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Earth and Planetary Science Letters 128 (1994) 183–197

EPSL

Helium and carbon geochemistry of hydrothermal fluids from the North Fiji Basin spreading ridge (southwest Pacific)

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Received 19 November 1993; accepted 12 September 1994

Abstract

The North Fiji Basin is one of the active marginal basins in the southwestern Pacific. Hydrothermal fluid emanations were located at two sites on the Central ridge of the basin. High-temperature fluids (230–290°C) venting from anhydrite chimneys at a 17°S site have end-member compositions of: 11.0–14.5 mmol/kg of CO₂; 30.4–43.5 μmol/kg of CH₄; and 2.3–4.5 × 10⁻⁵ cm³STP/g of He. Taking phase separation processes into account, the gas abundances are not enriched compared with the mid-oceanic ridge hydrothermal systems. Isotopic compositions of CO₂ (δ¹³C = -6.2 to -5.7‰PDB), CH₄ (δ¹³C = -20 to -18‰PDB), and helium (R/R_A = 9.0–10.0) are comparable to the mid-oceanic ridge signature. Together with basalt helium data, the helium isotopic signature may be attributed to the incorporation of a hotspot-like primitive component. Low-temperature shimmering fluids (the highest measured temperature was 5.2°C) associated with biological communities at a site at 18°50'S show slight chemical anomalies, in some species, in SiO₂, Mn, Li, pH and CH₄, and helium isotope ratios distinct from ambient seawater. Evaluated helium isotopic compositions prior to dilution fall between R/R_A = 8.4 and 8.9, supporting the suggestion of high-temperature hydrothermal activity at this site, although this was not observed by dive expeditions. The gas geochemistry of these two different types of fluids show several similar characteristics to the mid-oceanic ridge hydrothermal systems. This result is in accordance with previous petrological studies which demonstrated a dominant N-MORB source signature and a co-existing OIB source influence of the North Fiji Basin magmatism.

1. Introduction

Recently, several investigations of marginal basins in the southwest Pacific region have discovered a number of submarine hydrothermal

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Elsevier Science B.V.

SSDI 0012-821X(94)00204-5

ORSTOM Documentation



010000995

O.R.S.T.O.M. Fonds Documentaire

N° : 43130

Cote : B ex 1

systems (e.g., [1–6]). Hydrothermal systems have been revealed not as a phenomenon peculiar to the mid-oceanic ridge (MOR) system, but as ubiquitous in active regions related to various tectonic settings.

The North Fiji Basin is an active marginal basin located at the boundary of the Pacific and Indo–Australian plates (Fig. 1). The North Fiji Basin has had a complex, multi-stage tectonic history since the beginning of spreading at 10–12 Ma and the present spreading activity started about 1 Ma ago, along the 800 km long central ridge [7–10]. This spreading system can be divided into four segments; these trend, from north to south, N160°, N15°, N–S and the last section, offset to the east, also trending N–S [11,12]. The STARMER project (1987–1992), under the framework of Japanese–French–SOPAC cooperation, investigated the central ridge system and revealed it to be comparable to the MOR systems in several features, such as size, bathymetric pro-

files, morphologic variations and petrologic features [11–13].

Evidence for present hydrothermal activity along the central ridge was provided by the identification of hydrothermal plumes at several sites before and during the STARMER project [1,8,14,15]. During dive programs in 1989 by the French submersible *Nautilie* and in 1991 by the Japanese submersible *Shinkai6500*, active fluid emanations were observed at two stations [12,16]. One is a vigorous, high temperature fluid venting from anhydrite chimneys at 17°0'S, 173°50'E (station 4) and the other is a low temperature shimmering fluid associated with biological communities at 18°50'S, 173°30'E (station 14) (locations are shown in Fig. 1).

In this paper, we present the concentrations and isotopic compositions of carbon and helium dissolved in these fluids. This is the first data set for the hydrothermal fluid end-member obtained from the southwest Pacific marginal basins. The

