

Carbon isotope systematics of CO₂, CO and CH₄ in fumarolic gases from Satsuma-Iwojima volcanic island, Japan

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Carbon isotopic composition ($\delta^{13}\text{C}$) of CO₂, CO and CH₄ were determined for fumarolic gases from Satsuma-Iwojima, to range from -3.1 to -2.6‰ , from -11.6 to -2.8‰ and from -56 to -37‰ , respectively. Carbon isotope exchange equilibrium temperature between CO₂ and CO was calculated to be ranging from 896° to 950°C for high temperature (691° to 882°C) fumarolic gases, suggesting that CO₂ and CO were in isotopic equilibrium near the vent temperature. However, low temperature ($<650^\circ\text{C}$) gases were not in isotopic equilibrium between CO₂ and CO under any realistic conditions. The correlations of $\delta^{13}\text{C}(\text{CO})$, CO/CO₂ ratio and temperature can be explained in terms of kinetic conversion of CO to CO₂ with decreasing temperature. The $\delta^{13}\text{C}$ values of CH₄ and CO₂ revealed that the CH₄ was not equilibrated in carbon isotope exchange reaction with CO₂ even at fumarolic gas temperature near 900°C . Correlation of $\delta^{13}\text{C}(\text{CH}_4)$ and CH₄/C₂H₆ ratio indicate that CH₄ of the low CH₄/CO₂ ratio group ($<10^{-5}$) is mainly originated from thermogenic decomposition of organic matter, while the high CH₄/CO₂ ratio group (7.7×10^{-4} to 7.4×10^{-3}) is contaminated by the CH₄-rich gas with $\delta^{13}\text{C}$ value of about -40‰ .

1. Introduction

Satsuma-Iwojima is a volcanic island, located about 40 km south of Satsuma peninsula, Kyushu, Japan, forming northwestern part of the Kikai caldera. Ono *et al.* (1982) summarized geology of the Satsuma-Iwojima district. Iwodake, located on the eastern part of Satsuma-Iwojima, is one of central cones of the Kikai caldera, and is famous for intense volcanic gas emission. High temperature fumarolic gases have discharged from the summit area for more than 30 years (Kamada, 1964). Several chemical and isotopic studies on the fumarolic gases were conducted by Matsuo *et al.* (1974), Matsubaya *et al.* (1975) and Shinohara *et al.* (1993).

Carbon isotope studies of various species, such as CO₂, CO and CH₄, in fumarolic gases give us important information on sources of the carbon species and isotope exchange behavior during ascent of volcanic gas to the surface. There are many studies of chemical equilibrium thermometers and some studies of isotope exchange equilibrium thermometers (e.g.; Giggenbach, 1987; Symonds *et al.*, 1994; Ohba, 1997). However, $\delta^{13}\text{C}(\text{CO})$ and $\delta^{13}\text{C}(\text{CH}_4)$ in high temperature volcanic gases have not been measured due to their low contents. Although Matsubaya *et al.* (1975) already reported H, C, O and S isotopic composition of fumarolic gases from Satsuma-Iwojima, carbon isotope ratios were measured only for CO₂. In this paper, we will present first $\delta^{13}\text{C}$ data of CO and CH₄ in fumarolic gases from Satsuma-Iwojima together

with $\delta^{13}\text{C}$ of CO₂ and $^3\text{He}/^4\text{He}$, and will discuss carbon isotope exchange equilibrium and origin of the carbon species.

2. Sampling and Analytical Methods

Sampling of fumarolic gases was conducted in October 1996 and November 1997. Locations of the fumaroles are shown in Fig. 1. The highest temperature of the gases was close to 900°C at Ohachi-oku. Gas samples for the analyses of $\delta^{13}\text{C}$ of CO₂ and $^3\text{He}/^4\text{He}$ were collected as “dry gas” in a glass bottle with two stopcocks by flowing through the gases without any treatment. Samples for $\delta^{13}\text{C}$ measurement of CO and CH₄ were collected as “R-gas” using the method proposed by Ozawa (1968), where acid gases (e.g.; CO₂, SO₂, etc.) were dissolved into a NaOH solution. Concentrations and $\delta^{13}\text{C}$ -values of CO₂ in the dry gases, and those of CO and CH₄ in the R-gases were determined using a MAT delta-S GC/C/MS (combined gas chromatograph/combustion/mass spectrometer) system (Finnigan MAT Instrument Inc.; Sato *et al.*, 1999). Concentrations of CO in the dry gases, and C₂H₄ and C₂H₆ in the R-gases were also determined using a gas chromatograph in the GC/C/MS system. Analytical uncertainties are estimated to be 0.3‰ for $\delta^{13}\text{C}$ of CO₂ and CO, and 1.6‰ for $\delta^{13}\text{C}$ of CH₄. Analytical procedure of $^3\text{He}/^4\text{He}$ was the same as that by Sano *et al.* (1982).

