Radiocarbon content of carbon dioxide and methane in hydrothermal fluids of Okinawa Trough vents

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Here we quantify radiocarbon (^{14}C) content in CO_2 and CH_4 from hydrothermal fluids collected at 5 vent sites in the Okinawa Trough. These data provide preliminary insights on how different carbon sources and circulation processes contribute to vent fluids and take into consideration all potential contaminations during sample processing and analysis with accelerator mass spectrometer. For CO_2 , ^{14}C -dead values observed in fluids of most sites (Hatoma, Hitoshi, Noho) demonstrate the complete removal of the inorganic carbon in the recharged seawater. Conversely, the significantly positive $^{14}\text{CO}_2$ are detected in fluids from the Daiyon-Yonaguni site, which implies the persistence of the recharged seawater-derived inorganic carbon and/or a contribution from thermal degradation of sedimentary ^{14}C -containing carbon during fluid upwelling. The CH_4 in these fluids were predominantly ^{14}C -dead or nearly ^{14}C -dead, suggesting a source of deep-buried, ^{14}C -dead sedimentary carbon. The methods outlined in our study exemplify a useful way of elucidating radiocarbon contents of geofluids, and provide future studies with a means to improve our understanding of carbon circulation between hydrosphere and lithosphere.

Keywords: hydrothermal vent, C-14, subseafloor, carbon cycle

INTRODUCTION

Radiocarbon (^{14}C) is a cosmogenic radio-active nuclide with a half-life of 5730 years. Because no ^{14}C is detectable in a carbon reservoir that is isolated from atmospheric carbon after ~50,000 years, ^{14}C content serves as a critical indicator of evaluating relative contribution of various carbon reservoirs, especially at boundaries between the ^{14}C -rich hydrosphere and ^{14}C -poor lithosphere. Progressive improvement of accelerator mass spectrometry (AMS) and AMS-compatible sample processing enable us to quantify ^{14}C content with smaller sample size and shorter analytical time compared to traditional decay counting (Roberts *et al.*, 2007; Ruff *et al.*, 2010; Lang *et al.*, 2013; Synal, 2013; Pack *et al.*, 2015; Wacker *et al.*, 2016; Haghypour *et al.*, 2019). As such, AMS-based ^{14}C measurement and ^{14}C tracer have been established in recent years as a vital tool for understanding biogeochemical carbon cycles (Trumbore, 2009; Ishikawa *et al.*, 2013; Blattmann *et al.*, 2019).

Deep-sea hydrothermal activity drives elemental fluxes between seawater in oceans and the lithosphere (Elderfield and Schultz, 1996). At sites exhibiting high-temperature venting, concentrations of CO_2 and CH_4 in the hydrothermal fluid are commonly higher than those of the ambient seawater (e.g., Kawagucci, 2014), demonstrating a net input of CO_2 and CH_4 to the oceanic hydrosphere through hydrothermal activity. The precise origins of this abundant CO_2 and CH_4 in the hydrothermal fluid, however, remain unclear; the same applies to the fate of dissolved inorganic carbon in the seawater (SW-DIC), which penetrates into the lithosphere as the first step of subseafloor hydrothermal fluid circulation (e.g., Proskurowski *et al.*, 2004).

The ^{14}C content of CO_2 and/or CH_4 in these high-temperature hydrothermal fluids offer key constraints to answer these questions. Radiocarbon data have thus far only been reported from Endeavour vents in the northeastern Pacific (Proskurowski *et al.*, 2004) and the Guaymas Basin (Pearson *et al.*, 2005). Although radiocarbon contents have also been reported from moderate-temperature venting system at the Lost City site off-axis of the Mid-Atlantic Ridge (Proskurowski *et al.*, 2008) and the Von Damm site in the Mid-Cayman Spreading Centre

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Fig. 1. Purification and oxidation line. Abbreviation “P” and “TMP” respectively represent pressure gauge and turbomolecular pump.

(McDermott *et al.*, 2015), these 2 sites are unusual in having fluid CO_2 concentrations lower than or comparable to SW-DIC. Furthermore, little information was given on the possibility of ^{14}C contamination during sample processing in these studies, although this should be crucial due to atmospheric CO_2 and CH_4 being highly enriched in ^{14}C (Hua *et al.*, 2013; Wahlen *et al.*, 1989).

