

Sources of pore water in a Tanegashima mud volcano inferred from chemical and stable isotopic studies

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Pore waters at the depths of 0–590 cm below seafloor (bsf) were collected from four core samples at four different sites in a mud volcano off Tanegashima Island between Ryukyu trench and Ryukyu arc of Japan. Concentrations of Cl^- , SO_4^{2-} , CH_4 , C_2H_6 and stable isotopic composition of $\delta^{13}\text{C}_{\text{CH}_4}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta\text{D}_{\text{H}_2\text{O}}$ in the pore waters vary as a function of distance from seafloor. This paper reports and discusses the pore waters collected at the summit (CV) site. The concentrations of Cl^- decrease from 540 at the seafloor to 375 mmol/kg at a depth of ~200 cm and remain constant at around 350 mmol/kg (64% of the concentration of seawater) below the depth. The concentrations of CH_4 are two to three orders of magnitude higher than those at other sites and have a maximum value of 715 $\mu\text{mol/kg}$ at around 120–140 cm bsf. Core samples collected at depths deeper than 180 cm bsf show collapsing gas bubbles and empty voids when they were split open. It was also observed that liquid seeped out from the surface of the split core. Considering the physical condition is favorable for the formation of methane hydrate, the observations suggest the existence of methane hydrates. High concentration of C_2H_6 , which had similar depth profile to that of CH_4 , was also observed. $\text{C}_2\text{H}_6/\text{CH}_4$ ratio remained larger than 10^{-3} and $\delta^{13}\text{C}_{\text{CH}_4}$ also remained around -45‰ below 180 cm bsf. The data suggest presence of thermogenic methane in the CV site. $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ profiles exhibited an opposite depth dependence, and only $\delta\text{D}_{\text{H}_2\text{O}}$ showed a decreasing depth profile similar to the concentration profile of Cl^- . They were inversely correlated with the concentration of Cl^- . The data of these two isotope compositions suggest a dilute fluid originates mainly from clay mineral dehydration but meteoric water. A simple mixing model of fluids from three sources (ambient seawater, water dissociated from methane hydrates, and diagenetic water ascending from deeper depth) with isotopic fraction during methane hydrate dissociation was applied for the observation result below 280 cm bsf to constrain ranges of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ of diagenetic water. Using the observed depth profile of Cl^- as a conservative component of ambient seawater, contribution of ambient seawater is estimated to be 64% whereas 36% from other two sources. Considering an isotopic fractionation during methane hydrate dissociation and using the estimated source fractions and observed isotopic composition of pore water, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ of the diagenetic water were estimated to range from +15 to +22‰ and from –103 to –43‰, respectively, which are in good agreement with isotopic compositions of water formed from clay minerals during their dehydration but quite different from those of meteoric water, supporting negligible contribution of meteoric water in the Tanegashima mud volcano fluid.

Keywords: water chemistry, mud volcano, fluid migration, clay mineral dehydration, stable isotopic composition

INTRODUCTION

Submarine mud volcanoes have been found worldwide on continental shelves and slopes of accretionary wedges under compressional tectonic regime (Henry *et al.*, 1990; Martin *et al.*, 1996; Milkov, 2000; Dahlmann and de Lange, 2003). Mud volcanoes are considered to bring deep fluids together with mud to the surface and, provide useful information related to geochemical processes occur-

ring in deep accretionary sediments that are not readily available by other methods (Moore and Vrolijk, 1992; Henry *et al.*, 1996; Hovland *et al.*, 1998; Kopf *et al.*, 2001). It has been also pointed out that gas hydrates commonly exist around mud volcanoes since they allows efficient migration of gases from deep to shallow depths in sedimentary rocks (Milkov, 2000; Waseda and Fujii, 2007).

Several mud volcanoes have been found on Tanegashima Island and more than 30 diapirs have been identified at the depth of 1200 to 3500 m below sea surface by acoustic sea floor survey along the Ryukyu Trench (Ujiié, 2000, references therein). The mud volcano in the

