



Submarine venting of liquid carbon dioxide on a Mariana Arc volcano

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[1] Although CO₂ is generally the most abundant dissolved gas found in submarine hydrothermal fluids, it is rarely found in the form of CO₂ liquid. Here we report the discovery of an unusual CO₂-rich hydrothermal system at 1600-m depth near the summit of NW Eifuku, a small submarine volcano in the northern Mariana Arc. The site, named Champagne, was found to be discharging two distinct fluids from the same vent field: a 103°C gas-rich hydrothermal fluid and cold (<4°C) droplets composed mainly of liquid CO₂. The hot vent fluid contained up to 2.7 moles/kg CO₂, the highest ever reported for submarine hydrothermal fluids. The liquid droplets were composed of ~98% CO₂, ~1% H₂S, with only trace amounts of CH₄ and H₂. Surveys of the overlying water column plumes indicated that the vent fluid and buoyant CO₂ droplets ascended <200 m before dispersing into the ocean. Submarine venting of liquid CO₂ has been previously observed at only one other locality, in the Okinawa Trough back-arc basin (Sakai et al., 1990a), a geologic setting much different from NW Eifuku, which is a young arc volcano. The discovery of such a high CO₂ flux at the Champagne site, estimated to be about 0.1% of the global MOR carbon flux, suggests that submarine arc volcanoes may play a larger role in oceanic carbon cycling than previously realized. The Champagne field may also prove to be a valuable natural laboratory for studying the effects of high CO₂ concentrations on marine ecosystems.

Components: 10,100 words, 12 figures, 3 tables, 2 videos.

Keywords: carbon dioxide; Mariana; submarine; volcano.

Index Terms: 1031 Geochemistry: Subduction zone processes (3060, 3613, 8170, 8413); 3017 Marine Geology and Geophysics: Hydrothermal systems (0450, 1034, 3616, 4832, 8135, 8424); 4832 Oceanography: Biological and Chemical: Hydrothermal systems (0450, 1034, 3017, 3616, 8135, 8424).

Received 27 September 2005; **Revised** 26 April 2006; **Accepted** 16 May 2006; **Published** 10 August 2006.

Lupton, J., et al. (2006), Submarine venting of liquid carbon dioxide on a Mariana Arc volcano, *Geochem. Geophys. Geosyst.*, 7, Q08007, doi:10.1029/2005GC001152.

1. Introduction

[2] While considerable effort has been devoted to exploring for submarine hydrothermal activity along the global mid-ocean ridge (MOR) system where tectonic plates are diverging, very little is known about the distribution and intensity of similar submarine activity on volcanic arcs where plates converge. *de Ronde et al.* [2001] made the first systematic study of hydrothermal activity in this tectonic setting along the southern Kermadec Arc. Their water column plume surveys showed that a substantial portion of the submarine volcanoes there are hydrothermally active [*de Ronde et al.*, 2001]. Furthermore, in contrast to MOR activity that is mainly confined to the depth range of 2000–2500 m, the Kermadec Arc volcanoes were

found to be introducing hydrothermal effluent at a wide variety of ocean depths, ranging from 100 to 1800 m.

[3] During February–March 2003, as part of the Submarine Ring of Fire (SROF) project funded by NOAA's Ocean Exploration Program, the R/V *Thomas G. Thompson* conducted a comprehensive survey of submarine hydrothermal activity along a second volcanic arc, the Mariana Arc from 13.5°N to 22.5°N [*Embley et al.*, 2004]. Plume surveys were conducted in the water column above ~50 Mariana Arc submarine volcanoes using a CTD/rosette system that included an Eh sensor for measuring in-situ oxidation-reduction potential. A total of 70 CTD casts were completed, and discrete water samples were collected for analysis of a

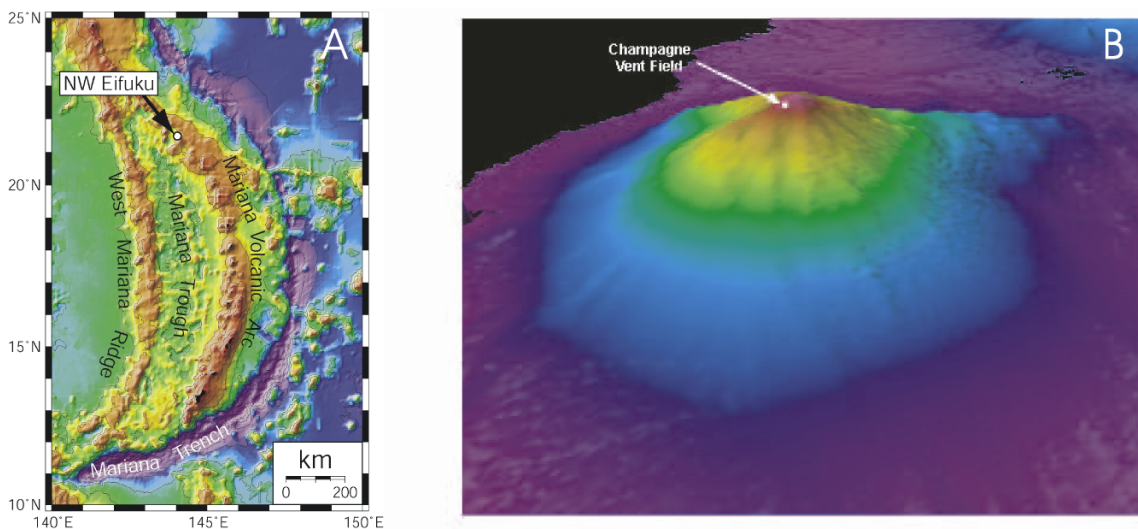


Figure 1. (a) Location map for NW Eifuku in the Mariana Arc. (b) Oblique 3-D representation of NW Eifuku viewed from the southwest, generated from EM300 bathymetry. No vertical exaggeration. Depths range from 1550 to 3000 m.

variety of hydrothermal tracers, including ^3He , CH_4 , CO_2 , H_2S , Fe, Mn, pH, and suspended particles. The analysis of these samples showed that 12 of the Mariana Arc submarine volcanoes surveyed had active hydrothermal discharge. Of these, 8 were new sites and 4 were volcanoes previously known to be hydrothermally active [see *Embley et al.*, 2004]. The newly discovered activity included that on NW Eifuku, a small volcanic cone located at 21.49°N , 144.04°E that rises to a depth of ~ 1535 m below sea level (Figures 1 and 2). NW Eifuku is the deepest in a cluster of 3 volcanoes that includes the larger neighboring volcanoes Daikoku and Eifuku. The water column samples collected over NW Eifuku in 2003 had excess concentrations of ^3He , CO_2 , CH_4 , Fe, and Mn, as well as pH, light backscattering (suspended particle), and Eh anomalies, all confined to the depth range of 1490 to 1620 m [Lupton *et al.*, 2003; Resing *et al.*, 2003].

2. Discovery of the Champagne Site

[4] The second phase of the SROF project consisted of a follow-up expedition aboard the R/V *T.G. Thompson* in March–April 2004 employing the remotely-operated vehicle (ROV) ROPOS to directly explore and sample a selected group of the Mariana Arc submarine volcanoes. Three ROV dives were devoted to exploring NW Eifuku. Approximately 8 hours into the first dive, at a depth of 1604 m, ROPOS discovered a remarkable

hydrothermal field (later named Champagne) with small white chimneys discharging buoyant milky fluid. Subsequent surveys with the ROV located several additional sites of hydrothermal discharge on NW Eifuku, although the most intense venting was found at the Champagne site ~ 80 m WNW of the volcano summit. The summit of NW Eifuku was mapped with an Imagenex scanning sonar on ROPOS (Figure 2c), following the methods described by *Chadwick et al.* [2001]. The high-resolution bathymetry shows that the Champagne vent field lies in the steep headwall of a gravitational slope failure that cuts across the top and SW side of the volcano [Chadwick *et al.*, 2004]. Although there were few vent animals right at the Champagne site, an extensive biological community was found within the surrounding few hundred meters, including mussels, shrimps, crabs and limpets.

[5] In addition to the vent fluid discharge at Champagne vent, droplets coated with a milky skin were rising slowly from the seafloor around the chimneys (Figure 3). The droplets were later determined to consist mainly of liquid CO_2 , with H_2S as a secondary component. The seafloor area of active CO_2 droplet flux was characterized by pumice and whitish/yellowish sulfur-rich material. The droplets were sticky and adhered to the ROV like clumps of grapes, although they did not tend to coalesce into larger droplets (Figure 3e). The film coating the droplets was assumed to be CO_2 hydrate (or clathrate) which is known to form