In the present study, we determined ^{14}C contents of CO_2 and CH_4 in high-temperature hydrothermal fluids collected at 5 vent sites in the Okinawa Trough in order to understand their source and behavior through the subseafloor hydrothermal processes. Furthermore, we carefully examined all potential and possible ^{14}C contaminations during sample processing all the way from hydrothermal fluid sampling to the AMS measurement, prior to discussing likely mechanisms controlling ^{14}C contents in Okinawa Trough vent fluids.

SAMPLING AND METHODS

Sampling

High-temperature hydrothermal fluids were collected between 2014–2017 during expeditions of KY14-02, NT15-02, and KR16-16 at five deep-sea vent sites in the

Okinawa Trough: Daiyon-Yonaguni (DY) (Konno *et al.*, 2006; Suzuki *et al.*, 2008), Hatoma (Toki *et al.*, 2016), Hitoshi (Nakamura *et al.*, 2015; Miyazaki *et al.*, 2017a), Noho (Nakamura *et al.*, 2015; Miyazaki *et al.*, 2017a), and Yokosuka (Miyazaki *et al.*, 2017b) (Fig. 1). The DY site is located in the low-point of a valley where high sedimentation rate is expected due to topographic effect by the surrounding high walls (Ishibashi *et al.*, 2014a; Wu *et al.*, 2019), while the main vents of the other four sites are located either at the top or on the slope of submarine knolls where less particles are to accumulate.

Radiocarbon content of the SW-DIC 1000 m below the sea surface in the Okinawa Trough was reported as ~85 pMC (defined by Eq. (2), see below) (Honda *et al.*, 2000). Radiocarbon dating by planktonic foraminifera buried in seafloor sediments yielded ~20 ky (~9 pMC) at 19 and 4 m below the seafloor near the DY site and the close-by sites Hitoshi and Noho, respectively (Kao *et al.*, 2005; Ijiri *et al.*, 2005; Shao *et al.*, 2016).

Seafloor fluid sampling was conducted with pressure-tight fluid samplers WHATS-2 (Saegusa *et al.*, 2006) or WHATS-3 (Miyazaki *et al.*, 2017a); on-board subsampling and processing followed procedures presented in previous publications using these samplers.

Flow-through mechanism implemented in the WHATS-series samplers allows sufficient substitution of pre-filled fluids by the target geofluid and prevents air-derived compounds from being retained in the sample bottles after fluid sampling (see (Miyazaki *et al.*, 2017a) for more details).

Sample processing onboard

Fluids contained in the pressure-tight sample bottles were subsampled immediately after the recovery on-board research vessels from the seafloor. Each sample bottle was connected to a vacuum line typically consisting of a gas extraction portion made from glass, subsampling bottles, pressure gauges, and an oil-rotary vacuum pump. The vacuum line exhibited inner pressure as low as 10^{-2} kPa and rate of pressure increase as low as 1×10^{-2} kPa every 10 minutes, before each fluid introduction. The entire body of fluid in a bottle was introduced into the extraction portion and mixed with solid reagents, sulfamic acid (H_3NSO_3) and cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2$), to extract inorganic carbon as CO_2 and precipitate H_2S as sulphide minerals. The gases extracted were diffused into a 2-L glass container as subsamples for ^{14}C analyses and 50-mL stainless-steel bottles for compositional and stable isotope analyses. Pressure at the time of sample gas diffusion to the sample canisters was no lower than 17 kPa, while water vapor pressure of ~ 3 kPa at laboratory temperature was included. Pressures after the gas extraction process (~ 15 minutes) fluctuated only by factors within the 10^{-2} kPa order, and air contamination was no greater than 0.1 kPa. Every whole-gas sub-sample contained $>50\%$ of CO_2 and exhibited CH_4/CO_2 ratios of $>1\%$, quantified by gas chromatograph analyses with $\sim 10\%$ analytical uncertainty. Stable isotope ratios of CO_2 and CH_4 were also quantified by isotope-ratio mass spectrometers (IRMS) with analytical uncertainty within 0.5 permil (Table 1). The liquid phase, remaining in the extraction portion, was also subsampled for onshore Mg concentration analyses with $\sim 2\%$ analytical uncertainty. Results from sample analyses without ^{14}C have already been partially reported (Miyazaki *et al.*, 2017a, b).