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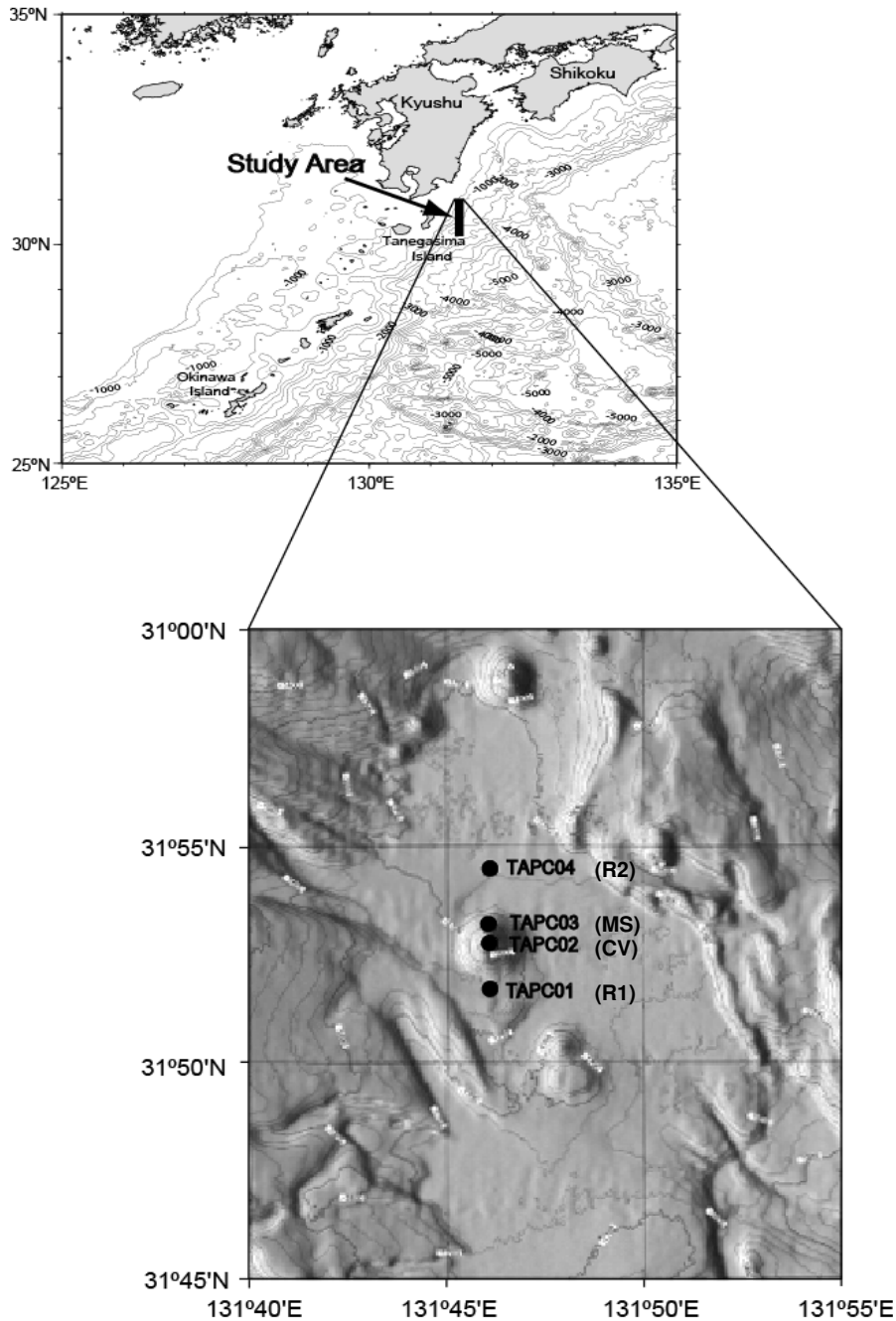


Fig. 1. Locations of four drill core sites in this study and seafloor topographic map. The bathymetric map was taken from Ujiie (2000). CV (TAPC02) and MS (TAPC03) refer the sites in the summit and the middle slope of the mud volcano, respectively. R1 (TAPC01) and R2 (TAPC04) refer sites off the volcano regarded as a reference of ambient seafloor.

present study is among the ones which were previously identified (Ujiie, 2000). Despite the discovery of increasing number of mud volcanoes by geophysical survey in this area, no geochemical study has been carried out for mud volcanoes around Tanegashima Island. Geochemical information, such as chemical and their isotopic composition of pore water, is valuable in elucidating the origin

of fluid below seafloor. This paper presents geochemical data of pore waters collected from four different sites in a Tanegashima mud volcano with special emphasis on a summit site, in which unusual depth profiles of chemical and isotopic compositions were observed. Using observed chemical and isotopic composition of the pore water, we will estimate relative contribution of different fluid

Table 1. Concentrations of chemical components and composition of stable isotopes as a function of distance from seafloor in the pore waters collected for different sites in Tanegashima Mud volcano

