DETERMINATION OF ^{14}C IN VOLCANIC GAS BY ACCELERATOR MASS SPECTROMETRY

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ABSTRACT. Radioactive nuclides such as radiocarbon can be good tracers for investigating the circulation of underground carbon and water. Volcanic gas can be sampled reliably for ^{14}C analysis and prepared for analysis by accelerator mass spectrometry (AMS). In this paper, we establish a method for the measurement of ^{14}C in volcanic gas, and measure the amounts of ^{14}C in various volcanic gases. Samples of fumarolic gas from some Japanese volcanoes were found to contain 0.5 to 4.2 pMC, while those from White Island in New Zealand contained 2.6 pMC. Dissolved gas from Lake Nyos, Cameroon, contained 0.4 to 4.8 pMC. The data indicate a mixing process between surface carbon and deep carbon.

INTRODUCTION

The main component of volcanic gas is water vapor. In this paper, we define "hot spring gas" as gas that evolved into bodies of water (such as small pools and rivers), and "fumarolic gas" as gas that evolved over dry areas. These 2 gas flows are collectively referred to as "volcanic gas" in this paper. The main components of volcanic gas (other than water vapor) are acidic gases, such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S). The origin of these acidic gases and the degree of mixing with surface water are not clearly known. Ellis et al. (1964) used a simulation experiment to show that the dissolved components in geothermal fluids originate from water-rock interactions at high temperature. The mechanism of formation of acidic gases may be explained by such reactions, but verification of the phenomena in nature is difficult to achieve in the laboratory. Clarifying the origin of these gases is important for understanding the behavior of the geothermal fluid and also for predicting volcanic eruptions. In this paper, we are interested in the origin of CO_2 in volcanic gases. The CO_2 may come from such sources as 1) the atmosphere, 2) organic carbon and bicarbonate in groundwater, 3) carbonate sediments or rocks in contact with geofluids, and 4) magma.

Radiocarbon, which has a half-life of 5730 yr, is generated by cosmic rays in the atmosphere and is suitable as a tracer for studies of the geochemical behavior of carbon in nature. The carbon in volcanic gas is generally considered to be derived from "dead" carbon sources, e.g. magma and ancient sediment. If ^{14}C can be detected in volcanic gas, it can be explained as additions from a surface carbon reservoir, such as the thermal decomposition products of organic material in Earth's surface layer or the bicarbonate dissolved in underground water in the geothermal zone. The former cause applies only to new volcanoes, while the latter applies to the majority of active volcanoes.

Jansen (1977) geochemically estimated the mixing of "modern carbon" to be less than 1% based on a proportional counter measurement of the gas in a geothermal well in New Zealand. The detection limit of the above technique using a proportional counter is estimated to be a few percent modern carbon (pMC), and applying this technique for the ^{14}C measurement in volcanic gas is certainly limited by the amount of collectable gas.

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To obtain new information about the sources of volcanic gas, we have attempted using accelerator mass spectrometry (AMS) to measure ^{14}C in volcanic gas. This method can be used to measure concentrations of ^{14}C for a limited amount of carbon sample at the geothermal area. The difficulty involved in applying AMS is in preventing contamination by modern carbon in the sampling and sample preparation steps. This paper describes the methods of sampling volcanic gas and the sample preparation steps for the AMS ^{14}C measurements, and presents some results from major volcanoes in Japan.

GAS SAMPLING METHOD

Sampling of volcanic gas is very difficult and dangerous because the temperature of a fumarole exceeds the boiling point of water (e.g. the highest temperature in this study was about 600 °C at Mt Use), and also because the environment is filled with very acidic and often poisonous gas, as the sampling location is sometimes in the volcano crater. The main component of volcanic gas is generally water vapor, amounting to more than 90% of the total gas volume. Other gas components are "non-condensed gas," and consist mostly of carbon dioxide (CO_2), sulfur dioxide (SO_2), hydrogen halides, carbon monoxide, nitrogen, and argon. We collected CO_2 gas using the Giggenbach method (Giggenbach 1975). The sampling apparatus was composed of a sampling pipe and a 200-mL gas sample bottle equipped with needle valves (see Figure 1a). To avoid contamination of the sample with modern carbon, we took special care in preparing the sampling bottle.