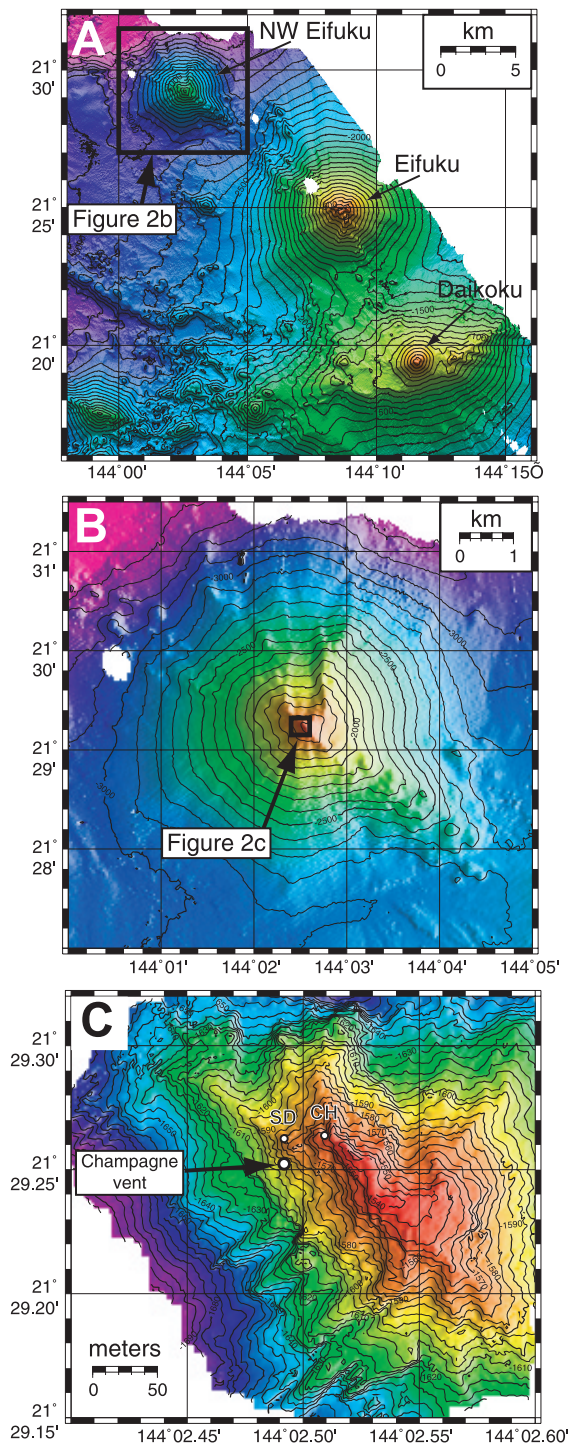


Figure 2. (a) Bathymetric map showing locations of Daikoku, Eifuku, and NW Eifuku submarine volcanoes. Box shows location of Figure 2b. (b) Detailed bathymetric map of NW Eifuku. Box shows location of Figure 2c. (c) High-resolution bathymetry of the summit of NW Eifuku, showing location of the Champagne site and Sulfur Dendrite (SD) and Cliff House (CH) vent sites. This high-resolution bathymetry was collected using the Imagenex sonar system mounted on the ROPOS ROV [Chadwick *et al.*, 2001, 2005].

whenever liquid CO₂ contacts water under these P, T conditions [Sloan, 1990]. Liquid CO₂ should be buoyant at the depth of the Champagne site, since it has a density less than seawater at depths shallower than about ~2600 m [Brewer *et al.*, 1999]. At NW Eifuku, droplets percolated out of crevices in the seafloor, and we did not observe the formation of small hydrate pipes as noted at the JADE site in the Okinawa Trough [Sakai *et al.*, 1990a]. The flux of liquid CO₂ droplets increased dramatically whenever the seafloor was disturbed by the ROV. This observation is consistent with the presence of a layer of liquid CO₂ beneath the surface capped by an impeding layer of CO₂ hydrate (see Figure 4). Thus any penetration of the hydrate cap releases the buoyant liquid CO₂ beneath. These observations are similar to those reported by Sakai *et al.* [1990a], who discovered venting of liquid CO₂ in the Okinawa Trough back-arc basin. A comparison of the video from both sites indicates a higher flux of CO₂-rich droplets at NW Eifuku compared to the JADE site (see Figure 3 caption).

[6] In October–November of 2005 we had a second opportunity to collect samples at NW Eifuku during cruise NT05-18 aboard the R/V *Natsushima*. During the *Natsushima* cruise, the ROV Hyper-Dolphin completed 6 dives on NW Eifuku, 2 on the volcano flanks and 4 on the summit area. During this expedition, the Hyper-Dolphin collected additional samples of both the vent fluids and liquid droplets at the Champagne site.

3. Methods

[7] Samples of the Champagne vent fluid were collected in special gas-tight, all-metal bottles constructed of titanium alloy. The bottles, which have an internal volume of ~150 ml, were initially evacuated. After the connecting lines were flushed, the bottle inlet was opened using a hydraulic actuator, and then hydrostatic pressure quickly forced the vent fluid sample into the bottle. At the end of the ROV dive, the samples were processed on board the ship using a high vacuum extraction line equipped with a low temperature (–60°C) trap and an all-metal bellows pump (Figure 5). The sample was first dropped from the gas-tight bottle into an evacuated glass flask containing ~1 g of sulfamic acid. The acid lowers the pH of the fluid, thereby aiding in the extraction of CO₂ and other dissolved gases. The bellows pump was then used to pump the exsolved gases

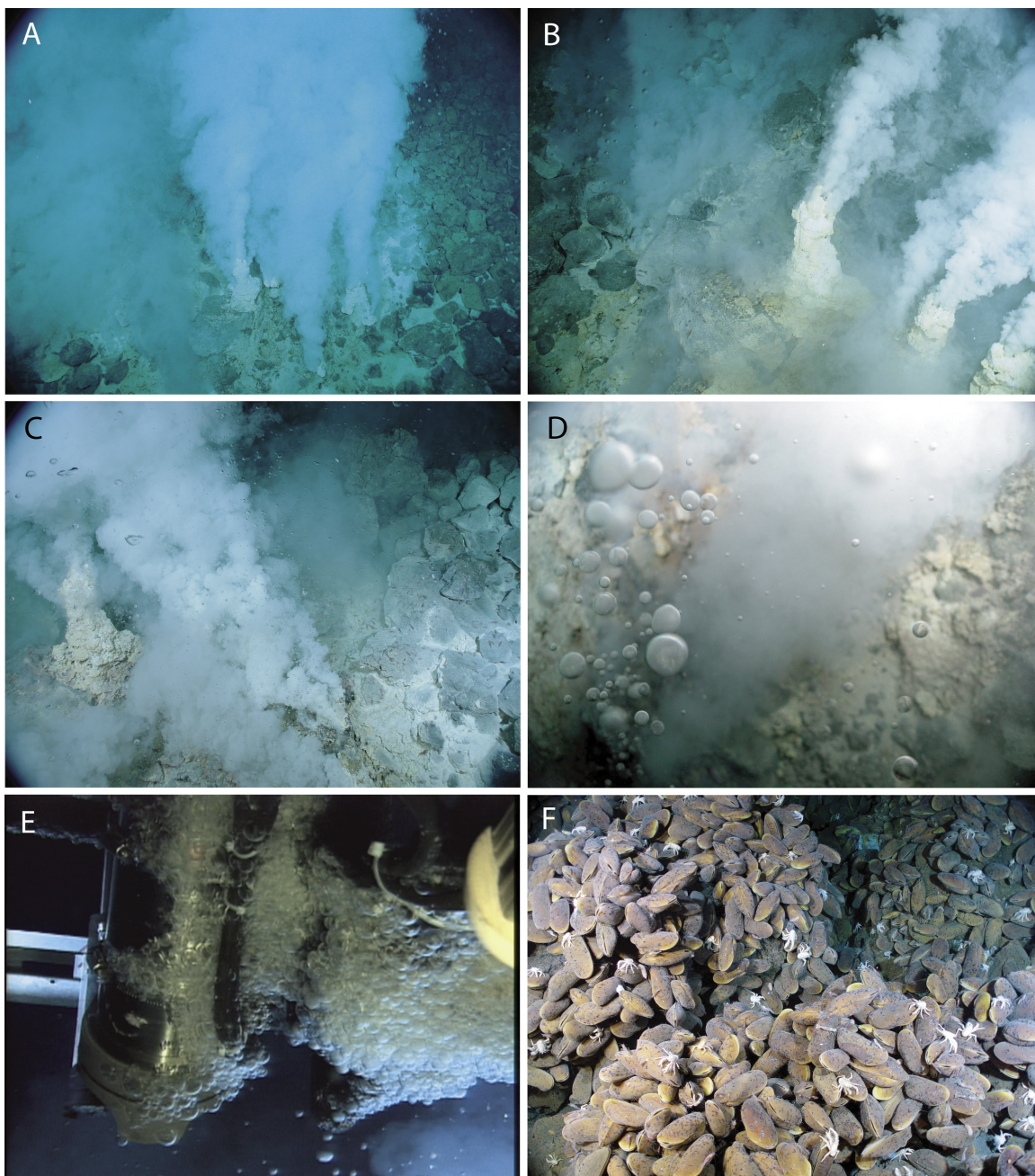


Figure 3. Photographs of the Champagne hydrothermal site taken with the ROPOS ROV. (a, b, and c) Small chimneys venting 103°C vent fluid. Liquid CO₂ droplets are also visible. (d) Close-up of liquid CO₂ droplets rising in a stream from the seafloor. (e) Liquid CO₂ droplets collecting on the underside of the ROV bumper-bar and camera. (f) Mussel bed only tens of meters from the Champagne vent site. See also Movies 1 and 2. Additional photographs and video clips from the 2004 Submarine Ring of Fire expedition and from NW Eifuku in particular are available at the Ocean Exploration Web site: <http://oceanexplorer.noaa.gov/explorations/04fire/logs/april10/april10.html> and <http://oceanexplorer.noaa.gov/explorations/04fire/logs/photolog/photolog.html>.

through the drying trap into a calibrated volume. After the pumping was completed, the total amount of gas was measured using a high precision capacitance manometer attached to the cali-

brated volume. Then splits of the dry gas were sealed into glass ampoules. For rare gas measurements, the ampoules were constructed of type 1720 or 1724 aluminosilicate glass with low heli-