Core No. Location Water depth	Interval (cmbsf)	Cl ⁻ (mmol/kg)	SO ₄ ²⁻ (mmol/kg)	δ ¹⁸ O (‰ VSMOW)	δD (‰ VSMOW)	CH ₄ (μmol/kg)	δ ¹³ C-CH ₄ (‰ VPDB)	C ₂ H ₆ (μmol/kg)	C2/C1
R1 (TAPC01)	0–5	541	27.5	-0.2	-1.0	0.06	-51.4	—	—
30°51.70' N	10–15	546	27.5	+0.2	-1.3	0.06	-51.4	—	—
131°46.02' E	70–90	548	27.5	-0.2	-1.5	0.04	-49.9	—	—
1697 m	100–110	542	28.0	+0.1	-1.7	0.26	-50.4	—	—
	115–130	554	28.0	-0.0	-1.2	0.11	-57.0	—	—
	130–145	547	27.5	+0.3	-1.8	0.21	-52.0	—	—
	150–170	551	28.0	+0.3	-0.6	0.18	-58.9	—	—
	230–250	543	28.1	+0.1	-1.1	0.10	-53.1	—	—
	275–290	546	27.1	+0.3	-1.2	0.48	-42.8	—	—
	355–375	543	26.0	+0.2	-1.2	0.36	-45.0	—	—
	400–420	541	26.0	+0.3	-1.2	0.25	-45.1	—	—
	460–480	546	25.9	+0.4	-1.0	0.23	-47.7	—	—
	520–540	546	26.1	+0.5	-1.2	0.10	-47.6	—	—
	570–590	546	26.1	+0.5	-1.2	0.09	-47.4	—	—
CV (TAPC02)	0–5	548	27.5	+0.1	+0.2	5.02	-49.3	1.7	0.338
30°52.74' N	10–15	555	27.3	+0.2	+0.5	3.04	-51.6	0.3	0.103
131°46.04' E	20–40	554	26.3	+0.2	+0.1	1.39	-46.6	0.8	0.577
1442 m	40–60	545	23.9	+0.5	-1.1	15.23	-39.7	3.2	0.210
	60–80	538	19.4	+0.5	-3.5	62.60	-43.3	16.8	0.269
	120–140	486	5.5	+1.1	-3.9	714.54	-42.6	264.6	0.370
	180–210	375	0.3	+3.2	-10.4	115.64	-40.7	22.2	0.192
	230–250	354	0.5	+4.1	-13.0	165.32	-39.2	17.8	0.107
	280–300	348	0.9	+5.4	-15.7	81.80	-41.9	6.0	0.074
	330–350	347	0.3	+5.3	-15.6	45.02	-39.0	3.5	0.078
	380–410	349	0.7	+5.5	-16.7	53.47	-42.7	3.3	0.061
MS (TAPC03)	0–10	551	27.9	+0.3	+0.1	1.37	-48.4	—	—
30°53.01' N	10–20	552	28.0	+0.2	-1.1	0.28	-48.0	—	—
131°46.01' E	20–40	554	28.0	+0.4	+0.0	0.06	-42.8	—	—
1564 m	40–50	553	27.4	+0.4	-0.1	5.66	-53.6	0.27	0.047
	60–80	562	28.0	+0.3	-1.0	1.80	-51.4	0.19	0.105
	80–100	556	27.1	+0.2	-2.0	0.72	-54.0	0.23	0.319
	100–120	559	27.1	+0.4	-1.2	0.67	-46.6	0.30	0.449
	150–170	554	25.8	+0.1	-1.1	2.91	-52.0	0.21	0.074
	200–210	556	25.1	+0.2	-1.0	0.73	-49.0	—	—
	210–220	558	24.7	+0.3	-2.2	0.29	-45.9	—	—
	250–270	553	24.0	+0.1	-1.2	3.12	-54.3	—	—
	300–310	556	24.3	+0.3	-1.7	0.18	-43.1	—	—
R2 (TAPC04)	0–5	548	27.0	+0.2	-0.1	0.25	-42.5	—	—
30°54.48' N	10–15	548	26.9	+0.2	-0.8	0.28	-47.0	—	—
131°46.06' E	35–55	550	27.1	+0.1	-1.6	0.20	-45.2	—	—
1730 m	55–75	556	27.1	+0.2	-2.1	0.11	-47.2	—	—
	85–100	550	26.6	+0.2	-2.0	0.10	-47.3	—	—
	110–130	559	26.4	+0.0	-1.9	0.10	-47.9	—	—
	130–135	550	26.4	+0.2	-1.6	—	—	—	—
	180–200	559	26.4	+0.2	-1.9	—	—	—	—
	260–280	554	27.7	-0.1	-2.1	0.23	-49.2	—	—
	310–330	555	26.5	-0.0	-2.2	0.28	-47.7	—	—
	370–390	554	26.5	+0.1	-1.6	0.20	-49.9	—	—

