Geochemical Journal, Vol. 38, pp. 527 to 534, 2004

Discovery of a new hydrothermal venting site in the southernmost Mariana Arc: Al-rich hydrothermal plumes and white smoker activity associated with biogenic methane

TOSHITAKA GAMO,[1,2]* HARUE MASUDA,[3] TOSHIRO YAMANAKA,[4,5]** KEI OKAMURA,[1]*** JUNICHIRO ISHIBASHI,[6,4] EIICHIRO NAKAYAMA,[7+] HAJIME OBATA,[7]**** KIMINORI SHITASHIMA,[8] YOSHIRO NISHIO,[6]***** HIROSHI HASUMOTO,[1] MASAHARU WATANABE,[1] KYOHIKO MITSUZAWA,[9]***** NOBUKAZU SEAMA,[10] URUMU TSUNOGAI,[6,2] FUMITAKA KOUZUMA[2] and YUJI SANO[1]

[1]Ocean Research Institute, The University of Tokyo, Nakano-ku, Tokyo 164-8639, Japan
[2]Graduate School of Science, Hokkaido University, N10 W8, Sapporo 160-0810, Japan
[3]Graduate School of Science, Osaka City University, Sugimoto, Osaka 558-8585, Japan
[4]Graduate School of Science, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan
[5]Institute of Geoscience, University of Tsukuba, Tsukuba 305-8571, Japan
[6]Graduate School of Science, The University of Tokyo, Hongo, Tokyo 113-0033, Japan
[7]University of Shiga Prefecture, Hikone 522-8533, Japan
[8]Central Research Institute of Electric Power Industry, Abiko, Chiba 270-1194, Japan
[9]Department of Deep Sea Research, JAMSTEC, Yokosuka 237-0061, Japan
[10]Research Center for Inland Seas, Kobe University, Kobe 657-8501, Japan

(*Received June 25, 2003; Accepted April 19, 2004*)

This paper reports a series of studies leading to the discovery of a submarine hydrothermal field (called Nakayama Field) at an arc seamount (12°43′ N, 143°32′ E) in the southernmost part of the Mariana Trough, western Pacific Ocean. We first detected hydrothermal plumes characterized by water column anomalies of temperature, light transmission, Mn, Fe, Al, O_2, CH_4, and $\delta^{13}C$ of CH_4 above the summit caldera of the seamount. Then deep-tow camera surveys confirmed the existence of hydrothermal activity inside the caldera, and an ROV dive finally discovered white smoker-type fluid venting associated with vent fauna. A high concentration of aluminum in the plume and white smoker-type emissions imply acidic hydrothermal activity similar to that observed at the DESMOS Caldera in the eastern Manus Basin, Papua New Guinea. Anomalously low $\delta^{13}C$ (CH_4) of –38‰ of a vent fluid sample compared to other arc hydrothermal systems along the Izu-Bonin and Mariana Arcs suggests an incorporation of biogenic methane based on a subsurface microbial ecosystem.

Keywords: submarine hydrothermal activity, southern Mariana Trough, hydrothermal plume chemistry, aluminum anomaly, biogenic methane

INTRODUCTION

The Mariana Trough is a present-day spreading back arc basin behind the Mariana Trench, where the Pacific plate subducts under the Philippine Sea plate (Fig. 1). The spreading rate is thought to be ~3 cm y^{-1} as a full rate for these 3 m.y. (Hussong and Uyeda, 1981). The Mariana Trough is also characterized by active hydrothermal circulation with heat and chemical fluxes from the seafloor (e.g., Ishibashi and Urabe, 1995). At 18°13′ N, 144°42′ E at a depth of 3,600 m, Alice Springs Field in the mid-Mariana Trough (Fig. 1) vents clear fluids with the maximum temperature of 280–287°C that have been known since the discovery by the submersible *Alvin* in 1987 (Craig *et al*., 1987; Campbell *et al*., 1987; Hessler *et al*., 1988; Gamo *et al*., 1993; Fujikura *et al*., 1997). In the southern Mariana Trough, clear fluids (maximum temperature: 202°C) were found at 13°24′ N, 143°55′ E at a depth of 1,470 m (Forecast Vent Field; Fig. 1) by the submersible *Shinkai 6500* in 1992 (Johnson *et al*., 1993; Gamo *et al*., 1993). It has been suggested from chemical and isotope characteristics of the hydrothermal fluids that the Alice Springs Field belongs to a sediment-starved back

*Corresponding author (e-mail: gamo@ori.u-tokyo.ac.jp)
**Present address: Graduate School of Social and Cultural Studies, Kyushu University, Roppon-matsu, Fukuoka 810-8560, Japan.
***Present address: Institute for Chemical Research, Kyoto University, Uji 611-0011, Japan.
****Present address: Ocean Research Institute, The University of Tokyo, Nakano-ku, Tokyo 164-8639, Japan.
*****Present address: Institute for Frontier Research on Earth Evolution, JAMSTEC, Yokosuka 237-0061, Japan.
+Deceased.