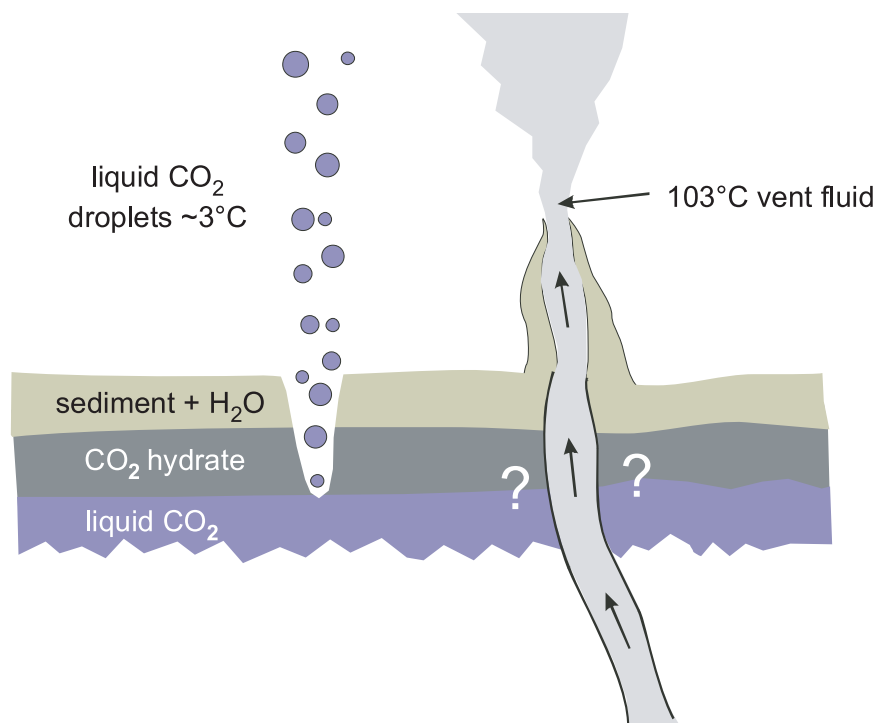


Figure 4. Diagram of near surface conditions at the Champagne vent field. The “?” indicates possible regions where liquid CO₂ and/or CO₂ hydrate are being entrained into the vent fluid flow.

um permeability. During the 2004 R/V *Thompson* cruise, our extraction line had the capability of handling about 1.5 l of total gas, which proved to be inadequate for some of the very gassy vent fluid samples. Thus for most gas-rich samples it was necessary to carry out the extractions in multiple steps. While this provided an accurate assessment of total gas content, the multiple step extraction fractionated the samples, making them unsuitable for gas composition or isotopic measurements. For the 2005 R/V *Natsushima* cruise, the extraction line was fitted with an additional tank increasing the calibrated volume to 11 l, thereby allowing us to extract the samples in one step.

[8] For analysis of dissolved species, additional samples of vent fluid were collected in non-gas-tight PVC pistons with pressure relief valves at the top to capture the water component. Careful measurements using a temperature probe integral with the sampler inlet gave temperatures of 103°C for the most vigorous vents, although several other vents in the area were discharging fluids at temperatures between 11 and 68°C. Careful probing into the seafloor where the liquid droplets were forming found temperatures <4°C, consistent with the existence of CO₂ in the liquid or hydrate state.

[9] Sampling of the liquid droplets proved to be even more challenging. On one of the 2004 ROPOS ROV dives we collected about 0.5 l of the liquid CO₂ droplets in an inverted plastic cylinder normally used for collection of sediment

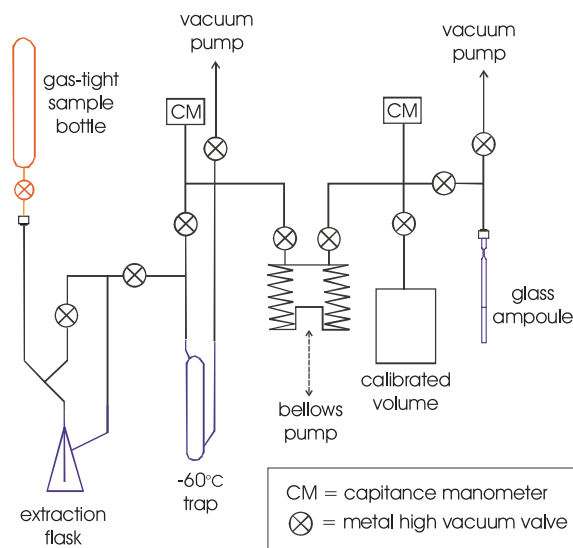


Figure 5. Schematic of the extraction line used for sample processing at sea.



Figure 6. Photographs of sampling at the Champagne site in 2004 and 2005. (a) Fluid sampler being inserted into 103°C hydrothermal vent. (b) Droplets of liquid CO₂ being collected in an inverted plastic cylinder held in the ROV arm. (c) Photograph of the plastic cylinder taken at about 400 m depth during the ROV’s ascent to the surface. Most of the liquid droplets have converted to hydrate, and the hydrate is beginning to sublime into gaseous CO₂. (d) Close-up of the “droplet catcher” used during the 2005 expedition attached to the small volume gas-tight bottle. (e and f) The ROV Hyper-Dolphin sampling liquid CO₂ with the droplet catcher and gas-tight bottle at the Champagne site.

cores (Figure 6b), and observed the droplets as the submersible ascended to the surface at the end of the dive (Figure 6c). This was similar to an experiment conducted by *Sakai et al.* [1990a] in the Okinawa Trough. We were able to first observe

the continuous conversion of liquid CO₂ into white “sherbet-like” hydrate in the cylinder. Then as the submersible passed through ~400 m depth (at ~4°C), we observed rapid conversion of both liquid CO₂ and hydrate into gaseous CO₂. This is

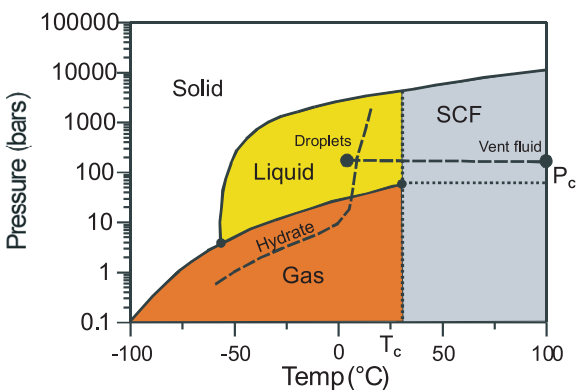


Figure 7. Phase diagram for CO₂ showing regions where solid, liquid, gas, and super-critical fluid (SCF) exist. P_c and T_c denote the critical pressure and temperature. The dashed line denotes the boundary of hydrate stability [Sloan, 1990]. The P, T conditions for the Champagne site liquid droplets and for the 103°C vent fluid are shown.

precisely the pressure depth at which this phase transition was expected, thus confirming our hypothesis that the droplets were composed mainly of liquid CO₂ (Figure 7). The plastic collection cylinder as well as some of the ROV camera face plates suffered permanent damage as a result of contact with the corrosive liquid droplets.

[10] In 2004, liquid CO₂ droplets were also collected by gluing a length of PEEK[™] tubing into the plastic cylinder mentioned above and connecting the other end to the inlet of a titanium gas-tight bottle. The ROV again collected about 500 ml of the liquid droplets by holding the plastic cylinder inverted above the buoyant droplet stream. Then the gas-tight bottle was opened, drawing liquid CO₂ into the bottle. As a safety precaution, we opened the bottle several times before the ROV surfaced to allow gas to escape and relieve the internal pressure. Because there was a mixture of liquid CO₂, hydrate, and water in the bottle, this led to fractionation of the sample gas composition. Furthermore, this liquid droplet sample had to be extracted in multiple steps, leading to further fractionation. However, we were still able to confirm that the droplets consisted of >90% CO₂ by volume.

[11] During the 2005 R/V *Natsushima* cruise, we employed a new method for the collection of the liquid droplets that was very successful. One of us (C. Young) designed a special “droplet catcher” consisting of a conical metal spring that was connected with PEEK[™] tubing to a special titanium gas-tight bottle with low (~10 cc) internal volume (Figure 6d). The spring coil was first filled

with liquid droplets by holding it over a stream of CO₂ droplets exiting the seafloor (Figure 6e). We knew from previous experience that the droplets are sticky and do not tend to coalesce. The droplets were visible through the spring coils but stayed in place inside the coils. Then the spring coil was compressed against a flat surface on the ROV, thereby expelling most of the excess water between the droplets. Finally, the small volume gas-tight bottle was triggered, drawing the droplet sample into the bottle. During the *Natsushima* cruise, we were able to collect 4 good samples of the liquid droplets with this technique. Subsequent analysis showed that each sample contained about 5 cc of liquid CO₂. This converted to about 7 l of gas at STP in the extraction line, which we were able to handle quite easily with our enlarged calibrated volume.

[12] In both 2004 and 2005, water column samples were collected using a CTD rosette package. Plume identification was accomplished using both a light scatter sensor and an Eh sensor. Samples were collected into Niskin type bottles and sub-sampled for helium isotopes, CO₂, and other plume components.

[13] He and Ne concentrations, ³He/⁴He ratios, and ¹³C/¹²C ratios were determined by mass spectrometry, while CO₂, CH₄, H₂, and other gas concentrations were determined by gas chromatography. Total CO₂ in the water column plume samples was analyzed by coulometry. Radiocarbon was measured on selected samples at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory. Hydrogen sulfide was analyzed on fluid samples collected with the non-gas-tight PVC pistons using the conventional methylene blue method. However, due to possible gas loss from the PVC pistons, these H₂S values represent only a lower limit. As an alternative, splits of the gases from selected gas-tight bottle samples were sent to Atmospheric Analysis and Consulting (AAC), Inc., Ventura, CA, for analysis of reduced sulfur compounds by sulfur chemiluminescence (method ASTM D-5504). In addition, AAC measured CO₂ abundances by conventional thermal conductivity gas chromatography on the same samples, thereby producing a measure of the H₂S/CO₂ ratio.

