

B-2.2 Studies for estimation of methane flux from volcanoes

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Abstract Volcanoes are one of most important source of gas components in nature. Although methane is minor component of volcanic gas with concentration of an order of ppm, the methane flux from volcanoes could be important for geochemical cycle of methane during geological time scale. Emission rate of volcanic methane was evaluated through measured flux of CO₂ and CH₄/CO₂ value representative to each source. On the basis of the chemical analyses of gases from high temperature and low temperature fumaroles, geothermal well, submarine hydrothermal vents and soil around volcanoes (as soil gas), the maximum CH₄/CO₂ value for each source were estimated to be 10²-10³. These ratios multiplied by the CO₂ flux gave us the global methane to be less than 0.04 Tmol/year.

Key Words Methane, Carbon dioxide, Volcanic gas, Soil gas

1. Introduction

Magmatism, metamorphism, and subduction of oceanic crust has acted an important role for recirculation of substances in earth crust for 46 billion years since the earth was born. Geological cycle involves atmosphere, hydrosphere, earth crust and mantle and operates in the time scale of several million years. Biological cycle modifies geological framework with much shorter term of several thousands' years. To understand the material cycle we have to evaluate quantitatively contributions from the geological, biological processes and human activities.

Berner's geological (geochemical) recycle model (BLAG model) ¹⁾ for carbon indicates that the most essential factor for changing atmospheric concentration of CO₂ is degassing rate from the earth's interior. Though yearly flux of CO₂ from the geological processes is much smaller than that from human activities (500Tmol/yr), the total contribution of geological processes to global CO₂ is principal because of their long duration time. This study aims to evaluate global flux of magmatic methane emitted from both terrestrial and submarine volcanisms.

2. Method

Emission of CO₂, which is genetically in close relation with methane, has been estimated by various methods (table 1). 1), 2), 3), 4), 5), 6), 7) Among many components in volcanic gases SO₂ is the only molecule we can measure remotely by spectroscopic methods. For instance TOMS (Total Ozone Mapping Spectrometer) and COSPEC (Correlation Spectrometer) use characteristic absorbance of ultraviolet light. Since earth's mantle, therefore magmatic process, is the only source for ³He, it can be used as a reference component. Flux of volcanogenic CO₂ can be estimated by multiplying thus measured flux

of SO₂ by ratios of CO₂ /SO₂. Similarly measured ³He flux and CO₂ /^βHe value are also used for evaluating CO₂ flux. Our basic idea in this study is to evaluate the global flux of volcanogenic methane using the CO₂ flux and the ratios of CH₄ /CO₂ in gases of relevant sources. For this purpose we determined the chemical composition of gases of various geological sources and estimated the representative CH₄ /CO₂ value for each source.

We covered volcanic gases from various environments in two volcanic arcs, Japan and Indonesia, from degassing domes such as Satsuma-Iwojima and Usu to extremely matured volcanic hydrothermal system like Osorezan. The temperatures of gases range between 900°C and 100°C. We studied 40 soil gas samples also at Satsuma-Iwojima volcano. Gases from both terrestrial and submarine hydrothermal systems were also examined. On the other hand, gas flux from metamorphic process was estimated mainly based on the previous works.

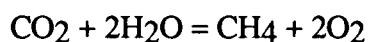
3. Results and Discussion

(1) Flux of CO₂ from volcanoes

Mode of emission of volcanic gas is classified into three types; eruptive emission related to volcanic explosion, steady emission from fumaroles, and diffusive emission from whole volcanic body as soil gas (Table 1). The presumption in table 1 is for steady state of present time. It is probable that in geologic history global flux of gases fluctuated in association with big tectonic event such as accelerated spreading of sea floor and breaking up of Pangaea. As evidenced by that Mt. Etna contributes 10-50% of global fumarolic emission of CO₂, gas sources are unevenly distributed. The gas flux by diffused emission is also comparable to that of fumarolic emission from the summit crater at Mt. Etna, Sicily. Gas flux data by diffused emission are not available yet for other volcanoes. Gas flux by eruptive emission is also unevenly distributed over space and time. For instance the flux by giant eruption sometimes exceeds global yearly flux of gases. Since the gas plume reaches 10 km at the time of giant eruption (VEI>3), the gas components tend to spread widely into the stratosphere.