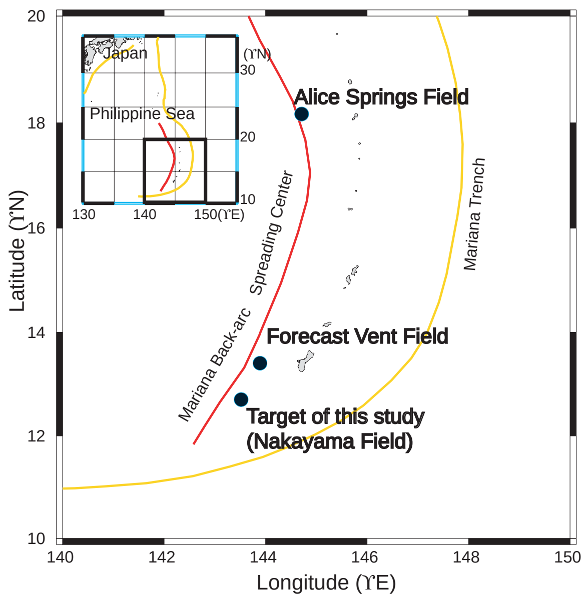

Fig. 1. A bathymetric map of the mid- and southern Mariana Trough, showing the location of the target area of this study together with so far reported high temperature hydrothermal active sites (Alice Springs Field and Forecast Vent Field).

arc type, while the Forecast Vent Field is a sediment-starved arc type (Gamo *et al.*, 1997a).

Little data are available, however, on whether submarine hydrothermal activity extends further south of 13°24′ N. It is of special interest that southward extension of the back-arc rift and that of the arc volcanic chain are sharply turned clockwise in the southernmost Mariana Trough as they approach to the trench axis. Martinez *et al.* (2000) elucidated the "fast spreading" geophysical and morphological characteristics of the southernmost Mariana Trough spreading center, suggesting additional magma supply from arc magmatic sources. We have been searching for current hydrothermal activity in the southernmost Mariana Trough as expected from its robust magmatic appearance (Martinez *et al.*, 2000). In this study, we focused our attention to a large seamount at 12°43′ N (Fig. 1), where hydrothermal deposits had been dredged (P. Fryer, personal communication). Chemical anomalies in bottom seawaters above the seamount, visual data from deep-tow camera surveys and a ROV dive for direct bottom observation were successfully conducted to find a new large scale hydrothermal venting field as described below.

We call this hydrothermal field "Nakayama Field", which is named after Prof. Eiichiro Nakayama, an analytical geochemist at the University of Shiga Prefecture who passed away in December 2001. He was a pioneer in trace metal analysis using chemiluminescence detection, and played an important role in characterizing the hydrothermal plume in this study. Hydrothermal plume surveys, chemical and isotopic characterizations of the new Nakayama fluids are the main themes of this paper.

Operations at Sea and Methods

Geographic features of the target

As shown in Fig. 2, the seamount locates ~5 miles southeastward from the back-arc spreading axis of the southern Mariana Trough, having an elliptic shape with the major axis of ~7 miles. The seamount belongs to the NNE-SSW arc volcanic chain extending along the eastern side of the spreading axis (Martinez *et al.*, 2000). The summit of the seamount forms a wide and deep caldera depression (called TOTO Caldera). The shallowest depth of the caldera rim is about 2,300 m, while the bottom of the caldera has a depth of more than 3,150 m.

A series of cruises

Three cruises were devoted for the survey of the seamount. First for the hydrothermal plume mapping, the R/V *Hakuho Maru* cruise KH-98-1 Leg-3 (Ocean Research Institute, the University of Tokyo) was conducted between March 2 and 16, 1998 as described in Subsection "Hydrothermal plume survey". Then, deep-tow camera surveys were performed during the R/V *Yokosuka* YK-99-11 cruise (Japan Marine Science and Technology Center: JAMSTEC) from Jan. 7 to Jan. 24, 2000 (Mitsuzawa *et al.*, 2000; Masuda *et al.*, 2001) as described in Subsection "Deep-tow camera survey". Finally, the ROV (Remotely Operated Vehicle) *Kaiko* of JAMSTEC was used for intensive dive observation and sampling inside the TOTO Caldera, during the R/V *Kairei* cruise KR-00-03 (JAMSTEC) from May 26 to June 11, 2000 as described in Subsection "Diving survey".

Hydrothermal plume survey

Seawater sampling was performed at almost the center of the TOTO Caldera (station Hyd-01 (12°43.1′ N, 143°32.0′ E) shown in Fig. 2), using a CTD (Conductivity, Temperature, Depth sensor package) multi-sampling system. The CTD system (Seabird, Carousel-32; SBE-9 plus CTD) was equipped with the following *in situ* instruments: a DO (Dissolved Oxygen) sensor (SBE-13B), a light transmissometer (Sea Tech, 25 cm light path), and an *in situ* flow-through Mn analyzer GAMOS-II (Okamura *et al.*, 2001). Nineteen Niskin bottles (General Oceanics, 12-liter type) were attached to the system for water sampling. In order to avoid the contamination from the bottles, the Niskin bottles had been coated with Teflon paint on their inside walls, and silicon tubing (Silastic tube, Dow Corning) is used as the rubber spring inside the bottles because of its contamination-free characteris-