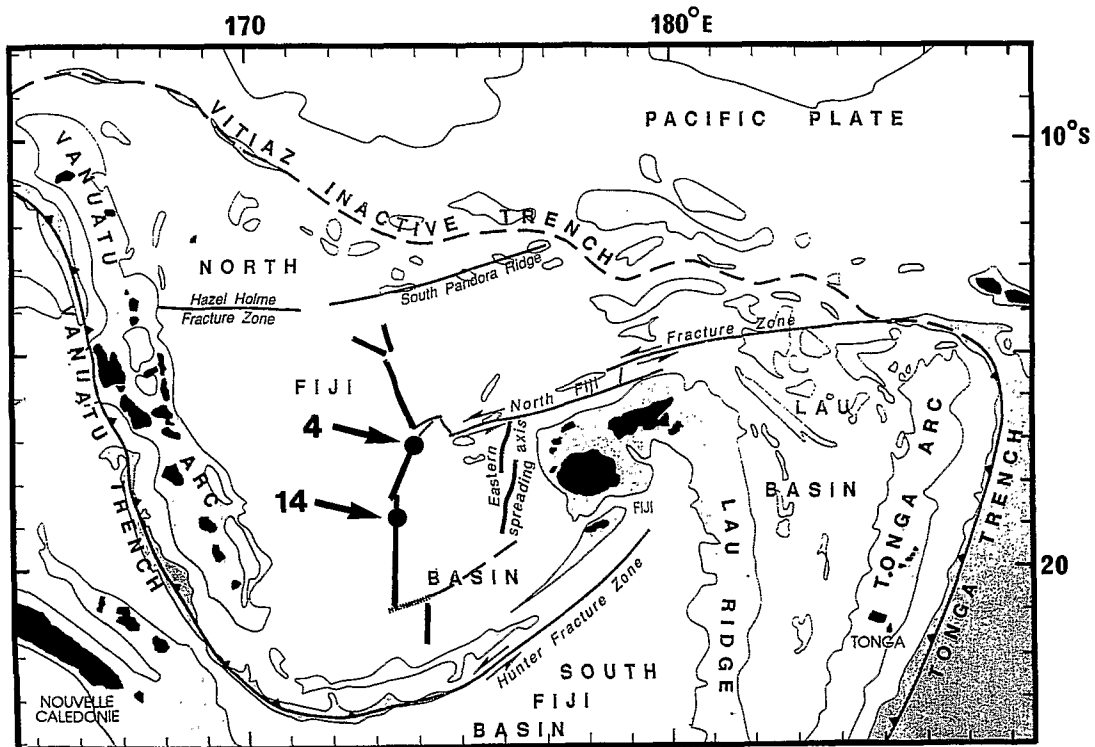


Fig. 1. Regional map showing the North Fiji Basin Central ridge and two fluid emanation sites (stations 4 and 14).

gas geochemistry of the MOR hydrothermal systems has been the subject of several previous studies (e.g., [17–20]), these revealed that the isotopic composition of helium and carbon reflect the MORB magma signature, as long as fluids were not significantly influenced by sedimentary organic material during hydrothermal circulation. Accumulation of gas geochemistry data for hydrothermal fluids in marginal basins could provide a basis for chemical comparison among hydrothermal systems in various tectonic settings.

2. Description of sampling site

2.1. Hydrothermal fluid venting at 17°0'S (station 4)

At the northern tip of the N15° segment, adjacent to the triple junction on the central ridge, an active hydrothermal vent site is located [12,16,21]. This site is situated at a bathymetrical rise of up to 1980 m, which seems an unusual characteristic in a spreading ridge context. Active anhydrite chimneys venting transparent fluids are scattered within a limited area with a radius of about 200 m. Around the active region, huge, extinct sulfide chimneys are distributed in a graben structure.

During the dive studies, several fluid samples were collected. Most of the 1989 samples were obtained from the 'White Lady' chimney (sample series ST). Two years later we re-visited the same anhydrite chimney and collected fluid samples (samples YK77 and YK78). During the latter dive program we also sampled fluids from two other anhydrite chimneys 'Kaiyo' (samples YK80) and 'LHOS' (samples YK93) at the STARMER II site, which is located about 150 m southwest of White Lady. The fluid temperature of these three chimneys range between 230° and 290°C. Geochemical studies of the elemental composition of the hydrothermal fluids have already been reported [22,23]. All of the three fluids show low chlorinity, 45–49% of seawater value, which is strong evidence of a phase separation process during hydrothermal circulation. The lack of any significant fluctuation in the elemental composition of the White Lady fluid in the 2 years be-

tween samples suggests that the phase separation process is occurring in a steady state [23].

2.2. Low temperature shimmering fluid at 18°50'S (station 14)

At station 14 a megaplume-like hydrothermal plume was observed in 1987 [15] and biological communities associated with low temperature fluid seepage were discovered by a towing video TV survey in 1988 [12,16]. During the dive studies, several biological communities, comprising mussels, galatheids and synaptic holothurians, were observed at the fissure or on lava debris resulting from the collapse of lava lakes [24]. This site is situated in the N–S trending segment of the central ridge, and has a morphology comparable to that of a fast spreading ridge. Recent volcanic activity is represented by fresh lava flows widely distributed throughout the axial graben, with hollowed-out lava lakes, lava pillars, sheet flows and lobate lava [12].

Fluid sampling was conducted during the 1991 *Shinkai6500* dive program. At that time, we could not find 'mussel valley' which had been a main target of the 1989 dive study. Thus, we collected fluids from a rather small (about 10 m in diameter) and sparse mussel bed named 'Sunset site' (samples YK87 and YK96). Fluid emanations were quite moderate and the highest temperature measured was only 5.2°C (ambient seawater was 1.6°C). From another colony named 'Refound Arch', about 100 m away from the former site, additional samples were collected (sample YK95). In this colony all the mussels were dead and the fluid temperature was about 3°C. Although we had expected hydrothermal activity with temperatures as high as 300°C, from the presence of the extinct sulfide chimneys [12], such activity was not identified, despite of intense effort, during the dive programs.

3. Sampling and analytical methods

3.1. Sample handling

Sampling equipment was described in the previous reports [22,23]. All of the 1989 samples and

some of the 1991 samples (whose sample name bears the suffix '-Ti') were collected by a titanium syringe of the French submersible *Nautilus*. The other samples were taken using a pumping sampler system developed for the Japanese submersible *Shinkai6500*.

Sample aliquots for gas species analyses were taken out from the sample bottles prior to those for elemental composition analyses. First, the sample for helium measurement was introduced into a copper tube (~30 ml), which was immediately sealed with two knife-edged clamps. A lead glass container with two stopcocks (volume about 40 ml) was sometimes used in place of the copper tubing. Aliquots for CO₂ and CH₄ analyses were drawn into glass vials (volume about 25 ml). After being poisoned by mercury chloride, each vial bottle was capped with a rubber septum, making sure no head space air was present. These bottles were stored in a refrigerator (at about 5°C) until their analysis in shore-based laboratories. Where

sample recovery was insufficient it was not possible to measure all gas species.