4. Results

[14] The analytical results for the 2004 and 2005 samples from NW Eifuku are summarized in

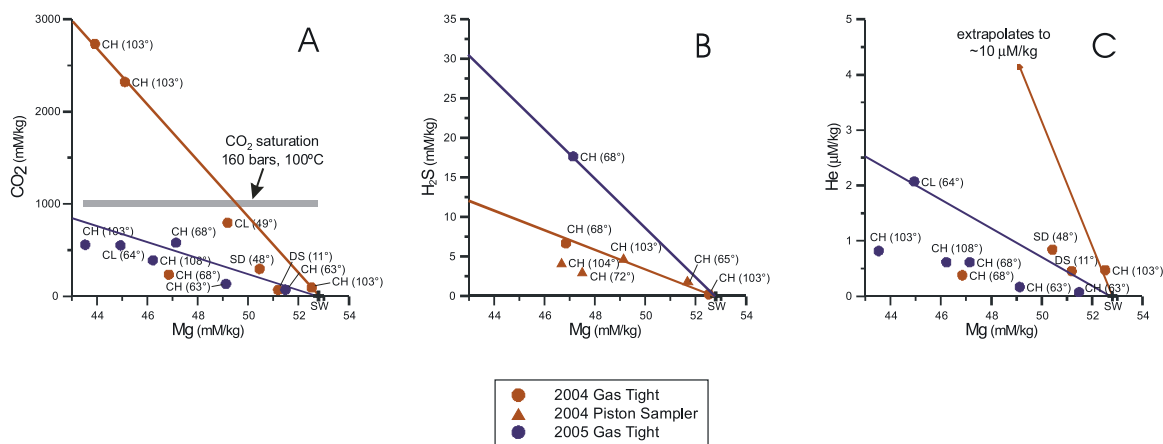


Figure 8. Vent fluid concentrations for CO₂, H₂S, and He versus Mg for NW Eifuku vent fluids. Vent designations are CH (Champagne), SD (Sulfur Dendrite), CL (Cliff House), and DS (Diffuse Site). The 2004 collections are shown in red; the 2005 collections are shown in blue. Fluid discharge temperatures are indicated in parentheses. All of these sites are near the Champagne vent field (see Figure 1b). Possible mixing lines are shown indicating end-member compositions for 2004 samples (red lines) and 2005 samples (blue lines). The solubility of CO₂ in water at these conditions (160 bars, 100°C) is shown for comparison.

Tables 1 and 2. By theory and observation, high-temperature hydrothermal fluids are nearly devoid of Mg, so pure “end-member” fluid compositions normally are estimated by extrapolating to zero Mg [Edmond *et al.*, 1979; Seyfried, 1987; Von Damm, 1990]. However, even though in-line temperatures of ~103°C were measured during sampling, none of the samples collected at the Champagne site had a Mg concentration less than 43 mmol/kg, although several samples approach this value. As we will explain in the Discussion section, we do not believe that a high temperature zero-Mg end-member exists at the Champagne site. Rather than extrapolate to zero magnesium, which would yield unrealistically high temperatures and CO₂ concentrations, we assign the value of 43 mmol/kg Mg to the undiluted 103°C vent fluid that exists at the seafloor. In adopting this approach, we assume that the range of Mg concentrations that we measure is due to entrainment of local seawater during sampling. In Figure 8, vent fluid properties are plotted versus Mg, and mixing lines are shown extrapolating the concentrations to the assumed end-member Mg value of 43 mmol/kg. By extrapolating to this value, we believe we are correcting each sample for seawater dilution during sampling.

[15] Turning our attention at first to the 2004 results, based on an extrapolation to 43 mmol/kg Mg, the 103°C Champagne hydrothermal fluid contained a surprising ~3.0 moles/kg of CO₂. This is an order of magnitude higher than any CO₂ values previously reported for submarine hydro-

thermal fluids (Figure 9). As will be discussed later, we believe that this very high CO₂ concentration in the vent fluid is the result of subsurface entrainment of liquid CO₂ and/or CO₂ hydrate. The overall gas composition of the 2004 vent fluid was ~3000 mmol/kg CO₂, ~12 mmol/kg H₂S, <0.2 mmol/kg CH₄ and H₂, and 0.01 mmol/kg ⁴He. Although we analyzed for CO, it was for the most part below our detection limit (Table 1). Concentrations of N₂, O₂, Ar, and Ne are also included in Table 1 as indicators of air or seawater contamination. Two of the samples collected in 2005 (H494-GT4 and H497-GT7) did suffer from air contamination on the basis of their N₂ and O₂ concentrations, but not enough to compromise the other gas measurements. The Champagne vent fluids have lithium concentrations in the range of 20 to 26 µmol/kg, significantly lower than the ambient seawater concentration (26.5 µmol/kg), and pH ranging from 3.4 to 4.8. The low end of measured pH of Champagne vent fluids is consistent with CO₂ buffering in the end-member fluid.

[16] As discussed above, we were not able to collect an unfractionated sample of the liquid droplets in 2004. However, analysis of the one liquid droplet sample that we collected confirmed that the droplets were composed of >90% CO₂, with the remaining gas assumed to be H₂S.

[17] As discussed above in the Methods section, determining H₂S concentrations in these NW Eifuku samples was challenging because of the

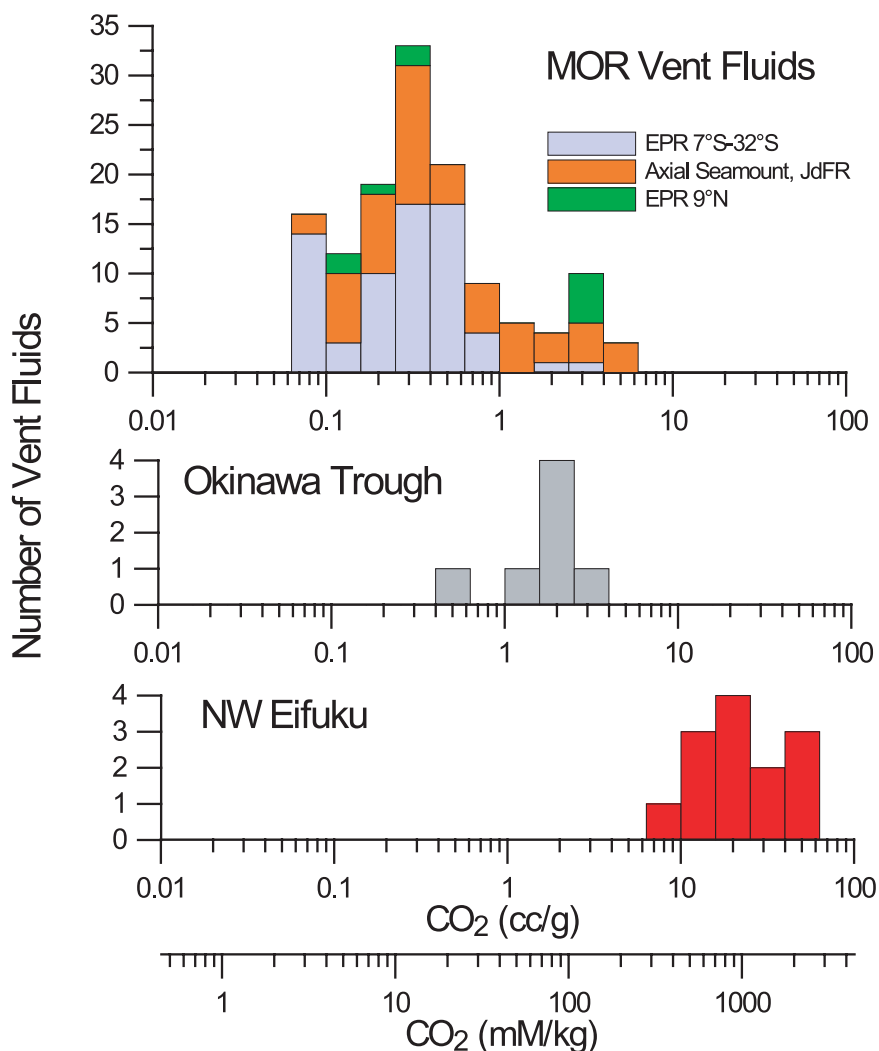


Figure 9. Histogram comparing estimated end-member CO₂ concentrations for vent fluids from mid-ocean ridges [Kelley *et al.*, 2004], the Okinawa Trough [Sakai *et al.*, 1990a, 1990b], and NW Eifuku (this work). For the MOR and Okinawa Trough samples, the end-member concentrations were derived in the usual way by extrapolating to zero Mg. For the NW Eifuku samples a value of 43 mmol/kg was used for this end-member extrapolation (see text for explanation).

high gas content of the samples. Shipboard analysis of samples collected with the non-gas-tight PVC pistons shows a roughly linear trend of increasing H₂S with decreasing Mg, with H₂S reaching approximately 4.5 mmol/kg in the water phase of the least diluted PVC piston samples (Figure 8b). However, because the PVC piston samples have lost significant gas volume in most cases, these are minimum values for H₂S in the fluids. One gas-tight sample collected in 2004 (R793-GT5) was analyzed by sulfur chemi-luminescence gas chromatography at Atmospheric Analysis and Consulting, Inc., and this value lies on the mixing line through the highest of the PVC piston results (Figure 8c). This suggests that the

end-member concentration (~12.5 mmol/kg H₂S) derived from this mixing line (the red mixing line) represents the best estimate for the 2004 Champagne fluid composition. In all of the samples analyzed at AAC, H₂S was the only sulfur species detected.