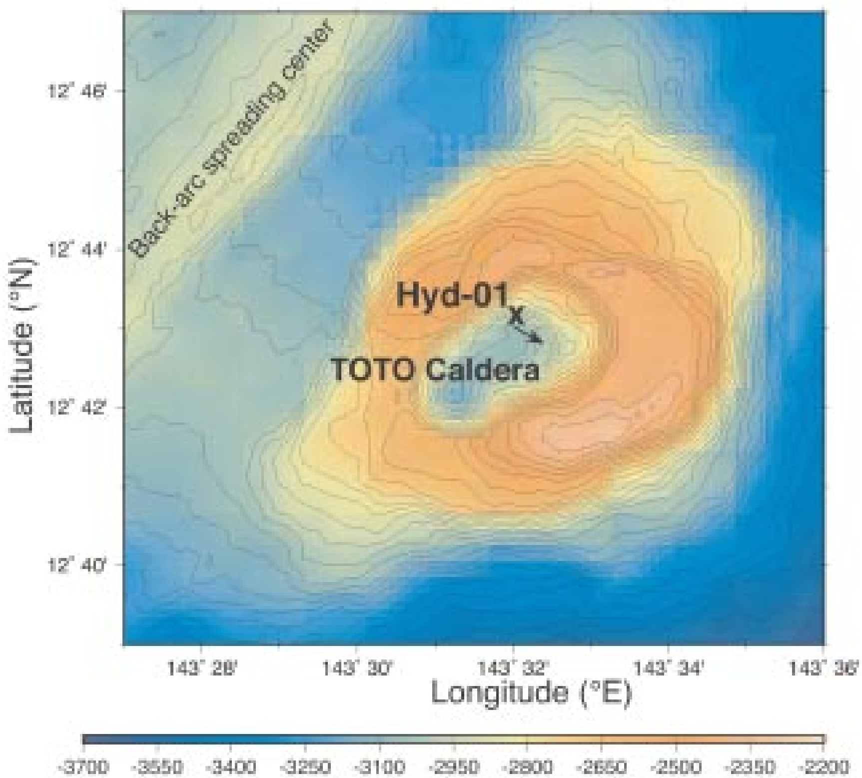

Fig. 2. A bathymetric map of the seamount (an arc volcano) with a big caldera (TOTO Caldera) surveyed by this study. The cross and the arrow show the location of station Hyd-01 and the rough track of the ROV Kaiko dive #163 (see Fig. 5 for details), respectively. Nakayama Hydrothermal Field locates at the northeastern crater of the caldera.

tics. An armored cable made of titanium was used for the hydrocast to minimize trace metal contamination during water sampling. In addition, the Niskin bottles were thoroughly cleaned using 2% Extran MA01 (Merck) solution, 0.1M HCl solution and Milli-Q pure water just before use.

Collected seawater samples were analyzed for Mn, and Fe(III) on board the ship. Dissolved Mn was determined for unfiltered seawater at pH = 5.0 using an automated Mn analyzer consisting of column electrolysis preconcentration and chemiluminescence detection system (Nakayama *et al*., 1989). The obtained Mn values were in good agreement with the *in situ* data by the GAMOS-II as reported by Okamura *et al*. (2001). Iron(III) in an acidified seawater sample (pH = 3.0) was measured for unfiltered seawater using an automated Fe analyzer consisting of chelating resin preconcentration followed by chemiluminescence detection (Obata *et al*., 1993).

In shorebased laboratories, dissolved Al was analyzed for unfiltered seawater by a flow-through fluorimetric method using lumogallion-Al complex (Obata *et al*., 2000). Methane and its carbon isotope ratio ($\delta^{13}C_{PDB}$) were measured by isotope-ratio-monitoring-GC/MS (Tsunogai *et al*., 1998, 2000). Helium isotope ratio ($^3He/^4He$) was measured by isotope mass spectrometry (Sano and Wakita, 1988). Subsamples for methane and $^3He/^4He$ measurements were taken without air contamination in 100 cm^3 glass vial bottles with $HgCl_2$ for disinfection, and in 40 cm^3 Pb-glass tubes with stopcocks at both ends, respectively.

Deep-tow camera survey

A 4000 m-class deep-tow camera system of JAMSTEC (Monma, 2000) was used for extensive bottom observation at and around the TOTO Caldera. The system includes a super harp TV color camera, two still cameras (Benthos, 372A), a CTD (Seabird, SBE-9plus), and an SSBL (Super Short Baseline) acoustic transponder (OKI, SB-1017A) to know the system's correct position during its operation.

Diving survey

The 10,000 m-type ROV *Kaiko* (JAMSTEC) dove once at the TOTO Caldera (dive #163) for detailed bottom observation and sampling. An Alvin-type titanium syringe sampler (Von Damm *et al*., 1985) was installed to *Kaiko* for hydrothermal fluid sampling. During the dive, continuous data of temperature, light transmission and pH were recorded using a sealogger CTD (Seabird, SBE-