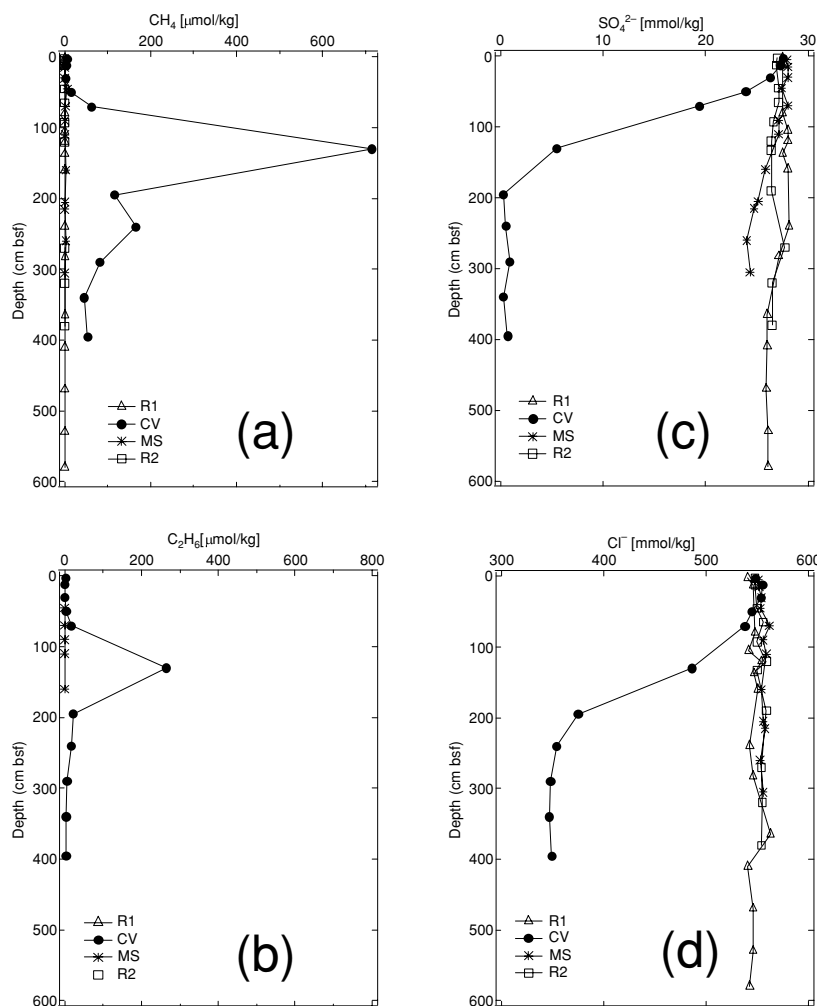


Fig. 2. Vertical profiles of concentrations of CH_4 , C_2H_6 , SO_4^{2-} , and Cl^- in the pore waters collected in the four different sites at a Tanegashima mud volcano. Solid circle, summit site (CV); star, middle of the volcano's slope (MS); open triangle and open square, off the volcano as a reference of ambient seafloor (R1, R2).

sources to the pore water and show the importance of clay mineral dehydration in the fluid of the Tanegashima mud volcano.

EXPERIMENTAL

Sampling and analytical methods

Sediment sampling was conducted as a part of Metal Mining Agency of Japan (MMAJ) geochemical survey by R/V Hakurei-maru II in January 2002. Figure 1 shows locations of sediment core sampling. This mud volcano ($30^\circ 53' \text{ N}$, $131^\circ 46' \text{ E}$) was chosen for this extensive investigation based on the early survey in this area (Ujiié, 2000). Four piston core samples (TAPC01, TAPC02, TAPC03, and TAPC04) were collected from different sites of the mud volcano. The recovered sediment cores were 310–520 cm in length (Table 1). After recovering, the core

samples were cut every 1 m interval. In the shipboard laboratory, pore waters were extracted from the sediment samples using a squeezer which was a modified version of one developed by Manheim (1966). After filtering the pore water through $0.45\text{-}\mu\text{m}$ Millipore filter, the water samples were processed immediately in the shipboard laboratory before storing in a refrigerator. For the analyses of CH_4 , C_2H_6 and $\delta^{13}\text{C}_{\text{CH}_4}$, about 2 ml of extracted pore water was immediately transferred to a 3 cm^3 poisoned serum glass vial under oxygen-free N_2 environment to prevent oxidation of methane. Then the glass vial was sealed with a butyl rubber septum with an aluminum caps and stored in a refrigerator. The remaining pore water was divided into two and put in a polypropylene bottle (for the analysis of Cl^- and SO_4^{2-}) and a glass vial (for the analysis of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$) and stored in a refrigerator. All chemical analysis was carried out in the labora-

