

## Diversity of fluid geochemistry affected by processes during fluid upwelling in active hydrothermal fields in the Izena Hole, the middle Okinawa Trough back-arc basin

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Two active hydrothermal fields, Jade and Hakurei fields have been discovered within the Izena Hole, a rectangular 6 km × 3 km shape depression located in the middle Okinawa Trough back arc basin. In both fields, intense hydrothermal activity is represented by venting of high-temperature fluid (>300°C) and occurrence of sulfide/sulfate ore deposits. We collected hydrothermal fluids during dive expeditions of ROV *Hyper Dolphin* conducted in 2003, 2010 and 2011, in order to analyze both elemental and gas species. The geochemistry of high temperature hydrothermal fluids collected from the Jade and Hakurei fields is very similar to each other with exceptions in minor gas composition. Little temporal variation was observed in geochemistry of the high-temperature hydrothermal fluid of the Jade field over two decades, since a previous study carried out in 1989. These results suggest that these fluids are derived from a common fluid reservoir where fluid chemistry is basically controlled by fluid-mineral equilibria and gas species are dominantly contributed from the same magma. Venting of low temperature fluid (about 104°C) was discovered in the distal part of the Jade field, which was named as the Biwako vent. Chemical composition of the Biwako vent fluid was distinctive from that of the high temperature fluid in the proximal part of the Jade field, and could not be explained by simple dilution or cooling. This intra-field chemical diversity could be caused by phase separation and segregation during fluid upwelling, based on relationships in concentrations of Cl and major cations. On the other hand, the chemical diversity recognized in minor gas composition between the Jade and Hakurei fields is in accordance with results from previous plume survey. Difference in concentrations of minor gases such as H<sub>2</sub> is attributed to contribution from thermal degradation of organic matter in the sediment, during fluid upwelling.

Keywords: hydrothermal fluid circulation system, phase separation, fluid-sediment interactions, magmatic volatiles, thermal decomposition of organic matter, Okinawa Through

### INTRODUCTION

Since discovery of high temperature fluid venting from the seafloor more than 35 years ago, numerous studies have established the key processes controlling fluid chemistry during fluid circulation beneath the seafloor (e.g.,

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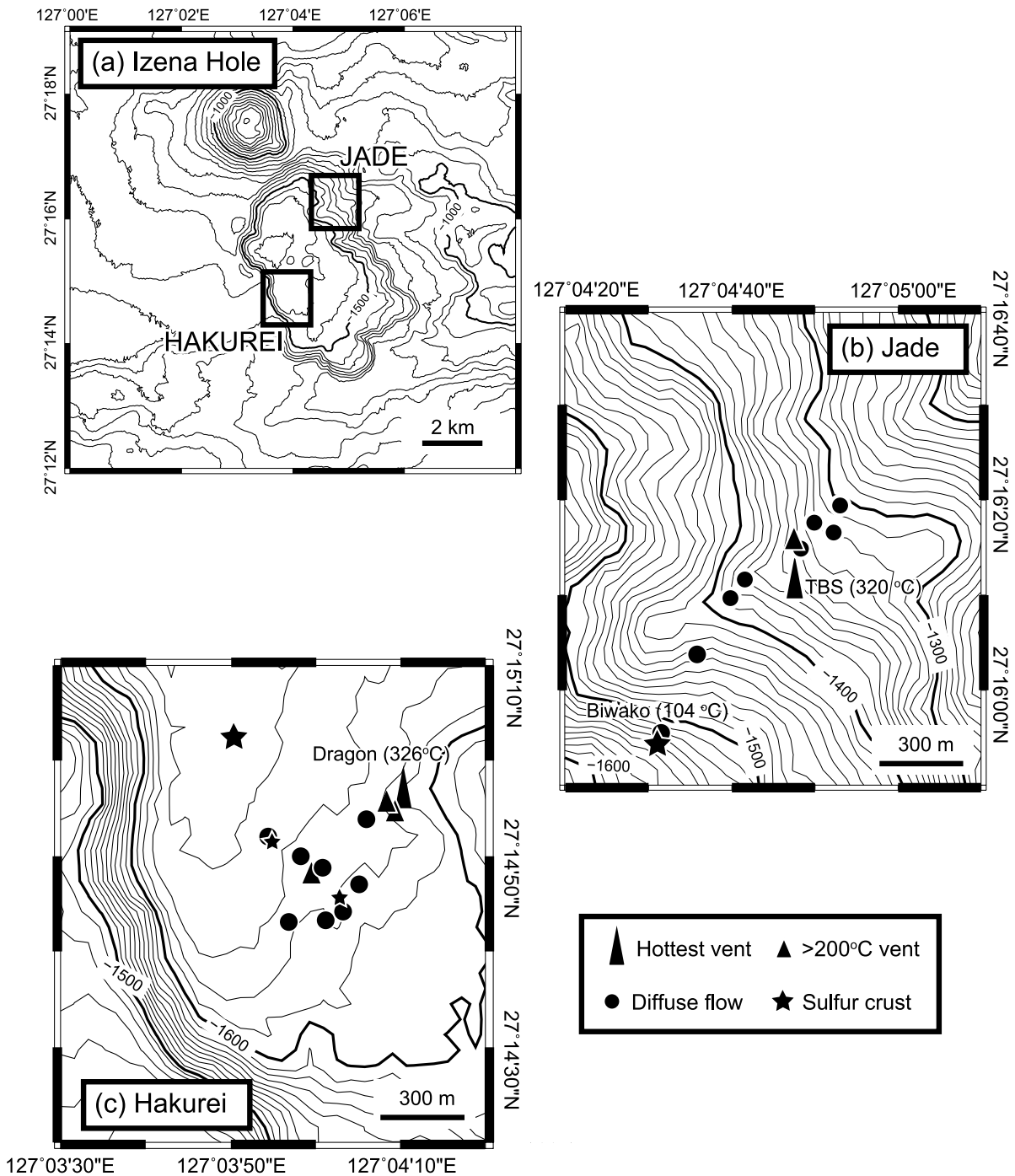


Fig. 1. Topographic maps of the Izena Hole (a), the Jade hydrothermal field (b), and the Hakurei hydrothermal field (c).

Butterfield *et al.*, 2003; German and Von Damm, 2004; Tivey, 2007). Cold seawater penetrating into the subsurface is altered significantly by chemical and microbial processes within crust and/or sediment at the fluid recharge stage (e.g., Tivey, 2007; Kawagucci *et al.*, 2011). High temperature fluid-mineral interactions at the reaction zone primarily constrain chemical characteristics of

venting fluid (e.g., Seyfried, 1987). In addition, processes during fluid upwelling at the discharge stage also impact on fluid chemistry (e.g., Proskurowski *et al.*, 2008).