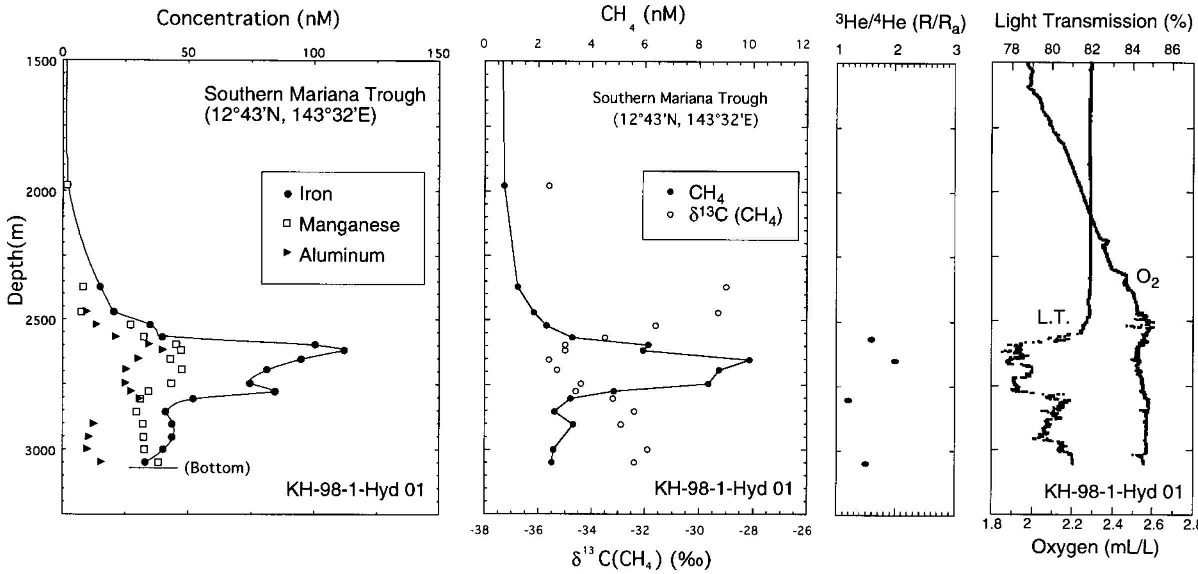

Fig. 3. Vertical profiles of Fe, Mn, Al, CH_4, $\delta^{13}C$ of CH_4, $^3He/^4He$ ratio, O_2, and light transmission observed at station Hyd-01 in March 1998.

25) with a transmissometer (WETLabs C-Star 25 cm) and a deep-sea *in situ* pH sensor attached to *Kaiko*. The pH sensor, which employs an ion sensitive field effect transistor (ISFET) as a pH electrode and a Cl-ion selective electrode as a reference electrode, has a quick response time of within a few milliseconds and a high accuracy of 0.01 to 0.005 pH (Shitashima and Kyo, 1998).

A collected fluid sample was analyzed for pH, alkalinity by a potentiometric titration method, Si and NH_4^+ by colorimetric methods (Gieskes *et al.*, 1991) on board the ship, and for ΣCO_2 (with a coulometer), CH_4, $^{13}C/^{12}C$ ratio ($\delta^{13}C$) of CH_4 and $^3He/^4He$ ratio in shorebased laboratories. CH_4, $\delta^{13}C$ (CH_4) and $^3He/^4He$ were measured using the same methods as described in Subsection "Hydrothermal plume survey".

Results and Discussion

Hydrothermal plumes

Strong signatures of hydrothermal plume were detected at station Hyd-01 within the TOTO Caldera. Figure 3 shows vertical profiles of trace metals (Fe, Mn, Al), CH_4, $\delta^{13}C$ (CH_4), $^3He/^4He$ ratio, O_2, and light transmission at station Hyd-01. A dominant plume existed at a depth of 2,600–2,650 m. The maximum values of Fe, Mn, Al, CH_4, and $^3He/^4He$ (R/R_a: the ratio to the atmospheric $^3He/^4He$ of 1.39×10^{-6}) are 112, 47, 40, 9.9 (nmol kg^{-1}), and 2.0, respectively. The temperature anomaly of +0.017°C was also observed at the plume center, as already published elsewhere together with the Mn anomaly detected by the *in situ* Mn analyzer GAMOS-II (Okamura *et al.*, 2001). The anomaly of the $^3He/^4He$ ratio clearly evidences the contribution of mantle-derived magma to the hydrothermal system at the TOTO Caldera.

The Al anomaly is a unique feature. High concentrations of Al have never been observed in general hot spring fluids on lands and at mid oceanic ridges, except for extremely acidic fluids with a pH of less than 2 (Ossaka *et al.*, 1977; Gamo *et al.*, 1997b). Aluminum is known to be leached from silicate minerals by acid attack (Stoffregen, 1987). A high sulfidation hydrothermal system at the DESMOS Caldera in the eastern Manus Basin, Papua New Guinea, is associated with the hydrothermal plume with aluminum anomaly of 1,500 nM at its maximum (Gamo *et al.*, 1993). Although the maximum Al concentration (40 nM) in Fig. 1 is much lower than that at the DESMOS Caldera, it strongly suggests the existence of an acidic hydrothermal fluid. This point remains unsolved in this study, because we have not inspected a high-temperature endmember fluid sample yet, as described in Subsection "Discovery of the Nakayama Field".

The turbidness of the plume as shown by the strong anomaly of light transmission, up to 4%, is suggestive of black smoker or white smoker type activities nearby to the station Hyd-01. This suggestion was confirmed by a ROV dive as mentioned in Subsection "Discovery of the Nakayama Field". It is noteworthy that the dissolved oxygen measured with the DO sensor showed an apparent negative anomaly at ~2,600 m depth as shown in Fig. 3, probably reflecting the oxygen consumption within the plume by oxidative reactions with electron acceptors such as H_2S, CH_4, and Fe(II).

The vertical profile of $\delta^{13}C$ of CH_4 also shows a clear negative anomaly (minimum value: –35.6‰), indicating

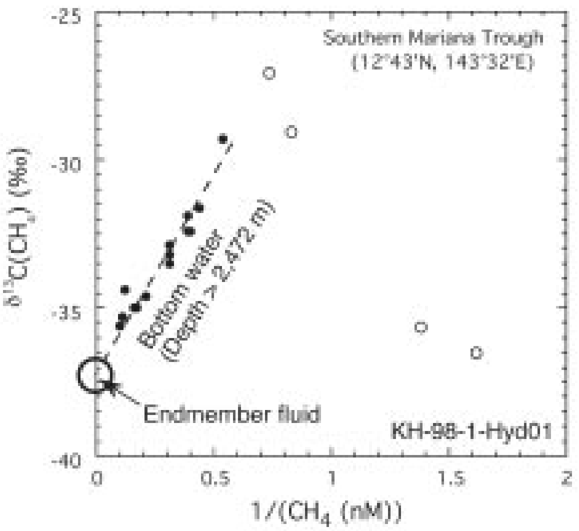

Fig. 4. Relationship between the reciprocal of CH_4 concentration in nmol kg^{-1} and the $\delta^{13}C$ (‰PDB) of CH_4 observed at station Hyd-01 in March 1998. Filled circles and open circles show the data for bottom waters below a depth of 2,472 m and those for deep waters between 993 m and 2,373 m depths, respectively.