3.2. Analytical procedures

Helium samples were sent back to the LEC laboratory (in Japan). Dissolved gas was extracted to an evacuated lead glass bottle (~50 ml) and its helium isotope ratio was measured by a VG 5400 mass spectrometer (after [25]). During the purification procedure, the abundance ratio of He/Ne and absolute helium content were measured using a quadrupole mass spectrometer (QMS) installed in the purification line. The helium contents were determined by comparing the peak intensity of the QMS with the result of standard air measurement. Some duplicate helium samples were sent to the DMS-CEA laboratory (in France) and measurements of abundance and isotopic ratio were carried out using a VG 3000 mass spectrometer (after [26]). Precision

Table 1
Chemical data for hydrothermal samples from station 4

Site	Sample	Mg ^{a)} (mmol/kg)	CO ₂ ^{a)} (mmol/kg)	CH ₄ (μmol/kg)	He (cm ³ STP/g)
White Lady 89	ST1-2	22.6	9.0	20.0	1.9×10 ⁻⁵
	ST4-1	51.7		0.93	2.4×10 ⁻⁶
	ST5-1	18.9	10.2	16.7	1.6×10 ⁻⁵
	ST5-2	8.6	11.8	23.6	3.3×10 ⁻⁵
	ST5-3	50.4	2.9	0.46	0.5×10 ⁻⁶
	ST6-1	25.7	8.2	25.2	2.0×10 ⁻⁵
	ST6-2	8.9	12.3		2.5×10 ⁻⁵
White Lady 91	YK77-6	49.8	2.2	0.09	
	YK78-Ti	18.5	9.7	16.9	1.8×10 ⁻⁵ c)
Kaiyo	YK80-Ti	52.0	2.3	0.24	0.2×10 ⁻⁶ c)
	YK80-3	31.5	5.0	14.2	2.1×10 ⁻⁵ c)
	YK80-4	8.5	10.2	37.6	
LHOS	YK93-2	51.0	2.3	0.51	0.4×10 ⁻⁶
	YK93-3	22.7	6.4	21.5	6.6×10 ⁻⁶
	YK93-4	33.9			
Reference ^{b)}	ST4-2	52.6	2.2	<0.01	

^a Data from [22,23].

^b Sample collected about 3 km north of the White Lady.

^c Results of measurements in the CEA laboratory, others are those from the LEC laboratory.

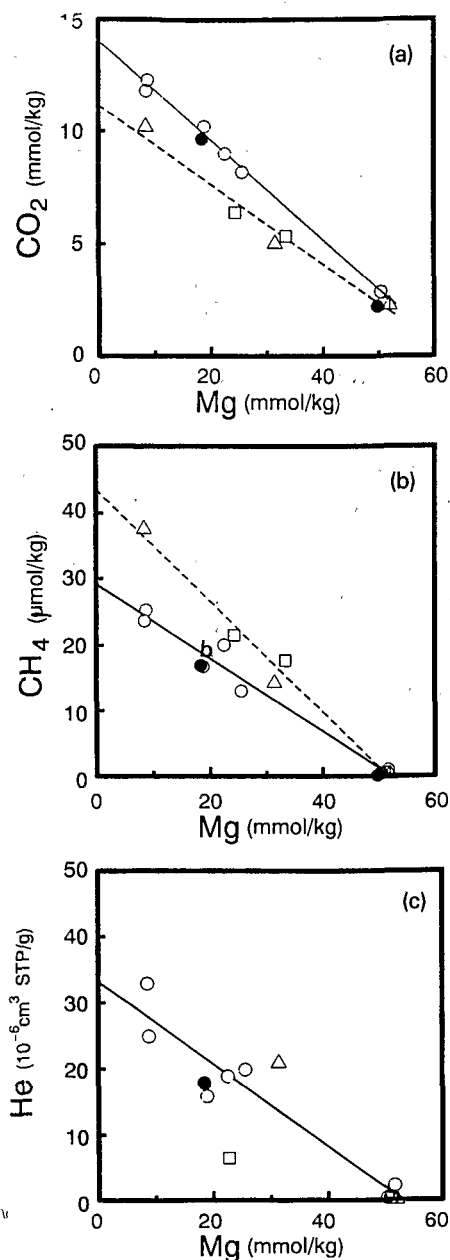


Fig. 2. Relationship between concentration of gas species versus Mg for the samples at station 4. \circ = White Lady in 1989; \bullet = White Lady in 1991; \triangle = Kaiyo; \square = LHOS; solid line = regression of the White Lady 1989 samples; dashed line = regression of the Kaiyo-LHOS samples. (a) carbon dioxide (b) methane (c) helium.

on the helium isotope ratio measurement is estimated to be within $\pm 1\%$ of the value for both the LEC and CEA laboratory, according to previous experiments. Determination of the total amount of helium has larger uncertainties, which are estimated to be around 10% for the LEC laboratory and 1% for the CEA laboratory.

CO₂ concentration of the 1989 samples was analyzed using GC-TCD [27]. After the analysis, the same CO₂ fraction was collected for carbon isotope measurement. We used a coulometer (UIC Inc. Model 5012) for CO₂ concentration determination of the 1991 samples. In this case, CO₂ for the isotope measurement was extracted from another aliquot by the addition of H₃PO₄. Reproducibility of CO₂ concentration determination is within $\pm 1\%$ of the value for the GC-TCD technique and $\pm 0.1\%$ for the coulometer analyses. Isotope measurements were made using a Finnigan MAT250 mass spectrometer. Its precision is estimated to be within $\pm 0.1\%$. All of the CO₂ analyses were carried out in the ORI laboratory.

The CH₄ concentration was analyzed by GC-FID, after extraction by bubbling through helium carrier gas, followed by collection in a charcoal trap at the temperature of dry ice [28]. Analytical precision is estimated to be within $\pm 5\%$ from replicate analyses. For carbon isotope measurement, CH₄ in the fluid sample was extracted into head space N₂ gas (about 10 ml), which was introduced into a glass vial by a needle through a rubber septum cap. After shaking it vigorously and leaving for about 1 h, 50–100 μl of the head space N₂ gas was injected into the GC/C/IRMS system (VG PRISM). The precision of the isotope measurement is estimated to be within $\pm 1\%$ from previous experiments [29]. In order to confirm no fractionation during the head space technique, we conducted a preliminary experiment using water samples saturated with the cylinder CH₄ gas, whose isotope ratio was known. The result showed agreement between the carbon isotope ratio of the head space gas and the original CH₄ gas within the analytical precision of the GC/C/IRMS system. All of the CH₄ analyses were conducted in the NIES laboratory.