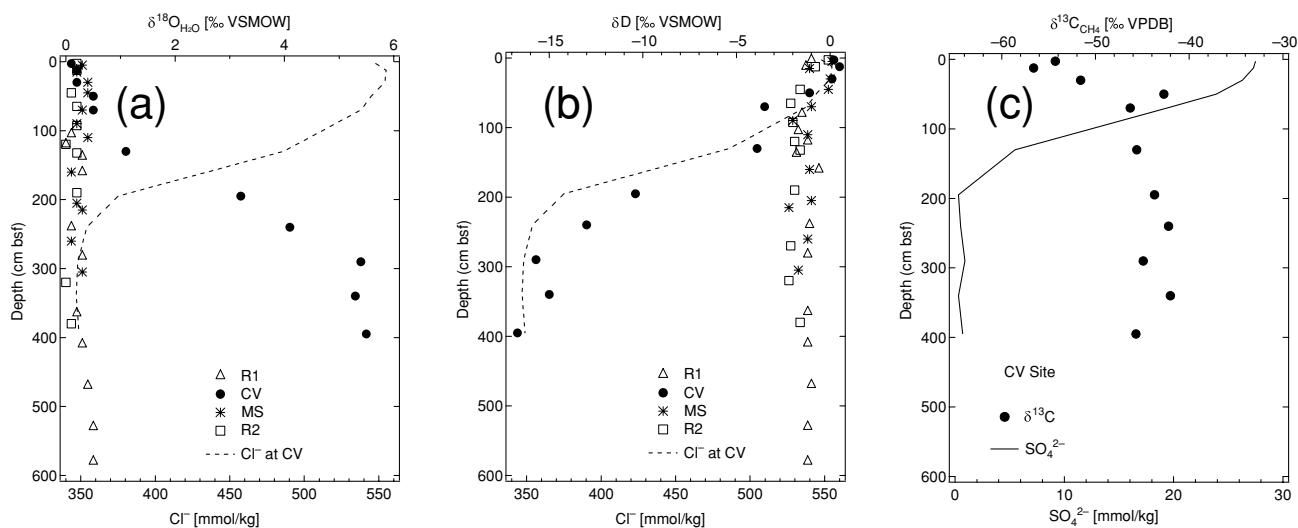


Fig. 3. Vertical profiles of (a) $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and (b) $\delta\text{D}_{\text{H}_2\text{O}}$ of the pore waters collected at four different sites. The data from the CV site was plotted for (c) $\delta^{13}\text{C}_{\text{CH}_4}$. Depth profiles of the concentrations of Cl^- (dashed line in (a) and (b),) and SO_4^{2-} (solid line in (c)) in the CV site were also plotted. The data are using the lower X-axis for the concentrations of Cl^- and SO_4^{2-} , and the upper X-axis for isotopic compositions of (a) $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, (b) $\delta\text{D}_{\text{H}_2\text{O}}$, and (c) $\delta^{13}\text{C}_{\text{CH}_4}$. Closed symbol, summit site (CV); cross symbol, middle of the volcano's slope (MS); open triangle and open square, off the volcano as a reference of ambient seafloor (R1, R2), respectively.

tory at Hokkaido University after the cruise. Totally, 48 samples of pore waters were obtained and analyzed in this study.

Concentrations and stable carbon isotope compositions of CH_4 and C_2H_6 were simultaneously determined by an isotope ratio monitoring gas chromatography/mass spectrometry system which was specially designed for the isotope analysis of trace low-hydrocarbon species ($\text{C}_1\text{--}\text{C}_3$) (Tsunogai *et al.*, 2002). Accuracy and precision for the isotope analysis was examined to be $\sim 0.3\%$ (1σ for 10 measurements) using a 200 pmol of CH_4 gas made from NIST RM8560 (IAEA NGS2). Precision of the CH_4 measurement was $\sim 6.5\%$ (1σ for 10 measurements) at the concentration level of 2 nmol/kg of methane. The analytical blank for CH_4 was negligibly small (< 1 pmol). A water- CO_2 equilibration method (Epstein and Mayeda, 1953) was used for the determination of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$. For the $\delta\text{D}_{\text{H}_2\text{O}}$ analysis, 2 μl of water was reduced to H_2 by reacting with 100 mg of Zn in a Pyrex tube at 500°C (Coleman *et al.*, 1982). Resultant H_2 gas was analyzed using Finnigan Mat 252 mass spectrometer equipped with a dual inlet system. Precision of the $\delta\text{D}_{\text{H}_2\text{O}}$ analysis was $\sim 1\%$. The concentrations of Cl^- and SO_4^{2-} were determined using an ion chromatograph with a precision of $\sim 3\%$.

RESULTS AND DISCUSSION

Figure 3 shows depth profiles of the concentrations of CH_4 , C_2H_6 , SO_4^{2-} and Cl^- in pore waters collected at the four sites. Only in the summit site (CV, TAPC02),

unusual depth profiles were observed, while monotonous depth profiles with concentrations similar to those of ambient seawater were observed in other sites.

At the CV site, CH_4 increased significantly from 5 to 715 $\mu\text{mol/kg}$ in the segment from 0 to 140 cm bsf, and dropped to 50–80 $\mu\text{mol/kg}$ at depths deeper than 140 cm bsf. In the other sites (R1, R2, and MS), CH_4 concentration was quite low and showed a rather uniform depth profile (0.1–0.5 $\mu\text{mol/kg}$ for R1 and R2, 0.1–5 $\mu\text{mol/kg}$ for MS, see Table 1). Collapsing gas bubbles and empty voids were observed in the core samples below 180 cm bsf at the CV site when the core was split open (National Oil Corporation, 2003). The evidence suggests gas escape from the core and the observed gas concentrations are much lower than the actual gas concentrations in the core. Therefore, reported gas concentrations represent minimum values. In spite of the escape of gasses, observed CH_4 concentrations at the CV site were two to three orders of magnitude higher than those in other sites, and more than six orders of magnitude higher than that in ambient seawater. A high concentration of ethane, which had similar depth profile to that of methane, was also observed in the CV site samples. The concentration ratios of C_2H_6 to CH_4 also remained above 10^{-3} at all depths. Since ethane is mainly produced through thermal decomposition of organic matter (Bernard *et al.*, 1978; Whiticar, 1999), the observed relationship of methane and ethane is indicative for a primary contribution of thermogenic methane in the CV site. The proposed interpretation is also supported by similar $\delta^{13}\text{C}_{\text{CH}_4}$ values of $\sim 45\%$ below