(2) Concentration of methane in volcanic gases

Chemical compositions of volcanic gases, including those from terrestrial and submarine hydrothermal systems, are listed in Table 2 for newly collected and studied samples. Generally speaking, volcanic gas involves methane from two different sources; 1) product of chemical reaction among CO₂, H₂O and O₂, 2) thermal decomposition product of organic materials in sedimentary rocks. Since the latter depend on the temperature-pressure condition and amount of organic material around the heat source, accurate estimation for the flux may be difficult. On the other hand major part of CO₂ in volcanic gas has its source in magma and affected little by shallow contamination by organic materials. Therefore, we can estimate the CO₂ /CH₄ ratios as a function of temperature, total pressure and partial pressure of O₂ with the assumption that the following inorganic reaction controls the CO₂ /CH₄ value:



Oxidation state of magma, which is buffered by Fayalite-Magnetite-Quartz assemblage (FMQ) in arc environment, looks to control partial pressure of O₂ (or H₂ /H₂O) in high temperature (>800°C) volcanic gases also (fig. 1). On the other hand, the partial pressures of O₂ (or H₂ /H₂O) in lower temperature gases are far from FMQ buffer because of the following quick reaction; $\text{H}_2\text{S} + 2\text{H}_2\text{O} = 3\text{H}_2 + \text{SO}_2$.

High temperature volcanic gases (>300°C) preserve equilibrium concentration of methane with FMQ buffer under 100 bars. Lower temperature gases contain much lower methane than the equilibrium concentration, indicating sluggishness of chemical reaction under lower temperature (<200°C).

Thus, we conclude that the recommended values for the maximum CH₄/CO₂ ratio in volcanic gases are 10⁻³ for high temperature gas (>800°C), 10⁻² for lower temperature gas (<800°C).

Combining these values with the volcanic CO₂ flux from eruptive and fumarolic activities, we can estimate the maximum flux of methane from volcanoes.

(3) Gas by diffused emission from volcanic bodies

Volcanoes emit gases not only from summit craters but also from all over the volcanic body as diffused flow through soil layer (soil gas). This was well evidenced at Etna, Sicily^{8),9)}, where diffused emission was responsible for almost half of total CO₂ from the volcano. Soil gas may be in chemical equilibrium (or in disequilibrium) under different temperature-pressure conditions and have different CH₄/CO₂ ratios from that of high temperature volcanic gases. No data has been available yet for the methane flux from this source. We conducted field sampling at Satsuma-Iwojima to investigate the chemistry and flux of soil gases. We collected 40 samples from 0.5~1.0m depth by plastic tubes 2 cm wide. We analyzed CO₂ and O₂ on site by portable gas detectors and other gases by gas-chromatography in the laboratory. Concentration of CO₂ ranges from 0.2 to 36% and that of CH₄ does < 10 to 2215 ppm. Excluding the data from warm ground to avoid shallow contamination from thermally decomposed organic substances, and regarding the high-CO₂ (22 mol%) and low-CH₄ (<10 ppm) specimen to be the least contaminated gas, we adopt 10⁻² as representative value of CH₄/CO₂ for soil gas.

(4) Gases from submarine hydrothermal systems

Submarine volcanoes emit various gases through hydrothermal activity. Hydrothermal fluid contains magmatic gas components, as suggested by the high ³He/⁴He value and carbon isotope data of CO₂. The CH₄/CO₂ ratios in the hydrothermal gases are 10⁻³ ~10^{-3.5} at Iheya, Okinawa trough (this study) and 10⁻² ~10⁻³ in other site¹⁰⁾. Thus we can use 10⁻² as the representative CH₄/CO₂ value for submarine hydrothermal fluids.