Purification and oxidation

Purification of CO_2 and CH_4 from the whole-gas sub-sample was conducted in shore-based laboratory at Japan Agency for Marine-Earth Science and Technology (JAMSTEC). The standard “swab test” confirmed negligible pollution in the purification room, although the building has a radio-active isotope laboratory (Kawagucci *et al.*, 2018b). A stainless-steel purification line, constructed based on Pack *et al.* (2015) and Okumura *et al.* (2016) with some minor modifications, functions as a conjunction between the vacuum line and a helium-flow gas chromatograph line (Fig. 1). The vacuum line was

Table 1. Radiocarbon contents of hydrothermal CO_2 and CH_4

Site name	Expedition	Dive No.	Bottle	Amount $\mu\text{g-C}$	ETH nr	F^{14}C	Standard deviation at AMS +/-	Mg mM	Mg-based f (SW) Eq. (4)	Conc. measured mM	Conc. (Mg = 0) Eq. (5)	Sampling artifact- subtracted F^{14}C Eq. (6)	$\delta^{13}\text{C}$ (IRMS) permil
CO_2													
Daiyon-Yonaguni	KY14-02	HPD1623	W1	139	80125.1.1	0.0162	0.0018	2.0	0.04	102	106	0.0155	-8.0
Hatoma	KY14-02	HPD1621	W4	180	80136.1.1	0.0007	0.0015	9.5	0.18	373	454	-0.0003	-8.7
Hitoshi	NT15-02	HPD1770	CWR	171	80127.1.1	-0.0018	0.0013	0.2	0.00	278	279	-0.0018	-2.6
Noho	NT15-02	HPD1772	W1	99	80129.1.1	-0.0006	0.0013	0.5	0.01	116	117	-0.0008	-4.7
Yokosuka	KR16-16	MkIV#718	W4	130	80131.1.1	0.0069	0.0017	1.2	0.02	270	276	0.0068	-11.1
Yokosuka	KR16-16	MkIV#719	W1	130	80133.1.1	0.0058	0.0015	12.2	0.23	343	446	0.0044	-6.0
Commercial tank				151	80135.1.1	0.0063	0.0014						
Blank Gas					41218.7.167	0.0062	0.0010						
Blank Gas					41218.7.168	0.0075	0.0015						
Oxa II gas ($n = 6$)						1.3397	0.0111						
CH_4													
Daiyon-Yonaguni	KY14-02	HPD1623	W1	13	80126.1.1	0.0388	0.0028	2.0	0.04	2.0	2.1	—	-26.6
Hatoma	KY14-02	HPD1621	W4	38	80137.1.1	0.0001	0.0013	9.5	0.18	9.7	11.8	—	-50.3
Hitoshi	NT15-02	HPD1770	CWR	100	80128.1.1	-0.0003	0.0014	0.2	0.00	13.7	13.8	—	-33.1
Noho	NT15-02	HPD1772	W1	56	80130.1.1	-0.0030	0.0012	0.5	0.01	2.8	2.8	—	-28.8
Yokosuka	KR16-16	MkIV#718	W4	62	80132.1.1	0.0027	0.0013	1.2	0.02	10.0	10.2	—	-25.8
Yokosuka	KR16-16	MkIV#719	W1	50	80134.1.1	0.0001	0.0013	12.2	0.23	18.2	23.7	—	-26.5

evacuated by a turbomolecular pump and baked for one day before operation for background pressure lower than 10^{-3} kPa. Ultra-pure grade He (>99.9999%) was further purified by Molecular Sieve 5A trap at LN₂ temperature (−196°C) for the helium-flow line.

For CO₂ purification, the conventional purification method was applied using the vacuum line. First, an aliquot of the whole-gas subsample, which contained ~1 mg-C CO₂, was introduced. After water removal at a trap held at −72°C (dry ice/ethanol slush), CO₂ was condensed on a 9 mm-OD glass finger held at −196°C (LN₂) followed by evacuation of the non-condensable gas. The CO₂ was evaporated once to quantify the amount barometrically, following which, an appropriate volume (~100 µg-C, Table 1) was condensed into a 4 or 6 mm-OD glass ampule, and finally this ampule was sealed with a blowtorch. Blank CO₂ levels, quantified by the same procedure above but without sample introduction, was negligible (<0.1 µg-C).