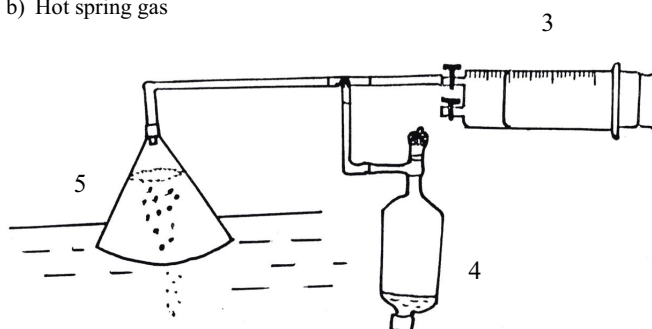a) Fumarolic gas
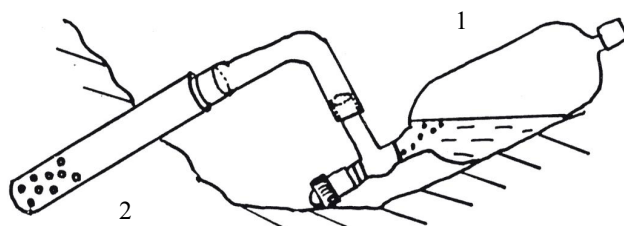
b) Hot spring gas

Figure 1 Sampling method of volcanic gas: a) for sampling fumarolic gas; 1: a 200-mL gas sampling bottle containing 10–20 mL 6M NaOH solution; 2: a titanium sampling pipe of 100 cm length; b) for sampling hot spring gas; 3: a 200-mL 2-inlet syringe for separation of non-condensed gas from water; 4: a 200-mL gas sampling bottle (Giggenbach bottle); 5: a glass funnel for collecting gas above the water.

In a glove box filled with pure nitrogen gas, a 10–20-mL 6M sodium hydroxide solution was prepared in order to avoid contact with the atmospheric CO_2. The solution was stored in a pre-weighed gas sampling bottle sealed using a greaseless stop-cock with a Teflon™ O-ring. The gas sampling bottle was initially filled with slightly pressurized nitrogen gas in the laboratory, and then evacuated by a hand pump before use in the field. The sodium hydroxide solution absorbed the acidic gas components of the non-condensed gas collected in the sampling bottle, and non-acidic residual gas was added to the space above the alkali solution.

The volcanic gas sample was introduced into the evacuated gas sampling bottle and was cooled during the sampling, so that the water vapor in the volcanic gas was condensed and the acidic gases were dissolved into the alkali solution. The amount of carbon obtained by this method was about 100 mg, and the time required for sampling was about 20 min.

At a hot spring, sampling was relatively easy because the gas always bubbled out of the water and the vapor had already been mostly condensed to water. We employed the 2-inlet syringe method proposed by Kamata (1961) for collection of the gas (Endo 1985) (Figure 1b). Ordinarily, we were able to sample about 200 mL of spring gas in a gas sampling bottle filled with an alkali solution while it was cooled to ambient temperature for measuring the volume. With this method, a 30–60-mg carbon sample could be collected when the CO_2 concentration of the non-condensed gas was in the range of 30–60%.

PREPARATION OF SAMPLE FOR AMS

The collected CO_2 gas was purified and transformed to a target (amorphous carbon) for AMS in the laboratory. A vacuum line was employed for purification of the gas sample in order to avoid contamination by ambient air. The vacuum line used to purify and reduce the sample is shown in Figure 2. A detailed description of the sample preparation and analysis method was reported in a previous paper written in Japanese (Yoshikawa et al. 1987), but a brief description is given below. The alkali solution that absorbed the sample gas was added to the line and mixed 1:1 with a sulfuric acid-$CuSO_4$ solution to recover CO_2 gas. The recovered CO_2 was then collected in a cold trap cooled by liquid nitrogen and regenerated by changing the refrigerant to a cooled ethanol trap of –50 °C (to avoid volatilizing the condensed H_2O). The purified CO_2 was collected in another sample bottle. Reduction to amorphous carbon was carried out by a reaction with metallic magnesium containing 5.9 ppm C (Nozaki 1983) at 650 °C for 4–6 hr. It was very important to avoid contamination with modern carbon in the sample preparation step, given the minute amount of carbon in volcanic gas.