Fluid chemistry of hydrothermal systems in the Okinawa Trough back-arc basin has been characterized by enrichment in  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{NH}_4^+$ , and K compared with those in typical sediment-free Mid Ocean Ridge (MOR)

hydrothermal fluids (Sakai *et al.*, 1990a; Gamo *et al.*, 1991; Ishibashi *et al.*, 1995; Konno *et al.*, 2006; Suzuki *et al.*, 2008; Kawagucci *et al.*, 2011, 2013). The difference in fluid chemistry has been related to the tectonic setting of rifting in the continental margin and fluid interactions with thick terrigenous/volcanic sediments on the seafloor (Gamo *et al.*, 2006). Moreover, a recent study pointed out compositional and/or isotopic variations among hydrothermal fluids collected from the Okinawa Trough, especially for species associated with fluid-sediment interactions such as H<sub>2</sub>, CH<sub>4</sub>, and Sr (Kawagucci *et al.*, 2013). As demonstrated in these previous studies, chemical processes across the entire sub-seafloor fluid circulation system control the fluid chemistry of hydrothermal fields in sediment-rich environments.

The Izena Hole is a rectangular shape depression with a size of about 6 km × 3 km (Fig. 1), which is located in the middle Okinawa Trough. Two active hydrothermal fields, Jade field and Hakurei field have been discovered in the Izena Hole. In both fields, hydrothermal activities were associated with venting of high-temperature (>300°C) fluid and abundant occurrence of sulfide/sulfate ore deposits. The Jade field is located at an inside slope of the northeastern wall of the Izena Hole (Fig. 1). Since its discovery in 1988 (Halbach *et al.*, 1989, 1993), the Jade field has been abundantly investigated (Nakamura *et al.*, 1989; Sakai *et al.*, 1990a, b; Ishibashi *et al.*, 1995; Kinoshita and Yamano, 1997; Marumo and Hattori, 1999). The Hakurei field is located at the southern part of the bottom seafloor of the Izena Hole. In this field, scientific research with manned submersible or Remotely Operated Vehicle (ROV) was not yet conducted until this study. Since 2008, the Hakurei field has been explored intensively by JOGMEC (Japan Oil, Gas and Metals National Corporation) under a framework of the ocean energy and mineral resources development program. Despite the vicinity of these two sites within 3 km, a previous water column survey above the Izena Hole revealed more than one-order higher H<sub>2</sub>/CH<sub>4</sub> ratio in the hydrothermal plume above the Hakurei field than that above the Jade field (Kawagucci *et al.*, 2010a). On the other hand, seismological investigations during the R/V Kaiyo KY02-11 cruise in 2002 reported notable geological differences between these two fields. The Hakurei field is covered with a thick sediment layer (more than 150 meters), whereas a few-meters thin sediment layer is recognized at the Jade field (Y. Nakamura, personal communication). The observed different chemical characteristics of the hydrothermal plumes between two fields could be related to difference in local sedimentary condition of the seafloor, because both H<sub>2</sub> and CH<sub>4</sub> are chemical species contributed from fluid-sediment interactions. A geochemical study of venting fluids was expected to reveal these processes.

We will report here a result of our investigation with ROV *Hyper Dolphin* that collected hydrothermal fluids from the Jade and Hakurei fields in the Izena Hole in 2003, 2010, and 2011 during the cruises of R/V *Natsushima* NT03-09, NT10-17, and NT11-15. We confirmed little temporal variation of geochemistry of high temperature hydrothermal fluid of the Jade field over two decades since the previous study (Sakai *et al.*, 1990a). We discovered venting of low temperature vent fluid in the distal part of the Jade field, which showed distinctive chemical characteristics from the high temperature fluid. We revealed geochemistry of high temperature hydrothermal fluid collected from the Hakurei field were very close to that of the Jade field, with a few exceptions. One of the exceptions was difference in minor gas composition that was expected by the previous plume survey. We will discuss factors to cause these diversities in fluid chemistry collected from the adjacent active hydrothermal fields, and demonstrate importance of chemical modification by fluid-sediment interactions during fluid upwelling.

#### GEOLOGICAL BACKGROUND AND OBSERVATIONS

Formation of the Izena Hole is considered to be related to rifting activity of the middle Okinawa Trough based on its peculiar topography. For example, steep gradient and horseshoe depressions were notable especially on the southeastern wall, which could be attributed to results of recent fault activities (Kato *et al.*, 1989; Kato, 1990). On the other hand, it is difficult to recognize whether magmatic activity in this area should be ascribed to a volcanic front or a back-arc rifting. The Izena Hole is situated along plausible southwestern continuation of a chain of Quaternary volcanoes of the Ryukyu arc (Shinjo *et al.*, 1999). Its location can be also considered as the eastern end of the Aguni rift graben segment (Halbach *et al.*, 1993). Abundant tuff breccia and woody pumice of dacitic composition were observed as exposed on the hole slopes. A center-cone like a small knoll consisted of dacite lava was recognized at the center of the hole during past dive surveys (Kato *et al.*, 1989; Kato, 1990). These observations suggest recent magmatic activity, although detailed petrology of volcanic rocks in the Izena Hole have not been studied.

Present hydrothermal activity in the Izena Hole was firstly discovered in 1988 by towed video camera surveys and dredges of hydrothermal ore deposits during SO-56 cruise lead by a German scientific team (Halbach *et al.*, 1989). This site was named as “Jade” in commemoration of Japan-Deutsche collaboration during this cruise. Geochemical studies on the hydrothermal activity were conducted during following dive missions in 1988 and 1989 (Sakai *et al.*, 1990a, b; Ishibashi *et al.*, 1995). The Jade field is located on the northeastern slope of the Izena

Hole at water depth of 1300–1550 m. Hydrothermal activity was recognized in an area of 500 m × 300 m. Venting of the fluid having recorded the highest fluid temperature of 320°C at “TBS” chimney was located at 1350 m in depth, where “black smoker” had been reported in 1989 (Sakai *et al.*, 1990a). Chimneys associated with moderate to high temperature fluid venting were concentrated in the neighbor of the TBS chimney, which is regarded as the proximal part of the Jade field (Fig. 1). Based on visible observations during 2003 and 2011 surveys, fluid venting and associated hydrothermal activity in the proximal part was as intense as observed in 1989. Other than these active chimneys, diffusive shimmering vents and inactive chimneys were recognized along a NE–SW direction (Nakamura *et al.*, 1989). Emission of CO<sub>2</sub> dominated liquid bubbles were identified in the distal part of the Jade field at both ends of the chimney line, one of which was previously reported in Sakai *et al.* (1990b). At the southwestern end of the Jade field, a notable layered and consolidated structure plausibly composed of amorphous silica and native sulfur was localized in 2003, and named as “sulfur crust”. In the vicinity of the sulfur crust, diffusive venting of hydrothermal fluid at 104°C associated with liquid CO<sub>2</sub> bubbling was recognized in 2003, which was named as the “Biwako vent” (Fig. 1).

The Hakurei field is located at the bottom of the depression of the Izena Hole, at water depths of 1600–1610 m (Fig. 1). The northern part of the Hakurei field is located at about 3 km far from the Jade field in the southwestern direction. Hydrothermal activities were observed in an area of at least 500 m × 300 m, during our dive expeditions. Vigorous high temperature fluid venting in the Hakurei field was often associated with a complex chimney structure of more than 10 meters height and showing a well-developed flange structure. At “Dragon” chimney at the depth of 1600 m (Fig. 1), we observed effluent from the edges of the flange, which recorded the highest temperature ever of 326°C among the Hakurei field. The seafloor away from these complex chimney structures is covered with sandy and silty sediment (Kato *et al.*, 1989). In some places, white-colored patched area and sulfur crust structure were recognized by visual observations.