3. Results

Table 1 shows the analytical results. The concentration ratio of CO/CO₂ of fumarolic gases ranges from 0.5×10^{-3} to 7.0×10^{-3} , which shows a positive correlation with the fumarolic temperature. The $\delta^{13}\text{C}(\text{CO}_2)$ is ranging from -3.1 to -2.6‰ , without any correlation with the fumarolic temperature. These values are higher than those reported by

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Table 1. Chemical and isotopic composition of fumarolic gases from Satsuma-Iwojima.

No.	Location	Date year/month/day	Temp. (°C)	composition in R-gas ^{*1}						composition in dry gas ^{*2}								
				CO (ppm)	CH ₄ (ppm)	C ₂ H ₄ (ppm)	C ₂ H ₆ (ppm)	$\delta^{13}\text{C}(\text{CO})$ (‰)	$\delta^{13}\text{C}(\text{CH}_4)$ (‰)	CO ₂ (%)	CO (%)	He (ppm)	$\delta^{13}\text{C}(\text{CO}_2)$ (‰)	$^3\text{He}/^4\text{He}$ (R/R _a)	$^4\text{He}/^{20}\text{Ne}$	CO/CO ₂ (10 ⁻³)	CH ₄ /CO ₂ (10 ⁻⁶)	CO ₂ ² /He (10 ¹⁰)
1	Ohachi-oku	1996/10/17	882	3700					-11.5									
2	Ohachi-oku	1996/10/18	882	4100					-11.7									
3	Ohachi-oku	1996/10/17	845	3800					-10.7									
4	Kodake-shita	1996/10/18	807	3700					-11.2									
5	crater rim	1996/10/18	100	3300					-4.0									
6	Ohachi-oku	1997/11/2	855	3500	7	0.2	0.07		-11.0	-40.2								7.26
7	Ohachi-oku	1997/11/5	834	4170	3590	2	1		-11.4	-43.7	30.5	0.20	3.0	7.08	11.0	6.6	5600	1.0
8	Kodake-shita	1997/11/3	788	3970	17	0.6	0.2		-10.9									
9	Hachima	1997/11/5	780	4140	4	0.1	0.04		-10.8	-43.9	28.5	0.20	2.5	7.29	8.1	7.0	6.8	1.1
10	Hachima	1997/11/5	691	2010	520	0.6	0.6		-11.6	-45.5	33.7	0.10	2.7	7.22	10.1	3.0	770	1.2
11	Ohachi-oku	1997/11/3	650	5540	6720	2	2		-5.5	-43.5	31.0	0.19	2.8	7.04	9.8	6.1	7400	1.1
12	Hachima	1997/11/4	573	1870	2	0.08	0.02		-7.7	-51.9								
13	Hachima	1997/11/3	410	3380	2	0.1	0.07		-7.4									
14	Ohachi-oku	1997/11/2	400	1220	2	0.09	0.04		-7.8	-55.9								
15	Hachima	1997/11/4	300	4340	<0.2	<0.07	<0.04		-4.5		49.9	0.12	5.0	7.85	21.6	2.4	<0.1	0.91
16	Hachima	1997/11/5	300	2990	1	0.09	<0.02		-4.4		49.0	0.11	5.3	6.67	11.6	2.2	0.8	1.0
17	Hachima	1997/11/4	115	4790	2	0.1	0.1		-5.2	-36.9	54.4	0.12	4.4	7.55	14.7	2.2	0.9	1.2
18	Kodake-shita	1997/11/5	101	1610	1	<0.06	<0.04		-2.8	-50.7	55.2	0.03	3.3	7.48	14.2	0.5	0.3	1.6

*1 Gas phase after removing acid gases dissolved in NaOH solution in the sample bottles.