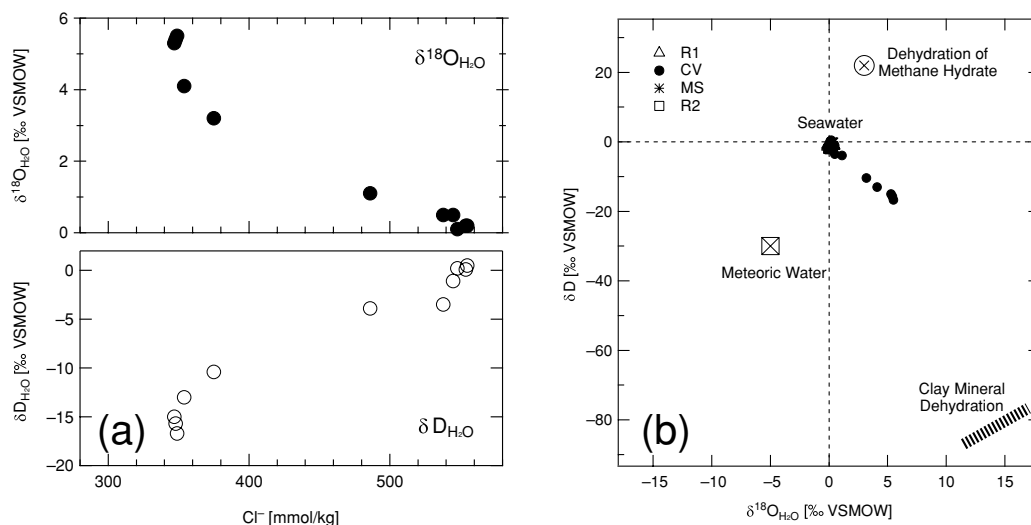


Fig. 4. (a) Correlation plot of isotopic compositions and Cl^- concentrations in pore waters collected at the CV site (solid circle, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$; open circle, $\delta\text{D}_{\text{H}_2\text{O}}$). (b) $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ of pore waters at four studied sites. Data from all depths at these sites were plotted on the figure. The data except for those from the CV site are similar to seawater values and overlapped each other on the plot. As a reference, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ of the local meteoric water, waters formed during the dehydration of methane hydrate and clay minerals are also plotted. Solid circle, summit site (CV); star, middle of the volcano's slope (MS); open triangle and square, off the volcano as a reference of ambient seafloor (R1, R2).

60 cm bsf (Fig. 3(c)). The thermogenic methane of $\delta^{13}\text{C}_{\text{CH}_4}$ ranges from roughly -50‰ to -20‰ , whereas that of the bacterial methane varying from -110‰ to -50‰ (Bernard *et al.*, 1978; Coleman and Risatti, 1981; Paull *et al.*, 1994; Tilbrook and Karl, 1995; Whiticar, 1999).

On the other hand, unusually steep gradient of sulfate concentration decreased from 27 to ~ 0 mmol/kg was also found in upper sediments at the CV site whereas the methane concentration increased by ~ 0.7 mmol/kg. It indicates the high rates of sulfate reduction compared to other sites (Fig. 2(c)). In methane-rich sediment, the concentration of SO_4^{2-} is commonly depleted since sulfate-reducing bacteria consume SO_4^{2-} during methane oxidation (Marty, 1993). In a closed system, the preferential removal of isotopically lighter methane during sulfate reduction results in a progressive shift in the C isotope compositions of residual methane towards ^{13}C -enriched values. However, high concentration of methane at the study site results in a negligible contribution of the biological sulfate reduction to the isotopic composition of methane as observed in the CV site even when most of sulfate was reduced. Actually, much higher concentration of methane should have been existed in the porewater in the CV site samples, which is consistent with the escape of gases from the core, as described above.

An unusual depth profile of Cl^- concentration was also observed at the CV site, whereas almost constant Cl^- concentration was observed for all depths at other sites. At

the seafloor (0 cm bsf), the concentrations of Cl^- were similar to that of seawater. At the CV site, the concentration of Cl^- declined as increasing depth down to around 200 cm bsf and became constant below the depth. Since Cl ion is a conservative chemical component of ambient seawater, the Cl^- concentration lower than the ambient seawater suggests a dilution of ambient seawater with fluids.

$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ exhibited clear depth-dependent variations at the CV site whereas no depth-dependent variation was observed in other sites (Figs. 3(a) and (b)). At the CV site, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ increased from 0 to $+5.4\text{‰}$, while $\delta\text{D}_{\text{H}_2\text{O}}$ decreased from 0 to -16‰ at depth from 0 to 280 cm bsf, showing that the two are inversely correlated. Below 280 cm bsf, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ became constant ($+5\text{‰}$ and -15‰ , respectively). In the other sites, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ stayed in the range from -0.2 to $+0.5\text{‰}$ and -2.2 to $+0.1\text{‰}$ in all depths, respectively. These values are similar to those of the seawater. It should be pointed out that $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ in the CV site samples show an inverse correlation when they were plotted against the concentration of Cl^- (Fig. 4(a)). The data demonstrate the dilute water originates from clay minerals during their dehydration rather than from gas hydrate dissociation. It has been shown that mixing of meteoric water results in decreasing $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ for water (Dahlman and de Lange, 2003), while they changed to the opposite direction in the CV site as shown in Fig. 4(b). Similar isotopic comparison has been used to elucidate possible ori-