For CH₄, first an aliquot of the whole-gas subsample was introduced into the vacuum line and concentrated onto a silica gel trap (silica gel packed into a tube 10 cm in length and 1/4"-OD), at −196°C (LN₂). A helium stream set at 50 mL/min was introduced to pass through the silica gel trap, which was then heated to 98°C (boiled water) to evaporate and blow the concentrated gases including CH₄. Sample gases on the stream were sequentially passed through: 1) a chemical trap, filled with magnesium perchlorate (Mg(ClO₄)₂) and Ascarite II (sodium hydroxide-coated silica gel) to remove water and CO₂; 2) a glass tube having CuO wires held at 290°C for the oxidation of CO to CO₂; 3) another chemical trap; 4) a coiled tube held at −130°C (*n*-pentane/LN₂ slush) for precipitation of volatile organic compounds without CH₄; and 5) a stainless-steel tube filled with HayeSepD (60/80 mesh, 3 cm-long, 1/8"-OD tube) held at −130°C (*n*-pentane/LN₂ slush) to capture the CH₄ while allowing H₂/N₂/O₂/Ar to pass through (Okumura *et al.*, 2016). After turning the 2-position valve to introduce another helium stream set at 3 mL/min for the HayeSepD trap, concentrated gases were evaporated by heating (boiled water) and transported to the main oxidation reactor consisting of a glass tube filled with CuO/NiO chips and Pt/Pd wires for CH₄ oxidation to CO₂, held at 1000°C. Ethane and other light molecular weight organic compound may also be oxidized to CO₂ whereas their mixing ratios are two or three orders of magnitude lower than CH₄ (e.g., Miyazaki *et al.*, 2017a). The H₂O produced was removed by a tube filled with Mg(ClO₄)₂ while the CO₂ produced was condensed at a U-shaped stainless-steel tube held at −196°C (LN₂). Headspace gas of the U-shaped trap was evacuated, followed by the transfer of CO₂ into a 4 or 6 mm-OD glass tube, and lastly this ampule was sealed with a blowtorch. Recovery rate of CH₄ as CO₂ was not lower than 80%.

Blank CH₄, probably derived from the traps, was quantified by the same procedure as above (without sample introduction) and was lower than 0.3 µg-C CO₂.

Radiocarbon contents of CO₂ in the ampules resulting from the above procedures were analyzed using MICADAS (the mini radiocarbon dating system), a gas ion source AMS, at the ETH-PSI laboratory in Zürich (Ruff *et al.*, 2010; Wacker *et al.*, 2016). The CO₂ in the 6 mm-OD ampule prepared at JAMSTEC was transferred to 4 mm-OD ampule at ETH for adaption for MICADAS manipulation. Device specification, analytical procedure, and data acquisition for the MICADAS ¹⁴C analyses followed in the present study have been reported in detail in previous publications (Ruff *et al.*, 2010; Wacker *et al.*, 2016). Laboratory standards of ¹⁴C-known modern oxalic acid OxII and ¹⁴C-dead ancient CO₂ were analyzed along with the samples. In this study, the radiocarbon content is presented in F¹⁴C (fraction of modern carbon) (Reimer *et al.*, 2004) and pMC (percent modern carbon) that are defined as follows:

$$F^{14}C = A_{SN}/A_{ON}, \quad (1)$$

$$pMC = F^{14}C \times 100, \quad (2)$$

where A_{SN} and A_{ON} represent the δ¹³C-normalized specific activities of the sample and OxII, respectively. Details of definition and calculation of F¹⁴C from the AMS measurement have been reported in previous publication (Reimer *et al.*, 2004). Standard deviation of each F¹⁴C determination during individual sample analysis at AMS are presented along with the F¹⁴C values (Table 1).

RESULTS

All ¹⁴C data acquired in our study are shown in Table 1. Figure 2a shows results along with chronological order of the AMS analyses. The ¹⁴C contents, without the modern OxII (Fig. 2b), were all lower than 4 pMC. If only considering the analytical uncertainties during the AMS analyses (Table 1), 5 of the 12 hydrothermal samples contained significant ¹⁴C, while the other 7 were completely ¹⁴C-dead (Fig. 2b). In order to interpret if the significant ¹⁴C seen in these 5 hydrothermal samples truly represents ¹⁴C contained in the seafloor hydrothermal fluids or is due to contamination, we must take into consideration and critically appraise the possible sources of ¹⁴C contamination, as discussed below.