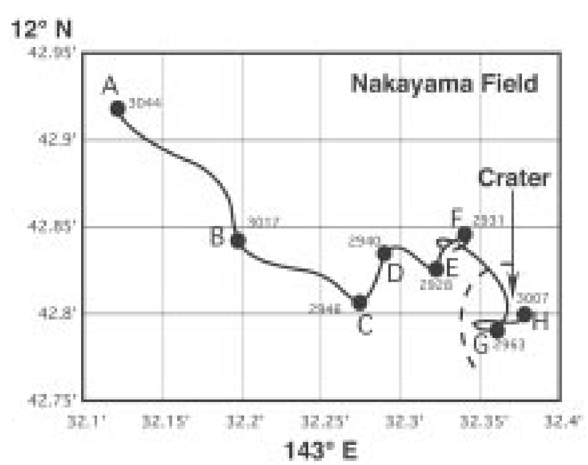

Fig. 5. The track of the ROV Kaiko dive #163 in June 2000. Points A and H are the locations of landing and leaving the bottom, respectively. White smoker chimneys were found at point G. Four-digit numbers mean the bottom depths.

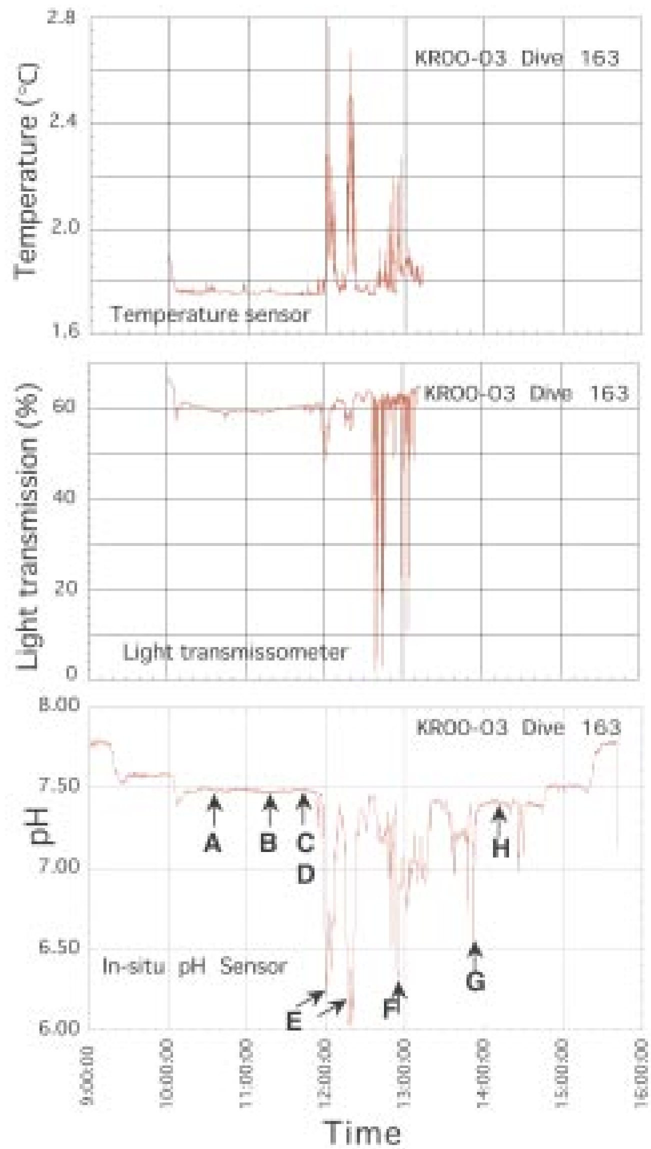

Fig. 6. Results of in situ measurements of temperature, light transmission and pH during the Kaiko dive #163. Letters A to H correspond to the locations shown in Fig. 5.

the supply of methane with a lesser $\delta^{13}C$ value. Figure 4 is the relationship between the reciprocal of CH_4 concentration and the $\delta^{13}C$ of CH_4, showing a simple mixing line between an imaginary endmember fluid and the ambient deep seawater below a depth of 2,400 m. The simple linearity suggests little existence of microbial CH_4 oxidation. The mixing line also suggests the endmenber $\delta^{13}C$ value to be –37 to –38‰, which was later confirmed by the direct measurement of a diluted hydrothermal fluid sample as described in the next section.