For the purpose of surveying possible contaminant routes of modern carbon, we measured $^{14}C/^{12}C$ ratios for the carbon in the organic solvents used for processing samples. Acetone, carbon tetrachloride, toluene, and rotary pump oil were each absorbed in a glass-fiber paper free of organic binder and burned into soot. Reagents and equipment with no modern carbon content were selected in order to prevent contamination. All operations were performed in a clean room to avoid contamination by airborne dust.

A sample of crystalline limestone from the Paleozoic era (originated at Kabaru, Fukuoka Pref, estimated age: ~300 million yr) was used as the reference sample of dead carbon for the CO_2 gas. First, the sample surface was etched with a diluted hydrochloric acid solution until a weight reduction of 10% was achieved, after which the sample was crushed. After storing the sample in a vacuum desiccator, CO_2 was generated through the reaction of 200 mg of this carbonate sample with 20 mL of 50% phosphoric acid solution and collected in the sample preparation line. The CO_2 sample was refined by repeating the cold trap operation. Amorphous carbon was prepared by reduction of CO_2
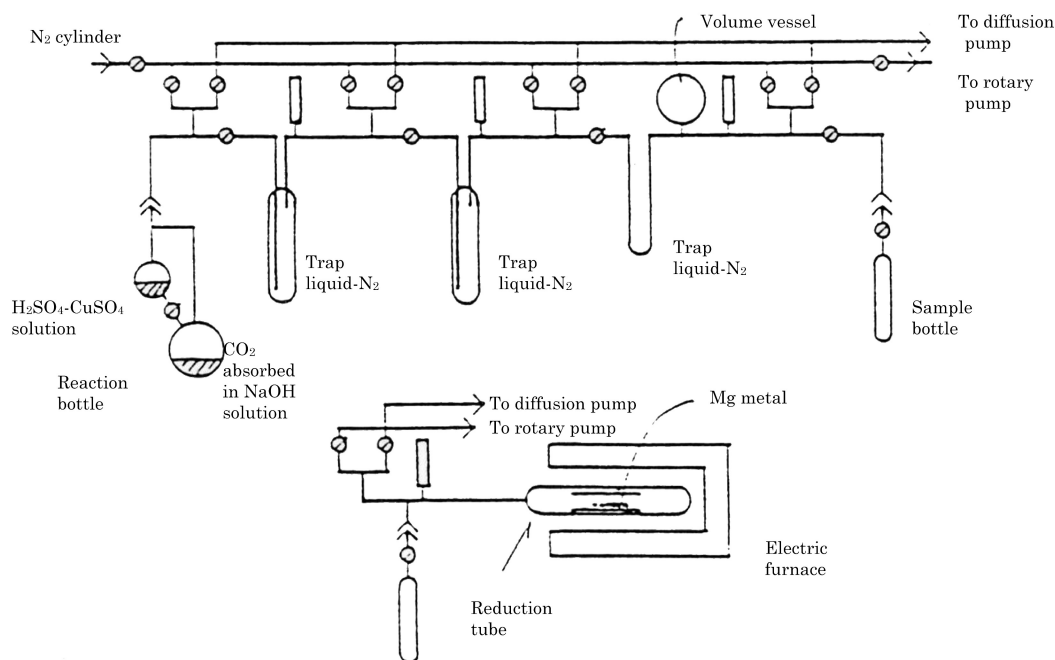
Figure 2 Sample production apparatus for CO_2 gas

with magnesium metal as the reducing agent at high temperature, as described above. The resulting detection limit using the entire sampling and preparation procedure was 0.16 ± 0.01 pMC.

MEASUREMENT OF ^{14}C

AMS was carried out with a Tandem van de Graff accelerator (3.5 MV) at the Research Center for Nuclear Science and Technology, University of Tokyo. This system was the first generation AMS system at Tokyo University (Imamura 1984; Kobayashi 1990). The detection limit of the AMS was about 10^{-16} in terms of the ^{14}C/^{12}C ratio, from the point of view of the performance of the ion source, optics, measuring system, etc. This suggests that, in principle, the ^{14}C content of samples more than 65 kyr old could be measured.