The ¹⁴C contents of the ancient CO₂ gas standards, measured in the same way as the modern standards, were significantly positive at 0.62 ± 0.10 and 0.75 ± 0.15 pMC (Table 1). This ¹⁴C level would correspond to the ¹⁴C blank during sample manipulation at the ETH-AMS laboratory, although memory effect from the OxII processing may

Fig. 2. All y axes represent ^{14}C content in pMC. (a) All the results of AMS analysis including modern carbon standards OxII are shown in chronological order. (b) Open and filled circles represent hydrothermal samples of CO_2 and CH_4 , respectively. Circles marked by DY are samples from Daiyon-Yonaguni site. Open squares and diamond represent ancient CO_2 provided directly to the ETH-AMS and processed at JAMSTEC laboratory, respectively. Symbol size is comparable to analytical errors at AMS. Shade represents a blank level at AMS analysis. (c) Samples arranged by sample size introduced to ETH-AMS system.

have resulted in such (slightly high) blank levels. The ^{14}C -dead-certified commercial CO_2 processed in JAMSTEC showed 0.63 ± 0.14 pMC, comparable to the ancient CO_2 provided at the ETH-AMS laboratory. When the ^{14}C blank as high as 0.9 pMC from MICADAS manipulation is ap-

plied, the ^{14}C contents in 2 samples collected at the DY site still remain significantly positive (Fig. 2b).

The highest ^{14}C value of 3.88 ± 0.28 pMC was acquired from the DY CH_4 -derived CO_2 sample containing $13 \mu\text{g-C}$ (Fig. 2c), the smallest sample size in this study, while the MICADAS used herein was certified to be able to reliably measure CO_2 samples containing carbon as small as $8 \mu\text{g}$ (Ruff *et al.*, 2010). The other significantly positive ^{14}C content of 1.62 ± 0.18 pMC was acquired from the DY CO_2 sample while all hydrothermal CO_2 samples were processed with $> \sim 100 \mu\text{g-C}$. The Yokosuka CO_2 contained ^{14}C as high as the AMS blank level, while CO_2 from the other three sites were determined to be completely ^{14}C -dead.

Seawater entrained at the time of seafloor sampling is another contaminant where modern CO_2 could be introduced into the fluid samples, as deep-sea water in the Okinawa Trough contains modern DIC (2.3 mM with 85 pMC) (Honda *et al.*, 2000). Since magnesium is enriched in seawater (53 mM-Mg) but depleted in the endmember hydrothermal fluid (0 mM-Mg), magnesium concentrations in the fluid samples can be used as a proxy of the contribution ratio of seawater (SW), f , to the discharging hydrothermal fluid (HF) in the samples collected:

$$[\text{Mg}]_{\text{sample}} = (1 - f) \times [\text{Mg}]_{\text{HF}} + f \times [\text{Mg}]_{\text{SW}} \quad (3)$$

$$f = [\text{Mg}]_{\text{sample}} / 53. \quad (4)$$

Using f , the isotope mass balance calculation for the subtraction of seawater-derived ^{14}C signature can provide $\text{F}^{14}\text{C}_{\text{CO}_2}$ of the fluid as followings:

$$[\text{CO}_2]_{\text{sample}} = (1 - f) \times [\text{CO}_2]_{\text{HF}} + f \times [\text{CO}_2]_{\text{SW}} \quad (5)$$

$$\text{F}^{14}\text{C}_{\text{sample}} \times [\text{CO}_2]_{\text{sample}} = (1 - f) \times \text{F}^{14}\text{C}_{\text{HF}} \times [\text{CO}_2]_{\text{HF}} + f \times \text{F}^{14}\text{C}_{\text{SW}} \times [\text{CO}_2]_{\text{SW}}. \quad (6)$$

For example, applying this calculation for the DY sample generates the endmember fluid CO_2 concentration and ^{14}C content of 106 mM and 1.55 pMC, respectively (Table 1). As only negligible CH_4 (< 1 nM) occurs in deep-sea water in the western Pacific (e.g., Kawagucci *et al.*, 2018a), its contribution should be negligible (not calculated).

