

## Gas geochemical characteristics of hydrothermal plumes at the HAKUREI and JADE vent sites, the Izena Cauldron, Okinawa Trough

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(Received July 14, 2009; Accepted June 4, 2010)

Hydrothermal plumes above the HAKUREI and JADE sites, two high-temperature hydrothermal vent sites in the Izena Cauldron at the mid-Okinawa Trough, were investigated in order to gain a preliminary understanding of gas geochemical characteristics at underlying hydrothermal vent sites. Three geochemical tracers, H<sub>2</sub>, CH<sub>4</sub> and δ<sup>3</sup>He, covary with each other above the HAKUREI site but only CH<sub>4</sub> and δ<sup>3</sup>He are correlated above the JADE site. The carbon isotope ratio of methane within the Izena Cauldron can be accounted by a combination of the fluid dilution by ambient seawater and microbial consumption with the kinetic carbon isotope effect (KIE) of 1.007. An estimated endmember δ<sup>13</sup>C value of -32‰ in the HAKUREI fluid was obtained. Both the plumes above the HAKUREI and JADE sites showed C<sub>1</sub>/C<sub>2</sub> ratios between 10<sup>3</sup>~10<sup>4</sup>. Only the bottom water around the HAKUREI site showed significant N<sub>2</sub>O excess with isotopically light δ<sup>15</sup>N and δ<sup>18</sup>O, suggesting N<sub>2</sub>O input from microbial activity in the sediment. A linear correlation between H<sub>2</sub> and CH<sub>4</sub> in the HAKUREI plume gives a H<sub>2</sub>/CH<sub>4</sub> ratio of the HAKUREI fluid of more than 0.022. The estimated H<sub>2</sub>/CH<sub>4</sub> ratio in the HAKUREI fluid is significantly higher than that of the JADE fluid, comparable with those of fluids venting at other sediment-related hydrothermal systems, and also comparable with those of thermogenic gases produced by hydrothermal sediment experiments. These facts suggest that fluid-sediment interaction during fluid upwelling appears to modify gas geochemical characteristics at the HAKUREI site but have little influence at the JADE site. This study demonstrates the availability of the Izena Cauldron hydrothermal field and the HAKUREI and JADE sites as a natural laboratory for investigating the fluid-sediment interaction during fluid upwelling.

Keywords: hydrothermal plume, gas geochemical characteristics, Okinawa Trough, H<sub>2</sub>/CH<sub>4</sub> ratio, fluid-sediment interaction

### INTRODUCTION

Hydrothermal fluid geochemistry in the Okinawa Trough backarc basin was first studied by the late Prof. Hitoshi Sakai and colleagues in 1989 at the JADE site in the Izena Cauldron (Sakai *et al.*, 1990a, b). Another six hydrothermal vent sites in the Okinawa Trough were found subsequently: CLAM (Gamo *et al.*, 1991), Minami-Ensei (Chiba *et al.*, 1993), Ihey North (Chiba *et al.*, 1996; Nakagawa *et al.*, 2005), Hatoma Knoll (Nakano *et al.*, 2001), Yonaguni Knoll IV (Kishida *et al.*, 2004; Konno *et al.*, 2006; Inagaki *et al.*, 2006; Hongo *et al.*, 2007; Suzuki *et al.*, 2008; Nunoura and Takai, 2009), and HAKUREI (Ishibashi *et al.*, 2009). A notable geological

feature of the Okinawa Trough is the existence of terrigenous sediment (Narita *et al.*, 1990), which is thought to affect the geochemical characteristics of the hydrothermal fluids (Gamo *et al.*, 1991; Gamo, 1995; Ishibashi *et al.*, 1995).

All the hydrothermal vents investigated in the Okinawa Trough demonstrated significantly elevated methane concentration of more than 1 mmol/kg with an isotopically light δ<sup>13</sup>C value lower than -20‰ (Sakai *et al.*, 1990a; Chiba *et al.*, 1993; Ishibashi *et al.*, 1995; Konno *et al.*, 2006; T. Toki, personal communication). High methane concentration with light δ<sup>13</sup>C values were also observed in several sediment-covered hydrothermal sites (e.g., Guaymas Basin, Welhan, 1988; Middle Valley, Cruse and Seewald, 2006) and unsedimented while sediment-influenced Endeavour site (Lilley *et al.*, 1993). In contrast to these "sediment-related" sites, sediment-starved sites generally show a methane concentration lower than 1 mmol/kg and/or δ<sup>13</sup>C values ranging from -20‰ to -5‰ (e.g., Welhan and Craig, 1983; Charlou *et al.*, 2002; Takai *et al.*, 2008; Kumagai *et al.*, 2008). The