#### SAMPLING AND ANALYTICAL METHODS

Fluid samples were collected during dive missions in 2003 (NT03-09 cruise), 2010 (NT10-17 cruise) and 2011 (NT11-15 cruise). Fluid sampling was conducted using WHATS sampler type JAM-3, which was developed for collecting fluid samples without loss of gas species (Saegusa *et al.*, 2006). The sampler was installed on ROV *Hyper Dolphin* and controlled from an operator onboard R/V *Natsushima*. A platinum resistance thermometer at

the end of the fluid inlet titanium tubing enabled temperature monitoring during collection of fluids. Plastic bag sampler (Kawagucci *et al.*, 2011) was also used for venting fluid sampling. In addition, 2.5-L Niskin bottles were employed for the sampling of ambient seawater.

The fluid samples were processed as quickly as possible after ROV recovery. Aliquots for each specific analysis were drawn from the sampler using silicon rubber tubing. Measurement of pH and colorimetry for silica (SiO<sub>2</sub>), ammonium (NH<sub>4</sub><sup>+</sup>), and hydrogen sulfide (H<sub>2</sub>S) were conducted onboard following Gieskes *et al.* (1991) procedure. Subsamples were transferred into two polyethylene bottles after filtration using 0.2-μm pore membrane filter. One of them, for cation analysis, was acidified to pH < 2. The other, for anion analysis, was kept in a refrigerator and analyses carried out ashore. Sulfate (SO<sub>4</sub><sup>2-</sup>) concentration was analyzed by ion chromatography after 300 times dilution. Chloride (Cl<sup>-</sup>) concentration and alkalinity was determined by titrations (Gieskes *et al.*, 1991). Concentration of cations was determined on flame emission spectrophotometry for potassium (K) and on ICP-AES for boron (B), sodium (Na), lithium (Li), magnesium (Mg), calcium (Ca), barium (Ba), iron (Fe), manganese (Mn), and strontium (Sr) after 200 times dilution of the acidified aliquots. Total selenium (Se) concentration was analyzed through high performance liquid chromatography with fluorescence detection (Nakaguchi *et al.*, 2004). Analytical errors for these chemical analyses, estimated from replicate analysis, were within ±5% for the instrumental analyses and alkalinity determination, and within ±0.5% for the chloride titration.

Fluid samples for gas analyses were obtained only in 2010. After recovery of the WHATS sampler, fluid in a stainless steel gas-tight bottle (150 mL) was immediately opened into a vacuum line (*ca.* 1.5 L) to extract dissolved gas species. In the vacuum line, ~2 ml of reagent-grade solid sulphamic acid (HOSO<sub>2</sub>NH<sub>2</sub>) was added to stimulate degassing, and ~2 ml of mercury chloride (HgCl<sub>2</sub>) powder was added to fix sulphide as mercury sulfide (HgS). After the degassing for over 10 minutes, the gas phase was collected in 50-mL stainless steel bottles for subsequent gas analyses. The degassed fluid sample was recovered and filtered using a 0.45-μm pore membrane filter, which was provided for Mg and sulphur isotope ratio measurements.

Concentrations of molecular hydrogen (H<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), carbon monoxide (CO), and ethane (C<sub>2</sub>H<sub>6</sub>) were determined by GC-HID analysis of the extracted gas phase, with errors of 10%. Helium (He) concentration was determined by GC-TCD analysis utilizing argon as a carrier gas, with a 10% error. Carbon isotope ratio of CO<sub>2</sub> was determined by continuous-flow isotope ratio mass spectrometry (Kawagucci *et al.*, 2005 with some modification) with analytical errors of 0.5‰

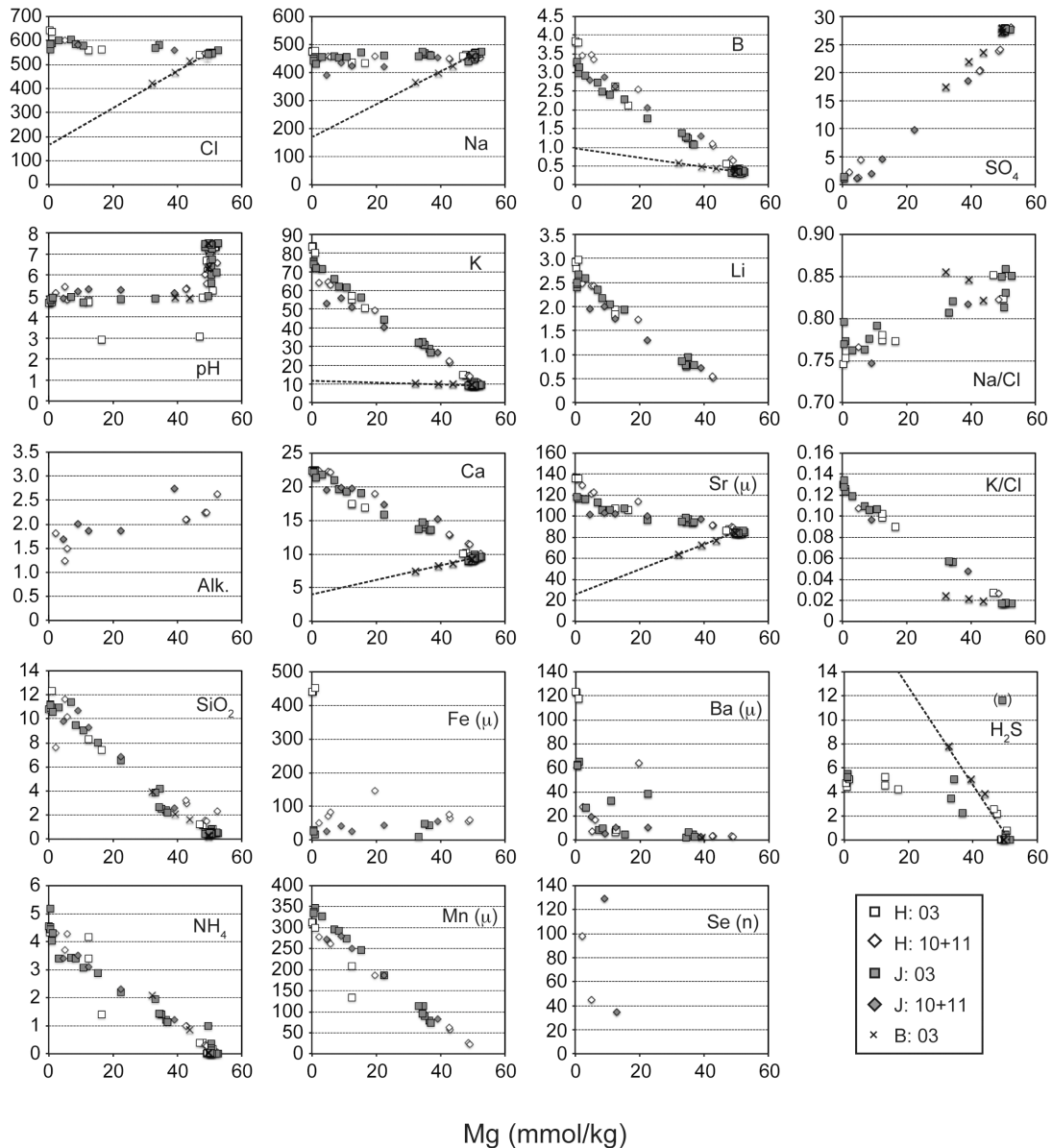


Fig. 2. Magnesium diagrams showing analytical results of elemental concentrations for all the studied samples. Open and grey symbols represent samples collected from the Hakurei and Jade fields, respectively. Square and diamond symbols represent samples collected in 2003 and 2010/2011, respectively. Cross symbol represents samples collected from the Biwako vent in 2003. Dashed lines represent linear regressions for the Biwako data set. Panels with signatures “(μ)” and “(n)” have units of μM and nM in y-axis, while those with no signature are in mM.