*2 Collected gas using two-mouth bottle.

*3 Corrected ratio for air components using $^4\text{He}/^{20}\text{Ne}$ ratio.

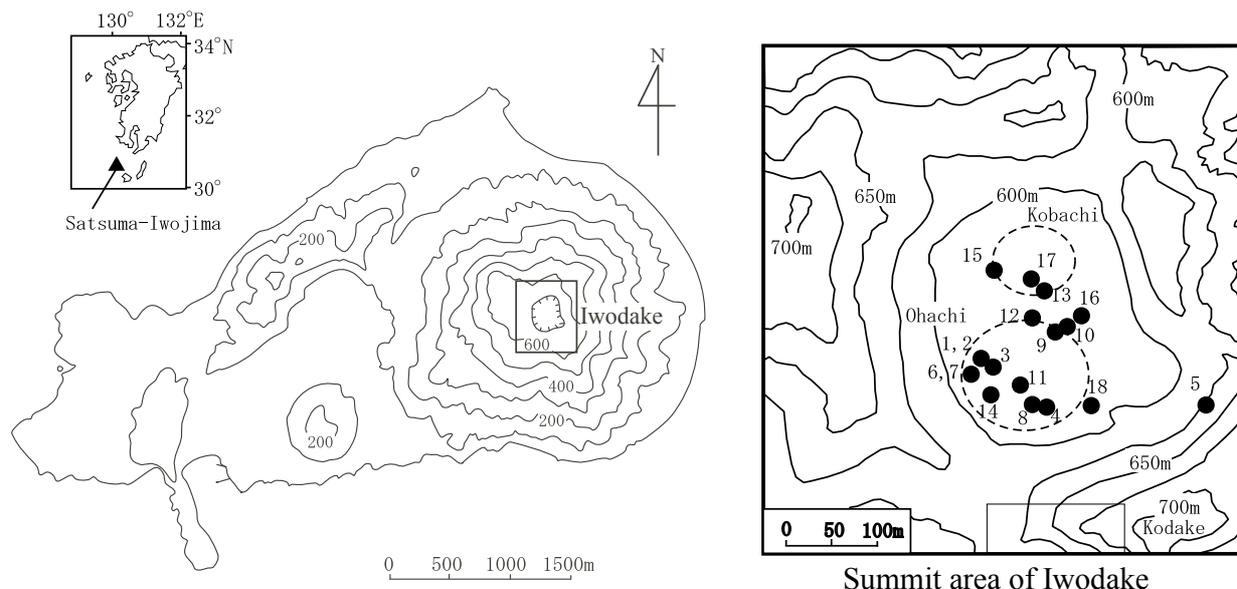


Fig. 1. Map of Satsuma-Iwojima (left) and summit area of Iwodake (right). Sample locations are shown by black dots with numbers. The numbers correspond to those in Table 1.

Matsubaya *et al.* (1975) ranging from -8.2 to -5.0‰ . The difference may suggest temporal change in carbon sources during 23 years. But the exact reason of the disagreement remains unclear, because differences in analytical procedures, mass spectrometers and standard materials used by each study may be another possibilities to lead the disagreement. The $\delta^{13}\text{C}(\text{CO})$ of high temperature fumarolic gases ($>650^\circ\text{C}$) was about -11‰ , whereas the $\delta^{13}\text{C}(\text{CO})$ of low temperature fumarolic gases was higher up to -2.8‰ , indicating negative correlation between $\delta^{13}\text{C}(\text{CO})$ and fumarolic temperature.

The CH_4/CO_2 ratio ranges from 1×10^{-7} to 7.4×10^{-3} , and the data can be divided into two groups; the high CH_4/CO_2 ratio group with the range from 7.7×10^{-4} to 7.4×10^{-3} , and the low CH_4/CO_2 group of $<10^{-5}$. These features were already pointed out by Shinohara *et al.* (1993). The $\delta^{13}\text{C}$ values of CH_4 are variable and show no correlation with the fumarolic temperatures nor with the CH_4/CO_2 ratios. The $\text{C}_2\text{H}_4/\text{CH}_4$ ratio was in the range from 2×10^{-2} to 9×10^{-2} for the low CH_4/CO_2 group, and from 3×10^{-4} to 1×10^{-3} for the high CH_4/CO_2 group. The $\text{CH}_4/\text{C}_2\text{H}_6$ ratio ranges from 20 to 100 for the low CH_4/CO_2 group, and from 800 to 3600 for the high CH_4/CO_2 group. The $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ ratio seems to be constant whereas the CH_4 contents are largely variable.