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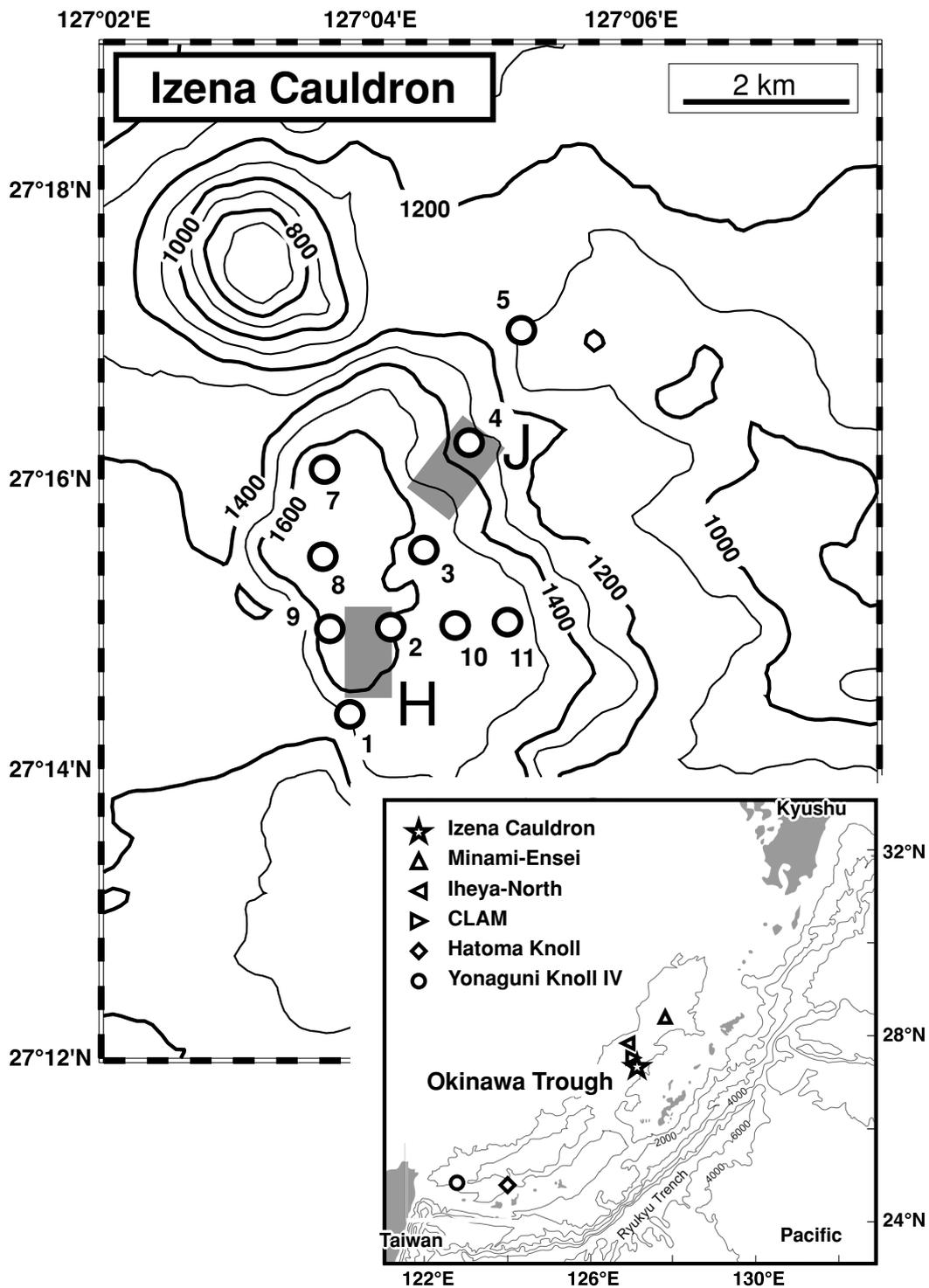


Fig. 1. Bathymetry maps of the Okinawa Trough (inset) and the Izena Cauldron. Hydrocast stations in this study are presented in the large map by open circles with station numbers. Gray squares indicate the location of the HAKUREI (H) and JADE (J) sites, respectively. The inset map shows the locations of the Izena Cauldron and the known hydrothermal sites in the Okinawa Trough (after Suzuki et al., 2008).

origin of the excess methane at sediment-related hydrothermal system was explained by methane production through thermal decomposition of sedimentary organic matter (e.g., Ishibashi *et al.*, 1995). Because of requirement of high temperature, thermal decomposition of sedimentary organic matter could occur at deep reaction zone and during fluid upwelling. Alternatively, microbial methanogenesis in low-temperature sediment environment during fluid recharge has also been discussed as the possible origin of isotopically light methane in vent fluids at sediment-related hydrothermal systems (Lilley *et al.*, 1993; Cruse and Seewald, 2006). Thus “sediment-derived methane” potentially represents both thermogenic and biogenic methane. To discuss the origin of the high methane concentration in sediment-related hydrothermal sites, information to distinguish these sediment-derived methane from each other is required.

The HAKUREI and JADE sites are located in the Izena Cauldron within 3 km of each other (Fig. 1) which suggests common hydrothermal characteristics at the deep root zones. A previous investigation by the ROV Hyper Dolphin in 2003 revealed almost same major composition (K, Ca, Si, and so on) between the HAKUREI and JADE fluids (Ishibashi *et al.*, 2009). In contrast, they have quite different sedimentary settings. Based on recent seismological observations during the R/V Kaiyo KY02-11 cruise, the HAKUREI site is covered by a sediment layer over 150 m in cover whereas little sediment layer, no more than several meters thickness, is found at the JADE site (Y. Nakamura, personal communication). The geological features indicate that thermogenic gas production during fluid upwelling is hypothesized to occur at the HAKUREI site but little at the JADE site; comparison of the gas geochemical fluid composition from these two sites is expected to show the influence of sedimentary processes on the HAKUREI fluids. The gas geochemistry of the venting fluid at the HAKUREI site, however, has not to date been investigated. In this study, because hydrothermal plume observations have been widely used in order to gain a preliminary understanding of gas geochemical characteristics at underlying hydrothermal vent sites (Jean-Baptiste *et al.*, 2004; Keir *et al.*, 2006; Love *et al.*, 2008; Kawagucci *et al.*, 2008), the gas geochemistry in the water column in the Izena Cauldron was investigated to understand the gas geochemical characteristics of the HAKUREI and JADE fluids.

## SAMPLING AND ANALYSES

### *Background of study sites*

The JADE hydrothermal site was located inside the north-eastern wall of the Izena Cauldron in the mid-Okinawa Trough backarc basin behind the Ryukyu arc-trench system (Fig. 1). The site has been the subject of

numerous studies to date (Halbach *et al.*, 1989; Sakai *et al.*, 1990a, b; Ishibashi *et al.*, 1995; Kinoshita and Yamano, 1997; Marumo and Hattori, 1999). A vigorous black smoker vent at 320°C was found at a depth of 1350 m, and active and inactive sulfide–sulfate chimneys and mounds were present around the black smoker vent at a depth of 1550 m to 1300 m. The HAKUREI site was studied in 2003 at the southern part of the bottom of the Izena Cauldron (Fig. 1) (Ishibashi *et al.*, 2009). Fluid at 326°C diffusing from a chimney structure was observed at a depth of ~1650 m that is 3 km from the “Black smoker vent” at the JADE site (Sakai *et al.*, 1990a). At the JADE site, direct fluid sampling using the submersible Shinkai 2000 and detailed geochemical analyses of the fluid were carried out in 1989 (Sakai *et al.*, 1990a, b; Ishibashi *et al.*, 1995) and methane in the water column was sampled in 1993 (Watanabe *et al.*, 1995).