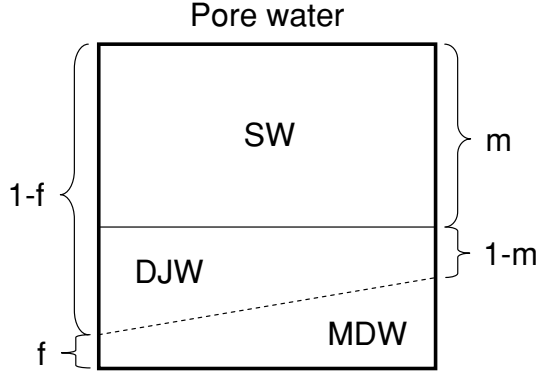


Fig. 5. Schematic diagram showing the simple mixing model of source waters used in this study. The model considers three sources: water generated by dehydration of methane hydrate (MDW) and a diluted of ambient seawater with fluid (FLD). The FLD is composed of SW (ambient seawater) and DJW (diagenetic water). f and m stand for the relative contribution of waters and SW, respectively. All acronyms used in the figure are the same as those in the equations in the text.

gins of sediment pore waters at the high methane flux areas over the Japan Sea (Hiruta *et al.*, 2009).

Origin of diagenetic water in the CV site

Observed depth profiles suggest that fluid from deeper depth migrated through the sediment and mixed with ambient seawater in the shallow layers below seafloor, although 350 mol/kg of Cl^- below 200 cm bsf indicates that the fluid also contains significant amount of seawater. Only summit site (CV) exhibited the unusual depth profiles, which show that the mud volcano also has a “pathway for fluid migration” from deep sediments to seafloor in the vent area as reported in other mud volcanoes (e.g., Milkov, 2000) and the fluid may be brought from the deeper layer to the shallow sediment zone together with various chemical components. What is the origin of the fluid? As already mentioned, contribution of meteoric water can be excluded in the current study. Since high concentration of CH_4 was observed and because the conditions in the site are in the stability field of methane hydrate, existence of methane hydrates should be also considered. Thus three possible sources of water are considered: (1) ambient seawater, (2) water dissociated from methane hydrates, and (3) water produced during the diagenesis of deep sediments.

A simple mixing model was applied to the observed results obtained below 280 cm bsf in the CV site to evaluate the sources of the water and estimate their relative contributions (Fig. 5). In our model, we assumed that methane hydrate below 200 cm bsf was formed by the interaction between methane and surrounding water (a

mixture of ambient seawater and diagenetically produced water), which is represented as *fluid* in the following model equations.

The relationship between observed isotopic compositions of the pore water can be written as follows:

$$\delta_{\text{obs}} = f \cdot \delta_{\text{mdw}} + (1 - f) \cdot \delta_{\text{fld}} \quad (1a)$$

$$\delta_{\text{mdw}} = \delta_{\text{fld}} + (\alpha - 1) \cdot 10^3 \quad (2a)$$

$$\delta_{\text{fld}} = m \cdot (1 - f) \cdot \delta_{\text{sw}} + (1 - m) (1 - f) \cdot \delta_{\text{djw}}. \quad (3a)$$

f is relative contribution of water generated by methane dehydration, while m is the relative contribution of ambient seawater in the fluid (see Fig. 5). δ represents isotope composition of oxygen and hydrogen. δ_{obs} is the observed isotopic composition. δ_{mdw} and δ_{fld} are isotopic compositions of water in methane hydrates and fluid (ambient seawater + diagenetically processed water), respectively. δ_{sw} is the isotopic composition of ambient seawater. δ_{djw} is the isotopic composition of diagenetically processed water. α is the isotope fractionation factor of water for methane dehydration. We adapted 1.003 and 1.022 as α values for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$, respectively (Matsumoto and Borowski, 2000; Pashkina, and Esikov, 1990).

Applying (2a) to (1a), Eq. (1a) can be rewritten as

$$\delta_{\text{obs}} = \delta_{\text{fld}} + f \cdot (\alpha - 1) \cdot 10^3. \quad (4)$$

Merging (4) and (3a) and since $\delta_{\text{sw}} = 0$ in the current study,

$$\delta_{\text{djw}} = (\delta_{\text{obs}} - f \cdot (\alpha - 1) \cdot 10^3) / (1 - m). \quad (5)$$

Equation (5) shows a relationship between δ_{obs} and δ_{djw} and is useful in estimating the range of δ_{djw} value and the origin of the fluid, however, unique values of f and m cannot be determined in the current study. Thus we constrained possible range of the δ_{djw} from the ranges of f and m . The ranges of f and m were constrained using concentrations of chlorine because water produced during methane hydrate and diagenesis of sediments contain essentially no chlorine and because chlorine is a conservative component of seawater,

$$[\text{Cl}^-]_{\text{obs}} = f \cdot [\text{Cl}^-]_{\text{mdw}} + (1 - f) \cdot [\text{Cl}^-]_{\text{fld}} \quad (1b)$$

$$[\text{Cl}^-]_{\text{mdw}} = 0 \quad \text{and} \quad [\text{Cl}^-]_{\text{djw}} = 0 \quad (2b)$$

$$[\text{Cl}^-]_{\text{fld}} = m(1 - f) \cdot [\text{Cl}^-]_{\text{sw}} + (1 - m) (1 - f) \cdot [\text{Cl}^-]_{\text{djw}}. \quad (3b)$$