[18] During the return visit to NW Eifuku in 2005, while the Champagne site still had a constant flow of vent fluid and liquid droplets, there seemed to be slightly less activity than observed in 2004. During our first visits to the Champagne site in 2004, the vent fluid was discharging through several small white chimneys (see Figures 3a, 3b, and 3c). We were surprised to find that these chimneys, which

Table 1. Gas Compositions for Vent Fluid and Liquid Droplet Samples From NW Eifuku^a

Sample	Vent	Collection	Temp, °C.	Mg	CO ₂	CH ₄	H ₂	N ₂	O ₂ ^b	Ar	CO	He, μmol kg ⁻¹	Ne, μmol kg ⁻¹	H ₂ S	H ₂ S/CO ₂
R791-GT7	Champagne	4/9/04	103	52.52	118	0.0138	0.00011	1.01	ND	0.0194	ND	0.475	0.0182		
R791-GT9	Champagne ^c	4/9/04	103	45.11	2308										
R791-GT11	Champagne ^c	4/9/04	103	43.93	2711										
R793-GT5	Champagne	4/11/04	68	46.85	254	0.00017	0.00071	1.63	0.0509	0.0168	ND	0.386	0.0325	6.69 ^d	0.0285
R793-GT11	Sulfur Dendrite	4/11/04	48	50.43	306	0.0137	0.00019	0.48	ND	0.0075	0.0104	0.843	0.0077		
R793-GT7	Cliff House	4/11/04	49	49.20	703										
R791-GT2	Diffuse Site	4/9/04	11	51.19	76.0	0.0111	0.00010	1.56	0.0040	0.0265	ND	0.460	0.0301	4.24 ^e	
R791-P24	Champagne	4/9/04	104	46.67										4.76 ^e	
R791-P4	Champagne	4/9/04	103	49.15										1.94 ^e	
R793-P5	Champagne	4/11/04	65	51.68										3.09 ^e	
R793-P4	Champagne	4/11/04	72	47.51											
H494-GT4	Champagne	10/29/05	68	47.14	564	0.00127	0.108	7.35	ND	0.0583	ND	0.652	0.132	17.87 ^d	0.0317
H497-GT10	Champagne, 2nd Site	11/1/05	56–63	49.12	136	0.00021	0.00326	0.69	0.0014	0.0599	ND	0.172	0.012		
H497-GT16	Champagne, 2nd Site	11/1/05	63	51.48	72.3	0.00016	0.00089	0.96	0.00018	0.0141	0.00054	0.077	0.014		
H497-GT6	Champagne	11/1/05	108	46.22	405	0.00059	0.00588	1.03	ND	0.0120	ND	0.621	0.027		
H497-GT7	Champagne	11/1/05	103	43.53	591	0.00169	0.0123	36.0	1.50	1.21	0.300	1.07	0.879		
H499-GT5	Champagne	11/2/05	47	48.64	174	0.00041	0.00181	1.01	ND	0.0126	0.103	0.259	0.017		
H499-GT15	Cliff House	11/2/05	64	44.94	567	0.0136	0.00316	1.15	ND	0.0133	0.0452	2.08	0.029		
SW	Seawater			52.8	2.34	0.0000003	0.0000003	0.593	0.050	0.0163	0.0000003	0.0019	0.0080		
Detection Limit					0.0001	0.000002	0.00002	0.004	0.0006	0.0001	0.000002	0.0018	0.0032		
H492-10cc#1	Champagne droplets ^f	10/27/05	≤ 4		%	%	%	%	%	%	%	ppm	ppm	%	
					98.7	0.00064	0.00032	0.0814	0.00285	0.00034	ND	5.15	0.0123		
H494-10cc#1	Champagne droplets ^f	10/29/05	≤ 4		98.6	0.00092	0.00017	0.206	0.0213	0.00103	ND	5.72	0.0460		
H497-10cc#2	Champagne droplets ^f	11/1/05	≤ 4		99.6	0.00088	0.00023	0.224	0.0192	0.00114	ND	5.37	0.0474		
H499-10cc#1	Champagne droplets ^f	11/2/05	≤ 4		98.9	0.00094	0.00023	0.140	ND	0.00128	ND	6.99	0.0161	0.5–0.8 ^d	0.005 –0.008

^a Units are mmol/kg unless noted otherwise. For the conventional gas chromatograph analyses (CO₂, CH₄, H₂, N₂, O₂, Ar, CO), the concentrations are precise to about ±5%.

^b The O₂ concentration is not a reliable indicator of air contamination since O₂ may have been reduced by reacting with H₂S in the ampoule.

^c For these samples, the gas content was more than our extraction system could easily handle, and some fractionation of the gases occurred. For this reason we are reporting only those gas compositions that are reliable.

^d Gas-tight bottle sample, H₂S analyzed by sulfur-chemiluminescence at AAC.

^e Samples collected with the piston sampler, H₂S analyzed by the conventional methylene blue method.

^f For the liquid droplets, which are essentially pure gas, we report the CO₂ content as a volume%.

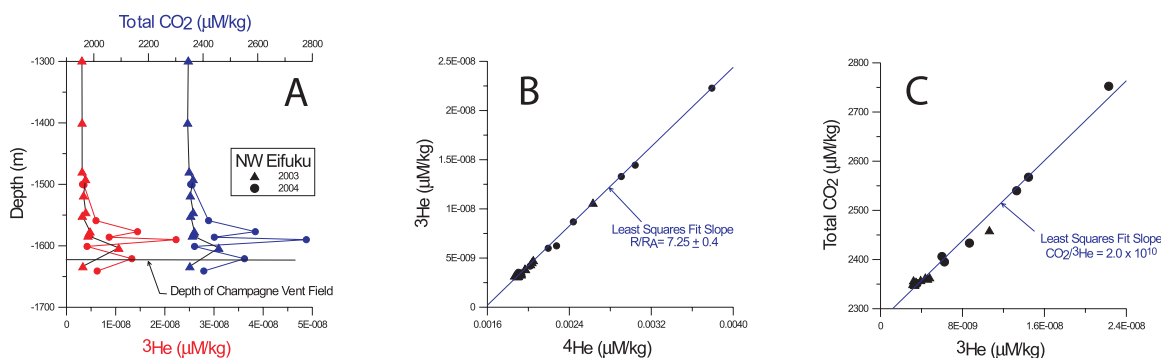


Figure 10. Plots showing ³He, ⁴He, and CO₂ data collected in the water column over NW Eifuku in 2003 (filled triangles) and 2004 (filled circles). (a) [³He] and ΣCO₂ versus depth. The depth of the Champagne vent field is indicated for comparison. (b) [³He] versus [⁴He] showing an estimate of the end-member ³He/⁴He ratio based on a linear regression fit. Here $R = {}^3\text{He}/{}^4\text{He}$ and $R_A = R_{\text{air}} = 1.39 \times 10^{-6}$. (c) ΣCO₂ versus [³He] showing a similar estimate of the end-member CO₂/³He ratio.

were destroyed by the ROV during the 2004 sampling, had not re-grown during the intervening 18 months. As shown in Tables 1, 2, and 3 and in Figure 8, on the basis of “end-member” extrapolations, compared to 2004 the CO₂ concentration was lower in 2005, accompanied by higher H₂S, lower He, and higher C/³He ratios. One of the major accomplishments of the 2005 Hyper-Dolphin dives was the successful collection of 4 uncontaminated samples of the liquid droplets (see Methods section above). The liquid droplets had a gas composition of ~98% CO₂, <0.01% CH₄ and H₂, ~6 ppm He, and ~0.8% H₂S (see Tables 1 and 3). While this composition is similar to that of the vent fluids, the liquid droplets collected in 2005 have lower H₂S/CO₂ and higher He/CO₂ ratios than the 2005 vent fluids (Table 3).

[19] The helium in both the Champagne vent fluid and in the liquid droplets had an isotopic ratio of $R/R_A = 7.31 \pm 0.05$, a value typical of subduction zone systems ($R = {}^3\text{He}/{}^4\text{He}$ and $R_A = R_{\text{air}}$) [Poreda and Craig, 1989; Hilton *et al.*, 2002]. During the 2003 water column surveys over NW Eifuku, helium samples were collected that allowed an estimate of the end-member helium isotope ratio based on the co-variation of [³He] versus [⁴He]. This estimate gave $R/R_A = 7.25 \pm 0.4$, in remarkably good agreement with direct measurements of the vent fluids (see Figure 10). Furthermore, the C/³He ratio estimated from measurements of ΣCO₂ and [³He] in the water column plumes differed only by 10% from that determined from the vent fluids (Figure 10c). This suggests that reliable estimates of the ratios of certain vent fluid properties can be made from samples of the

overlying water column plumes, even though these plumes typically contain only 0.1% or less of the pure vent fluid.

[20] Isotopic analysis of the CO₂ in the Champagne vent fluid gave $\delta^{13}\text{C} = -1.75\text{‰}$, while the carbon in the liquid droplets was slightly heavier ($\delta^{13}\text{C} = -1.24\text{‰}$). The C/³He ratio ranged from 1.6 to 9.7×10^{10} for the Champagne vent fluids, and from 1.4 to 1.9×10^{10} for the liquid droplets (Table 2). A sample of the CO₂ from the Champagne site 103°C vent fluid was analyzed for radiocarbon at the CAMS facility at Lawrence Livermore National Laboratory. The result was $\Delta^{14}\text{C} = -998.7\text{‰}$, corresponding to an age of 53450 ± 3200 years, or a fraction of modern carbon of only 0.0013 (see Table 2). Analyses of the 68°C vent fluid and of the liquid CO₂ droplets yielded similar results. Thus the carbon in the Eifuku CO₂ is “dead” (age $\geq 50,000$ years).