### *Sampling*

A detailed plume survey in the Izena Cauldron was carried out during the R/V Tansei-maru KT-08-4 cruise in March 2008 by using a wired CTD-CMS (CTD-carousel multiple sampling system). The wired CTD-CMS used during the cruise consisted of a CTD (Model 9 Plus, Sea-Bird Electronics), a CMS (Carousel-32, Sea-Bird Electronics), 12 Niskin-X bottles (12-liter type, General Oceanics), a pinger (Benthos, model 2216), and a turbidity meter (Seapoint Sensors Inc.). The system can detect *in-situ* turbidity (hydrothermal) anomalies in the water column and simultaneously obtain hydrothermal plume water for onboard and onshore geochemical analyses. We carried out 10 hydrocasts in the Izena Cauldron at Stns. 1–11 (Stn. 6 was missed) (Fig. 1) and 1 hydrocast to the north of the cauldron (Stn. 12: 27°21' N, 127°08' E). Note that Stns. 2 and 4 were just above the HAKUREI and JADE hydrothermal vent sites, respectively.

### *Analyses*

The samples in the Niskin bottles were immediately subsampled into optimized bottles for various geochemical analyses. For reduced gases analyses, sample water from a Niskin bottle was directed to the bottom of a 120 mL glass vial with no air bubbles through a Teflon tube. The vial was allowed to overflow by 2 volumes before the tube was slowly withdrawn. After the addition of 0.5 mL HgCl<sub>2</sub>-saturated solution for poisoning, a Teflon-coated butyl-gum septum (for H<sub>2</sub> and CO analyses) or untreated butyl-gum septum (for CH<sub>4</sub> and N<sub>2</sub>O) were used to cap the vials. The duplicate vial samples were taken for each measurement (H<sub>2</sub>/CO and CH<sub>4</sub>/N<sub>2</sub>O). The vials were kept in a dark refrigerator (~5°C) until just prior to analysis.

Molecular hydrogen (H<sub>2</sub>) and carbon monoxide (CO) were analyzed onboard within six hours after subsampling

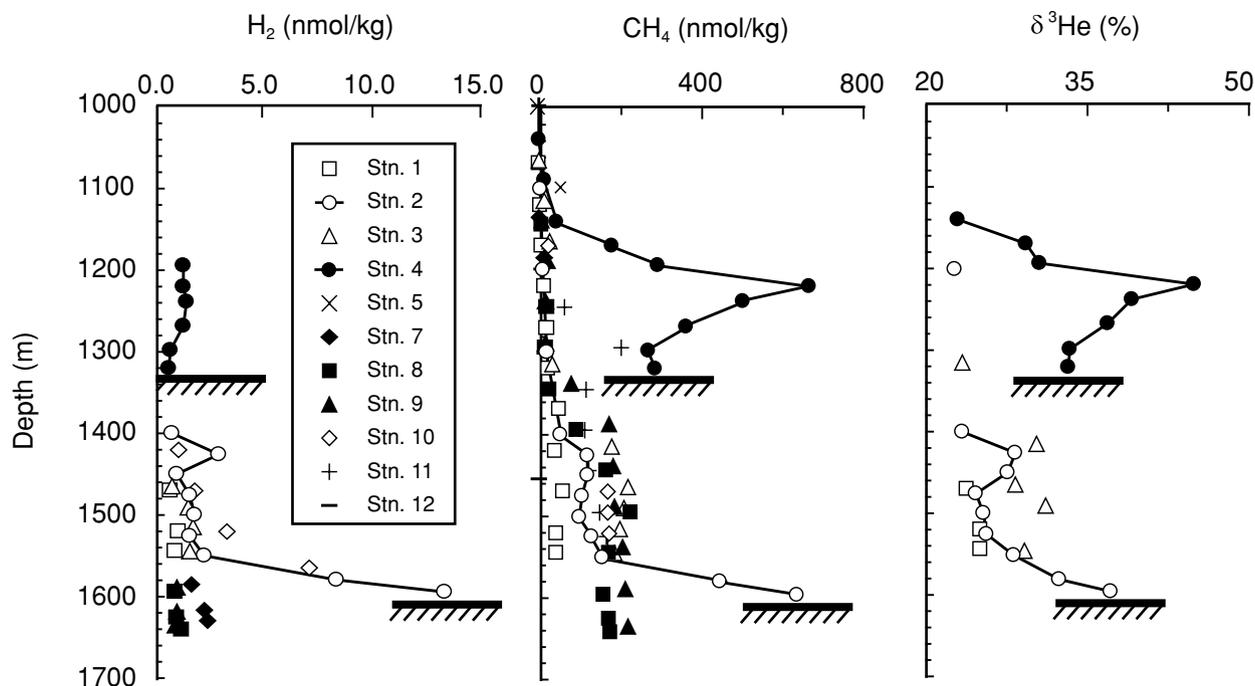


Fig. 2. Vertical profiles of  $H_2$  concentrations,  $CH_4$  concentrations, and  $\delta^3He$  values. Samples at Stn. 2 and Stn. 4 are connected by solid lines. Seafloor depths at Stn. 2 and Stn. 4 are also shown.

to avoid sample alteration during storage. To make head space in the vial, 20 mL of sample water was substituted by  $H_2$ - and  $CO$ -free air using gas-tight syringes; the vial was then shaken for 6 min. to achieve equilibrium between the dissolved and head space gases. An aliquot (4 mL) of the equilibrated headspace was taken by a gas-tight syringe and then 1.2 mL was injected into a gas chromatograph equipped with a trace reduced gas detector (TRD-1: Round Science Inc., Japan). Hydrogen and carbon monoxide were separated at  $50^\circ C$  on a 3 m column packed with Silicagel and subsequently at  $70^\circ C$  on a 3 m column packed with Molecular sieve 5A giving retention times of 4 min. and 12 min., respectively. Dissolved gas concentration is calculated from measured gas mixing ratio in the headspace using a solubility coefficient (Wiesenburg and Guinasso, 1979; Xie *et al.*, 2002). The overall analytical uncertainties and detection limits are examined respectively by repeated analyses of vials from a Niskin bottle and measurements of commercial gas standard with barometric dilution of the standard, and estimated for both gases as  $\pm 10\%$  and 0.5 nmol/kg.

At an onshore laboratory at Hokkaido University, Japan, the concentrations and carbon, nitrogen, and oxygen isotope ratios of methane ( $CH_4$ ), nitrous oxide ( $N_2O$ ), and ethane ( $C_2H_6$ ) were simultaneously determined from one sample vial. The measurement consisted of a combination of purge-and-trap technique, continuous-flow iso-

tope ratio mass spectrometry, a gas chromatograph (HP6850), and an isotope ratio mass spectrometer (Finnigan MAT252) (Tsunogai *et al.*, 2000, 2008). The stable carbon, nitrogen, and oxygen isotope ratios are presented in the standard delta-notation in the permil scale with respect to Vienna-PDB, Air, and Vienna-SMOW, respectively. Analytical errors ( $1\sigma$ ) of concentrations and  $\delta^{13}C$  for methane are estimated as 5% and 0.2‰, respectively.