Isotopic ratio of $^3\text{He}/^4\text{He}$ ranges from 6.67 to 7.85 R/R_a regardless of the fumarolic temperature and the CO_2 contents. This range is consistent with the previous results on Satsuma-Iwojima gases (Sano and Wakita, 1985; Marty *et al.*, 1989) and with the typical ratio of island arc volcanic gases (Lupton, 1983).

4. Discussion

4.1 The origin of CO_2

Figure 2 shows variation of the $\text{CO}_2/^3\text{He}$ ratio and the $\delta^{13}\text{C}(\text{CO}_2)$ to identify source components of volcanic gas.

Data of Satsuma-Iwojima gases are plotted within the common range of volcanic gases from island arc volcanoes (Sano and Marty, 1995). This indicates significant contribution of CO_2 from the mantle and recycled limestone as in other volcanic gases from island arcs. Contribution of the MORB-type mantle CO_2 is calculated to range from 9 to 17%, and that of the recycled limestone CO_2 to range from 77 to 82%.

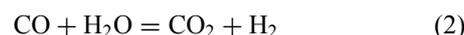
4.2 CO_2 -CO isotopic equilibrium temperature

Assuming that the carbon isotopic compositions of CO_2 and CO in the fumarolic gases are controlled by the following isotope exchange reaction,



the apparent equilibrium temperature (AET) of the reaction can be calculated using the analyzed $\delta^{13}\text{C}$ of CO_2 and CO. Using the fractionation factor as a function of temperature given by Richet *et al.* (1977), the AET can be calculated for the 1997 samples (Fig. 3, Table 2). For the high temperature ($>650^\circ\text{C}$) gases, the AET were calculated to range from 896° to 950°C . This temperature range is close to the temperature of rhyolitic magmas (Miyashiro and Kushiro, 1977), and the highest temperature of the fumaroles of Satsuma-Iwojima, suggesting that CO_2 and CO, which reached in isotopic exchange equilibrium just after degassing from the magma, are released from fumaroles with gas temperature almost with AET. On the other hand, $\delta^{13}\text{C}(\text{CO})$ values of low temperature ($<650^\circ\text{C}$) gases are higher than those of the high temperature gases and the calculated AETs were unrealistically high (Fig. 3), suggesting that the relationship between $\delta^{13}\text{C}(\text{CO}_2)$ and $\delta^{13}\text{C}(\text{CO})$ was not controlled by the isotopic exchange equilibrium.