(1σ). Carbon and hydrogen isotope ratios of CH<sub>4</sub> were determined by continuous-flow isotope ratio mass spectrometry (Popp *et al.*, 1995; Umezawa *et al.*, 2009 with some modification) with analytical errors of 0.5‰ and 5‰ (1σ), respectively. Hydrogen isotope ratio of H<sub>2</sub> was determined by continuous-flow isotope ratio mass spectrometry with analytical error of 5‰ (1σ) (Kawagucci *et al.*, 2010b). Helium isotope ratio was measured with a conventional noble gas mass spectrometer (Sano *et al.*,

2008). Hydrogen and oxygen isotope ratios of water (H<sub>2</sub>O) were determined by a wavelength-scanned cavity ring down spectroscopy analyzer (Liquid Water Isotope Analyzer, Los Gatos Research, Inc.) with analytical precision within 1.0‰ and 0.5‰ (1σ), respectively. Sulfur isotope ratios of mercury sulfides (HgS) recovered from the degassed fluid sample were determined by EA/IRMS (IsoPrime coupled with Euro Vector EA3000, GV Instruments). This ratio is considered equivalent to that of hy-

Table 1. Elemental species composition of estimated hydrothermal fluid end-members of active hydrothermal fields in the Izena Hole

Hydrothermal site	Sampling year	Temp. °C	pH	Cl mM	Na mM	K mM	Li mM	Ca mM	Sr μM	Mn mM	B mM	NH <sub>4</sub> mM	Si mM	H <sub>2</sub> S mM	Na/Cl	K/Cl
Hakurei	2003–2011	326	4.7	608	458	75	2.8	23	129	0.29	3.7	4.4	11.3	5.2	0.75	0.123
Jade	2003–2011	320	4.7	590	442	72	2.5	22	115	0.34	3.2	4.2	11.8	5.6	0.75	0.122
Jade [a]	1989	320	4.7	550	425	72	2.5	22	—	0.11	—	5.0	12.9	13	0.77	0.131
Biwako	2003–2011	104	4.8	167	173	12	—	4.3	27	—	1.0	5.0	11.0	23	1.04	0.072
Yonaguni IV	[b]	325	5.7	614	416	86	—	23	—	1.1	3.9	14.7	11.3	—	0.68	0.140
Minami Ensei	[c]	280	4.9	562	436	53	—	23	260	0.10	—	5.4	11.1	0.4	0.78	0.094
Hatoma	[d]	240	5.2	381	285	55	—	17	62	0.48	3.3	7.2	12.0	—	0.75	0.144
Iheya North	[e]	309	5.0	557	407	72	—	22	73	0.65	—	1.7	12.3	—	0.73	0.129
(seawater)			7.5	540	460	10	0.03	11	91	—	0.43	<0.01	0.1	—	0.85	0.019

[a] Sakai *et al.* (1990a), Gamo *et al.* (1991). [b] Data for Lion vent, Suzuki *et al.* (2008). [c] Kawagucci *et al.* (2013) and references therein. [d] Kishida *et al.* (2004). [e] Kawagucci *et al.* (2011).

drogen sulfide (H<sub>2</sub>S) dissolved in the original hydrothermal fluid. Following the previous study (Yamanaka *et al.*, 2008), the mercury sulfide precipitation was oxidized using mixture of concentrated nitric acid and bromine (10:1 in volume), and sulfur was then precipitated as barium sulfate (BaSO<sub>4</sub>) by addition of 0.5 M BaCl solution. Collected BaSO<sub>4</sub> was wrapped within a tin capsule with V<sub>2</sub>O<sub>5</sub> powder and directly subjected to the EA/irMS. Sulfur isotope ratio of the native sulfur samples was directly measured by EA/irMS, without treatment. Analytical precision for the sulfur isotope measurements is estimated as 0.2‰ (1σ) (Yamanaka *et al.*, 2008).

## RESULTS

Analytical results of elemental (ion) concentrations for all the studied samples are reported as two-component diagrams where concentration of each chemical species is plotted against the magnesium concentration (Fig. 2). In these so-called Mg diagrams, mixing between two end-members, namely hydrothermal fluid ([Mg] = 0 mM) and seawater ([Mg] = 54 mM) is expressed as a mixing line (Von Damm *et al.*, 1985). In Fig. 2, samples are categorized into groups by sampling time, 2003 (03) and 2010/2011 (10), and by sampling sites, Hakurei field (H), the proximal part of Jade field (J), and Biwako vent located in the distal part of the Jade field (B).

The plots are likely to form good linear relationships in the Mg diagrams for each vent field regardless the sampling time. As for exceptions, Fe, Se and Ba concentrations in Mg diagrams showed significant scatter, which are plausibly due to the non-conservative behavior (e.g., precipitation) of these species during sampling or post-sampling processes. The good linear relationships in the Mg diagrams suggest that all the fluids from each vent site originate from a single hydrothermal fluid source.

No systematic difference is observed between the plots of 2003 and of 2010/2011, which suggests chemistry of the fluid source is stable for at least this duration. Chemical composition of the fluid source can be estimated from the y-intercept of the least-squares linear regression in the Mg diagrams. In the case that data points are too few to estimate regression, the end-member composition is assumed to be equal to that of the higher temperature fluid sample with [Mg] < 5 mM. The calculated end-member chemical compositions for each vent field are summarized in Table 1.

Chemical composition of the high-temperature fluids from the Jade field was reported in a previous study (Sakai *et al.*, 1990a), although with large uncertainty related to the sampling device used (Sakai *et al.*, 1990a). As shown in Table 1, difference in concentrations of major species (Cl, Na, K, Ca and Si) measured in this study is within 10% of the estimated end-member composition determined previously (from the 1989 samples). This accordance suggests that high-temperature fluids from the Jade field have not changed significantly for this duration. Moreover, chemical composition of high-temperature fluids from the Hakurei field shows good similarity to that of the Jade fluid. On the other hand, six samples collected from the Biwako vent site in the distal part of the Jade field show clearly distinctive trend in the Mg diagrams from high temperature fluid samples in the proximal part of the Jade field (Fig. 2). Good linear relationship among the plots of the Biwako site provides the hydrothermal end-member chemical composition with little ambiguity. The Biwako fluid is represented by notably low Cl concentration (167 mM), which is approximately one third of the seawater concentration (Table 1).