Samples for the helium isotope ratio were transferred from a Niskin bottle into  $\sim 20$  mL copper-tubing storage containers without exposure to atmosphere. At an onshore laboratory of the Ocean Research Institute at the University of Tokyo, dissolved gas in the sample water was extracted into a stainless steel vacuum line. After the helium in the exsolved gases was purified using hot titanium-zirconium getters and charcoal traps held at liquid nitrogen temperature and 40K, the  $^3He/^4He$  ratios were measured by a conventional noble-gas mass spectrometer (Helix-SFT, GV Instruments) (Sano and Wakita, 1988; Takahata *et al.*, 2004; Takahata *et al.*, this issue, *Geochemical Advances: Following Prof. Sakai*, 2010). The observed  $^3He/^4He$  ratios are presented by delta notation of  $\delta^3He = \{ (^3He/^4He)_{seawater} / R_{atm} - 1 \} \times 100$ , where  $R_{atm}$  is the atmospheric ratio of  $1.39 \times 10^6$  (Lupton, 1998). Parts of  $\delta^3He$  values (Stn. 2) have been presented elsewhere (Lan *et al.*, 2009).

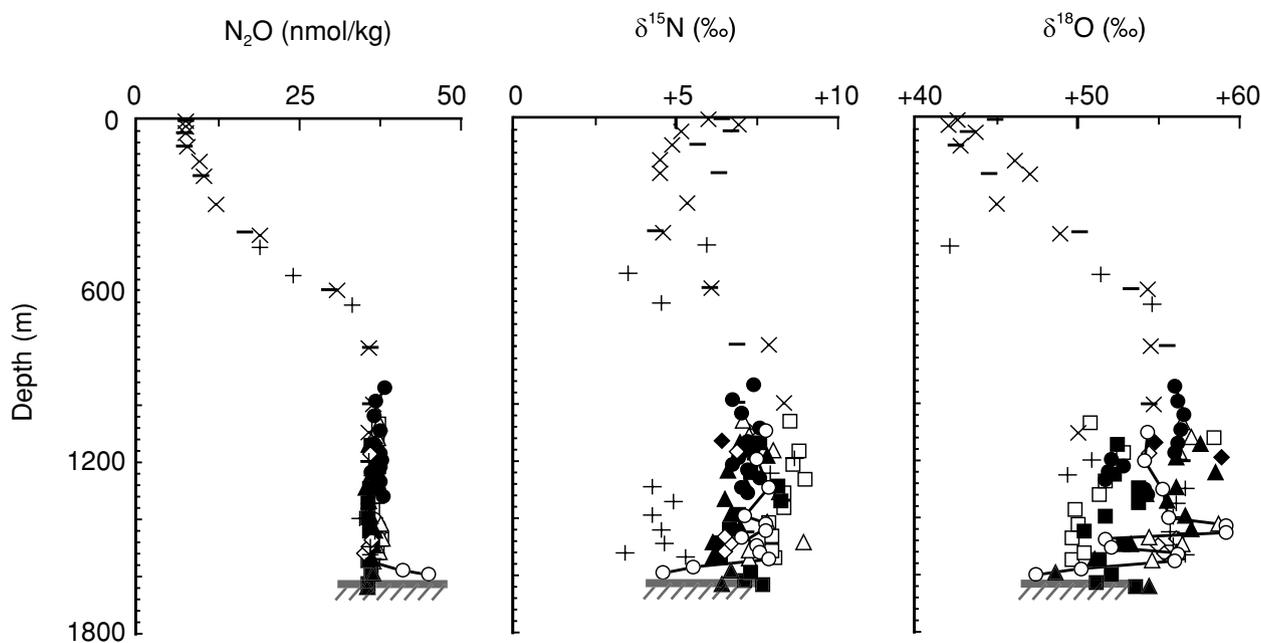


Fig. 3. Vertical profiles of  $N_2O$  concentrations and their nitrogen and oxygen isotope ratios. Samples at Stn. 2 are connected by solid lines. A seafloor depth at Stn. 2 is also shown.

## RESULTS

Vertical profiles of the  $H_2$  concentrations,  $CH_4$  concentrations, and  $\delta^3He$  values below a 1000 m depth are presented in Fig. 2. Methane concentrations higher than 10 nmol/kg were observed at all the stations 1–11 below 1100 m depth, which is the approximate depth of the cauldron's edge (Fig. 1). This fact suggests that the hydrothermal signature expanded entirely through the Izena Cauldron. At Stn. 2 (Fig. 1), the vertical profiles of  $H_2$ ,  $CH_4$ , and  $\delta^3He$  demonstrate strong peaks near the seafloor (1595 m depth) (Fig. 2). These trends imply diffusive hydrothermal fluid venting from the seafloor which is consistent with hydrothermal fluid diffusing from the chimney structure at the HAKUREI site. The  $H_2$  concentration reached 13.4 nmol/kg. Because  $^3He$  is inert against any chemical and biological processes while  $H_2$  and  $CH_4$  can be consumed by aerobic microbial activity in plumes, the observed covariation among the  $H_2$  concentrations,  $CH_4$  concentrations and  $\delta^3He$  values at Stn. 2 (Fig. 2) suggests a dominance of two endmember mixing controlling their behavior in the plume rather than *in-situ* biological alteration. At Stn. 4 (Fig. 1), the  $CH_4$  concentrations and  $\delta^3He$  values show strong positive anomalies at a depth of around 1220 m, while the  $H_2$  concentrations show only a slight peak relative to that at Stn. 2 (Fig. 2). The plume center depth, at ~110 m above the seafloor (Figs. 1 and 2), is similar to that previously observed above the JADE site (Watanabe *et al.*, 1995), consistent

with vigorous upward venting. The highest  $\delta^3He$  of 44.9% was observed at Stn. 4, indicating more magmatic volatile-enriched composition than Stn. 2, although  $CH_4/\delta^3He$  and  $H_2/\delta^3He$  ratios at Stn. 4 were lower than those at Stn. 2. Through out the Izena Cauldron, carbon monoxide was not detectable ( $<0.5$  nmol/kg); therefore the  $CO/CH_4$  ratio is less than  $10^{-3}$ . In addition, detectable amounts of  $C_2H_6$  (~0.2 nmol/kg) were observed at both Stn. 2 and Stn. 4 at methane peak depths, resulting in  $C_1/C_2$  ratios between  $10^3\sim 10^4$ .