The AET is calculated also for the following chemical equilibrium reaction,



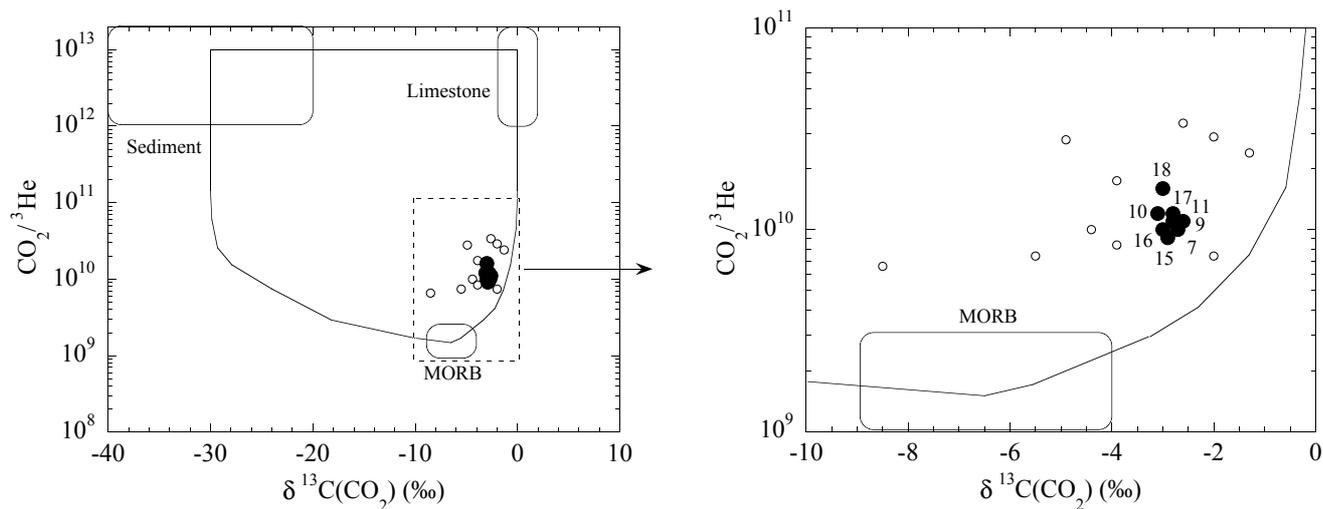


Fig. 2. Variation of $\text{CO}_2/{}^3\text{He}$ and $\delta^{13}\text{C}(\text{CO}_2)$ in Satsuma-Iwojima fumarolic gases. Model end-members are MORB (Mid-Ocean Ridge Basalt), marine limestone and organic sediment. Solid circles show the results of Satsuma-Iwojima gases and open circles indicate volcanic gas data from subduction settings (Sano and Marty, 1995). Lines show mixing lines among the end-members.

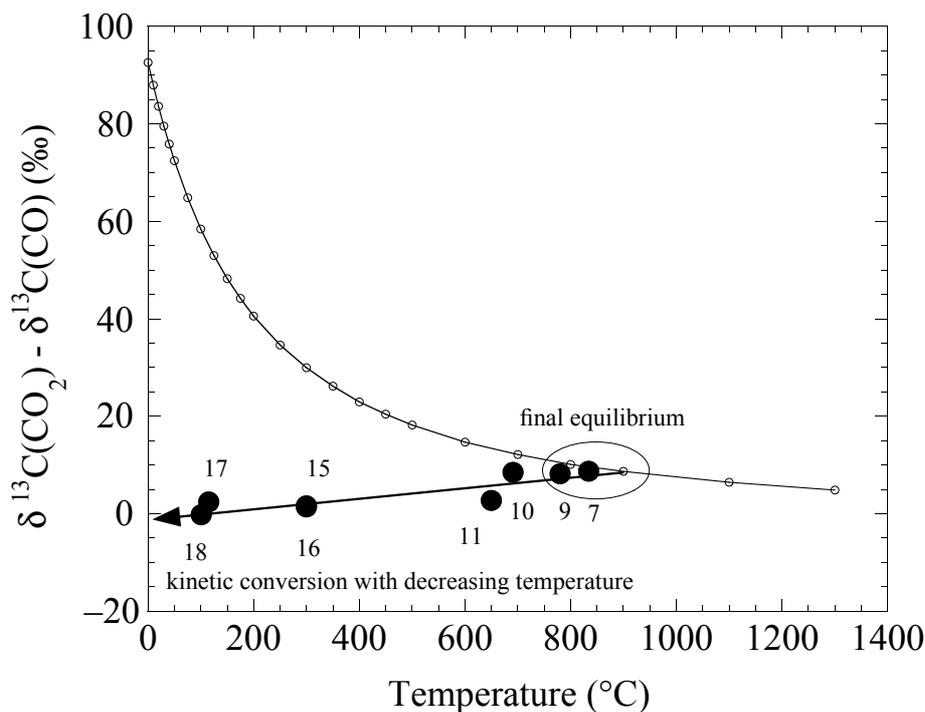


Fig. 3. Variation of $\delta^{13}\text{C}(\text{CO}_2) - \delta^{13}\text{C}(\text{CO})$ and fumarolic temperature. Solid circles show the analytical results and open circles are the $\delta^{13}\text{C}$ differences under isotopic equilibrium condition (Richet *et al.*, 1977).

Since we did not measure H_2O and H_2 contents in our sample gases, we could not calculate the AET using our own data. Ohba (1997) calculated the AET for Satsuma-Iwojima gases using the Shinohara *et al.* (1993)'s data, to range from 581° to 737°C for fumarolic gases with temperatures from 505° to 877°C . This shows that the AETs based on chemical equilibrium reaction (2) are commonly lower than the fumarolic temperatures, in contrast that the AET for the CO_2 and CO isotope exchange reaction (1) are slightly higher

than the fumarolic temperatures.