Furthermore, contamination of air during sample processing may have serious impacts, because CO_2 and CH_4 make up ~ 400 ppmv and ~ 2 ppmv of air and exhibit ^{14}C content of 110 and 130 pMC, respectively (Hua *et al.*, 2013; Wahlen *et al.*, 1989). Sensitivity of the F^{14}C values of the subsample (that was analyzed with AMS) against air contamination into the sample can also be calculated using isotope mass balance, as follows:

Fig. 3. Possible variation of radiocarbon content associated with air contamination. (a) Possible radiocarbon contents as a function of relative contribution of contaminant for the sample gas (assuming 0 pMC in both CO₂ and CH₄) at onboard gas extraction (curves) and shore-based CO₂ purification (line). For DY CO₂, g is expected at <0.001. (b) Possible radiocarbon contents of CH₄ as a function of sample size processed at the purification and oxidation line. Curves represent mixings between the 0.3 μg-C blank with radiocarbon contents of 130 pMC ($=F^{14}C_{air}$) or 13 pMC ($=0.1 \times F^{14}C_{air}$) and ideal CH₄ sample having 0 pMC.

$$[C]_{\text{subsample}} = (1 - g) \times [C]_{\text{sample}} + g \times [C]_{\text{air}} \quad (7)$$

$$F^{14}C_{\text{subsample}} \times [C]_{\text{subsample}} = (1 - g) \times F^{14}C_{\text{sample}} \times [C]_{\text{sample}} + g \times F^{14}C_{\text{air}} \times [C]_{\text{air}}, \quad (8)$$

where $[C]$ and g represent $[CO_2]$ or $[CH_4]$ (in ppmv) and the relative contribution of air, respectively. Assuming $F^{14}C_{\text{sample}}$ is zero, Eq. (8) can be rewritten as:

$$F^{14}C_{\text{subsample}} = \{g \times F^{14}C_{\text{air}} \times [C]_{\text{air}}\} / [C]_{\text{subsample}}. \quad (9)$$

The barometrical monitoring during the ship-board processing (<0.1 kPa-blank for >17 kPa-subsample, see Subsection “Purification and oxidation”) demonstrated that the actual value of g was <0.01. It is known that local $[CO_2]_{\text{air}}$, $[CH_4]_{\text{air}}$, $F^{14}C_{CO_2, \text{air}}$, and $F^{14}C_{CH_4, \text{air}}$ were no

Fig. 4. Radiocarbon contents and concentrations of hydrothermal fluid CO₂. Open symbols represent radiocarbon contents of hydrothermal fluid CO₂ from Guaymas Basin (square) (Pearson et al., 2005), Endeavour (diamond) (Proskurowski et al., 2004), Von Damm (hexagon) (McDermott et al., 2015), and Daiyon-Yonaguni (circle, this study). Filled circle represents seawater dissolved inorganic carbon (SW-DIC). Line and broken line respectively represent mixings of SW-DIC or a tenth of it with ¹⁴C-dead magmatic CO₂. Contribution of thermogenic CO₂ originating from ¹⁴C-containing sediment can increase both concentration and ¹⁴C content of CO₂.

higher than 1000, 5, 1.1, and 1.3, respectively. Given that $[CO_2]_{\text{subsample}}$ and $[CH_4]_{\text{subsample}}$ were not lower than 500,000 and 10,000 (see Subsection “Purification and oxidation”), respectively, the calculated $F^{14}C_{\text{subsample}}$ values were lower than 0.001 (0.1 pMC) for both CO₂ and CH₄ even for g as large as 0.1 (Fig. 3a).

To evaluate the blank effect at the shore-based purification stage based on barometrical monitoring of accumulated CO₂, where every (C) were the same due to purification (100% CO₂), Eq. (9) was simplified to the following:

$$F^{14}C_{\text{sample}} = x \times F^{14}C_{\text{contaminant}} \quad (10)$$

where x represents the relative contribution of the line blank CO₂ to the CO₂ in the ampule. The quantity of CO₂ sealed into the glass ampule was estimated based on the barometrical monitoring during processing (<0.1 μg-C-blank for ~100 μg-C-sample in the vacuum line, see Subsection “Purification and oxidation”), demonstrating that $x < 0.001$. Even when assuming $F^{14}C_{\text{contaminant}}$ as high as $F^{14}C_{\text{air}_CO_2}$ of 1.1 (110 pMC), the calculated $F^{14}C_{\text{subsample}_CO_2}$ value was lower than 0.0013 (0.13 pMC) (Fig. 3a). As such, contamination alone cannot explain the significantly positive $F^{14}C_{CO_2}$ value detected from the DY sample (Fig. 3a).