Vertical profiles of the  $N_2O$  concentration, and  $\delta^{15}N$  and  $\delta^{18}O$  values from the sea surface to the seafloor are presented in Fig. 3. The  $N_2O$  concentration gradually increases from the sea surface to a depth of about 1000 m, and is constant at ~37 nmol/kg below 1000 m depth, with almost constant  $\delta^{15}N$  and  $\delta^{18}O$  values of ~+7.5‰ and ~+53‰, respectively (Fig. 3). It is of note that only the bottom water at Stn. 2 shows a significant positive anomaly in  $N_2O$  concentration up to 45 nmol/kg with isotopically light  $\delta^{15}N$  and  $\delta^{18}O$  signatures (Fig. 3) whereas isotopically light  $N_2O$  without concentration anomaly was observed at Stn. 11.

The methane concentration and its carbon isotope ratio are presented on a correlation plot between inverse concentration and the isotope ratio, the so-called Keeling plot (Fig. 4) (Keeling, 1958). On the Keeling plot, linear distribution indicates a simple two endmember mixing whereas a logarithmic curve results from the kinetic isotope effect upon microbial consumption. At full

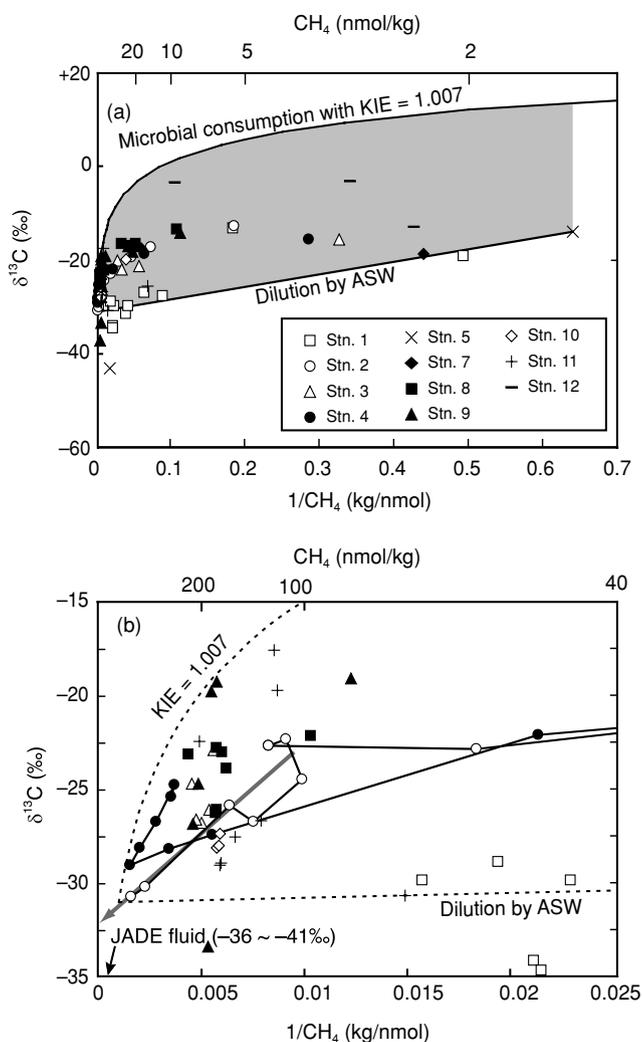


Fig. 4. Keeling plots for methane concentrations and carbon isotope ratios are presented at (a) full concentration range and (b) higher concentration range, respectively. Samples from Stn. 2 and Stn. 4 in (b) are respectively connected by solid lines in depth order. Solid straight lines and curves respectively represent a dilution by ambient seawater (ASW) and microbial consumption at  $KIE = 1.007$  for a methane concentration of 1000 nmol/kg with  $\delta^{13}C = -31\text{‰}$ . Gray zone in (a) indicates a range that possibly occurred during a mixing of fresh fluid, aged plume, and ambient seawater. The gray arrow in (b) indicates a probable endmember  $\delta^{13}C$  value of the HAKUREI fluid (see text).

concentration range (Fig. 4a), the observed methane distribution is non-linear. This suggests that the carbon isotope composition of methane in the Izena Cauldron water was controlled not only by a simple mixing between hydrothermal fluid and ambient water (1000 m depth at Stn. 5 in this study, Fig. 1), but also a kinetic isotope effect on microbial methane consumption in the plumes and

a complicated mixing of fresh hydrothermal fluid, aged plume, and ambient seawater. Assuming microbial methane consumption in a closed system at an initial composition of  $[CH_4] = 1000$  nmol/kg and  $\delta^{13}C = -31\text{‰}$ , which is similar to those in the highest methane concentration samples at Stns. 2 and 4 (Fig. 4b), almost all the methane we observed could be explained by a combination of the plume dilution by ambient seawater and a kinetic carbon isotope effect (KIE) of 1.007. The KIE of 1.007 is slightly higher, but comparable with those determined by previous plume observations in the Myojin Knoll Caldera hydrothermal field ( $1.005 \pm 0.001$ : Tsunogai *et al.*, 2000), the Yonaguni Knoll IV hydrothermal field (1.005 and 1.012: Gamo *et al.*, this issue, *Geochemical Advances: Following Prof. Sakai*, 2010), and the East Pacific Rise 27.5°–32.5°S area (1.004~1.006: Gharib *et al.*, 2005). Parts of samples at Stns. 1 and 9 seem to show more  $^{13}C$ -depleted methane than those at other stations (Fig. 4), implying an additional methane source outside of the HAKUREI site at the southwest side of the cauldron (Fig. 1). Methane at Stn. 5 also shows  $^{13}C$ -depleted methane, implying a possible methane source near the station.