4. Results and discussion

4.1. Gas abundance of the hydrothermal fluids at station 4

Concentrations of CO₂, CH₄ and He of the fluid samples obtained from station 4 are presented in Table 1. The relationships of each gas concentration to Mg concentration are illustrated in Fig. 2. The White Lady samples and the southwestern STARMER II site (Kaiyo–LHOS chimneys) samples show different mixing lines in these diagrams. This result is consistent with the previous elemental composition study [23].

End-member values are estimated according to the conventional method (extrapolation of the linear regression to Mg = 0). For the White Lady fluid, the CO₂ concentration is estimated to be 14.5 mmol/kg and CH₄ to be 30.4 μmol/kg, for the Kaiyo–LHOS fluid, CO₂ concentration is estimated at 11.0 mmol/kg and CH₄ at 43.5 μmol/kg. Good linear relationships in these magnesium diagrams (Fig. 2a,b) suggest that this is a reliable estimation of these end-member values.

In contrast to these, the He–Mg diagram shows a somewhat poor relationship (Fig. 2c). Moreover, the cross-check of helium concentration between LEC (Japan) and CEA (France) laboratories shows rather disagreeable results. For all three samples checked (YK78-Ti, YK80-Ti and YK80-3), the LEC results were substantially lower than CEA results. However, results of the 1989 samples, which were also measured in LEC, showed good agreement with the CEA results of the 1991 samples. Therefore, the disagreement is not attributed to difference between the two laboratories. As some previous studies have mentioned [17,18], the determination of the helium content of hydrothermal fluid samples is difficult due to the large pressure decrease after sample recovery. For instance, congregation of small gas bubbles during sample handling may lead to large uncertainties, since helium is subject to partition into the bubbles, if formed. Less helium in the second aliquot, which was analyzed in LEC, may be responsible for the lack of correlation between our results. In this study, we adopt CEA results for the three cross-checked samples (marked in Table 1).

Table 2
Isotopic data of hydrothermal samples from station 4

Site	Sample	R/R _A	$\frac{\text{He/Ne}}{(\text{He/Ne})_A}$	R _C /R _A ^{a)}	δ ¹³ C(CO ₂) (‰PDB)	δ ¹³ C(CO ₂) _h ^{b)} (‰PDB)	δ ¹³ C(CH ₄) (‰PDB)
White Lady 89	ST1-2	10.04	220	10.0	-5.6	-6.2	
	ST4-1				-2.1		
	ST5-1	9.83	250	9.86	-5.6	-6.0	-19.5
	ST5-2	9.72	300	9.75	-5.9	-6.1	-18.3
	ST5-3				-1.6		
	ST6-1	9.86	170	9.90	-5.3	-6.0	
	ST6-2	9.87	300	9.90	-6.0	-6.2	
White Lady 91	YK78-Ti				-5.3	-5.7	
Kaiyo	YK80-Ti				-6.7		
	YK80-3	9.04	27	9.28			-20.4
	YK80-4				-5.6	-5.7	
LHOS	YK93-3						-19.2
	YK93-4	8.99	120	9.04			
Reference	ST4-2				-0.7		

^a Corrected R/R_A for the addition of an atmospheric component from ambient seawater mixing (see text).

^b Corrected δ¹³C(CO₂) for mixing with ambient seawater (see text).

Such a bubble formation effect might be responsible for the poor correlation in the He–Mg diagram (Fig. 2c). It is impossible to estimate exactly this bias effect during the sample handling because it would depend on various factors, such as volume of the sampler, pressure of the sample, velocity of sample moving, and so on. However, we may expect that the sample with lower magnesium concentration, in other words more diluted with ambient seawater, would show less bias effect due to helium loss. However, in the He–Mg diagram, plots seem to be scattered along a single mixing line unrelated to their Mg concentration. This relationship suggests that the influence of helium loss is minimal and would allow us to evaluate the hydrothermal fluid end-member composition. Taking account of the scattering of data, the end-member helium concentration is estimated to lie in the range $(3.4 \pm 1.1) \times 10^{-5}$ cm³STP/g ($= 1.5 \pm 0.5$ μmol/kg).

4.2. Isotopic composition of the hydrothermal fluids at station 4

4.2.1. Helium

Helium isotope data from fluid samples obtained from station 4 are listed in Table 2. ³He/⁴He ratios and He/Ne ratios are presented as ratios relative to the atmospheric values (³He/⁴He ratio of 1.4×10^{-6} and He/Ne ratio of 0.288). Correction for the addition of an atmospheric component was calculated according to the conventional formula:

$$R_C = (R \times N - R_a \times N_a) / (N - N_a) \quad (1)$$

where R and N are ³He/⁴He ratio and He/Ne ratio of the sample, and R_a and N_a are those of the atmospheric component. Corrected helium isotopic compositions are presented as R_C/R_A in Table 2. This correction is based on the assumption that all the neon comes from the atmospheric component with the atmospheric helium [30]. In this study we selected the samples with high He/Ne ratios (> 20) to exclude the possibility of the addition of the atmospheric component derived from air during sample handling. We consider only the mixing of ambient seawater before sampling as source of the atmospheric

component and take the values of air-saturated seawater at 5°C ($R_a = 0.985$ and $N_a = 0.797$, calculated from the data in [31,32]).

Helium isotopic composition is known not to fractionate significantly during its partition into liquid and gas phases. Thus, the isotopic composition of the original hydrothermal fluid is estimated with confidence, even considering the possibility that the samples obtained might have suffered from helium loss. The cross-check of the isotopic measurements between the LEC and CEA laboratories did not show either significant disagreement or systematic bias, in contrast to the disagreeable results of the abundance determination. We report results from the LEC laboratory in Table 2 because the He/Ne ratio was measured during the same procedure.