Discovery of the Nakayama Field

Mitsuzawa *et al*. (2000) and Masuda *et al*. (2001) showed visual evidence for the existence of large-scale hydrothermal activity within the TOTO Caldera, based on the deep-tow camera surveys during the YK99-11 cruise. They observed white suspended matter, dead chimneys, warm water shimmering, talus fields covered with whitish material, biological communities (tube worms and shrimps), as well as water temperature anomalies up to

Table 1. Chemical and isotope data for the clear shimmering fluid taken from the Nakayama Field during the Kaiko dive #163 in May 2000

Components	Data	Analytical method	References
pH	5.16	pH meter	
Alkalinity (mM)	2.42	Potentiometric method	Gieskes *et al.* (1991)
Cl (mM)	547	Ion chromatography	
SO_4 (mM)	29	Ion chromatography	
Mg (mM)	49	ICP emission spectrometry	
Ca (mM)	9.2	ICP emission spectrometry	
K (mM)	9.7	ICP emission spectrometry	
Si (mM)	0.79	Colorimetry	Gieskes *et al.* (1991)
NH_4 (μM)	N.D. (<10)	Colorimetry	Gieskes *et al.* (1991)
ΣCO_2 (mM)	15.3	Coulometry	
$\delta^{13}C$ of ΣCO_2 (‰PDB)	–1.5	Mass spectrometry	Tsunogai *et al.* (1998)
CH_4 (μM)	2.0	Mass spectrometry	Tsunogai *et al.* (1998)
$\delta^{13}C$ of CH_4 (‰PDB)	–38.1	Mass spectrometry	Tsunogai *et al.* (1998)
$^3He/^4He$ (R/R_a)	8.1	Mass spectrometry	Sano and Wakita (1988)

Table 2. Comparison of isotope data among the three arc-type hydrothermal systems along the Izu-Bonin and Mariana Arcs

Location	Nakayama Field (Mariana Arc) (12°43′ N, 143°32′ E)	Forecast Vent (Mariana Arc) (13°24′ N, 143°55′ E)	Suiyo Seamount (Izu-Bonin Arc) (28°34′ N, 140°39′ E)
$^3He/^4He$ (R/R_a)	8.1	8.1	8.1
$\delta^{13}C$ (CO_2) (‰PDB)	–1.5	–0.6	–1.0
$\delta^{13}C$ (CH_4) (‰PDB)	–38.1	–11.0	–8.5
Reference	This study	Tsunogai (1996)	Tsunogai *et al.* (1994)

~0.1°C inside the caldera. These data suggested the northeastern side of the caldera near to the station Hyd-01 is the most feasible area to be directly observed using submersibles.

Then, the diving observation by the ROV *Kaiko* (dive #163) was performed along the northeastern side of the caldera as shown in Fig. 5 (from waypoints A to H), whose area is shown as a small rectangle in Fig. 2. At waypoint A, the ROV landed on the bottom of a talus field which is partly covered with whitish material. The marker "163-1" was deployed here. As the ROV proceeded from points A to C, the visibility became lower and lower due to white smoke coming from the forward direction. At points E and F, clear shimmering fluids were observed together with hydrothermal vent communities of tube worms, shrimp, and galatheid crabs. At point E, the marker "163-2" was deployed. Since the ROV was not installed with a thermometer, no temperature data are available for the clear fluids. There was a steep down-slope (probably toward the bottom of a crater) from points F to G, and the visibility became much lower than before. At point G (D = 2,963 m), several chimneys were barely observed at the bottom, erupting white smoke vigorously. This point may be the origin of the hydrothermal plume detected at Hyd-01 (Fig. 3). The dive ended at point H, still on the way toward the deeper zone of the crater. Poor visibility inside the crater made it difficult for the ROV to approach the chimney for taking fluid samples.

The CTD system with the transmissometer and the pH sensor attached to the ROV clearly recorded an increase of temperature and decreases of light transmission and pH during approach to the fluid venting sites, as shown in Fig. 6. Unfortunately, the records of temperature and light transmission after 13:13 were not recovered due to some memory trouble.

A clear shimmering fluid sample was taken at point F using the Alvin-type sampler. The results of chemical and isotopic analyses are summarized in Table 1, together with the analytical methods and references. The concentrations of major cations and anions are almost the same as that of seawater, probably because the sample was seriously diluted by ambient seawater during sampling. On the other hand, data of Si, ΣCO_2 and CH_4 showed significantly higher values than those of seawater, demonstrating the incorporation of a hydrothermal fluid. The $^3He/^4He$ ratio of 8.1 (R/R_a) clearly indicates helium of mantle-origin.

The rock samples from the rim of the crater were covered with sulfur particles on the surface, suggesting the white smoke partly consists of native sulfur, as previously observed at the DESMOS Caldera in the eastern Manus Basin (Gamo *et al.*, 1997b).

Biological communities were observed at the clear fluid venting sites. These consist of galatheids, tube worms (vestimentifera), shrimp, small bivalves and gastropods. However, there is no big gastropod, *Alviniconcha Hessleri*, which have been commonly observed at the mid-Mariana Trough (18°12′ N; Alice Springs Field) and southern Mariana Trough (13°24′ N; Forecast Vent Field) hydrothermal sites.

Unique features of hydrothermal activity at the Nakayama Field

Hydrothermal fluid data from the vents at Suiyo Seamount (28°34′ N, 140°39′ E) (Tsunogai *et al.*, 1994), Kasuga Seamounts (21°24–36′ N, 143°37′ E) (McMurtry *et al.*, 1993), as well as that from the Forecast Vent Field in the southern Mariana Trough (Tsunogai, 1996) should be good references to be compared with the data from the Nakayama Hydrothermal Field, because these four hydrothermal sites are all associated with submarine volcanoes along the common arc volcanic chain extending south of Japan (Izu-Bonin arc and Mariana arc). Although it is almost difficult at the present stage to estimate the fluid endmember composition at the Nakayama Field using one extremely diluted sample only (Table 1), we could regard the $\delta^{13}C$ values of ΣCO_2 and CH_4 (Table 1) as those of the endmember, because the concentrations of ΣCO_2 and CH_4 observed (15.3 mM and 2.0 μM, respectively) are overwhelmingly higher than those of common deep seawater (2.4 mM and <1 nM, respectively).