For CH₄, the blank level was as high as 0.3 μg-C. On one hand, analysis of 13 μg-C of ¹⁴C-dead CH₄ can

achieve ^{14}C content of 3.4 pMC when applying $F^{14}\text{C}_{\text{air_CH}_4}$ of 1.3 for $F^{14}\text{C}_{\text{contaminant_CH}_4}$ (Fig. 3b). This calculated ^{14}C content of 3.4 pMC seemed comparable to 3.88 pMC acquired from the DY CH_4 sample analysis. On the other hand, although the $F^{14}\text{C}$ value of the blank gas cannot be quantified due to its small quantity, it would be an order of magnitude lower than 1.3, as demonstrated by four other samples with $F^{14}\text{C}_{\text{CH}_4}$ values of <0.001 (Fig. 3b). Indeed, the purification line has so far only been used for geological and geofluid-derived samples, which would contain little $^{14}\text{CH}_4$ and $^{14}\text{CO}_2$. Nevertheless, the above calculation suggests that contamination alone may explain the significantly positive ^{14}C content of CH_4 from the DY sample.

DISCUSSION

The critical evaluation of sample quality and contamination potentials indicated that the hydrothermal gas collected at the DY site undoubtedly contained a significant amount of ^{14}C in CO_2 , and possibly in CH_4 . Subseafloor hydrothermal fluid circulation includes four carbon reservoirs: seawater, magma, host rocks, and sediment (McCollom, 2008). Of these, carbon in magma and host rocks must be ^{14}C dead, as these carbon sources have a geological-scale age. In addition to seawater DIC (2.3 mM, 85 pMC), sediments younger than 20 ky old within ~20 m below the seafloor of the Okinawa Trough likely contains significant ^{14}C in the form of organic matter. Thermal degradation of this ^{14}C -containing, sedimentary organic matter by interaction with ascending fluids results in the simultaneous production of CO_2 and CH_4 that contains ^{14}C (e.g., Kawagucci and Seewald, 2019). Dissolved organic matter in the deep-sea water also contains some ^{14}C (~40 μM , 50 pMC) (Williams and Druffel, 1987), but is negligible in quantity.

Seawater DIC recharged at the initial stage of hydrothermal circulation may serve as a source of $^{14}\text{CO}_2$ in the venting fluid CO_2 (Fig. 4), although quantitative conservation of the recharged DIC has been much debated (Proskurowski *et al.*, 2004). A simple calculation for magmatic ^{14}C -dead CO_2 addition to seawater DIC can indeed yield values that characterize the DY CO_2 (106 mM, 1.55 pMC) (Fig. 4). The quantitative conservation of SW-DIC is, however, not supported by other fluids with ^{14}C -dead CO_2 reported herein or from a previous study (Proskurowski *et al.*, 2004) (Fig. 4). The possible removal of DIC during subseafloor fluid circulation is implied, for example, from calcium carbonate veins in altered oceanic crust (Alt and Teagle, 1999), whereas active high-temperature hydrothermal system differs from the off-axis oceanic crust with respect to residence time, temperature, and host rock acidity.

Two possible explanations are feasible to account for

the presence/absence of ^{14}C in the Okinawa Trough vent fluids: i) the degrees and persistence of recharged SW-DIC during subseafloor fluid-rock interaction are variable among different hydrothermal sites and happens to be high at the DY site, and ii) recharged seawater DIC is completely removed at every site while the thermogenic $^{14}\text{CO}_2$ input via subseafloor fluid-sediment interaction is significant at some sites, including DY. The apparently ^{14}C -dead CO_2 in other Okinawa Trough vent sites (Hatoma, Hitoshi, Noho) indicate that the recharged DIC has been completely removed and only negligible sedimentary carbon has been provided in these sites. The $^{14}\text{CO}_2$ in the DY fluid can reflect either the recharged DIC or sedimentary carbon, or a combination of both.

Thermal degradation of sedimentary ^{14}C -containing carbon may contribute to $^{14}\text{CO}_2$ and $^{14}\text{CH}_4$ in the fluid of DY site. An example of thermogenic $^{14}\text{CO}_2$ and $^{14}\text{CH}_4$ input has been reported from the Guaymas Basin site in the Gulf of California, where the upwelling fluid passes through a >1 km-thick sediment layer (Pearson *et al.*, 2005) resulting in abundant $^{14}\text{CO}_2$ (50 mM, 5.6 pMC) (Fig. 4) as well as $^{14}\text{CH}_4$ (53 mM, 7.5 pMC) in the venting fluids (Pearson *et al.*, 2005; Proskurowski *et al.*, 2008). Topographical characteristics of the DY site, a valley where high sedimentation rate is expected due to particles coming from the surrounding walls, enables an environmental setting suitable for relatively young sediment interaction with upwelling fluid beneath the hydrothermal vent. On the other hand, vents of the other four Okinawa Trough sites studied here are located at the top or on the slope of knolls (Nakamura *et al.*, 2015; Toki *et al.*, 2016; Miyazaki *et al.*, 2017b). Presumably, negligible fluid-sediment interaction within the upwelling zone in this environmental setting (Ishibashi *et al.*, 2014b) results in negligible $^{14}\text{CO}_2$ and $^{14}\text{CH}_4$ as observed for fluids from these sites.