Our data clearly show that the CO/CO_2 ratio decreases with decreasing temperature, meaning that the reaction (2) shifts to the right with decreasing temperature. Since kinetic reaction enriches ^{13}C in the residual species, $\delta^{13}\text{C}(\text{CO})$ increases by progress of kinetic conversion of CO to CO_2 . Therefore, the correlation of $\delta^{13}\text{C}(\text{CO})$, CO/CO_2 ratio and fumarolic temperature seems to be the result of kinetic conversion of CO to CO_2 with decreasing temperature.

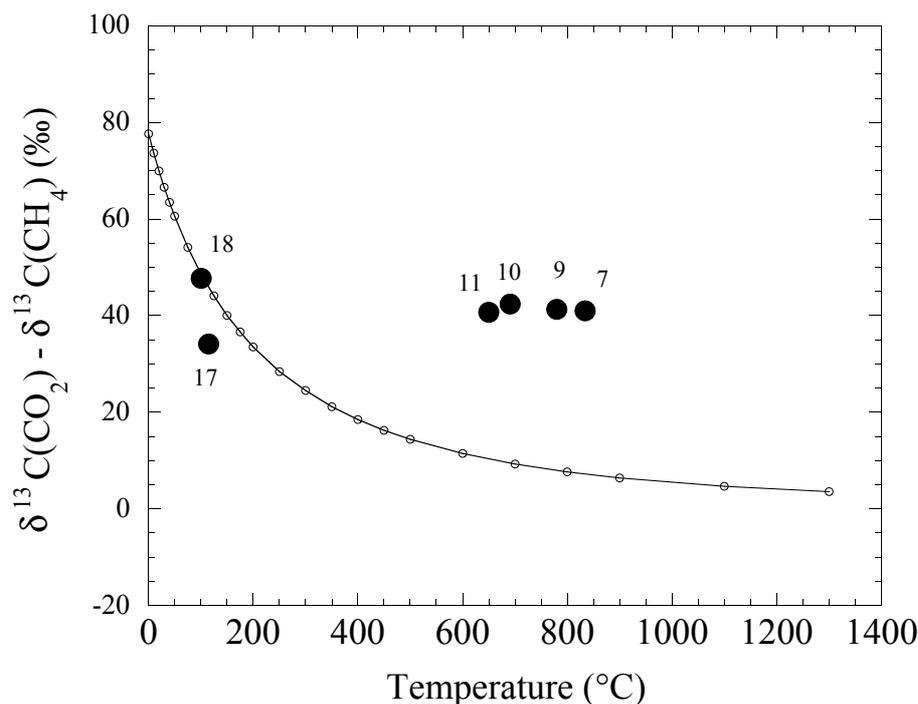


Fig. 4. Variation of $\delta^{13}\text{C}(\text{CO}_2) - \delta^{13}\text{C}(\text{CH}_4)$ and fumarolic temperature. Solid circles show the analytical results and open circles are the $\delta^{13}\text{C}$ differences under isotopic equilibrium condition (Richet *et al.*, 1977).

Table 2. Isotopic AET of Satsuma-Iwojima fumarolic gases.

No.	Fumarolic temp. (°C)	AET (CO_2 -CO) (°C)	AET (CO_2 - CH_4) (°C)
7	834	896	143
9	780	934	141
10	691	910	134
11	650	>1300	145
15	300	>1300	
16	300	>1300	
17	115	>1300	193
18	101	>1300	105

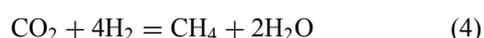
4.3 CO_2 - CH_4 isotopic exchange equilibrium and other hydrocarbons

Similar to the discussion of CO_2 -CO isotopic equilibrium temperature, the AET can be calculated for the following isotopic exchange reaction:



The calculated AETs are lower than 200°C independent of the fumarolic temperature, as shown in Fig. 4 and Table 2. Because the calculated AETs are unrealistically low even for the fumarolic gases of about 900°C, the $\delta^{13}\text{C}$ values of CH_4 are concluded not to be controlled by the isotopic exchange equilibrium between CH_4 and CO_2 .