The corrected isotopic compositions of the seven samples collected at station 4 fall in the range $R/R_A = 9.0$ – 10.0 . The isotopic ratio of basaltic glass helium at the same station was reported as $R/R_A = 10.0$ [33], which is in agreement with this range. These isotopic compositions seem to be higher than the average range of the MORB helium ($R/R_A = 8.18 \pm 0.73$ [34]). Taking account of the previous assessment [29], which determined the accuracy of the LEC laboratory isotopic measurements as well as experimental errors (about 5%), we cannot neglect overlap between the range of the analytical results and the MORB values. Comparison of the helium isotopic signature of the North Fiji Basin with the MORB range is discussed in a later section, together with data obtained from other sites.

4.2.2. Carbon

Results of carbon isotopic measurement are also presented in Table 2. In order to discuss the isotopic signature of the hydrothermal fluid, an isotopic composition free from the influence of dissolved CO₂ in deep seawater should be evaluated. Assuming simple mixing between the hydrothermal end-member and ambient seawater, the CO₂ concentration and isotopic composition of each sample can be expressed by the following equations:

$$[\text{CO}_2]_s = (1 - m) \times [\text{CO}_2]_a + m \times [\text{CO}_2]_h \quad (2)$$

$$\delta^{13}\text{C}_s \times [\text{CO}_2]_s = (1 - m) \times \delta^{13}\text{C}_a \times [\text{CO}_2]_a + m \times \delta^{13}\text{C}_h \times [\text{CO}_2]_h \quad (3)$$

where m is the mixing ratio of hydrothermal fluid estimated from the magnesium concentration; and subscripts s , a and h refer to sample, ambient seawater and hydrothermal end-members, respectively. Using these two equations, the isotopic composition of $\text{Mg} = 0$ end-member can be estimated from CO_2 concentration, $\delta^{13}\text{C}(\text{CO}_2)$ value and Mg concentration. The values of ambient seawater in this area are determined as: CO_2 concentration = 2.2 mmol/kg and $\delta^{13}\text{C}(\text{CO}_2) = -0.7\text{‰}$, from analytical results of the sample collected at the reference site (ST4-2). The estimated end-member isotopic compositions are listed as $\delta^{13}\text{C}(\text{CO}_2)_h$ in Table 2. They fall in a narrow range of $\delta^{13}\text{C}(\text{CO}_2)$ between -6.2‰ and -5.7‰ .

Since the fluids obtained have experienced subsurface phase separation processes, we should examine the effect of isotopic fractionation during these processes. The most dominant species of CO_2 dissolved in the fluids is considered to be H_2CO_3 . Only a small portion of CO_2 can be dissociated to bicarbonate ion due to the strong fluid acidity and the low dissociation constant of bicarbonate at high temperatures. Isotopic fractionation between gaseous CO_2 and dissolved H_2CO_3 is expressed according to the experimental results [35] as:

$$\delta^{13}\text{C}(\text{CO}_2, \text{gas}) - \delta^{13}\text{C}(\text{CO}_2, \text{dissolved}) = -0.373 \times 10^3 / t + 0.19\text{‰} \quad (4)$$

where t is temperature in degrees Celsius. In the case that this fit is valid up to higher temperatures, around 300°C , the carbon isotopic fractionation would be limited to within less than 0.5‰ [36]. Therefore, the original carbon isotopic signature of the hydrothermal system at station 4 would not seem to be different to the measured values of $\delta^{13}\text{C}$, around -6.0‰ .

With respect to CH_4 , mixing with ambient seawater will have a negligible effect on the $\delta^{13}\text{C}(\text{CH}_4)$ values of the samples because deep

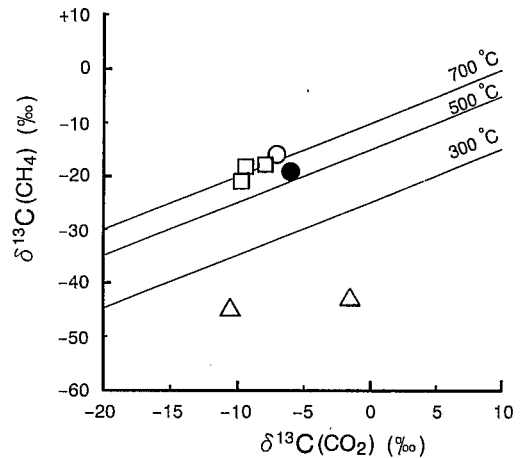


Fig. 3. Carbon isotope ratios in hydrothermal methane versus carbon dioxide. Isotherms for hypothetical isotopic equilibrium are calculated from Bottinga [37]. ● = North Fiji Basin (this study); ○ = East Pacific Rise 21°N [17]; □ = Southern Juan de Fuca Ridge [19]; △ = Guaymas Basin [47].

seawater contains only minor amounts of CH_4 (less than 10 nmol/kg). Thus, the end-member isotopic composition of the fluids can be directly evaluated from the analytical results of four samples; that is $\delta^{13}\text{C}(\text{CH}_4) = -20.4\text{‰}$ to -18.3‰ (Table 2).

While the helium isotopic composition shows distinct characteristics, the carbon isotopic composition of the fluids indicates a quite similar signature to the mid-oceanic ridge (MOR) hydrothermal systems. Both the $\delta^{13}\text{C}(\text{CO}_2)$ value around -6.0‰ and the $\delta^{13}\text{C}(\text{CH}_4)$ value between -20‰ and -18‰ are in the range of MOR systems. Deviation of 13‰ between CO_2 and CH_4 corresponds to isotopic equilibrium for ^{13}C exchanges at 550°C , according to the calculation of Bottinga [37]. Fig. 3 illustrates this relationship to the carbon isotopic data from other hydrothermal systems so far reported. Although the estimated temperature for the North Fiji Basin system is slightly lower than those for the MOR systems (EPR: $620\text{--}770^\circ\text{C}$ and SJFR: $640\text{--}750^\circ\text{C}$), this high apparent equilibrium temperature suggests the co-existence of CO_2 and CH_4 in a magmatic reservoir before their incorporation into hydrothermal fluids, as in the MOR systems.