Applying (2b) for (1b), Eq. (1b) becomes

$$[\text{Cl}^-]_{\text{obs}} = m(1 - f) \cdot [\text{Cl}^-]_{\text{sw}}. \quad (1c)$$

$[Cl^-]_{sw}$ is the concentration of Cl^- in ambient seawater, 547 mmol/kg in bottom seawaters. $[Cl^-]_{obs}$ is the observed concentration below about 200 cm bsf (350 mmol/kg). The relative contribution of ambient seawater $m(1-f)$ is calculated to be 0.64, while that of other waters (diagenetic and methane dehydration waters) is calculated to be 0.36. This constrains possible ranges of f and m to $0 \leq f \leq 0.36$ and $0.64 \leq m \leq 1$. Applying these ranges of f and m and the observed values of $\delta^{18}O_{H_2O}$, +5‰, and δD_{H_2O} , -15‰, to Eq. (5), possible ranges of $\delta^{18}O_{djw}$ and δD_{djw} were estimated: $+15‰ \leq \delta^{18}O_{djw} \leq +22‰$ and $-103‰ \leq \delta D_{djw} \leq -43‰$.

Mizota and Kusakabe (1994) reported that the average values for $\delta^{18}O_{H_2O}$ and δD_{H_2O} of meteoric water in the southern Japan are around -5‰ and -30‰, respectively. These values are quite different from the ranges of $\delta^{18}O_{H_2O}$ and δD_{H_2O} of diagenetic water estimated in this study as shown in Fig. 4(b) (Craig, 1961; Mizota and Kusakabe, 1994). It clearly supports that meteoric water had negligible contribution to the diagenetically processed fluid in the current study. The estimated ranges of $\delta^{18}O_{H_2O}$ and δD_{H_2O} of diagenetic water have been reported in various geological settings and explained by the formation of water by mineral dehydration (Magaritz and Gat, 1981; Capuano, 1992; Sheppard and Gilg, 1996; Hensen *et al.*, 2007). Capuano (1992) predicted that water from dehydrating smectite has $\delta^{18}O_{H_2O}$ values ranging from +7 to +14‰ and δD_{H_2O} from -45 to -25‰. Magaritz and Gat (1981) reported that clay mineral dehydration in oceanic sediments yielded water with $\delta^{18}O$ ranging from +11.5 to +28.5‰ and δD from -87 to -55‰. These values are comparable to our estimated $\delta^{18}O_{djw}$ and δD_{djw} , which supports clay mineral dehydration as the primary source of diagenetic water in the Tanegashima mud volcano.

Fluids from deeper depth migrated through the sediment usually undergo various complicated diagenetic processes under different environmental conditions and geological settings. Thus in many cases it is quite difficult to isolate a specific fluid and identify its origin or processes that it experiences (Dahlmann and de Lange, 2003; Hensen *et al.*, 2007). However, current study shows that different sets of geochemical data, such as chemical and isotopic compositions are useful to characterize diagenetic processes.

SUMMARY

In a mud volcano off Tanegashima Island between Ryukyu trench and Ryukyu arc of Japan, pore waters were collected at four sites. Concentrations of Cl^- , SO_4^{2-} , CH_4 , and C_2H_6 in pore waters, and the stable isotopic composition of $\delta^{13}C_{CH_4}$, $\delta^{18}O_{H_2O}$, and δD_{H_2O} of pore waters show variations with distances from seafloor. A simple mixing model was applied to explain the observed results below

280 cm bsf in the summit site (CV), in which unusual depth profiles of chemical concentrations and isotopic compositions were observed. Because unusually high concentration of CH_4 compared to other sites and the conditions at the site is in the stability field of methane hydrate, the existence of methane hydrates is suggested at the CV site. The depth profiles of $\delta^{18}O_{H_2O}$ and δD_{H_2O} of the pore water showed an opposite depth dependence, and only $\delta^{18}O_{H_2O}$ showed a decreasing depth profile similar to that of the concentrations of Cl^- . These relationships could not be explained by a simple dilution of the pore water by water dissociated from methane hydrates. Thus a mixing model of three different source waters was considered; ambient seawater, water dissociated from methane hydrates, and diagenetic water ascending from deeper depth. Isotopic fractionation during methane hydrate dissociation was also considered and applied to the model. Using the concentrations of Cl^- as a conservative component of seawater, contribution of ambient seawater was estimated to be 64%, whereas 36% from diagenetic fluid and water dissociated from methane hydrates. The estimated relative contributions constrained the possible ranges of isotopic compositions of the diagenetic water to range from +15 to +22‰ for $\delta^{18}O_{djw}$ and from -103 to -43‰ for δD_{djw} . The data support that clay mineral dehydration contributes to the diagenetic water.

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