5. Discussion

[21] In order to put the very high CO₂ concentration of the Champagne vent fluids in perspective, Figure 9 compares the end-member CO₂ concentrations at NW Eifuku with those at the Okinawa Trough and at various mid-ocean ridge hydrothermal sites. Although Sakai *et al.* [1990a] observed liquid CO₂ venting at the JADE site in the Okinawa Trough, the 320°C vent fluid at the JADE site contained only 200 mmol/kg of CO₂. As shown in Figure 9, the end-member CO₂ concentrations at the Champagne site are an order of magnitude higher than any values reported for other hydrothermal fluids, and 100 times higher

Table 2. Isotope Ratios for Vent Fluid and Liquid Droplet Samples From NW Eifuku

Sample	Vent	Collection	Temp, °C.	Mg, mmol/kg	CO ₂ , mmol/kg	He, μmol/kg	³ He, pmol/kg	³ He/ ⁴ He ^a (R/R _A)	C/ ² He	δ ¹³ C(CO ₂), ‰	Δ ¹⁴ C, ‰	¹⁴ C Age, years
R791-GT7	Champagne	4/9/04	103	52.52	118	0.472	4.81	7.33	1.93E+10	-1.75	-998.7	53450 ± 3200
R791-GT9	Champagne	4/9/04	103	45.11	2308							
R791-GT11	Champagne	4/9/04	103	43.93	2711							
R793-GT5	Champagne	4/11/04	68	46.85	254	0.379	3.86	7.33	6.06E+10	-1.76	-991.9	38600 ± 520
R793-GT11	Sulfur Dendrite	4/11/04	48	50.43	306	0.843	8.45	7.22	3.23E+10	-1.74		
R793-GT7	Cliff House	4/11/04	49	49.20	703			7.32				
R791-GT2	Diffuse Site	4/9/04	11	51.19	76.0	0.454	4.63	7.34	1.48E+10			
H494-GT4	Champagne	10/29/05	68	47.14	564	0.614	6.19	7.26	8.99E+10	-1.76		
H497-GT10	Champagne, 2nd Site	11/1/05	56-63	49.12	136	0.168	1.70	7.29	7.77E+10			
H497-GT16	Champagne, 2nd Site	11/1/05	63	51.48	72.3	0.0730	0.742	7.31	9.40E+10			
H497-GT6	Champagne	11/1/05	108	46.22	405	0.613	6.18	7.25	6.31E+10			
H497-GT7	Champagne	11/1/05	103	43.53	591	0.819	8.21	7.22	6.79E+10			
H499-GT5	Champagne	11/2/05	47	48.64	174	0.254	2.57	7.28	6.47E+10			
H499-GT15	Cliff House	11/2/05	64	44.94	567	2.07	20.9	7.26	2.63E+10			
SW	Seawater			52.8	2.34	0.0019	0.0014	0.98				
H492-10cc#1	Champagne droplets	10/27/05			%	ppm	ppm					
H494-10cc#1	Champagne droplets	10/29/05			98.7	5.15	5.22E-05	7.31	1.83E+10	-1.28		
H497-10cc#2	Champagne droplets	11/1/05			98.6	5.72	5.82E-05	7.33	1.63E+10			
H499-10cc#1	Champagne droplets	11/2/05			99.6	5.37	5.45E-05	7.30	1.77E+10			
					98.9	6.99	7.09E-05	7.30	1.32E+10	-1.20		

^a Helium isotope ratio expressed as R/R_A, where R = ³He/⁴He and R_A = R_{air} = 1.39 × 10⁻⁶. The solubilities of the two isotopes in water are slightly different, with the result that for air saturated water R/R_A = 0.98.

Table 3. Estimated End-Member Compositions, Based on Extrapolating to a Mg Concentration of 43 mmol/kg

Vent	Collection	Temp, °C.	Mg, mmol/kg	CO ₂ , mmol/kg	CH ₄ , mmol/kg	H ₂ , mmol/kg	H ₂ S, mmol/kg	He, μmol/kg	³ He/ ⁴ He ^a (R/R _A)	H ₂ S/CO ₂	C/ ² He	δ ¹³ C(CO ₂), ‰
Champagne Fluid	2004	103	43	3000	<0.2	<0.2	12.5	10	7.31	0.004	2-4E+10	-1.75
Champagne Fluid	2005	108	43	800	<0.2	<0.2	30	2.5	7.31	0.03	6-9E+10	-1.75
Champagne droplets	2005	<4	-	98%	-	-	0.8%	5-6 ppm	7.31	0.008	1.5E+10	-1.24
Seawater		2	52.8	2.34	0.0003	0.0003	-	.0019	0.98	-	-	-

^a Helium isotope ratio expressed as R/R_A, where R = ³He/⁴He and R_A = R_{air} = 1.39 × 10⁻⁶. The solubilities of the two isotopes in water are slightly different, with the result that for air saturated water R/R_A = 0.98.

than average values at MOR systems. The structure of the hydrothermal system at NW Eifuku is clearly different from that at the JADE site, where high-temperature, zero-magnesium fluids are produced in a reaction zone with low water/rock ratio [Sakai *et al.*, 1990a, 1990b].

[22] The CO₂ concentration at NW Eifuku is even more remarkable when it is compared against the CO₂ solubility at these P, T conditions. The solubility of CO₂ in seawater at 160 bars, 100°C is ~1.0 mole/kg [Wiebe and Gaddy, 1939; Takenouchi and Kennedy, 1964], much lower than the concentrations we measured in 2004. The most plausible explanation for the apparent supersaturation of CO₂ is that the Champagne vent fluid is entraining small amounts of liquid CO₂ and/or CO₂ hydrate as the hot vent fluid penetrates the layers of CO₂ liquid and hydrate that we propose exist beneath the seafloor (Figure 4). Incorporation of only 6% by volume of liquid CO₂ into the vent fluid would increase the CO₂ concentration from 1 to 2.7 moles/kg, and this liquid CO₂ would likely not be visible as a separate phase in the vent fluid stream.

[23] The 2005 vent fluid samples had lower CO₂ concentrations and different relative proportions of dissolved gases compared to the earlier 2004 collections. In fact, none of the 2005 water samples had CO₂ concentrations above the 1.0 mole/kg solubility of CO₂ at the conditions at the Champagne site. Furthermore, as discussed above, the 2005 vent fluid samples had higher end-member H₂S/CO₂ ratios, and higher C³He ratios compared to the 2004 samples (Table 3). For whatever reason, the liquid droplets have lower H₂S/CO₂, lower C³He, and are heavier in δ¹³C compared to the vent fluids. This difference between the vent fluid compositions in 2005 versus 2004 may be due to temporal changes in the degree of entrainment of liquid CO₂ and/or hydrate into the rising vent fluid. Our results indicate that all of the vent fluid samples are actually a mixture of the pure “subsurface” hydrothermal fluid combined with varying amounts of entrained liquid CO₂ or CO₂ hydrate. The end-member compositions estimated for the 2005 samples (see Table 3) may thus represent a form of the Champagne vent fluid relatively un-contaminated with entrained liquid CO₂, while the gas-rich 2004 vent fluids had more entrained liquid CO₂. For the 2004 vent fluid samples with ~2.7 moles/kg CO₂, most of the CO₂ came from the entrained liquid droplets and/or hydrate, while most of the H₂S and He was

already dissolved in the hot fluid before it reached the near surface liquid CO₂ layer.

[24] In many cases, diffuse hydrothermal fluids are located near high-temperature fluids or their chemistry indicates that they are dilutions of high-temperature fluids, with overprinting low-temperature reactions [Edmond *et al.*, 1979; Butterfield and Massoth, 1994; Butterfield *et al.*, 1997, 2004; Sedwick *et al.*, 1992]. That is not the case at NW Eifuku. If we were to extrapolate the temperature and fluid composition to a zero-magnesium value, the results would be nothing like a fluid produced in a high-temperature water/rock reaction zone. For example, a zero-Mg extrapolation at NW Eifuku would yield temperatures of 500–600°C, CO₂ concentrations of 10–20 mol/kg, and zero Li concentration. The implication of this is that we are not dealing with a high-temperature aqueous system, but with a high-temperature CO₂ system, entraining some water that undergoes incomplete reaction to remove some seawater magnesium and extract some elements from the rock. CO₂ migrating upward from a gas pocket in a magma chamber must cool as it ascends through volcanic rock and may entrain small amounts of seawater (Figure 11). Water and CO₂ are immiscible at 500 bars at temperatures below 310°C [Takenouchi and Kennedy, 1964; Bowers, 1991] and separate into a CO₂-rich vapor and a water-rich liquid. As pressure increases, immiscibility of H₂O-CO₂ occurs at lower temperatures [Bowers, 1991]. In a system dominated by the flux of hot CO₂ from a magma chamber, the penetration of water into the core of the system will be limited at typical hydrothermal temperatures (up to ~350°C) due to the immiscibility. If seawater is not first heated by hot rock (and the water chemistry at the Champagne site indicates minimal high-T water/rock reaction), then the outer portions of the CO₂ column will be in the P-T region of H₂O-CO₂ immiscibility. As long as the flux of hot CO₂ from the magma chamber and cooling in the pathway to the seafloor is maintained, the penetration of water into the CO₂ –rich zone is inhibited. The presence of a gas hydrate phase at temperatures below 10°C may also inhibit penetration of water into the sub-seafloor CO₂-rich zone.