4.3. Comparison of gas geochemistry of the hydrothermal fluids at station 4 with other hydrothermal systems

Chemical and isotopic compositions, measured exit temperature and calculated $^3\text{He}/\text{heat}$ ratio of end-members of the hydrothermal fluids at station 4 are summarized in Table 3. Data on the MOR hydrothermal fluids are presented in the same table for comparison. Previous studies have revealed that hydrothermal fluids from aged systems in equilibrium have converged $^3\text{He}/\text{heat}$ ratios in the range $0.5\text{--}1.5 \times 10^{-12} \text{ cm}^3\text{STP/g } ^\circ\text{C}$ [38] and a common range of gas contents: CO_2 around 10 mmol/kg, CH_4 in the range 30–120 $\mu\text{mol/kg}$ and helium in the range $2\text{--}5 \times 10^{-5} \text{ cm}^3/\text{g}$. This signature would suggest that magma beneath these hydrothermal systems has similar gas abundances and that the mechanism for the process by which gas species are introduced into the circulation of these hydrothermal systems (from the magma beneath the systems) is common.

Compared with MOR fluids, the North Fiji Basin hydrothermal fluids show comparable or slight enrichment in gas abundances. Since the hydrothermal fluids at station 4 are vapor-rich components after phase separation [22,23], it

would be quite reasonable to expect high gas concentrations due to preferential gas partition. The ASHES vent field in the Juan de Fuca Ridge is known as the first observation of subseafloor phase separation. Significant enrichment in gas species of the vapor-rich fluids is one of unique geochemical characteristics of the ASHES vent fluids among the ridge systems [39]. Butterfield et al. [39] attributed their high CO_2 concentrations (285 mmol/kg) to two causes: the gas partition into the vapor phase and the magmatic exsolution of a CO_2 -rich fluid. They estimated the effect of the gas partition during phase separation to be an enrichment factor of 4–5 by 15–20% boiling of the initial fluid. If we assume a similar enrichment factor by phase separation processes, based on similar chlorinity to the ASHES fluids, we could evaluate the gas abundance of the initial North Fiji Basin fluid as being comparable to the lower levels in the range of MOR fluids.

The isotopic data from the fluids at station 4 indicate that gas species predominantly originate from the mantle component. The MORB-like carbon isotopic composition fluids show no evidence for the involvement of the subducted components of organic material and/or altered carbonates. Negligible contamination of radiogenic helium from the crustal component is supported

Table 3
Comparison of the gas composition of hydrothermal fluids

		North Fiji Basin	EPR 21°N	EPR 13°N	SJFR	MAR
fluid temperature	(°C)	285/290	350	335	285	325–345
CO_2	(mmol/kg)	14.5/11.0	8.0	10.8–16.7	3.9–4.4	---
CH_4	($\mu\text{mol/kg}$)	30.4/43.5	45–65	27–55	82–118	61.6
He	($\times 10^{-5} \text{ cm}^3/\text{g}$)	2.3–4.5	2.1–2.9	3.0–4.5	---	4.6
$\delta^{13}\text{C}(\text{CO}_2)$	(‰PDB)	-6.2 to -5.7	-7.0	-5.5 to -4.1 ^a)	-9.7 to -6.8	---
$\delta^{13}\text{C}(\text{CH}_4)$	(‰PDB)	-20 to -18	-17.6 to -15.0	-19.5 to -16.6	-20.8 to -17.8	---
R/R _A		9.0 to 10.0	7.8	7.4 to 7.6	---	8.4
$^3\text{He}/\text{heat}$	($\times 10^{-12} \text{ cm}^3\text{STP/g}^\circ\text{C}$)	1.4	0.4 ^b)	0.7 to 1.4 ^b)	---	1.2

^a Not corrected for the involvement of seawater bicarbonate.

^b From [45].

Data sources: EPR 21°N = East Pacific Rise 21°N [17,46]; EPR 13°N = East Pacific Rise 13°N [18]; SJFR = Southern Juan de Fuca Ridge [19]; MAR = Mid-Atlantic Ridge, the Snake Pit site at 23°N [20].

Table 4
Chemical data of low temperature fluid samples from station 14

Site	Sample	SiO ₂ (mmol/kg)	pH	Li (μmol/kg)	Mn (μmol/kg)	CO ₂ (mmol/kg)	CH ₄ (μmol/kg)
Refound arch	YK95-2	0.148	7.57	24.9		2.20	0.01
	YK95-3	0.141	7.61	26.7	0.12		0.08
Sunset	YK87-M	0.127		22.5	0.09		
	YK87-Ti	0.156	7.63	25.2	1.01	2.24	
	YK87-2	0.192	7.45	26.8	1.08	2.23	0.04
	YK87-3	0.193	7.43	26.4	1.15		
	YK87-4	0.187	7.50	25.4	1.17	2.29	0.05
	YK96-2	0.264	7.10	30.7	2.95	2.22	0.14
Reference a)	YK96-3	0.272	7.05	30.3	3.28	2.29	0.18
	YK96-4	0.272	7.07	32.3	3.33		
	YK86-3	0.116	7.71	21.6	0.12		
	YK86-4	0.120		20.3	0.13	2.08	0.02

^a Sample collected about 2.5 km south of the Sunset site.