Table 2 compares the carbon isotope data (together with the helium isotope data) among the three hydrothermal areas where the isotope data are available. These hydrothermal fields belong to a sediment-starved type, where the interaction between fluid and sediment is hardly expected to occur. It should be noted that the $\delta^{13}C$ of CH_4 (–38.1‰) at the Nakayama Field is much lower than those at the Suiyo Seamount (–8.5‰) and at the Forecast Vent Field (–11‰), while the $^3He/^4He$ ratio and the $\delta^{13}C$ of ΣCO_2 are quite similar among the three venting sites. The lower $\delta^{13}C$ (CH_4) for the clear shimmering fluid at the Nakayama Field suggests the incorporation of biogenic methane, in addition to the magmatic CH_4 which is the major component at the Forecast Vent Field and the Suiyo Seamount (Tsunogai, 1996; Tsunogai *et al.*, 1994). There is little probability of thermogenic CH_4 at the Nakayama Field because the C_2H_6/CH_4 ratio is less than 0.006. It is known that biogenic CH_4 formation by CO_2 reduction in various environments should cause large carbon isotope fractionation (depletion of ^{13}C) of between 40‰ and 90‰ (Whiticar *et al.*, 1986; Sugimoto and Wada, 1993). The $\delta^{13}C$ difference between CO_2 and CH_4 of 37‰ is suggestive of the existence of methanogenesis through the CO_2 reduction in a subsurface microbial ecosystem at the Nakayama Field. More data accumulation, including those for the white smoker fluid, is necessary to investigate this point in more detail.

Acknowledgments—We sincerely thank three reviewers: H. Chiba, G. McMurtry, and J.-L. Charlou for their useful comments to revise the initial manuscript. Thanks are also due to the captains, crew and scientific parties of KH-98-1, YK-99-11 and KR-00-03 cruises for their invaluable collaboration. This study was supported by a Grant-in-Aid for Scientific Research (A)(2) (No. 11308020), a Special Coordination Fund "Archaean Park" project, and a 21st Century COE Program on "Neo-Science of Natural History" (program leader: H. Okada) financed by the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

Campbell, A. C., Edmond, J. M., Colodner, D., Palmer, M. R. and Falkner, K. K. (1987) Chemistry of hydrothermal fluids from the Mariana Trough back arc basin in comparison to mid-ocean ridge fluids. *EOS Trans. AGU* **68**(44), 1531 (abstract).

Craig, H., Horibe, Y., Farley, K. A., Welhan, J. A., Kim, K.-R. and Hey, R. N. (1987) Hydrothermal vents in the Mariana Trough: Results of the first Alvin dives. *EOS Trans. AGU* **68**(44), 1531 (abstract).

Fujikura, K., Yamazaki, T., Hasegawa, K., Tsunogai, U., Stern, R. J., Ueno, H., Yamamoto, H., Maki, Y., Tsuchida, S., Kodera, T., Yamamoto, H., Sun, C.-H. and Okutani, T. (1997) Biology and earth scientific investigation by the submersible "Shinkai 6500" system of deep-sea hydrothermalism and lithosphere in the Mariana back-arc basin. *JAMSTEC J. Deep-Sea Res.* **13**, 1–20 (in Japanese with English abstract).

Gamo, T. and Y9204 Shipboard Scientific Party (1993) Revisits to the mid-Mariana Trough hydrothermal site and discovery of new venting in the southern Mariana region by the Japanese submersible *Shinkai 6500*. *InterRidge News* **2**, 11–14.

Gamo, T., Tsunogai, U., Ishibashi, J., Masuda, H. and Chiba, H. (1997a) Chemical characteristics of hydrothermal fluids from the Mariana Trough. *JAMSTEC J. Deep-Sea Res. Spec. Volume: Deep Sea Research in Subduction Zones, Spreading Centers and Backarc Basins*, JAMSTEC, 69–74.

Gamo, T., Okamura, K., Charlou, J.-L., Urabe, T., Auzende, J.-M., Shipboard Scientific Party of the ManusFlux Cruise, Ishibashi, J., Shitashima, K. and Kodama, Y. (1997b) Acidic and sulfate-rich hydrothermal fluid from the Manus basin, Papua New Guinea. *Geology* **25**, 139–142.

Gieskes, J. M., Gamo, T. and Brumsack, H. (1991) Chemical methods for interstitial water analysis aboard Joides Resolution. *ODP Technical Note*, No. 15, 60 pp.

Hessler, R., Lonsdale, P. and Hawkins, J. (1988) Patterns on the ocean floor. *New Scientist* **24** (March), 47–51.

Hussong, D. M. and Uyeda, S. (1981) Tectonic processes and the history of the Mariana arc: A synthesis of the results of Deep Sea Drilling Project Leg 60. *Initial Reports of the Deep Sea Drilling Project, 60* (Hussong, D. M., Uyeda, S. *et al*., eds.), 909–929, Deep Sea Drilling Project, Washington, D.C.

Ishibashi, J. and Urabe, T. (1995) Hydrothermal activity related to arc-backarc magmatism in the western Pacific. *Backarc Basins: Tectonics and Magmatism* (Taylor, B., ed.), 451–495, Plenum Press, New York and London.