## DISCUSSION

### Excess $N_2O$

A notable excess of  $N_2O$  was observed in the hydrothermal plume at Stn. 2 (Fig. 3). A positive anomaly of  $N_2O$  concentration together with the positive anomalies of  $CH_4$  and  $\delta^3He$  (Fig. 2) implies a vent fluid origin for the excess  $N_2O$ . The plume at Stn. 4, however, showed no anomaly in  $N_2O$  concentration in spite of more magmatic volatile-enriched composition demonstrated by  $\delta^3He$  values, suggesting  $N_2O$  sources other than magmatic input. Strong redox gradient at around hydrothermal vent orifice is favorable for both nitrification and denitrification that produces  $N_2O$ . Excess  $N_2O$  was also observed in hydrothermal fluid observed at the Galapagos Spreading Centre and thought to result from microbial denitrification at hydrothermal ecosystem (Lilley *et al.*, 1982). Moreover, even when hydrothermalism is absent, microbial denitrification in the sediment produce  $N_2O$  (e.g., Usui *et al.*, 1998; Laverman *et al.*, 2007) and could result in positive  $N_2O$  concentration anomaly in bottom water. These facts suggest that biological  $N_2O$  production likely account for the  $N_2O$  excess observed at Stn. 2. Although Keeling plot analyses (Keeling, 1958) for the plume dataset provides estimated endmember  $\delta^{15}N$  and  $\delta^{18}O$  values respectively of  $-8\text{‰}$  and  $+17\text{‰}$  for the  $N_2O$  source at Stn. 2, several possible N-substrates ( $NH_4^+$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $NH_2OH$ , and Org-N) and variable isotope fractionation factors on microbial metabolisms (e.g., Sutka *et al.*, 2006) limit further discussion about the  $N_2O$  source using stable isotopes. On the other hand, past ex-

periments revealed that thermal decomposition of sedimentary organic matter release N compound mainly as ammonium but  $N_2O$  was not investigated (Seewald *et al.*, 1990, 1994); thus fluid-sediment interaction during fluid upwelling at the HAKUREI site cannot be ruled out as a possible  $N_2O$  source.

#### Carbon isotope ratio in endmember fluid

The methane in the plume at Stn. 2 (HAKUREI plume) and Stn. 4 (JADE plume) are presented on the Keeling plot with data points connected in order of depth by solid lines (Fig. 4b). A Keeling plot analysis provides an estimated endmember  $\delta^{13}C$  value of the methane source as an extrapolated y-intercept of a mixing line through plume samples. The methane in the HAKUREI plume at concentrations  $>100$  nmol/kg seemed to show a linear trend (gray arrow in Fig. 4b). The y-intercept of this line, at  $-32\text{‰}$ , can be regarded as the endmember value of the HAKUREI fluid. In contrast, methane in the JADE plume has two linear trends. The samples collected above the depth of the highest methane concentration, and those collected below followed separate trends (Figs. 2 and 4b). These separate trends were likely derived from geographical settings (Fig. 1) that the shallower part was ventilated with ambient seawater outside of the Cauldron while the deeper part was surrounded by inside wall of the Cauldron and inhibited to mixing with fresh ambient seawater. Thus the shallower portion was mixed and diluted more with ambient seawater while the deeper portion would be mixed with aged plume at the Cauldron bottom which had  $^{13}C$ -enriched methane due to microbial consumption. The linear trends of the shallower and deeper samples seemed to be directed to the y-intercept at around  $-29\text{‰}$ – $-31\text{‰}$  (Fig. 4b).

The estimated endmember  $\delta^{13}C$  values of the HAKUREI and JADE plumes is more  $^{13}C$ -depleted than that in the Yonaguni Knoll fluid ( $\sim -27\text{‰}$ ; Konno *et al.*, 2006), slightly  $^{13}C$ -enriched than those of  $^3He$ -rich natural gases in north-east Japan ( $\delta^{13}C = \sim -35\text{‰}$ , Wakita and Sano, 1983; Wakita *et al.*, 1990). Notably, the estimated endmember  $\delta^{13}C$  values of the JADE plumes ( $-29\text{‰}$ – $-31\text{‰}$ ) are more enriched than those previously observed in the JADE fluid ( $-36\text{‰}$ – $-41\text{‰}$ ; Ishibashi *et al.*, 1995). If the endmember  $\delta^{13}C$  value in the JADE fluid has been constant for last two decades, the more enriched  $\delta^{13}C$  value in the JADE plume would be accounted by microbial consumption in the plume. Moreover, the estimated endmember  $\delta^{13}C$  value for the HAKUREI fluid ( $-32\text{‰}$ ) was also enriched than that in the JADE fluid. Although microbial contribution accounts for the  $\delta^{13}C$  value in the HAKUREI plume as well as that in the JADE plume, the enriched  $\delta^{13}C$  value in the estimated endmember HAKUREI fluid can be also derived from involvement of isotopically heavy methane from the fluid-sediment

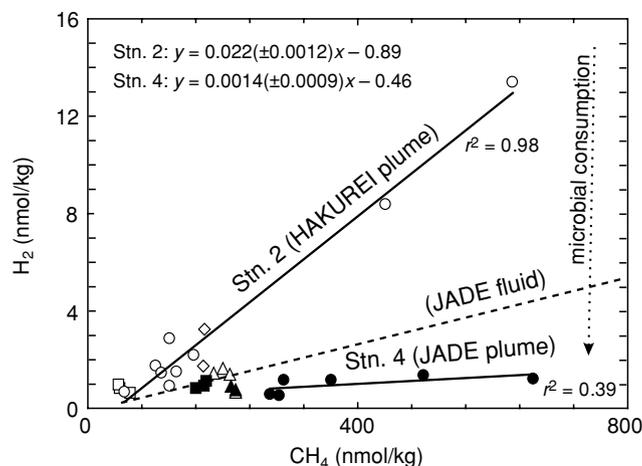


Fig. 5. A correlation plot between  $H_2$  and  $CH_4$ . The symbols are the same as in Fig. 2. Least-square regressions are respectively shown for the samples at Stn. 2 (open circle) and Stn. 4 (solid circle) with equations and  $r^2$  values. A  $H_2/CH_4$  of 0.007 observed in the JADE fluid in 1989 (Ishibashi *et al.*, 1995) is also presented by a dashed-line.

interaction ( $\sim -23\text{‰}$ ; Seewald *et al.*, 1994) into upwelling fluid, which has  $\delta^{13}C$  value as low as that observed in the JADE fluid ( $-36\text{‰}$ – $-41\text{‰}$ ). Alternatively, temporal change of the endmember  $\delta^{13}C$  value in the JADE fluid for last decades is also possible (e.g., Proskurowski *et al.*, 2008). If the  $\delta^{13}C$  value in the JADE fluid at 2008 is similar to those estimated from our plume observation, involvement of plume alteration and fluid-sediment interaction is not required to explain the plume data.