Analytical methods (and their precisions). SiO₂: colorimetry, silico-molybdate method (3%); pH: potentiometric (0.5%), Li: ICP-AES, standard additions (3%); Mn: ICP-AES (3%); CO₂: coulometer (0.1%); CH₄: GC-FID (5%).

by the helium isotopic composition. For ³He/heat ratios, the fluids at station 4 show a similar range to the MOR fluids, although the influence of significant conductive cooling and phase separation may have shifted the observed value from the original ³He/heat signature.

Both the gas abundance and isotopic composition of the hydrothermal fluids at station 4 have several similar characteristics to the MOR hydrothermal systems. This gas geochemistry was consistent with the petrological studies which in-

dicate predominant N-MORB features [40]. They demonstrated that the influence of subduction contamination is apparent in only a few samples and this influence is attributed not to present subduction but to partial melting of a mantle source suffering from remnant subduction.

4.4. Fluid geochemistry of low temperature fluids at station 14

The shimmering fluid discovered at station 14 is slightly warmer than ambient seawater. Chemi-

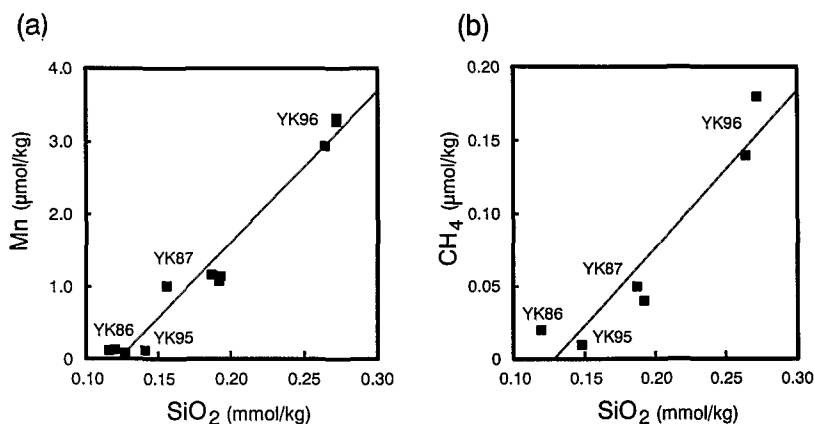


Fig. 4. Relationship between concentration of (a) manganese and (b) methane versus silica concentration for samples at station 14.

cal anomalies are detected in some components of Li, Mn, Si and pH, as listed in Table 4. Concentrations of other elements were equivalent to those of ambient seawater, within the analytical uncertainties, or lower than the detection limits. Among gas species, CH₄ indicates notable enrichment compared with ambient seawater, while CO₂ concentration does not show clear anomalies. All of the samples showed helium abundance comparable to that of air-saturated seawater (4×10^{-8} cm³/g) and our analytical procedure was too uncertain to discuss anomalies of helium contents in this range.

Fig. 4 illustrates relationships among chemical anomalies of the fluid samples. We took the SiO₂ concentration as an indicator of fluid mixing ratio and plotted the relationship of Mn and CH₄ concentrations against it. The YK87 and YK96 samples collected from the same 'Sunset site' show a linear trend in both plots. This linear relationship suggests that the samples obtained were a mixture of one fluid end-member and ambient seawater. Of course, it is impossible to evaluate the chemical composition of an end-member fluid because the anomalies in all the samples are quite small. However, we may discuss abundance ratios among these hydrothermal indicators. For instance, CH₄/Mn molar ratio of the fluid is calculated as 0.051 from slopes of the linear regressions in Fig. 4. We can also obtain information about relationships between chemical anomalies and the temperature anomaly from the temperature data. The Mn/heat ratio is estimated as 0.88 nmol/g °C and the CH₄/heat ratio as 0.046 nmol/g °C. The abundance ratios of heat, CH₄ and Mn of hydrothermal fluids and

hydrothermal plumes have been discussed in several previous studies. The Mn/heat ratio of the shimmering fluids at station 14 is in a range of the diffuse-type hydrothermal discharges. For example, Baker et al. [41] reported an average Mn/heat ratio for the diffuse low temperature vents at the north Cleft segment in the Juan de Fuca Ridge as 0.92 ± 0.67 nmol/g °C.

Moreover, these abundance ratios of chemical anomalies show a correspondence between the shimmering fluid and the hydrothermal plume observed in the same station. Nojiri et al. [15] reported two distinct hydrothermal plumes during the site survey conducted in 1987. They revealed different CH₄/Mn ratios in the plumes at different depths: 0.386 mol/mol for the upper megaplume-like plume and 0.056 mol/mol for the lower steady-state plume. The good agreement between the shimmering fluids at station 14 and the lower plume is shown not only in the CH₄/Mn ratio but also in the Mn/heat ratio (0.92 nmol/g °C) and CH₄/heat ratio (0.05 nmol/g °C). Although it is difficult to compare the plume in 1987 and the diffuse discharge in 1991 directly this agreement may suggest that these chemical ratios do not change significantly during the dilution process that takes place when a low-temperature type hydrothermal discharge develops into a plume.

4.5. Helium isotopic composition of low temperature fluid at station 14

Isotopic data on carbon and helium from the fluid samples at station 14 are listed in Table 5. While carbon isotopic compositions are difficult

Table 5
Isotopic data of low temperature samples from station 14

Site	Sample	R/R _A	$\frac{\text{He/Ne}}{(\text{He/Ne})_A}$	R _C /R _A	$\delta^{13}\text{C}(\text{CO}_2)$ (‰PDB)
Refound arch	YK95-2	2.40	1.00	7.96	0.01
	YK95-3	2.08	1.29	3.84	0.02
Sunset	YK87-2	5.44	1.84	8.86	0.04
	YK96-2	6.38	2.90	8.43	-0.51
	YK96-3	6.80	3.22	8.72	-0.38
	YK96-4	7.37	4.53	8.73	

to distinguish from ambient seawater values, helium isotope ratios provide useful information. As is well known, helium is chemically inert and also has little chance for isotope fractionation. Its isotopic composition changes only by mixing with helium from other sources. Thus, in the case of mixing only with ambient deep seawater, we can evaluate the original helium isotopic composition of fluids even when they are much diluted. The evaluated helium isotopic compositions, according to the same correction calculation described in section 4.2.1., are listed in Table 5. Although the samples were significantly diluted, the evaluated values of four samples from the Sunset site converged into a narrow range of $R_C/R_A = 8.4$ – 8.9 .