Large variations of ^{13}C content of CO_2 and CH_4 (Table 1) are known among the Okinawa Trough sites (Kawagucci *et al.*, 2013), however, their sources remain consistent with the almost ubiquitously ^{14}C -dead signatures reported here. For CO_2 , magmatic gas is considered to be the predominant source for CO_2 in vent fluids at hydrothermal sites located at convergent plate boundaries (e.g., Lupton *et al.*, 2008). The ^{13}C content of magmatic CO_2 is controlled by the mixing ratio between ^{13}C -rich subducting carbonate and ^{13}C -depleted subducting organic matter (Sano and Marty, 1995), while both types of subducting carbon have spent geological time sufficient to extinguish ^{14}C . Conversely, for CH_4 , the ^{13}C variation among the Okinawa Trough vent sites has been explained by differences in processes, instead of the carbon source. When based on deeply-buried sedimentary organic carbon which is dominated by ^{13}C -rich ^{14}C -dead carbon, variations in ^{13}C content with consistently ^{14}C -dead sig-

natures can result from larger/smaller kinetic isotope effects on the two processes of methanogenesis, namely microbial metabolism (Valentine *et al.*, 2004; Okumura *et al.*, 2016) and thermal decomposition (Seewald *et al.*, 1994; Kawagucci and Seewald, 2019).

SUMMARY AND CONCLUDING REMARKS

Our analyses of CO₂ and CH₄ radiocarbon contents in hydrothermal fluids collected at 5 vent sites in the Okinawa Trough provide preliminary insights on how different carbon sources and circulation processes contribute to vent fluids. The ¹⁴C-dead CO₂ values observed in fluids at three Okinawa Trough sites (Hatoma, Hitoshi, Noho) demonstrate that the recharged DIC had been completely removed during seafloor hydrothermal circulation, while the persistence of seawater DIC until the venting has been discussed. Factors controlling the persistence of the recharged DIC, such as residence time, temperature, and host rock type, remain unidentified. The significantly positive ¹⁴CO₂, and possibly ¹⁴CH₄, of the fluids detected in the DY site implies a contribution from thermal degradation of sedimentary ¹⁴C-containing carbon during fluid upwelling, and is consistent with its topographic setting at the bottom of a valley. The abundant CH₄ in Okinawa Trough vent fluids were ¹⁴C-dead or nearly ¹⁴C-dead, which suggests a predominant source from deeply-buried ¹⁴C-dead sedimentary carbon.

These results serve as evidence that the procedures described herein, which combine deep-sea geofluid sampling, gas extraction onboard, purification at laboratory in JAMSTEC, and AMS analyses based in ETH, can quantify ¹⁴CO₂ content in CO₂-rich geofluids as low as 0.9 pMC (Fig. 3a). The accumulation of blank CO₂ throughout the procedure of F¹⁴C_{CH₄} analysis was as low as 0.3 μg-C, while F¹⁴C values of the blank could not be determined. In this situation, the accurate quantification limit of F¹⁴C, three times higher than the blank level, is as low as 1.5 pMC when processing >100 μg-C of CH₄ (Fig. 3b). Sampling using the WHATS-series samplers (50 or 150 mL) for >0.1 mM concentrations of carbon compounds in seafloor geofluids bring >~60 μg-C on-board the research vessel. This appears to be sufficient for carrying out the ¹⁴C analyses using our procedure, although not quite ideal when the blank levels during CH₄ processing is considered. This will be the target of methodological improvements, especially to reduce blank levels at the JAMSTEC laboratory. Nevertheless, we consider the procedures reported here to be a useful approach for studying radiocarbon contents in geofluids. Future research applying this method or an improved version of it to elucidate radiocarbon contents of deep-sea hydrothermal fluids in settings lacking sediments will be a valuable window to understand carbon circulation beneath the seafloor.

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