[25] Some insight into the origin of the high CO₂ concentrations at NW Eifuku can be gained from the isotopic composition of the CO₂ and the relation of CO₂ to ³He. The δ¹³C of the Champagne vent fluids (–1.75‰) is much heavier than the δ¹³C = –13 to –4‰ typical for carbon in MOR

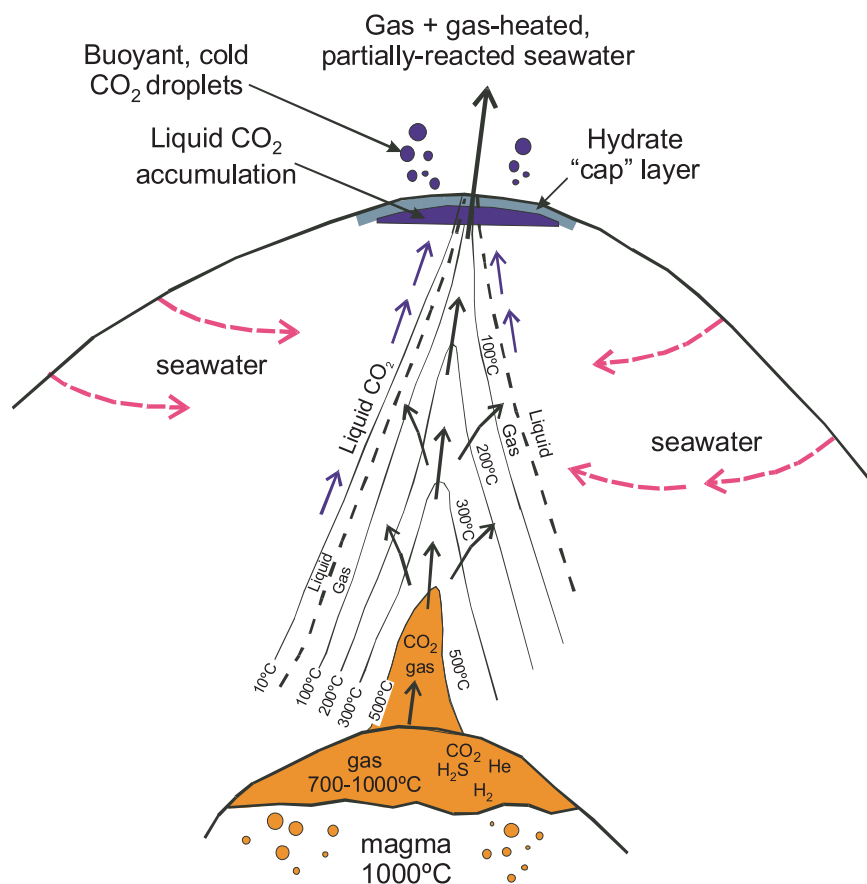


Figure 11. Diagram showing a model proposed for the gas flux from NW Eifuku, in which a CO₂-rich gas is directly degassing from the magma chamber. As this hot gas rises through the system, it cools, and CO₂ condenses as a separate liquid phase on the periphery of the main conduit. Seawater circulates through the system, but the penetration of water into the core of the system is limited at temperatures below 250°C due to CO₂-H₂O immiscibility. At the volcano summit the liquid CO₂ collects beneath a hydrate "cap" layer that forms where the liquid CO₂ comes in contact with seawater. Because the penetration of water is limited and the enthalpy is carried by the CO₂ gas, there is little high-temperature water-rock interaction.

vent fluids [Kelley *et al.*, 2004]. The NW Eifuku CO₂ is also heavier than that reported for the Mid-Okinawa Trough (−5.0 to −3.7‰) [Sakai *et al.*, 1990a, 1990b], falls at the heavy end of the range reported for arc volcanoes in general (−7 to −2‰) [Sano and Williams, 1996; van Soest *et al.*, 1998], and at the lighter end of the range for marine carbonates (−2 to +1‰) (Figure 12) [Hoefs, 1980]. The C³He ratio for the Champagne vent fluids and liquid droplets (1.3 to 9.4 × 10¹⁰) is similar to that reported for the Mid-Okinawa Trough [Sakai *et al.*, 1990a, 1990b], but an order of magnitude higher than the average value of 2 × 10⁹ found in MOR vent fluids [Resing *et al.*, 2004]. These δ¹³C and C³He values indicate that the majority of the carbon flux originated from marine carbonates incorporated into the melt as part of the subduction zone melting process rather than from mantle carbon. Using the method outlined by Sano

and Marty [1995] based on δ¹³C and C³He values, and taking sedimentary organic matter to have a δ¹³C value of −30‰ as did Sano and Marty [1995], we estimate that the NW Eifuku CO₂ was derived 88% from marine carbonates, 9% from mantle carbon, and 3% from sedimentary organic matter. If instead we assume that the δ¹³C of sedimentary organic matter is −20‰, then we calculate 87% from marine carbonates, 9% mantle, and 4% from sedimentary organics. These fractions are similar to those observed at subaerial arc volcanoes [Hilton *et al.*, 2002]. The fact that the radiocarbon is "dead" suggests that the CO₂ flux is mainly derived from subducted carbonates incorporated into the melt at depth and that local sediments are not responsible.

[26] It is a simple matter to show that the extremely high concentrations of CO₂ at NW Eifuku cannot

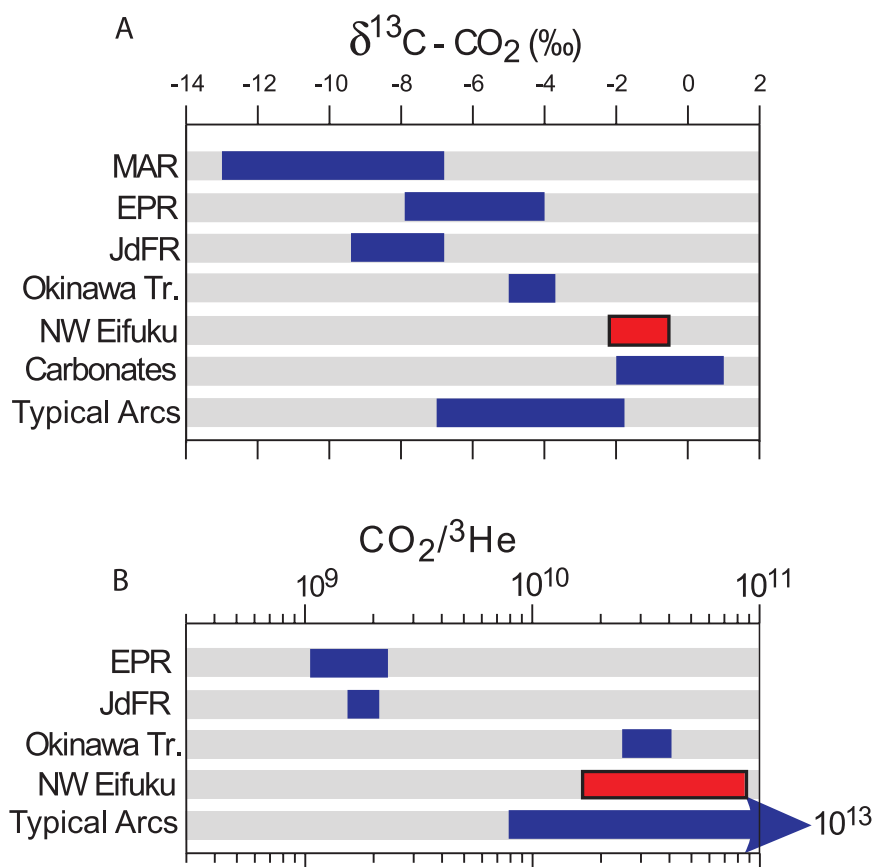


Figure 12. (a) Chart comparing $\delta^{13}\text{C}$ (‰) for CO₂ from various MOR sites [Kelley et al., 2004], the Okinawa Trough [Sakai et al., 1990a, 1990b], NW Eifuku (this work), marine carbonates [Hoefs, 1980], and typical volcanic arcs [Sano and Williams, 1996; van Soest et al., 1998]. (b) Similar chart comparing CO₂/³He ratios for MOR vents [Kelley et al., 2004], the Okinawa Trough [Sakai et al., 1990a, 1990b], and typical volcanic arcs [Sano and Williams, 1996; van Soest et al., 1998].

be easily derived from either water/rock reaction or from dissolution of putative carbonates within the volcanic edifice. On the first count, it has already been shown [Butterfield et al., 1990; Sedwick et al., 1994] that by extracting all of the CO₂ from 1 kg of MORB, assuming the maximum reported level of 8 mmol CO₂/kg rock [Dixon et al., 1988], into 1 kg of water (a typical water/rock ratio), the total CO₂ concentration in the aqueous phase would not exceed ~8 mmol/kg. However, according to Wallace [2005], undegassed arc magmas contain ~3000 ppm of CO₂. Using the same water/rock ratio of 1, this would produce only 68 mmol/kg of CO₂ in the hydrothermal fluid, still far below the 900–2700 mmol/kg we observe. Furthermore, the Champagne vent fluids have lithium concentrations lower than the ambient seawater concentration, indicative of minimal high-temperature water-rock reaction (a high water/rock ratio). Thus it appears to be impossible to extract enough CO₂ from basaltic or andesitic lava by water/rock interaction

to reach the levels of CO₂ found in the Champagne vent fluids, or even in some MOR vents (e.g., Axial Volcano on the Juan de Fuca Ridge or 9°N East Pacific Rise). On the second count, the low pH of Champagne vent fluids is inconsistent with calcium carbonate dissolution. In addition, dissolution of carbonates is self-limiting unless there is an additional source of acid to drive more dissolution. In that case, the calcium concentration would also be very high, but it is lower than seawater concentration in the Champagne vent fluids. We conclude that the CO₂ at this site must be derived from magma degassing, as there is no other plausible source.