GEOLOGICAL SETTING OF SAMPLING LOCATIONS

Including undersea volcanoes, there are 80 active volcanoes in Japan. We collected gas samples at 6 well-known active volcanoes in Japan (Figure 3a) and 1 sample from a volcano in Cameroon (Figure 3b). These volcanoes show constant fumarolic activity, and the presence of magma is indirectly indicated by the presence of hot springs in neighboring areas.

Mt Use and Mt Hokkaido-Komagatake are located in the southern part of Hokkaido Island. Mt Use last erupted at its top in 1977 and at its base in 2000, while the last eruption of Mt Hokkaido-Komagatake was in 2000. The main chemical components and the δ^{13}C of carbon dioxide were analyzed and reported by Matsuo (1982) and Mizutani (1982). We carried out a ^{14}C analysis of the CO_2 of 5 fumarolic gas samples collected at the I-crater, in which some fumaroles at temperatures up to 600 °C exist. One sample collected at the crater edge at Mt Hokkaido-Komagatake was also analyzed.
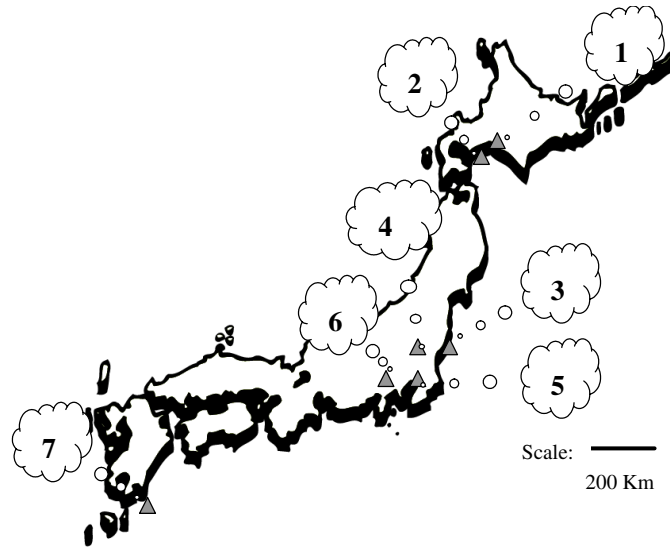
a). Sampling locations in Japan

b). Sampling locations

Figure 3   Sampling locations: 1–Mt Usu; 2–Mt Hokkaido-Komagatake; 3–Mt Nasudake; 4–Mt Kusatsu-Shiranesan; 5–Mt Hakoneyama; 6–Mt Ontakesan; 7–Mt Satsuma-Iwojima; 8–White Island in New Zealand; 9–Lake Nyos and Lake Kuchai-tium in Cameroon.

Mt Nasudake is located in the northeastern Kantou region, about 150 km from Tokyo. There are a number of hot springs around the mountain, including several well-known hot spa resorts (such as Nasuyumoto). Fumaroles at up to 300 °C occur outside the crater, e.g. at Okufun, Mugen, and Ush-ikubi. Because the high-temperature fumaroles are wide in area (about 4 m^2), it is difficult to take gas samples. We sampled gas at about 130 °C, near the high-temperature fumarole at Mugen.

Mt Kusatsu-Shiranesan is located 150 km from Tokyo in the north Kantou region, and has a main crater named Yugama which is filled with hot acidic water. We collected gases from a fumarole named Kitagawa at about 100 °C.

Owakidani is a geothermal area containing mud pools and hot springs on Mt Hakoneyama, a triple volcano composed of 2 overlapping calderas and 7 post-caldera cones. The eruption of Mt Hakon-

eyama began about 4 million yr ago. We carried out chemical analyses and measurements of ^{222}Rn in the hot spring gas.

Mt Ontakesan is located in the central part of Honshu. Its only recorded eruption was in 1979. There is still a small fumarole on the southern part of the cone.

Satsuma-Iwojima is a volcanic island about 50 km south of Kyushu and covers an area of about 12 km^2. Mt Iodake, a 700-m-high active volcano on the island, has erupted often since 1998. Sampling was performed at the Kuromoe geothermal area, where some fumaroles exhibited temperatures near 700 °C in 1987, in between periods of volcanic activity.

