CH4} values of the hydrothermal fluid CH_4 can be calculated using the thermally equilibrated δD_{H2} values according to rxn. 3. Indeed, all the known δD_{CH4} range of hydrothermal fluid CH_4 is comparable to the thermal isotopic equilibrium range calculated from the fluid temperatures and the temperature-dependent isotope fractionation factors on the CH_4–H_2 and H_2–H_2O equilibriums (Horibe and Craig, 1995) assuming δD_{H2O} = +0‰ (Shanks III et al., 1995) (Fig. 7). This result suggests that the δD_{CH4} values of the hydrothermal fluid may be controlled by the hydrogen isotope equilibrium between H_2O–H_2–CH_4. Given that the hydrogen isotope equilibrium between CH_4 and H_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 δD_{CH4} values between a part of the proposed thermogenic range (Schoell, 1980) and the observed hydrothermal range (Fig. 7) was probably circumstantial because of similar δD_{CH4} values observed even in sediment-starved hydrothermal systems (Logatchev and EPR21°N: Welhan and Craig, 1983; Proskurowski et al., 2006). However, a difference among the observed hydrothermal δD_{CH4} values is small (~34‰) but significant (analytical errors of ~10‰) so that the other factors controlling the δD_{CH4} values than the isotopic equilibriums at endmember hydrothermal temperatures might be involved for hydrothermal δD_{CH4} values. In any cases, the use of δD_{CH4} 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 δD_{CH4} values and the biogenic δD_{CH4} range reported previously (Fig. 7: Schoell, 1980; Sugimoto and Wada, 1995; Valentine et al., 2004b) does not deny biogenic origin of methane in the Iheya North hydrothermal field.

Based on the compositional and isotopic properties of the hydrothermal fluid CH_4 and other gas components in the Iheya North field, it is very likely that most CH_4 should be produced by microbial methanogenesis prior to the high temperatures hydrothermal reaction probably utilizing H_2 and CO_2 which are provided from the sedimentary organic matters by functions of co-existing fermentative microorganisms. This generation model of hydrothermal fluid CH_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_4 concentrations in the fluids are similar with those in the Iheya North field while the higher H_2 concentrations (>1 mmol/kg) and more ^{13}C-enriched CH_4 ($\delta^{13}C$ = –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_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_4. However, it would be important to know where the CH_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_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_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 recharging areas hosting the hydrogenotrophic methanogenesis have been hypothesized to be either in the valley-filling deposits of

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 CH_4 emitting flux (F_{CH4}) by the discharging hydrothermal fluids using a following equation:

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

where [Conc.], [Area], [Vel.], [N_{vent}], and [L/H] represent the endmember concentration of CH_4, 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 CH_4 flux between diffusing hydrothermal fluids and high temperatures fluids, respectively. The [Conc.] is determined to be 3 [mmol/L]. The [Area] is estimated by the seafloor observation (~2 cm in radius of a vent orifice) to be 12 [cm^2]. The [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 [N_{vent}] is 5. The diffusing hydrothermal fluids are recognized to convect more than one order of magnitude greater than the high temperature fluids (Elderfield and Schultz, 1996). Since numerous diffusing 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 × 10^7 [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:

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

where the [Vol.] is the total valley-filling deposit volume, the [Density] is a density of the deposit and the [TOC] is a total organic carbon content of deposit. The [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 × 10^8 [m^3]. The [Density] and [TOC] are determined for the pumicious deposit obtained from the Central Valley and are 2 [g/cm^3] and ~1 × 10^{-5} [g/g], respectively. These values lead to C_{pot} of 5.23 ×10^8 [mol-CH_4].

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 (Monma *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 impractial assumptions: the whole organic carbons in the valley-filling deposits convert to CH_4 without any conversion to CO_2 and other inorganic and organic carbons and the whole produced CH_4 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 CH_4 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 CH_4, 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 CH_4 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 NH_4 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 δD_{CH4} values in hydrothermal fluids that the CH_4 produced at the recharge zone had initially shown δD_{CH4} value within biogenic range (−350‰–−250‰: Sugimoto and Wada, 1995; Valentine *et al.*, 2004b) and the hydrogen isotope exchanges among H_2O–H_2–CH_4 at high temperature reaction zone made the δD_{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 CH_4 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 CH_4 concentrations (1.8–3.4 mmol/kg), high C_1/C_2 ratios (449–539), highly ^{13}C-depleted CH_4 (–55.0~–48.4‰) and moderate H_2 concentrations (0.16–0.42 mmol/kg), are very comparable to those in the Iheya North field. However, Lilly *et al.* (1993) suggested that most of the hydrothermal fluid CH_4 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 CH_4 may be more strongly associated with the venting CH_4 at the Endeavour field. Our MMR model would be not only an implication for the generation and incorporation of hydrothermal fluid CH_4 in the deep-sea hydrothermal systems but also for those of cold seep CH_4 (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.

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