[27] Although it is clear that the venting at the Okinawa Trough and NW Eifuku Champagne sites locally produces very high CO₂ concentrations, the question remains as to how significant the overall carbon flux is on a global scale. We estimated the volume flux of liquid CO₂ droplets at the Champagne site by examining video collected during the

2004 ROV dives. We first estimated that there were about 300 droplet streams rising from the 10 m² area of the Champagne site, and that each stream contained 2 droplets/s, each with an average diameter of ~1.5 cm. This gives a total liquid CO₂ flux of ~1 liter/s or 1 kg/s (assuming a density of 1g/cm³), equivalent to ~23 moles CO₂/s. Using a similar method, we estimate the CO₂ flux from the Champagne hot vents to be ~ 0.5 mole/s or only about 2% of the liquid CO₂ flux. The CO₂ flux from the liquid droplets at the Champagne site (8×10^8 moles/yr) approximately equals the combined carbon flux from all of the Endeavour Ridge vent fields on the Juan de Fuca Ridge [Rosenberg *et al.*, 1988; Lilley *et al.*, 1993], or about 0.1% of the global MOR carbon flux which is estimated at $0.5\text{--}2.0 \times 10^{12}$ moles/yr [Resing *et al.*, 2004]. The carbon flux from the Champagne site is also about 0.1% of the global CO₂ flux from subaerial arc volcanoes, estimated at $\sim 1.6 \times 10^{12}$ moles/y [Hilton *et al.*, 2002]. Although these flux estimates for NW Eifuku are admittedly only accurate to a factor of 2 or so, this carbon flux is surprising, since NW Eifuku is a small, young arc volcano and not a major volcanic edifice. Furthermore, the fact that NW Eifuku is a submarine volcano suggests that carbon fluxes based on observations of subaerial volcanoes may have underestimated the global fluxes from arcs. If there are many such submarine sites active along volcanic arcs and back arcs, then there is potential for a significant impact on oceanic carbon cycling. For completeness it should be noted that Hilton *et al.* [2002] estimated the carbon flux from an average subaerial arc volcano at 2×10^{10} moles/y, about 25 times higher than the carbon flux at NW Eifuku. They arrived at this estimate by normalizing the CO₂ flux to the measured SO₂ flux at various subaerial arc volcanoes, rather than by direct measurements of the CO₂ outgassing rate. Thus the carbon flux at NW Eifuku may be significant for submarine carbon cycling, but not necessarily for the global subaerial carbon flux.

[28] Additional visits and possibly long-term monitoring of the site are required to determine if this high CO₂ flux is time dependent. For example, Miyakejima volcano (Japan) underwent a months-long extremely high-volume magmatic degassing event following a caldera collapse in 2000 [Kazahaya *et al.*, 2004]. Recent mass-wasting at the summit of NW Eifuku could have been triggered by movements along what appears to be a NW-SE fracture underlying the volcano (Figure 2c). Deep conduits could be enlarged and

new ones opened during this process. Alternatively, long-term degassing during non-eruptive periods on some volcanoes has been tied to endogenous growth by magmatic intrusion [Allard, 1997].

[29] Recently there has been considerable interest in the possible oceanic disposal of fossil fuel CO₂ as a means to alleviate the increase of atmospheric CO₂ [Brewer, 2000]. One important question concerns the fate of the CO₂ after it is introduced into the ocean. Brewer *et al.* [2002] measured the rate of dissolution of liquid CO₂ injected into the ocean at a depth of ~800 m, and found that 90% of the buoyant CO₂ droplets dissolved within 200 m above the injection point. As shown in Figure 10, our water column measurements in the vicinity of NW Eifuku are in basic agreement with the Brewer *et al.* [2002] results. On several hydrocasts collected over the volcano in 2003 and 2004 we found large excesses in ³He and CO₂ that co-varied almost perfectly [Lupton *et al.*, 2003; Resing *et al.*, 2003]. In every case the excess ³He and CO₂ was confined to the depth range of 1490 to 1620 m and returned to background values about 150 m above the depth of the NW Eifuku vent fields (Figure 10).

6. Summary and Conclusions

[30] In summary, we have discovered a site at ~1600 m depth on NW Eifuku, a submarine volcano on the northern Mariana Arc, which is venting droplets of liquid CO₂ at an estimated rate of 8×10^8 moles/yr. This is only the second locality where submarine venting of liquid CO₂ has been observed, the other being the mid-Okinawa Trough [Sakai *et al.*, 1990a, 1990b]. The Champagne site on NW Eifuku is also venting hot (~100°C) vent fluid with CO₂ contents up to 2.7 moles/kg, far above the solubility (~1.0 mole/kg) at these P, T conditions. Observations at the site indicate the presence of a subsurface liquid CO₂ layer under a capping layer of CO₂ hydrate. We attribute the apparent CO₂ super-saturation in the vent fluid to entrainment of small amounts of liquid CO₂ and/or CO₂ hydrate into the ascending vent fluid stream. The liquid droplets are composed of >98% CO₂, ~1% H₂S, with only trace amounts of H₂ and CH₄. The dissolved gases in the vent fluid have a similar composition, with a slightly greater concentration of H₂S (~3%). The δ¹³C (CO₂) and CO₂/³He ratios fall in the range typical for volcanic arcs, and indicate that the carbon is derived ~90% from marine carbonates, the remainder being mantle carbon and sedimentary organic

matter. The fact that the radiocarbon is dead (age \geq 50,000 years) suggests that the source is subducted carbonates incorporated into the melt at depth in the subduction zone and not local carbonates on the volcano edifice.

[31] Sakai *et al.* [1990a, 1990b] explained their observations in the mid-Okinawa Trough in terms of separate CO₂-rich and H₂O-rich fluids that formed as the result of magma chamber degassing. They also discussed subsurface boiling as a possible mechanism for generating these two phases. It is clear that separate cold CO₂-rich and hot H₂O-rich fluids exist at the same site in close proximity at NW Eifuku. At the vent site, we envision a mechanism in which hot water is venting through an area of liquid CO₂ and CO₂ hydrate and entrains these, generating hot fluids with CO₂ contents higher than predicted by the limits of CO₂ solubility. In contrast to the 320°C fluids found in the Okinawa Trough, the 103°C fluid temperatures at NW Eifuku are \sim 250°C below the boiling point at 1600-m depth, and thus shallow subsurface boiling is unlikely. The 103°C fluids do not show signs of intense water/rock interaction, and their low alkali metal content is indicative of a high water/rock ratio. Given that we do not find a zero-magnesium, high-temperature fluid at NW Eifuku, it is impossible to extract enough CO₂ from the rock into circulating seawater to form an aqueous fluid saturated with CO₂. Instead, the extreme CO₂ concentrations at NW Eifuku require direct degassing of CO₂ from a magma chamber, cooling and migration to the seafloor, resulting in the generation of the CO₂-rich and H₂O-rich fluids that we observed. The physical/chemical model we have proposed (Figure 11) differs substantially from the mid-ocean ridge model of extraction of gases from rock by circulating hot water. If our model is correct, then elemental and isotopic fractionations that occur as a result of magma degassing, CO₂ condensation, hydrate formation, H₂O-CO₂ mixing, and phase separation add considerable complexity to the interpretation of gas ratios and isotopic ratios.

[32] The Champagne vent field and the other sites of hydrothermal activity on NW Eifuku clearly merit further study. As mentioned above, NW Eifuku is only the second locality where natural venting of liquid CO₂ has been reported, the other being the Okinawa Trough, a back-arc basin environment. At the time of its discovery, the Champagne site was the only arc volcano where the phenomenon of liquid CO₂ venting had been

found. However, venting of a separate CO₂ gaseous phase was recently observed at 3 other submarine arc volcanoes: Nikko volcano in the Mariana Arc [Lupton *et al.*, 2005], and Giggenbach volcano and Volcano 1, both in the Kermadec Arc [Lupton *et al.*, 2005; Stoffers *et al.*, 2006]. Furthermore, to our knowledge liquid CO₂ venting has never been found on mid-ocean ridges, suggesting that this type of activity is more prevalent on volcanic arcs and the associated back-arc basins. Experiments are being designed to accurately measure the flux and oceanic dispersal of CO₂ at NW Eifuku. In addition to physical and chemical measurements, the hydrothermal sites on NW Eifuku are a valuable natural laboratory for studying the effects of high CO₂ concentrations on marine ecosystems.

Acknowledgments

[33] We thank K. Shepard, K. Tamburri, and the other members of the Canadian ROPOS team, and the captain and crew of the R/V *Thompson* for their excellent support during the 2004 SROF expedition, and K. Chiba and the other members of the Hyper-Dolphin team and the Captain and crew of the R/V *Natsushima* for their support during the NT05-18 expedition. We thank S. Merle for help with the figures and Tom Brown and the Natural ¹⁴C Group at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory. V. Salters, D. Hilton, C. German, and T. Fischer provided constructive reviews of the manuscript. Radiocarbon measurements were supported in part by funding from CAMS through the University Collaborative Research Program. This publication was partially funded by the Joint Institute for the Study of the Atmosphere and Ocean (JISAO) under NOAA cooperative agreement NA17RJ1232, contribution 1154. This work was supported by the NOAA Ocean Exploration Program and by the NOAA VENTS Program. This is PMEL contribution 2843.

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