Isotopic fractionation of carbon between CH₄ and CO₂ in these samples suggests equilibrium formatin of CH₄ with CO₂ under the temperature range of 500~700°C¹⁰⁾.

(5) Geothermal gas

Geothermal gases are expected to be in equilibrium with surrounding rocks and the partial pressures of O₂ in the gas are buffered by Fe²⁺/Fe³⁺ = 1¹¹⁾. This is in good contrast to high-temperature volcanic gases of which the partial pressures of O₂ are controlled by FMQ buffer.

Since boiling and subsequent phase separation happen commonly in hydrothermal systems and modify gas ratio according to their liquid-vapor fractionation, we have to analyze geothermal fluid prior to phase separation to know the original CH₄/CO₂ ratio. Previous study for many geothermal fluids and this study on Indonesian geothermal system (Kamojan KMJ-45) revealed the values are between 10⁻² ~ 10⁻³. This suggests that the CH₄/CO₂ ratio reflect Fe²⁺/Fe³⁺ buffer under the temperature conditions of <300°C. Thus we can adopt 10⁻² as a typical value for CH₄/CO₂ for geothermal gas.

(6) Gas emitted from metamorphic processes

Subducting oceanic crust transports marine sediments to trench system to form accretional prism at the front of arc. The oceanic sediment partially travels into upper mantle along the subduction zone and discharges CO₂ ~due to thermal decomposition of carbonate and organic substances in it. Rate and extent of metamorphism depend on temperature-pressure conditions attained and variable from place to place. The flux of CO₂ from metamorphic

process was evaluated through the volume of metamorphosed rocks in which carbonate was eroded by thermal decomposition ⁷⁾. Since reducing condition prevails in metamorphism, CH₄/CO₂ ratio can be very high ¹²⁾ as evidenced by methane-rich fluid inclusions in metamorphic minerals ¹³⁾. Ratio of CH₄/CO₂ can be theoretically estimated as a function of temperature, pressure, partial pressure of O₂ and metamorphic history, though it is not realistic without knowledge for the emission mechanism of CO₂ from the metamorphic rocks. In any case metamorphic CH₄ cannot exceed CO₂ flux estimated by the decomposition rate of carbonates. Therefore, we can regard the CO₂ flux to be the maximum value for the CH₄ flux from the metamorphic process.

4. Summary

The global flux of methane from various geological sources was calculated from the representative CH₄/CO₂ ratios and global CO₂ flux for each process (table 1). As a conclusion the total methane flux from volcanic processes is estimated to be 0.04 Tmol/yr. Metamorphic process is another source of methane for which we were not able to access with enough accuracy. Since the flux of metamorphic CO₂ is about 1Tmol/yr, the flux of metamorphic CH₄ may not be ignored if CH₄ /CO₂ ratio is much higher than the value estimated for volcanic processes. Chemical composition and mode of emission of metamorphic gases are not yet clear and left for future study.

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Table 1 CO₂ and CH₄ flux from geological sources

	Method	Measured Component	CO ₂ flux (Tmol/yr)	Ref.	CH ₄ /CO ₂	CH ₄ flux (Tmol/yr)
Total	BLAG Model	CO ₂	6-11	1, 2	—	—
Volcano Erupcion	TOMS	SO ₂	1	3	<0.001	<0.001
	Fumarole	COSPEC	SO ₂	3	<0.01	<0.01
	Diffusive		CO ₂	(1)	<0.01	<0.01
Oceanic Ridge	³ He distribution	³ He	1	5	<0.01	<0.01
Geothermal		Heat	(1)	6	<0.01	<0.01
Metamorphic		Carbonate	(1)	7	?	?