Gas geochemistry data are summarized in Table 2. Stable isotope ratios of carbon, hydrogen, oxygen, and sulfur are represented by the delta-notation in per-mil

Table 2. Gas species composition of hydrothermal fluids from active hydrothermal fields in the Izena Hole

(a) Analytical results of the studied samples

Site	Sample ID	Mg mM	CO <sub>2</sub> mM	$\delta^{13}\text{C}(\text{CO}_2)$ ‰	CH <sub>4</sub> mM	$\delta^{13}\text{C}(\text{CH}_4)$ ‰	$\delta\text{D}(\text{CH}_4)$ ‰	H <sub>2</sub> mM	$\delta\text{D}(\text{H}_2)$ ‰	C <sub>2</sub> H <sub>6</sub> $\mu\text{M}$	CO $\mu\text{M}$	He $\mu\text{M}$	<sup>3</sup> He/ <sup>4</sup> He R <sub>atm</sub>
Hakurei	#1191	9.9	124	-6.2	5.6	-32.1	-113	1.17	-379	2.04	52	0.44	5.81
Hakurei	#1187	40.8	n.a.	n.a.	1.2	-32.0	-114	0.34	-384	n.d.	23	n.d.	n.a.
Jade	#1184	13.0	119	-6.2	3.7	-30.8	-113	0.05	-381	0.25	23	0.55	4.65

n.a. = not analyzed, n.d. = not detected.

(b) Estimated hydrothermal fluid end-members

Site	CO <sub>2</sub> mM	$\delta^{13}\text{C}(\text{CO}_2)$ ‰	CH <sub>4</sub> mM	$\delta^{13}\text{C}(\text{CH}_4)$ ‰	$\delta\text{D}(\text{CH}_4)$ ‰	H <sub>2</sub> mM	CO $\mu\text{M}$	He $\mu\text{M}$	<sup>3</sup> He/ <sup>4</sup> He R <sub>atm</sub>	H <sub>2</sub> /CH <sub>4</sub>	CH <sub>4</sub> /C <sub>2</sub> H <sub>6</sub>	CH <sub>4</sub> / <sup>3</sup> He* $\times 10^6$	CO <sub>2</sub> / <sup>3</sup> He* $\times 10^9$
Hakurei	151	-6.2	6.8	-32.1	-113	1.4	63	0.53	5.81	0.21	2730	1434	32
Jade	156	-6.2	4.9	-30.8	-113	0.06	30	0.72	4.65	0.013	14900	761	25
Jade [a]	209	-4.9	7.1	-40.7	—	0.05	—	0.89	6.5	0.007	—	920	26
Minami Ensei [b]	42	-5	2.3	-25	-105	0.04	—	—	7.0	0.017	>1710	—	—
Itheya North [c]	227	-10	7.6	-54.0	-132	0.23	—	—	7.1	0.03	>3700	—	—

[a] Ishibashi *et al.* (1995). [b] Kawagucci *et al.* (2013). [c] Kawagucci *et al.* (2011).

\*Helium isotope ratio was assumed as 6.5 for calculation.

scales against the international standards of VPDB, VSMOW, VSMOW, and CDT, respectively. Helium isotopic ratio (<sup>3</sup>He/<sup>4</sup>He) is normalized to that of the atmosphere of  $1.39 \times 10^{-6}$ . As a previous study demonstrated for the Jade field (Ishibashi *et al.*, 1995), the high temperature fluids in both fields are characterized by very high concentrations in gas species. Concentration of CO<sub>2</sub> which is the most dominant gas specie is about 150 mM in these two sites. Concentrations of CH<sub>4</sub> (6.8 mM for the Hakurei fluid and 4.9 mM for the Jade fluid) and He (0.53 and 0.72  $\mu\text{M}$ ) are also comparable between the two sites. Stable carbon and hydrogen isotope ratios of CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> are mostly identical between the two sites:  $\delta^{13}\text{C}_{\text{CO}_2} = -6.2\text{‰}$ ,  $\delta^{13}\text{C}_{\text{CH}_4} = -32\text{‰}$ ,  $\delta\text{D}_{\text{CH}_4} = -113\text{‰}$ , and  $\delta\text{D}_{\text{H}_2} = -380\text{‰}$  for the Hakurei fluid, and  $\delta^{13}\text{C}_{\text{CO}_2} = -6.2\text{‰}$ ,  $\delta^{13}\text{C}_{\text{CH}_4} = -31\text{‰}$ ,  $\delta\text{D}_{\text{CH}_4} = -113\text{‰}$ , and  $\delta\text{D}_{\text{H}_2} = -380\text{‰}$  for the Jade fluid. Isotope ratios of He show slight difference; <sup>3</sup>He/<sup>4</sup>He =  $4.02 \pm 0.12$  R<sub>atm</sub> for the Jade field and  $5.80 \pm 0.13$  R<sub>atm</sub> for the Hakurei field. Contrary to this, H<sub>2</sub> is notably enriched in the Hakurei fluid (1.4 mM) compared to the Jade fluid (0.06 mM). Measured C<sub>2</sub>H<sub>6</sub> concentration for the Hakurei fluid is also higher (2  $\mu\text{M}$ ) than that for the Jade fluid (0.3  $\mu\text{M}$ ). Sulfur isotopic composition of hydrogen sulfide shows higher diversity between sampling fields and times.  $\delta^{34}\text{S}$  values of H<sub>2</sub>S of the high temperature fluids in the Jade field are from +3.6‰ to +6.8‰ in 2010, which are somehow lower than those in 1989 (from +7.4‰ to +7.7‰: Gamo *et al.*, 1991). In the Hakurei field,  $\delta^{34}\text{S}$  values of hydrogen sulfide of high temperature fluids are from +5.5‰ to +7.8‰. Iso-

tope ratios of H<sub>2</sub>O of the high temperature fluids were analyzed for only a few samples;  $\delta\text{D}_{\text{H}_2\text{O}} = -0.3\text{‰}$  and  $\delta^{18}\text{O}_{\text{H}_2\text{O}} = +1.8\text{‰}$  for the Jade field ( $n = 1$ ) and  $\delta\text{D}_{\text{H}_2\text{O}} = -0.6\text{‰}$  and  $\delta^{18}\text{O}_{\text{H}_2\text{O}} = +1.6\text{‰}$  for the Hakurei field (averaged values from  $n = 4$ ).