Johnson, L., Fryer, P., Masuda, H., Ishii, T. and Gamo, T. (1993) Hydrothermal vent deposits and two magma sources for volcanoes near 13°20′ N in the Mariana backarc: a view from Shinkai 6500. *EOS Trans. AGU* **74**(43), Fall Meet. Suppl., V51C-14 (abstract).

Martinez, F., Fryer, P. and Becker, M. (2000) Geophysical characteristics of the southern Mariana Trough, 11°50′ N–13°40′ N. *J. Geophys. Res*. **105**, 16591–16607.

Masuda, H., Mitsuzawa, K., Seama, N., Masumoto, S. and YK-99-11 Shipboard Scientific Party (2001) Bathymetry and hydrothermal activities in the southern Mariana Trough—reconnaissance results of YK-99-11. *JAMSTEC J. Deep-Sea Res*. **18**, 83–88 (in Japanese with English abstract).

McMurtry, G. M., Sedwick, P. N., Fryer, P., VonderHaar, D. L. and Yeh, H.-W. (1993) Unusual geochemistry of hydrothermal vents on submarine arc volcanoes: Kasuga Seamounts, Northern Mariana Arc. *Earth Planet. Sci. Lett*. **114**, 517–528.

Mitsuzawa, K., Masuda, H., Seama, N., Hasegawa, Y., Miyamoto, M., Togashi, N., So, A. and Yamanobe, H. (2000) Preliminary report of Deep-Tow/*Yokosuka* Cruise at hydrothermal areas in the Mid and Southern Mariana. *JAMSTEC J. Deep-Sea Res*. **17**, 73–87 (in Japanese with English abstract).

Monma, H. (2000) Deep ocean technology at JAMSTEC. *MTS Journal* **33**, 49–63.

Nakayama, E., Isshiki, K., Sohrin, Y. and Karatani, H. (1989) Automated determination of manganese in seawater by electrolytic concentration and chemiluminescence detection. *Anal. Chem*. **61**, 1392–1396.

Obata, H., Karatani, H. and Nakayama, E. (1993) Automated determination of iron in seawater by chelating resin concentration and chemiluminescence detection. *Anal. Chem*. **65**, 1524–1528.

Obata, H., Nozaki, Y., Okamura, K., Maruo, M. and Nakayama, E. (2000) Flow-through analysis of Al in seawater by fluorometric detection with the use of lumogallion. *Field Anal. Chem. Technol*. **4**, 274–282.

Okamura, K., Kimoto, H., Saeki, K., Ishibashi, J., Obata, H., Maruo, M., Gamo, T., Nakayama, E. and Nozaki, Y. (2001) Development of a deep-sea *in situ* Mn analyzer and its application for hydrothermal plume observation. *Mar. Chem*. **76**, 17–26.

Ossaka, J., Ohira, Y., Hirabayashi, J. and Mori, A. (1977) Comparison of amorphous hydro-alumina-silicate, formed in seawater, with precipitated allophane. *J. Mineralog. Soc. Jpn*. **13** (Spec. Issue), 178–186 (in Japanese).

Sano, Y. and Wakita, H. (1988) Precise measurement of helium isotopes in terrestrial gases. *Bull. Chem. Soc. Jpn*. **61**, 1153–1157.

Shitashima, K. and Kyo, M. (1998) Application of Chemical Sensors to Oceanography—Development of Deep Sea pH Sensor Using ISFET—. *Chikyukagaku* (*Geochemistry*) **32**, 1–11 (in Japanese with English abstract).

Stoffregen, R. (1987) Genesis of acid-sulfate alteration and Au-Cu-Ag mineralization at Summitville, Colorado. *Econ. Geol*. **82**, 1575–1591.

Sugimoto, A. and Wada, E. (1993) Carbon isotopic composition of bacterial methane in a soil incubation experiment: Contributions of acetate and CO_2/H_2. *Geochim. Cosmochim. Acta* **57**, 4015–4027.

Tsunogai, U. (1996) Geochemical studies of migration process and source of fluids in the crust. Ph.D. Thesis, University of Tokyo, 116 pp.

Tsunogai, U., Ishibashi, J., Wakita, H., Gamo, T., Watanabe, K., Kajimura, T., Kanayama, S. and Sakai, H. (1994) Peculiar features of Suiyo seamount hydrothermal fluids, Izu-Bonin Arc: Differences from subaerial volcanism. *Earth Planet. Sci. Lett*. **126**, 289–302.

Tsunogai, U., Ishibashi, J., Wakita, H. and Gamo, T. (1998) Methane-rich plumes in Suruga Trough (Japan) and their carbon isotope characterization. *Earth Planet. Sci. Lett*. **160**, 97–105.

Tsunogai, U., Yoshida, N., Ishibashi, J. and Gamo, T. (2000) Carbon isotopic distribution of methane in deep-sea hydrothermal plume, Myojin Knoll caldera, Izu-Bonin arc: Implications for microbial methane oxidation in ocean and applications to heat flux estimation. *Geochim. Cosmochim. Acta* **64**, 2439–2452.

Von Damm, K. L., Edmond, J. M., Grant, B., Measures, C. I., Walden, B. and Weiss, R. F. (1985) Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise. *Geochim. Cosmochim. Acta* **49**, 2197–2220.

Whiticar, M. J., Faber, E. and Schoell, M. (1986) Biogenic methane formation in marine and freshwater environments: CO_2 reduction vs. acetate fermentation—Isotope evidence. *Geochim. Cosmochim. Acta* **50**, 693–709.