If the CH_4 content is controlled by the following reaction:



the CH_4/CO_2 ratio should be about 10^{-8} under the FeO- $\text{FeO}_{1.5}$ rock buffer at 877°C and 100 bar (Shinohara *et al.*, 1993). As described previously, the CH_4/CO_2 ratios fall into two groups; the high CH_4/CO_2 group (7.7×10^{-4} to 7.4×10^{-3}) and the low CH_4/CO_2 group ($<10^{-5}$). Even for the low CH_4/CO_2 group, the CH_4/CO_2 ratio is higher the estimated value (about 10^{-8}) under the magmatic condition, suggesting that the CH_4 of the low CH_4/CO_2 group cannot be of magmatic origin. Moreover, the CH_4/CO_2 ratio of the high CH_4/CO_2 group is more than 10^2 times of that of the low CH_4/CO_2 group. The excess- CH_4 might be originated from an additional source and must be contaminated to the low CH_4/CO_2 group gas. Shinohara *et al.* (1993) attributed the high CH_4 to near-surface contamination, reaction with sampling materials or addition of hydrothermal CH_4 .

Schoell (1980) showed that the origin of methane from natural gases can be classified into biogenic and thermogenic sources based on the variation of δD , $\delta^{13}\text{C}$ of CH_4 and contents of CH_4 and C_2 to C_4 hydrocarbons. Kiyosu *et al.* (1992) evaluated the origin of light hydrocarbons in Matsukawa (Japan) geothermal gases based on the variations of $\delta^{13}\text{C}(\text{CH}_4)$ and $\text{CH}_4/\text{C}_2\text{H}_6$ ratio, suggesting these gases to be a mixture of thermogenic and abiogenic (magmatic) components as shown in Fig. 5. Kiyosu *et al.* (1992) estimated the isotopic and chemical equilibrium composition of hypothetical magmatic gas under a condition of f_{O_2} controlled by fayalite-magnetite-quartz buffer at 1000 K, to be $\text{CH}_4/\text{C}_2\text{H}_6$ ratio of 2631 and $\delta^{13}\text{C}(\text{CH}_4)$ of -12.6‰ assuming $\delta^{13}\text{C}(\text{CO}_2)$ of -6.8‰ . In Fig. 5, the $\text{CH}_4/\text{C}_2\text{H}_6$ ratios and $\delta^{13}\text{C}(\text{CH}_4)$ values of geothermal gases in New Zealand (Giggenbach, 1997) are also shown for comparison. Giggenbach (1997) explained that these gases are derived

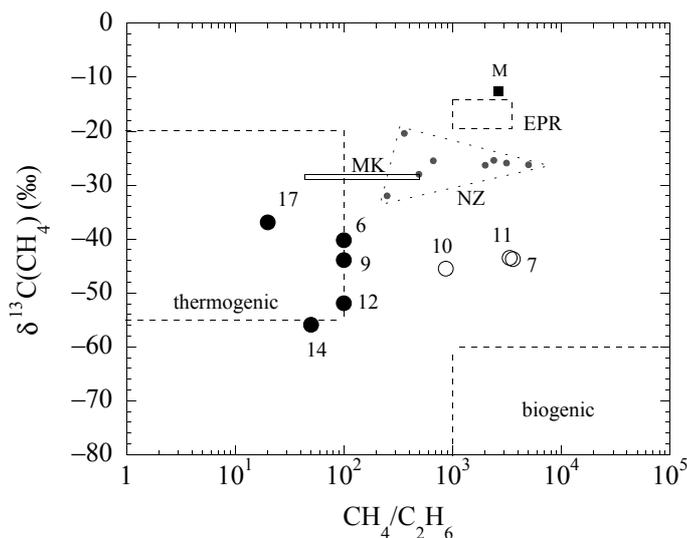


Fig. 5. Variation of $\delta^{13}\text{C}(\text{CH}_4)$ and $\text{CH}_4/\text{C}_2\text{H}_6$ ratios of fumarolic gases from Satsuma-Iwojima. Solid circles indicate the low CH_4/CO_2 group and open circles the high CH_4/CO_2 group. EPR: East Pacific Rise (Welhan and Craig, 1983). M: hypothetical magmatic gas (Kiyosu *et al.*, 1992). MK: Matsukawa geothermal gas (Kiyosu *et al.*, 1992). NZ: New Zealand geothermal gas (Giggenbach, 1997). Thermogenic and biogenic: (Schoell, 1980).

from 250°C hydrothermal equilibrium component contaminated by a small amount of natural gas component based on $\text{CH}_4/\text{C}_2\text{H}_6\text{-C}_2\text{H}_6/\text{C}_3\text{H}_8$ discussion.