## DISCUSSION

### Chemistry of high temperature hydrothermal fluids from the Izena Hole

The high temperature fluids collected from both the Jade and Hakurei fields showed strong similarities in fluid geochemistry. SiO<sub>2</sub> concentrations were 11.3 and 12.0 mM in the Jade and Hakurei fluids. These values correspond to the expected quartz solubility concentrations at pressure and temperature conditions of each site (Von Damm *et al.*, 1991). The moderate acidity of both the Jade and Hakurei fluids (pH = ~4.7) was comparable to those in other hydrothermal fields in the Okinawa Trough (Table 1). Alkalinity was about 1.5 mM, which suggests being neutralized at high temperature condition. This rather neutral pH is contrary to geochemical characteristics of hydrothermal fields in the Manus Basin, which is considered as a back arc basin in a rifting tectonic stage as well as the Okinawa Trough. However active hydrothermal fields in the Manus Basin are located in a sediment-poor environment compared to the Okinawa Through, because they are located far from any continents. Strong acidity was remarkable in high temperature fluid in the Pacmanus field (Reeves *et al.*, 2011) and low temperature fluid in

the Desmos field (Gamo *et al.*, 1997). These previous studies demonstrated the acidity is attributed to significant contribution of magmatic volatiles, especially SO<sub>2</sub> into the hydrothermal fluids (Reeves *et al.*, 2011). On the other hand, contribution of magmatic volatile species into hydrothermal fluid was also notable in the Jade and Hakurei fluids as discussed later. Therefore, to explain the discrepancies in the pH between the Manus Basin fluids and those of the Jade and Hakurei fluids, fluid-sediment interactions could be the factor controlling the pH as well as dissolved gas species.

Chemical compositions of major ion species (Cl, Na, K, and Ca) in the Jade and Hakurei fluids were very similar. The hydrothermal end-member Cl concentration as the y-intercept of the Mg–Cl diagram was estimated as 590 mM for the Jade fluid, while the observed maximum was 604 mM. For the Hakurei fluid, the end-member Cl concentration was estimated as 608 mM, while the observed maximum was 643 mM. Both Cl concentrations were higher than that of seawater (=540 mM). Sodium concentrations were 442 mM and 458 mM in the Jade and Hakurei fluids, respectively. Molar ratios of Na/Cl were in the range from 0.75 to 0.80 for both fluids, which were substantially lower than that of ambient seawater (=0.86). This lower Na/Cl ratio would be attributed to Na uptake during fluid-mineral interactions involving plagioclase minerals, as proposed by Reeves *et al.* (2011). Concentrations of Ca were around 22 mM for both fluids, and concentrations of K were 72–75 mM. Both Ca and K concentrations were much higher than those of seawater. Enrichment in K for high temperature fluid was one of the common characteristics observed in hydrothermal fields in the Okinawa Trough (Table 1). End-member K/Cl ratios were 0.12 for both the Jade and Hakurei fields, which was comparable for K/Cl ratios found in the Yonaguni IV field (=0.14; Suzuki *et al.*, 2008), Hatoma field (=0.14; Kishida *et al.*, 2004) and Iheya North field (=0.13; Kawagucci *et al.*, 2011). These ratios are clearly higher than K/Cl ratios found in typical MOR hydrothermal fields (around 0.05; Von Damm, 1995). The high K/Cl ratios of high temperature fluids from the Okinawa Trough are likely to reflect high K contents in surrounding rocks with which fluid interacts during hydrothermal circulation (Sakai *et al.*, 1990a).

Also for the minor element compositions, no large discrepancies were recognized between the Jade and Hakurei fluids. Concentrations of Li were from 2.5 to 2.7 mM and concentrations of B from 3.2 to 3.7 mM for high temperature fluids. These concentrations are significantly higher than those in typical MOR fluids (Li = 0.5–1.5 mM and B = 0.5–1.0 mM; Von Damm, 1995). Since these concentrations are also higher than those of high temperature fluids collected from the Manus Basin (Reeves *et al.*, 2011), contribution from fluid-sediment interac-

tions could be important. Concentrations of Se around 120 nM and of Mn around 300 μM were also comparable to the concentration range among hydrothermal fields in the Okinawa Trough.

Gas concentrations for the Jade and Hakurei fluids show also some similarity, but with a few notable exceptions. Concentrations of CO<sub>2</sub> and He, as well as carbon and helium isotope ratios were similar between the two fields. As discussed in a previous study (Ishibashi *et al.*, 1995), the carbon and helium systematics of the high temperature fluids are attributed to significant contribution of volatile species of magmatic origin. Calculated CO<sub>2</sub>/<sup>3</sup>He ratios of (20–30) × 10<sup>9</sup> can be interpreted as reflecting molar ratio of magmatic fluid generally observed in arc-backarc settings. Concentrations of H<sub>2</sub>S of the high-temperature fluid were around 5–6 mM in the Jade and Hakurei fields, and concentrations of CH<sub>4</sub> were 4–7 mM for both high-temperature fluids. It is notable to find no large discrepancy for concentrations and isotope ratios of CH<sub>4</sub> and H<sub>2</sub>S between these two fluids, since these species derive from various sources during fluid-sediment interactions at the recharge zone (Kawagucci *et al.*, 2013). Distinctive difference was found only in concentrations of H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub>, which will be discussed later.

In summary, chemical composition of the high temperature fluids collected from the Jade field and Hakurei field were very similar with exception of a few minor species. This similarity could be explained by a model in which venting fluids are derived from the same fluid reservoir beneath the seafloor. The highly similarities in gas geochemistry supports the idea that hydrothermal activities in the Jade field and Hakurei field shares a common hydrothermal circulation system at depth. Similarities in magmatic species (CO<sub>2</sub> and He) imply that a single magma beneath the Izena Hole acts as a heat source, which contributes also magmatic volatiles into the fluid circulation system. Similarities in minor gas species (CH<sub>4</sub> and H<sub>2</sub>S) are well explained by a common fluid circulation system sharing at least the recharge zone. This model is reasonable considering that the distance between the two fields is about 3 km. Beneath the Jade fields, a previous heat flow study demonstrated the existence of a heat source at very shallow depth (a few hundred meters), which would be attributed to an intruded dyke (Kinoshita and Yamano, 1997). The hydrothermal activity in the Jade field may be considered as a satellite activity, while the Hakurei field may represent one of the main activities of the hydrothermal system in the Izena Hole.

#### *Intra-field diversity in fluid chemistry caused by phase separation*

We found distinctive chemistry between the low temperature fluid collected from the Biwako site in the distal part of the Jade field (called as the Biwako fluid hereaf-



ter) and the high temperature fluids collected from the proximal part of the Jade field (called as the Jade fluid hereafter). Cl concentration of the estimated hydrothermal end-member of 167 mM for the Biwako fluid was approximately one third of seawater level. Along with Cl, concentrations of Na (=173 mM), K (=11.9 mM) and Ca (=4.3 mM) in the Biwako fluid were close to one third of the level of the Jade fluids (Table 1). On the other hand, enrichment in H<sub>2</sub>S (=23 mM) and comparable concentrations of NH<sub>4</sub><sup>+</sup> (=5.0 mM) and SiO<sub>2</sub> (=11.0 mM) compared with the Jade fluid are notable.