#### $H_2/CH_4$ ratio

The correlation between the  $H_2$  and  $CH_4$  concentrations in the HAKUREI plume is linear ( $r^2 = 0.98$ ) (Fig. 5). The slope of the least square linear regression (Fig. 5), which can be regarded as the  $H_2/CH_4$  ratio of the HAKUREI plume, is  $0.022 \pm 0.0012$  ( $1\sigma$ ). A similar estimate for the JADE plume yields an estimated  $H_2/CH_4$  ratio of  $0.0014 \pm 0.0009$  ( $1\sigma$ ). The  $H_2/CH_4$  ratios observed in the plumes, however, cannot be directly regarded as those of venting fluid from the underlying hydrothermal sites because of possible  $H_2/CH_4$  ratio alteration in the water column. Among other possible processes, aerobic microbial activity consuming  $H_2$  and  $CH_4$  would likely dominate  $H_2/CH_4$  ratio change (Kadko *et al.*, 1990; McLaughlin-West *et al.*, 1999; Punshon *et al.*, 2007).  $H_2$  can be rapidly consumed by microbes over a timescale of a day (Kadko *et al.*, 1990; McLaughlin-West *et al.*, 1999; Punshon *et al.*, 2007) compared with that of more than a week for methanotrophs (Kadko *et al.*, 1990; Watanabe *et al.*, 1995; Cowen *et al.*, 2002), resulting in decrease of

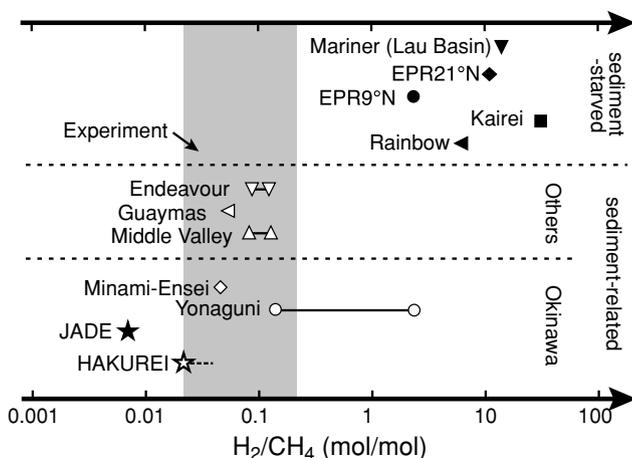


Fig. 6. Comparison of  $H_2/CH_4$  ratios among selected hydrothermal sites. An x-axis  $H_2/CH_4$  ratio is presented in log-scale. The gray zone represents a range of results from hydrothermal experiments using the sediment from the Guaymas Basin (Seewald *et al.*, 1994). Data are from the literature as follows: Mariner, Takai *et al.*, 2008; EPR21°N, Welhan and Craig, 1983; EPR9°N, Proskurowski *et al.*, 2008; Kairei, Kumagai *et al.*, 2008; Rainbow, Charlou *et al.*, 2002; Endeavour, Lilley *et al.*, 1993; Guaymas, McCollom, 2008; Middle Valley, Cruse and Seewald, 2006; Minami-Ensei, Chiba *et al.*, 1993; Yonaguni, Konno *et al.*, 2006; JADE, Ishibashi *et al.*, 1995.

$H_2/CH_4$  ratio. Oceanic processes which produce  $H_2$ , including photo-degradation of colored dissolved organic matter (Punshon and Moore, 2008a) and nitrogen fixation (Punshon and Moore, 2008b), are unlikely in the dark and nutrient-enriched deep sea environment. Thus, the  $H_2/CH_4$  ratio should steadily decrease after fluid emerges from the seafloor. This fact suggests that the  $H_2/CH_4$  ratio of the HAKUREI fluid should be no lower than that of the HAKUREI plume of 0.022. The lower  $H_2/CH_4$  ratio of the JADE plume (0.0014) than the JADE fluid observed in 1989 (0.007) can be also explained by microbial activity in water column while possible temporal change of  $H_2/CH_4$  ratio in endmember fluid at the JADE site can be not ruled out.

The  $H_2/CH_4$  ratios at the HAKUREI site (estimated from plume data) and other hydrothermal sites (observed in vent fluid) are presented along with results of hydrothermal experiment (Seewald *et al.*, 1994) in Fig. 6. The estimated  $H_2/CH_4$  ratio of the HAKUREI fluid (0.022) is significantly lower than those of sediment-starved hydrothermal sites ( $>1$ , Welhan and Craig, 1983; Charlou *et al.*, 2002; Kumagai *et al.*, 2008; Proskurowski *et al.*, 2008; Takai *et al.*, 2008) that correspond to abiotic gas. Notably, the  $H_2/CH_4$  ratio of the HAKUREI fluid was comparable with those of thermogenic gases produced by hydrothermal experiment using the Guaymas Basin sediment

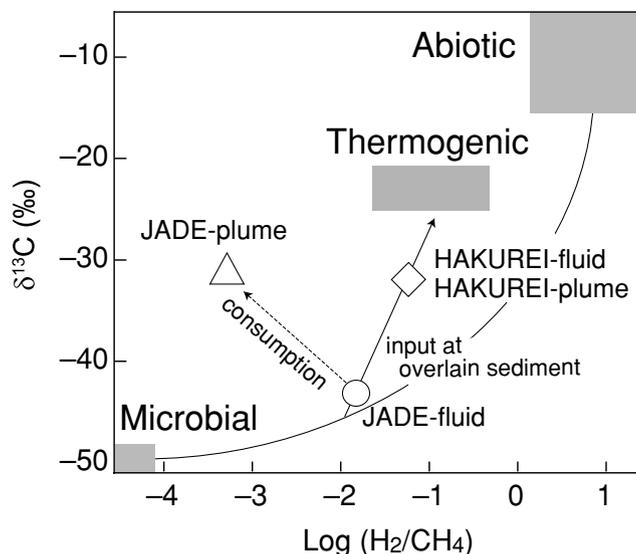


Fig. 7. Schematic illustration of gas geochemical characteristics at Izena Cauldron. Open circle, diamond, triangle represents the JADE fluid, the HAKUREI fluid (also plume), and the JADE plume, respectively. Each gray square represents approximate ranges of endmember composition from abiotic, thermogenic, and microbial processes. A curve represents possible composition of a deep subseafloor fluid resulted from microbial and abiotic inputs at hydrothermal recharge and reaction zones. An arrow represents thermogenic input during fluid upwelling at overlain sediment. A dashed arrow represents microbial consumption in water column.