In order to evaluate the origin of CH_4 from Satsuma-Iwojima volcanic gases, the data are also plotted in Fig. 5. The low and high CH_4/CO_2 groups are separately plotted on this diagram. The $\delta^{13}\text{C}(\text{CH}_4)$ of the low CH_4/CO_2 group ranges from -56 to -37‰ and $\text{CH}_4/\text{C}_2\text{H}_6$ ratio ranges from 20 to 100, indicating thermogenic origin. On the other hand, the high CH_4/CO_2 group has variable $\text{CH}_4/\text{C}_2\text{H}_6$ ratios (7×10^2 to 8×10^3) and the similar $\delta^{13}\text{C}(\text{CH}_4)$ with the low CH_4/CO_2 group. These gases can be formed by addition of CH_4 -rich gas with $\delta^{13}\text{C}(\text{CH}_4)$ of about -40‰ to the low CH_4/CO_2 group, which is consistent with the conclusion by Shinohara *et al.* (1993). However, the source of this CH_4 -rich gas is not clear. As the CH_4 -rich gas has composition at middle of the magmatic and biogenic components (Fig. 5), this CH_4 -rich gas could be a mixture of these source gases, although the mixing mechanism is not clear and, therefore, its probability cannot be evaluated. Since the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio of the hydrothermal equilibrium component was calculated to be 10^6 at 250°C by Giggenbach (1997), this component can be also a candidate of the CH_4 -rich gas. However $\delta^{13}\text{C}(\text{CH}_4)$ in equilibrium with $\delta^{13}\text{C}(\text{CO}_2)$ of -3‰ at 250°C is calculated to be -31‰ (Fig. 4), that is more positive than the observed values (-55 to -40‰).

Ethylene was detected in the most of samples. Kiyosu and Asada (1995) reported that $\text{C}_2\text{H}_4/\text{CH}_4$ ratio is relatively high (about 10^{-1} to 10^{-3}) in fumarolic gases and low ($<10^{-3}$) in geothermal gases. The $\text{C}_2\text{H}_4/\text{CH}_4$ ratio of the low CH_4/CO_2 group ranges from 10^{-1} to 10^{-2} , that is consistent with the reported range for fumarolic gases by Kiyosu and Asada (1995). The $\text{C}_2\text{H}_4/\text{CH}_4$ ratio of the high CH_4/CO_2 group ranges from 3×10^{-4} to 1.2×10^{-3} , that is closer to geothermal gases rather than fumarolic gases, although the temperatures are above 650°C. This also supports the considerable addition of CH_4 in the high CH_4/CO_2 ratio group. It

must be mentioned that ratios $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ ratios are constant (~ 1) regardless of the CH_4 contents. This may also suggest that addition of CH_4 -rich component causes the variation in $\text{C}_2\text{H}_4/\text{CH}_4$ ratio.

5. Conclusions

Carbon isotopic compositions of CO_2 , CO and CH_4 were measured for fumarolic gases from Satsuma-Iwojima volcano with various temperatures up to 900°C. The AET for carbon isotope equilibrium between CO_2 and CO in high temperature gas is calculated to be 896° to 950°C, which is a little higher than fumarolic temperature, suggesting that the carbon isotopic compositions are controlled by the isotopic exchange equilibrium. In contrast, the AET for the low temperature gases is calculated to be unrealistically high. The variations of $\delta^{13}\text{C}(\text{CO})$, CO/CO_2 ratio and temperature suggest that kinetic conversion of CO to CO_2 occurred with decreasing temperature.

Carbon isotopic ratio of CH_4 is not controlled by isotopic exchange equilibrium between CH_4 and CO_2 even up to 900°C. Combined with $\text{CH}_4/\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ data, contribution from thermogenic CH_4 is significant for low CH_4/CO_2 group and contamination of CH_4 -rich gas is significant for high CH_4/CO_2 group. However, origin of CH_4 -rich gas component is not clear. $^3\text{He}/^4\text{He}$ shows a typical island arc magma value and does not vary with gas temperature nor gas chemistry.

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