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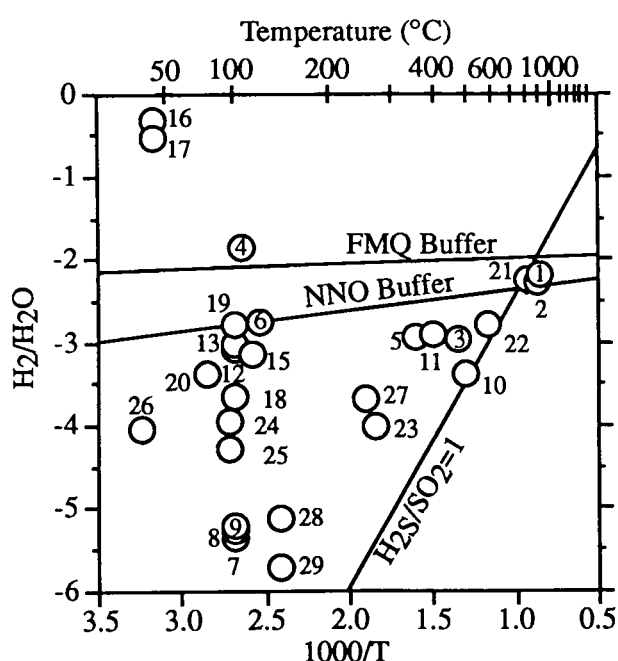


Figure 1 Variation of H₂/H₂O ratio with temperature of fumaroles

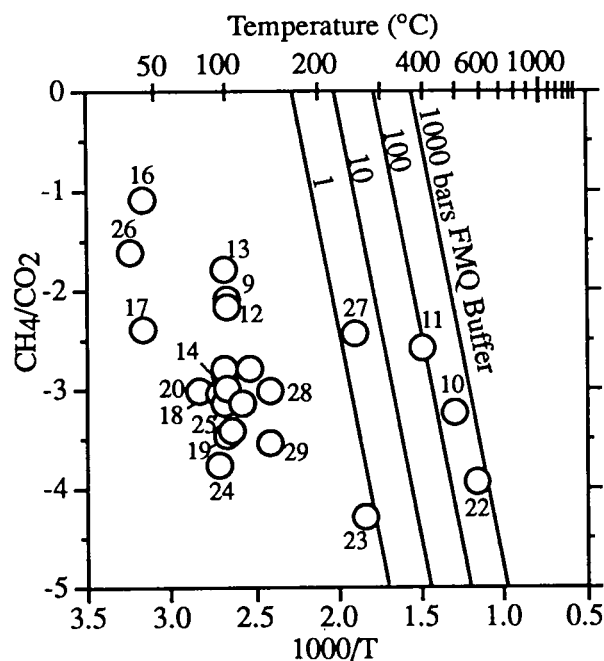


Figure 2 Variation of CH₄/CO₂ ratio with temperature of fumaroles

Sample No.: SATUMA-IWOJIMA, 1:O-hachioku901, 2:O-hachioku881, 3:O-hachinaka467, 4:O-hachinaka106, 5:Kuromoe351, 6:Ohachifuchi121, 7:Monogusa, 8:Monogusa, 9:NE-fumarole, USU, 10:I-crater495, 11:I-crater393, 12:Gin-numa, 13:Gairinn-uchi, 14:Gairinn-soto, NOBORIBETU, 15:Hoyoriyama, 16:A-1, 17:A'-1, OSOREZAN, 18:No.1 Spring, 19:Genkisen, 20:Shinta-choubu, Indonesia, 21:Merapi Gendol, 22:Merapi Woro, 23:Papandayang, 24:Tankubang Perahu, 25:Dieng Sikidang, 26:Dieng Senila, 27:Kamojang KMJ-45, Okinawa Trough IKEYA, 28:D684-2a, 29:D-684-1a.