Proportional variation of major ion concentrations between the high and low temperature fluids from the Jade field strongly suggests that the intra-field variation is caused by phase separation beneath the seafloor. A previous study on fluid inclusions of sulfide/sulfate ore deposits collected from the proximal part of the Jade field demonstrated that phase separation occurred at 1500 to 2000 m water depth, based on varying salinities of the fluid inclusions (Lüders *et al.*, 2001). Phase separation of hydrothermal fluids in such subcritical condition forms the vapor phase of substantially low Cl concentration and the liquid phase which Cl concentration is slightly higher than that of seawater. Dissolved ion species are distributed preferably into the liquid phase, while volatile species into the vapor phase (Butterfield *et al.*, 2003). The low concentrations of major ion species (Cl, Na, K, and Ca) and high H<sub>2</sub>S concentrations are attributed to that the low temperature Biwako fluid is dominantly composed of the vapor-phase of the hydrothermal fluid. On the other hand, the Jade fluid may be basically composed of the remaining liquid-phase of the original hydrothermal fluid, because it shows ~10% higher Cl concentration than seawater. Comparable SiO<sub>2</sub> concentrations between these two fluids may be attributed to no preferential distribution of silica due to electrically-neutral chemical speciation or quick dissolution of silicate minerals just prior to venting of the hydrothermal fluid. If phase separation completely controls the observed diversity of fluid chemistry, cation/anion ratio should be identical in these two fluids. However, the Biwako fluid showed slightly higher Na/Cl ratio and lower K/Cl ratio than those of the Jade fluid. This disagreement may be a result of the quick dissolution of silicate minerals or the involvement of seawater just prior to the hydrothermal fluid venting.

Formation of liquid CO<sub>2</sub> bubbles and sulfur crust within the surface sediment were noticed in the distal part of the Jade field. As demonstrated in a previous study in the Yonaguni IV field (Konno *et al.*, 2006), formation of liquid CO<sub>2</sub> bubble would be explained by accumulation of CO<sub>2</sub> delivered by the vapor-phase of the hydrothermal fluid. In similar way, formation of the sulfur crust would be related to the high H<sub>2</sub>S concentration of the Biwako fluid. Range of sulfur isotope ratios of the sulfur crust

from +5.6‰ to +6.3‰ overlaps with that of the hydrogen sulfide dissolved in the Jade high temperature fluid (from +3.6‰ to +7.8‰). This agreement may support the idea of a hydrothermal origin of the sulfur crust, although we have no sulfur isotope data for the Biwako fluid to confirm this hypothesis. Contribution of microbial reduction of seawater sulfate may be alternative process to contribute formation of the sulfur crust. It is reasonable to expect abundant CH<sub>4</sub> in the Biwako fluid due to phase separation (again despite of no data), which could stimulate microbial reduction of seawater sulfate ( $\delta^{34}\text{S} = +20\text{‰}$ ) within the sediment. Since microbial sulfate reduction generally generates approximately 10–30‰ <sup>34</sup>S-depleted sulfide relative to the substrate sulfate, the observed sulfur isotope (from +5.6‰ to +6.3‰) can be interpreted also as microbial process, although SO<sub>4</sub><sup>2-</sup> concentration of the seawater (=28 mM) would limit availability as a sulfur source. On the other hand, input of SO<sub>2</sub> derived directly from the magmatic volatile is excluded, because the disproportionation of SO<sub>2</sub> induces native sulfur of more <sup>34</sup>S-depleted isotope ratio (Kusakabe *et al.*, 2000). Based on the obtained data, plausible explanation for the significantly high H<sub>2</sub>S concentration of the Biwako fluid (23 mM) is a combination of hydrothermal source and effect of the microbial sulfate reduction. Further studies on sulfur and carbon cycles in the low-temperature hydrothermal environment in the distal part of a hydrothermal field are required. Occurrence of sulfur crusts was located also in the Hakurei field, and the sulfur isotope ratio was from +9.2‰ to +10.6‰. This result implies similar phase separation process may occur (or have occurred) beneath the Hakurei field, although no evidence was observed.

Similar intra-field variation of fluid chemistry has been identified in other hydrothermal fields in the Okinawa Trough, such as the Iheya-North field (Nakagawa *et al.*, 2005; Kawagucci *et al.*, 2011) and the Yonaguni IV field (Konno *et al.*, 2006; Suzuki *et al.*, 2008). As demonstrated in these previous studies, geographical distribution of Cl-rich fluid vents and Cl-depleted fluid vents is likely similar to the distribution of fluid emanations observed in onland geothermal fields. Venting fluid of the highest temperature located in the center of the active hydrothermal field is usually revealed as Cl-rich chemistry. Contrary to such vigorous venting in the proximal part, fluid venting in the distal part is often diffusive, of low temperature and of Cl-depleted chemistry. Our observation in the Jade field recognized common geographical distribution. The Cl-depleted venting of 104°C at the Biwako vent site was located in the distal part of the Jade field, about 400 meters apart from the activity center. Such diffusive emanation could be an analogue to as acid-sulfate type vapor emanation in a geothermal system. This geographical distribution is accordance with the model that hydrothermal activity in the Jade field is driven by an intruded dyke.

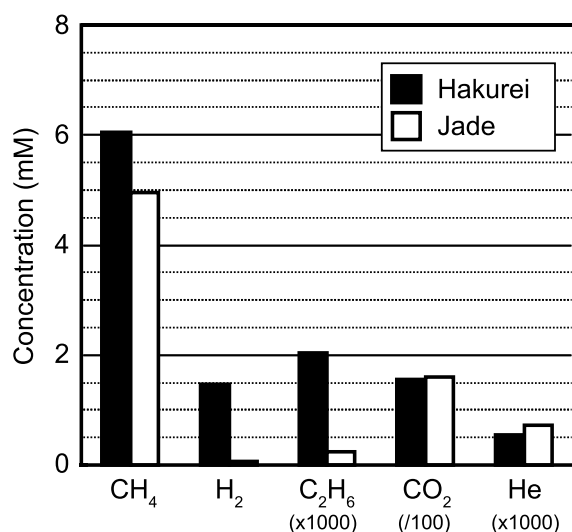


Fig. 3. Comparison of gas concentrations of hydrothermal fluids collected from the Hakurei and Jade fields.

Intrusion of a heat source of a small size could stimulate phase separation and segregation of the hydrothermal fluid.

#### *Intra-field diversity in minor gas chemistry caused by fluid-sediment interactions*

The exceptional difference between fluid chemistry of the Jade and Hakurei fields was recognized in composition of minor gas species such as H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub>. Concentration of H<sub>2</sub> of the Hakurei fluid was more than one order higher than that of the Jade fluid (Fig. 3). This difference is in agreement with the chemical signature of the hydrothermal plumes above these fields; an order of magnitude higher H<sub>2</sub>/CH<sub>4</sub> ratio in water column above the Hakurei field than the Jade field (Kawagucci *et al.*, 2010a).