White Island is a volcanic island in New Zealand. The samples were collected over a vent situated at the western border of the Donald Mound fumaroles field in December 1988.

Lake Nyos is located in the North-West Province of Cameroon. Nyos is a crater lake and has a volcanic cone in its northeastern corner. It is famous for a recent eruption of CO_2 gas generated from the lake, which caused a large number of fatalities. We analyzed some samples collected in 1987 of CO_2 dissolved in the deep-layer water from Lake Nyos.

RESULTS AND DISCUSSION

The background shows that contamination of modern carbon for the preparation method using CO_2 followed by the magnesium reduction method was about 0.16%, or 53,000 yr old in terms of the dating age. In terms of the ^{14}C/^{12}C ratio, the background was $(2.0 \pm 0.5) \times 10^{-15}$.

Table 1 and Figure 4 show the results of ^{14}C measurements in the volcanic gas. The range of pMC varies widely, from 0.8 to 4.2 pMC, and differs even among fumaroles of the same volcano. There is no guarantee that the value directly indicates the age of the magma; rather, it shows the degree of carbon mixing caused by groundwater, which contains modern C, into the magmatic CO_2 gas, which contains no ^{14}C. Measurement of the tritium contents also indicates that the H_2O in fumarolic gas contains some groundwater. Kakiuchi (1987) measured the tritium content in the condensed water of fumarolic gas at Mt Use and reported 4.4–6.6 TU (Kakiuchi 1987). Such tritium data clearly indicate the admixture of modern groundwater and geothermal fluid. The main components of the volcanic gas at the I-crater of Mt Use were H_2O (994 mmol per mole of non-condensed gas) and CO_2 (3.3–3.6 mmol per mole of non-condensed gas) (Giggenbach 1991). If the origin of the water in the fumarolic gas on Mt Use is groundwater containing modern bicarbonate, the observed ^{14}C is the result of oxidation of the bicarbonate and indicates mixing of the groundwater into the fumarolic gas. We observed ^{14}C in the range of 0.9–4.2 pMC in the fumarolic gas of Mt Use. These data also point out that the major part of the water, which constitutes the majority of the geothermal fluid, is groundwater circulating near the surface. The groundwater at relatively shallow depth is expected to be sucked into the uprising flow of the magmatic gas, and the origin of a large fraction of the CO_2 in the fumarolic gas of Mt Use can be attributed to bicarbonate in the groundwater. In order to calculate the mixing ratio accurately, we require more information, including the concentration and pMC of bicarbonate and inorganic carbon in shallow groundwater near the fumarole. Therefore, we can only present the possibility of using ^{14}C data as a mixing parameter of the groundwater into the fumarolic gas. On the other hand, we can see the effect of volcanic gas on groundwater by using the ^{14}C content as a marker for the origin of the gas. Our data from Lake Nyos indicate that the ^{14}C content at the 150-m level is less than that at the 125-m level, indicating that the CO_2 originated from volcanic gas emerging into the bottom of the lake. In this case, the pMC value demonstrates the influence of geothermal fluids on the volcanic lake.

Table 1 Results of ^{14}C measurements in volcanic gas.

Sampling location	^{14}C content (pMC)
Mt Usu I-crater nr 2 600 °C	1.4 ± 0.5
Mt Usu I-crater nr 4	0.9 ± 0.3
480 °C	0.9 ± 0.6
455 °C	3.8 ± 1.9
Kousu 370 °C	4.2 ± 2.1
Mt Hokkaido-Komagatake	2.5 ± 0.7
Mt Nasudake	2.1 ± 0.6
Mt Kusatsu-Shirane	
Kitagawa fumarole (1)	0.5 ± 0.1
Kitagawa fumarole (2)	0.8 ± 0.1
Kitagawa fumarole (3)	1.4 ± 0.5
Kitagawa fumarole (4)	1.2 ± 0.4
Kitagawa fumarole (5)	0.9 ± 0.3
Mean	*1.0 ± 0.1*
Mt Hakone (Mt Kamiyama)	
Owakidani hot spring (1)	1.5 ± 0.5
Owakidani hot spring (2)	0.7 ± 0.1
Mt Ontakesan	0.8 ± 0.1
Mt Satsuma-Iojima	1.8 ± 0.6
White Island (New Zealand)	2.6 ± 1.6
Lake Nyos (Cameroon)	
150 m below lake surface	0.4 ± 0.2
125 m below lake surface	4.8 ± 1.2
Lake Kuchaitium (Cameroon)	3.6 ± 0.5