The helium isotopic compositions of station 14 are comparable to the MORB helium range, although they are lower than the value of basaltic glass helium at the same station ($R/R_A = 9.4$ [33]). This result strongly suggests magmatic helium involvement in the fluid during its circulation and implies present or at least recent high temperature hydrothermal activity around this area. The chemical anomalies of the fluids described in the previous section are additional evidence because these components are difficult to leach by low temperature fluid circulation.

4.6. Helium isotope signature of the North Fiji Basin central ridge

Craig et al. [1] identified helium isotope anomalies in a hydrothermal plume at $18^{\circ}08'S$ on the central ridge during the PAPTUA expedition in 1986 and evaluated the helium isotopic composition of the added source end-member at $R/R_A = 8.4$. For basalt glass helium, Poreda and Craig [42] reported $R/R_A = 9.2$ and Hirose et al. [33] reported $R/R_A = 9.3$ – 10.0 . Together with our hydrothermal fluids results ($R/R_A = 9.0$ – 10.0 at station 4 and $R/R_A = 8.4$ – 8.9 at station 14), the helium isotope signature of the North Fiji Basin central ridge is characterized as higher than, or on the high side of, the average MORB range ($R/R_A = 8.18 \pm 0.73$ [34]). Because of the low number of data it is difficult to confirm helium isotope variation along the central ridge.

The helium isotopic signature could be related to the trace element geochemistry of basalt samples from the North Fiji Basin central ridge. Previous studies [39,43] have indicated a co-variation of incompatible element abundances and Sr–Nd isotope systematics and attributed it to the mixing of a dominant N-MORB signature source with a co-existing enriched OIB source, whose influence increases towards the northern segments. Since the whole range of these compositions, as well as the helium isotopic composition, are not so large, it is difficult to exclude the possibility of heterogeneity within the MORB source. However, the isotopic variations in both incompatible elements, such as Sr and Nd, and volatile elements, such as helium, are best explained by the incorporation of a hotspot-like primitive component into the magmatic source of the North Fiji Basin central ridge.

In several other places in the southwest Pacific region, Poreda and Craig [42,44] have reported elevated helium isotope signatures; such as the Manus basin ($R/R_A = 10.9$) and the northeastern part of the Lau Basin ($R/R_A = 8$ – 22). They suggested this high ^3He province stretches from the Manus Basin to the Easter Microplate, including the Samoan hotspot. The spreading process of the North Fiji Basin, especially the unique topographic uplifted dome in the triple junction near station 4, might be related to the upwelling of a ^3He -rich, hotspot-like component.

5. Conclusions

On the central ridge of the North Fiji Basin, hydrothermal fluid emanations were located at two sites, station 4 ($17^{\circ}0'S$) and station 14 ($18^{\circ}50'S$). The chemical composition and isotopic ratio of helium and carbon were studied in the fluid samples obtained from these stations.

The hydrothermal fluids from station 4 (venting temperatures were 230 – 290°C) did not show such significant gas enrichment, like that observed in the ASHES field in the Juan de Fuca Ridge, although there are vapor-rich fractions after phase separation. The carbon isotopic signatures of $\delta^{13}\text{C}(\text{CO}_2)$, of around -6.0‰ (PDB),

and $\delta^{13}\text{C}(\text{CH}_4)$, around -19% (PDB), were comparable to the mid-oceanic ridge (MOR) hydrothermal systems. On the other hand, the helium isotopic composition ($R/R_A = 9.0\text{--}10.0$) suggests the influence of a hotspot-like primitive component.

The low-temperature fluids from station 14 (the highest measured temperature was 5.2°C) showed slight chemical anomalies in some species of SiO_2 , Li, Mn, pH and CH_4 . The original helium isotopic composition (R/R_A) was estimated to be between 8.4 and 8.9. These geochemical indicators of the fluids suggest the existence of high temperature hydrothermal activity in this area.

In summary, the gas geochemistry of these fluids from the North Fiji Basin central ridge was similar in several characteristics to that of the MOR hydrothermal systems. They did not show evidence of the influence of a subducted component. The results are in agreement with the previous petrological studies on basaltic rocks, which demonstrated a N-MORB-like signature with little affinity to back-arc basin basalt. This is quite reasonable since the central ridge is 150–500 km away from the present subduction of the New Hebrides Trench and its spreading occurs free from the present subduction process. The gas geochemistry of the fluid emanations, which is similar to the MOR fluids, clearly reflect the mature signature of the North Fiji Basin spreading activity.

Acknowledgements

We are very grateful to the captains and crews of R/V *Nadir* and R/V *Yokosuka*, and to the submersible teams of *Nautila* and *Shinkai6500*. This study was conducted as a part of 'STARMER Project' funded by the Science and Technology Agency (STA) of Japan and IFREMER of France. We wish to thank the shipboard scientists for their cooperation, especially for the sample collecting. We thank Mr. T. Nakayama for CH_4 concentration analyses; Dr. Y. Zeng for assistance in CH_4 isotope measurements by GC/C/IRMS; Mr. M. Tsutsumi for assistance in CO_2

isotope measurements. We also thank Dr. Hirose for allowing to cite his unpublished manuscript, and to Drs. Y. Sano and G. Igarashi for fruitful discussions. This manuscript was much improved by valuable comments from Prof. H. Craig and an anonymous reviewer. [MK]

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