Concentration of H<sub>2</sub> in hydrothermal fluids is considered to be primarily controlled by redox condition of the fluid reservoir. In case the surrounding rocks are silicic volcanic material, H<sub>2</sub> concentration is expected to be less than 0.1 mM (Kawagucci *et al.*, 2013). Indeed, the observed H<sub>2</sub> concentration of the Jade fluid was 0.06 mM. Increase of contribution from magmatic volatiles derived from rather oxidic silicic magma would not account for the high H<sub>2</sub> concentration of the Hakurei fluid, although enrichment in H<sub>2</sub> in the periods following the magmatic event was observed in some hydrothermal fields in the mid-oceanic ridge setting (e.g., Haase *et al.*, 2007). The high H<sub>2</sub> concentration in the Hakurei fluid cannot be explained by phase separation, because the Cl-rich chemistry suggests it experienced loss of the vapor phase. Phase separation can result in increase of H<sub>2</sub> concentration in the vapor phase as demonstrated in the Yonaguni IV field

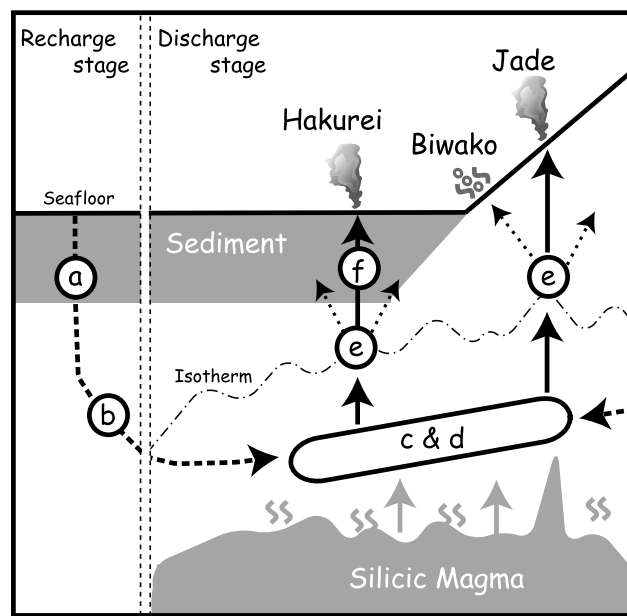
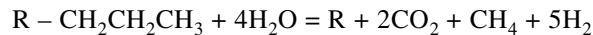


Fig. 4. Schematic cartoon illustrating the geochemical processes during the fluid circulation at the Izena Hole, which follows the original cartoon proposed by Reeves *et al.* (2011). a: low temperature water/rock reactions and involvement of organic-derived species at the recharge zone, b: high temperature reactions at the reaction zone, c: involvement of magmatic volatiles in the vicinity of the magma intrusion, d: high temperature reactions to attain equilibrium in the fluid reservoir (reaction zone), e: phase separation (and segregation) during fluid ascent in the discharge zone, f: fluid-sediment interaction including thermal degradation of organic matter in the discharge zone.

(Konno *et al.*, 2006), but would decrease H<sub>2</sub> concentration in the residual liquid phase. Microbial fermentation is another potential H<sub>2</sub> source, however the observed  $\delta D_{H_2}$  value of  $-380\text{‰}$  suggesting that the fluid temperature above 300°C (Kawagucci *et al.*, 2010b) is not in agreement with a contribution from such microbial process. Geological productions of H<sub>2</sub> by water radiolysis (Lin *et al.*, 2005) and mechano-chemical reaction associated with fault activity (Kita *et al.*, 1982; Hirose *et al.*, 2011) have been proposed, but negligible in this case due to their weak and intermittent occurrence.

The most likely process to cause H<sub>2</sub> enrichment in the Hakurei fluid is thermal degradation of sedimentary organic matter during the fluid upwelling (Seewald *et al.*, 1994; Cruse and Seewald, 2006), as pointed out in the previous plume study (Kawagucci *et al.*, 2010a). This process could be represented by a general reaction of hydrocarbons degradation as following,



where R is some hydrocarbon moiety (Seewald, 2003). Considering stoichiometry of this reaction, the observed differences between the Hakurei fluid and Jade fluid would be considered as evidence for the thermal degradation. Hydrocarbon composition of the Hakurei fluid was significantly enriched in ethane ( $C_1/C_{2+}$  ratio = 2700) compared to the Jade fluid ( $C_1/C_{2+}$  ratio = 14900), and  $CH_4/{}^3He$  ratio of the Hakurei fluid ( $1410 \times 10^6$ ) is higher than that of the Jade fluid ( $750 \times 10^6$ ). Although  $CO_2$  should be also produced during the thermal degradation as reported for other sediment-hosted hydrothermal system (Cruse and Seewald, 2006), overwhelming abundance of the magmatic  $CO_2$  prevents detection of difference neither in  $CO_2$  concentrations nor carbon isotope ratios.

As discussed previously, the Jade and Hakurei fluids are likely to share a common reservoir, which means that they share a common fluid circulation system at the recharge and reaction zones. Therefore, the distinctive minor gas composition should reflect process during fluid upwelling at the discharge zone. Because organic-derived species such as  $CH_4$  and  $NH_4^+$  would be involved into the hydrothermal fluid by microbiological activity during fluid-sediment interactions at the recharge zone (Kawagucci *et al.*, 2013), effect of thermal degradation would not obviously appear in concentration of these species. Distinguishable difference was recognized specifically in concentrations of a few minor gas species such as  $H_2$  and  $C_2H_6$  which is sensitive to thermal degradation of organic matter.

As described in the geological background section, observations during dive expeditions revealed different geological environments for the Jade and the Hakurei field. The Jade field is located on the slope where tuff breccia and woody pumice were often observed as exposed outcrop, whereas the Hakurei fields is located on the bottom seafloor of the depression. Here, the seafloor is covered with sediment except for the hydrothermal mounds. A thick sediment layer of more than 150 meters was recognized by a previous geophysical investigation (Y. Nakamura, personal communication). It is reasonable to expect that organic-derived species are added during upwelling of the high temperature fluid through such a thick sediment layer.

## CONCLUSION

This study reports chemistry of hydrothermal fluids collected from the Jade and Hakurei fields both located in the Izena Hole, the middle Okinawa Trough. Their chemical characteristics are attributed to various geochemical processes during the fluid circulation, which are summarized in a schematic cartoon (Fig. 4). Fluid chemistry recognized in these two sites was common to other hydrothermal fields in the Okinawa Trough, which

is explained by primary control by fluid interactions with surrounding silicic rocks. High similarity in chemical composition of major ions and gas species between these fluids suggests that they are derived from the same reservoir and share a common fluid circulation system. Whereas, diversity of geochemistry in the Jade and Hakurei hydrothermal fluids is attributed to chemical modification during fluid upwelling at the discharge zone. Intra-field diversity was found between the high temperature fluid at the proximal part and low temperature fluid in the distal part of the Jade field. Proportional variation of major ion concentrations is attributed to phase separation during fluid upwelling from the reservoir. Diffusive emanation of low temperature and vapor-rich fluid in the distal part is commonly observed in other hydrothermal fields in the Okinawa Trough. Another diversity of fluid chemistry was noted in the concentration of minor gas species between the high temperature fluids collected from the Jade and Hakurei fields. Enrichment in a few minor gas species in the Hakurei fluid is attributed to contribution from thermal gradation of organic matter during fluid upwelling through a thick sediment layer. The observed similarity and diversity in fluid chemistry are in agreement with a model based on geological and geophysical observations; the hydrothermal activity in the Jade field is supported by a satellite system related to an intruded dyke, while the Hakurei field is supported by a main fluid circulation system possibly located beneath thick sediment layer. This study shed light on importance of the Izena Hole as a natural laboratory for studying seafloor processes at the discharge zone, by which chemical characteristics of hydrothermal activity are substantially affected.

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