CONCLUSION

We attempted using ^{14}C as a tracer for investigating the circulation of underground carbon and water in geothermal fields using AMS. We studied sampling methods of volcanic gas and the sample preparation method of the carbon target for AMS while minimizing contamination by modern carbon. The results can be summarized as follows:

- Methods for sampling of volcanic gas and for preparing carbon samples for AMS measurements were developed with a detection limit of 0.16 ± 0.05 pMC for measuring ^{14}C in the CO_2 in volcanic gas.
- The Japanese fumarolic gas samples included carbon originating from groundwater as modern carbon on the order of a few pMC in the CO_2 component.
- Some data suggest the possibility of estimating the degree of mixing between groundwater and geothermal fluid from the ^{14}C content in the volcanic gas.
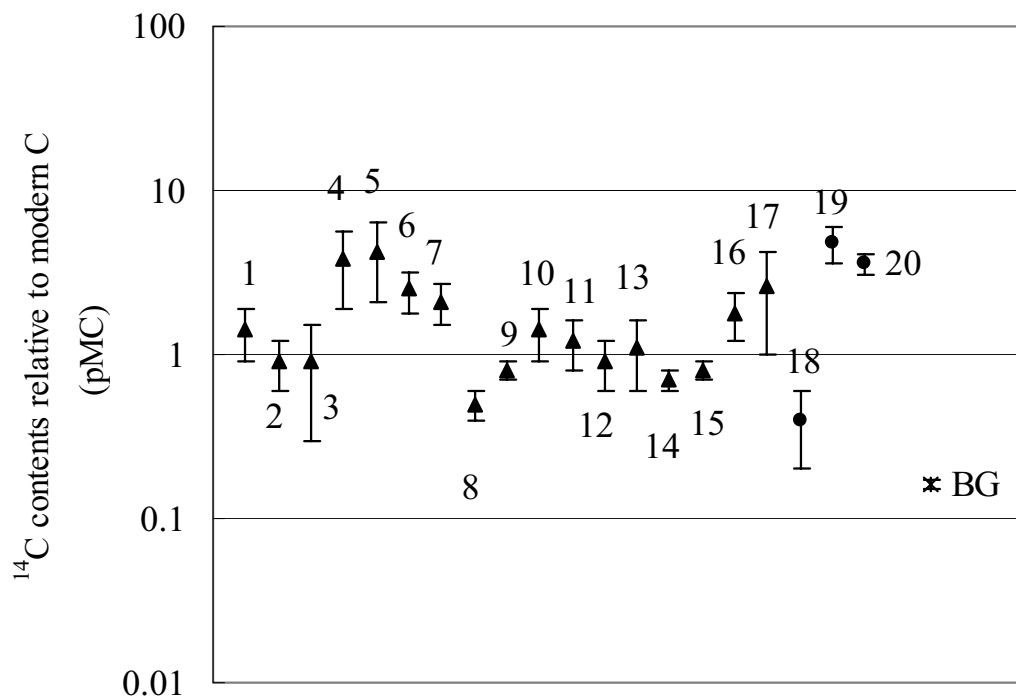
Figure 4 Results of ^{14}C measurement in volcanic gas (triangles: fumarolic gas; circles: hot spring gas): 1: Mt Usu I-crater nr 2 600 °C; 2: Mt Usu I-crater nr 4; 3: Mt Usu I-crater 480 °C; 4: Mt Usu I-crater 445 °C; 5: Mt Usu Kousu 370 °C; 6: Mt Hokkaido-Komagatage; 7: Mt Nasudake; 8–12: Mt Kusatsu-Shiranesan Kitagawa fumarole; 13–14: Mt Hakoneyama Owakidani hot spring; 15: Mt Ontakesan; 16: Mt Satsuma-Iojima; 17: White Island; 18: Lake Nyos at 150 m depth; 19: Lake Nyos at 125 m depth; 20: Lake Kuchaitium.

ACKNOWLEDGMENTS

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