Table 2 Results of volcanic gas analyses

Location	Date	Temp. Sample (°C)	Sample (g)	H ₂ O ppm-mol	CO ₂	H ₂ S	SO ₂	HCl	He	H ₂	O ₂	N ₂	Ar	CH ₄	CO
Satsuma-Iwojima															
1	O-hachioku901	94/10/29	6.19	969 785	4 758	214	12 184	6 057	0.021	6 625	0	287	4.87	0	33.7
2	O-hachioku881	94/10/29	12.29	974 129	3 804	323	9 853	6 410	0.016	5 327	0	107	1.09	0	26.8
3	O-hachinaka467	94/10/31	22.89	951 369	48	8 278	16 269	13 531	0.025	1 030	0	69	0.77	0	4.95
4	Ohachinaka106	94/10/31	5.21	950 343	4 050	8 656	16 350	191	0.374	13 480	0	101	12.2	1.58	2.34
5	Kuromoe351	94/10/31	45.23	976 043	3 100	1 431	6 537	11 603	0.019	1 133	7	103	0.87	0	3.12
6	O-hachifuchi121	94/11/1	33.63	974 042	266	307	12 636	10 746	0.052	1 761	0	169	1.55	0.44	1.99
7	Monogusa	94/10/30	3.39	968 903	4 085	-	4 014	43	0.161	5	3 325	19 324	352	6.6	0
8	Monogusa	93/3/4	3.74	968 983	4 984	-	3 983	36	0.159	4	3 127	18 809	228	3.7	0
9	NE-fumarole	93/3/6	83.69	990 220	3 101	96	5 859	0	0.066	6	0	685	7	25	0
Usu															
10	I-crater495	94/11/30	40.55	997 263	1 339	1 552	173	601	0.001	429	0	40	0.42	0.79	0.24
11	I-crater393	94/11/30	31.53	995 993	1 655	1 836	115	610	0.004	1 290	0	119	1.42	4.10	0.58
12	Gin-numa	94/12/1	35.02	997 212	1 472	2 370	148	3	0.009	829	0	117	2.30	10.1	0.50
13	Gairinn-uchi	94/12/1	58.34	997 669	821	5 487	177	0	0.005	851	0	103	10.4	13.7	0
14	Gairinn-soto	94/12/1	1.15	973 895	2 996	0	0	131	0.023	0	4 699	18 045	230	4.30	0
Noboribetu															
15	Hiyoriyama	93/9/24	13.39	984 222	11 005	3 390	282	9	0.037	701	0	382	2	8	0
16	A-1	93/9/24	0.15	402 105	65 324	1 983	50	1 051	22.2	193 792	1 218	325 105	4 130	5 242	0
17	A'-1	93/9/24	0.43	388 137	358 141	5 591	4 825	1 083	5.33	116 751	0	122 323	1 744	1 478	0
Osorezann															
18	No.1Spring	93/11/6	6.77	805 650	149 558	37 197	4 136	21	0.63	187	1	3 087	11	153	0
19	Gennkisen	93/11/6	2.79	86 390	743 451	131 560	23 801	470	2.44	149	2	13 895	20	259	0
20	Shinta-choubu	93/11/6	4.35	618 032	292 866	76 216	6 418	307	0.94	261	5	5 595	14	285	0
Indonesia															
21	Merapi Gendol	94/7/27	1.18	874 681	61 882	403	10 072	3 931	0.523	5 017	5	41 678	475	0	328
22	Merapi Woro	94/7/27	10.39	936 717	45 803	2 198	5 217	1 986	0.160	1 533	9	2 685	25.6	5.20	74
23	Papandayang	94/7/23	26.89	965 128	24 067	4 734	1 470	1 840	0.211	97	1	445	0.76	1.25	0
24	Tankubang Perahu	94/7/21	84.50	992 756	3 895	9 682	254	2	0.096	112	0	189	1.16	0.67	0
25	Dieng Sikidang	94/7/25	69.79	986 199	7 079	10 782	479	56	0.313	53	0	179	0.50	6.36	0
26	Dieng Senila	94/7/25	2.49	820 772	172 428	-	126	128	1.562	73	43	2 253	7.22	4 185	0
27	Kamojang KMJ-4	94/7/22	92.73	995 392	4 064	117	45	2	0.13	207	1	154	1.10	14.9	0
Okinawa trough Iheya															
28	D684-2a	93/6/1	1.20	963 448	34 770	909	-156	158	0.252	7	134	683	11	35	0
29	D684-1a	93/6/1	15.07	951 411	34 812	882	-236	12 428	0.063	2	158	518	15	10	0