(0.02~0.2; Seewald *et al.*, 1994) as well as other sediment-related hydrothermal sites (Fig. 6) (Chiba *et al.*, 1993; Lilley *et al.*, 1993; Cruse and Seewald, 2006; McCollom, 2008). This thermogenic signature at the HAKUREI site is consistent with the thick layer of sediment present. Alternatively, the  $H_2/CH_4$  ratio in the JADE fluid (0.007; Ishibashi *et al.*, 1995) is lower than thermogenic range (Fig. 6). The low  $H_2/CH_4$  ratio in the JADE fluid would result from involvement of microbial methanogenesis at recharge zone (Lilley *et al.*, 1993; Cruse and Seewald, 2006) that provides  $CH_4$  with little  $H_2$ .

#### Gas biogeochemistry at the Izena Cauldron

Gas characteristics in hydrothermal plumes at the Izena Cauldron we observed can be consistently explained by following processes (Fig. 7). Microbial methane input at recharge zone ( $H_2/CH_4 \ll 0.02$ ,  $\delta^{13}C = \sim -50\text{‰}$ ) and abiotic  $H_2$ ,  $CH_4$ , and  $^3He$  input at reaction zone ( $H_2/CH_4 > 1$ ,  $\delta^{13}C = \sim -10\text{‰}$ ) results in gas geochemical composition of a deep subseafloor fluid prior to upwelling as  $H_2/CH_4 < 0.007$  and  $\delta^{13}C = -41 \sim -36\text{‰}$ . Then significant thermogenic gas input ( $H_2/CH_4 = 0.02 \sim 0.2$ ,  $\delta^{13}C = -23\text{‰}$ )

during fluid upwelling at the HAKUREI site induces an increase of  $H_2/CH_4$  ratio to 0.022 and  $\delta^{13}C$  value to  $-32\text{‰}$ , whereas little thermogenic input during fluid upwelling at the JADE site results in gas geochemical characteristics in vent fluid as same as that in the fluid before upwelling. Microbial consumption in the JADE plume decreases  $H_2/CH_4$  ratio to 0.0014 and enriches  $\delta^{13}C$  value to  $-29\text{‰}\sim-31\text{‰}$ . Higher  $CH_4/\delta^3He$  and  $H_2/\delta^3He$  ratios in the HAKUREI plume compared to those in the JADE plume (Fig. 2) are accounted by a combination of thermogenic gas input at the HAKUREI site and microbial consumption in the JADE plume. Although lacks of  $H_2$  and  $CH_4$  concentrations in the HAKUREI fluid inhibits mass-balance consideration among these parameters, the model (Fig. 7) can quasi-quantitatively describe the plume observation at the Izena Cauldron.

### CONCLUDING REMARKS

We carried out an observation of the HAKUREI plume and gained a preliminary understanding of gas geochemical characteristics of the HAKUREI fluid. Although the HAKUREI and JADE sites are located within 3 km distance, which suggests common hydrothermal characteristics at the deep root zones, significant differences were found. Fluid-sediment interaction during fluid upwelling appears to modify gas geochemical characteristics at the HAKUREI site but have little influence at the JADE site. This study demonstrates the availability of the Izena Cauldron hydrothermal field, the HAKUREI and JADE sites, as a natural laboratory for investigating the fluid-sediment interaction during fluid upwelling. At present, however, we cannot deduce further details of the underlying fluid geochemistry due to limitation of sample collection using the CTD-CMS. Direct gas tight sampling using submersibles or ROVs and subsequent gas analyses of nearly endmember vent fluids at both the HAKUREI and JADE sites will provide further details of the gas geochemical differences between the sites. Ocean drilling near the HAKUREI site and fluid sampling beneath the 150 m sediment layer would enable us to compare fluid geochemistry between the venting fluid and a fluid not modified by the fluid-sediment interaction during upwelling, thus revealing the net impact of the fluid-sediment interaction on fluid geochemistry.

In summary, our observation revealed the following:

- Strong hydrothermal plumes accompanied with positive anomalies in  $H_2$ ,  $CH_4$ , and  $\delta^3He$  were observed just above the HAKUREI and JADE sites. The  $H_2$  concentration reached 13.4 nmol/kg, whereas carbon monoxide was not detectable ( $<0.5$  nmol/kg). The  $C_1/C_2$  ratio ranged between  $10^3\sim 10^4$ .
- The nitrous oxide concentration below 1000 m within the Izena Cauldron is generally constant at  $\sim 37$

nmol/kg with  $\delta^{15}N$  and  $\delta^{18}O$  values of  $\sim +7.5\text{‰}$  and  $\sim +53\text{‰}$ , respectively. Bottom water around the HAKUREI site, however, did show a significant positive anomaly in the  $N_2O$  concentration with isotopically light  $\delta^{15}N$  and  $\delta^{18}O$  values. The estimated endmember  $\delta^{15}N$  and  $\delta^{18}O$  values for the anomalously enriched  $N_2O$  are  $-8\text{‰}$  and  $+17\text{‰}$ , respectively. The anomaly is likely accounted by microbial activity in the sediment, although  $N_2O$  production through a fluid-sediment interaction during fluid upwelling cannot be ruled out.

- The carbon isotope ratio of methane within the Izena Cauldron can be explained by a combination of the plume dilution by ambient seawater and the kinetic carbon isotope effect (KIE) of 1.007. The Keeling plot analysis provides an estimated endmember  $\delta^{13}C$  value of the HAKUREI fluid of  $-32\text{‰}$ .

- A linear correlation between  $H_2$  and  $CH_4$  at Stn. 2 provided a  $H_2/CH_4$  ratio of the HAKUREI fluid of more than 0.022. The  $H_2/CH_4$  ratio in the HAKUREI fluid was significantly higher than that of the JADE fluid, comparable with those of venting fluids at sediment-influenced hydrothermal systems, and also comparable with those of thermogenic gases produced by hydrothermal sediment experiments. These facts suggest that fluid-sediment interaction during fluid upwelling appears to modify gas geochemical characteristics at the HAKUREI site but have little influence at the JADE site.

**Acknowledgments**—We are grateful to the captain, crew, and onboard scientists of the KT-08-4 cruise of R/V Tansei-maru for their support. Comments from Drs. Hattori, Leybourne, and Love improve the manuscript. This research was supported by a Ministry of Education, Culture, Sports, Science and Technology Grant-in-Aid for Scientific Research (Nos. 16204045, 19253006, and 17101001) 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).

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