Interaction between magmatic fluid and meteoric water, inferred from $^{18}O/^{16}O$ and $^{36}Ar/H_2O$ ratios of fumarolic gases at the Kusatsu Shirane volcano, Japan

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Fumarolic gases from the Kusatsu Shirane volcano, Japan were analyzed for the content and isotopic compositions of H_2O, the abundances and isotopic compositions of noble gas. The observed $\delta^{18}O$ and $^{36}Ar/H_2O$ ratios could not be explained by an existing hydrothermal model in which a mixing between magmatic vapor (MAV) and meteoric water (ASW), a single-step separation to vapor and liquid phases and a subsequent partial H_2O vapor removal from the vapor phase have been considered. We constructed a revised model in which two-step mixing-separation and a subsequent partial H_2O vapor removal by condensation were considered. In the model, the first step was the mixing between MAV and ASW, and a subsequent separation to a primary vapor and liquid phases. In the secondary step, the primary vapor mixed with another fluid which has a $\delta^{18}O$ lower than the primary vapor phase and a low $^{36}Ar/H_2O$ ratio relative to ASW. The mixture separates to secondary vapor and liquid phases. The fluid with low $^{36}Ar/H_2O$ ratio could be ASW partially vaporized in the geothermal area. The secondary vapor ascended and discharged as fumarolic gas. In the ascending process, the secondary vapor suffers a partial H_2O vapor removal by condensation in various degrees.

1. Introduction

Mt. Kusatsu Shirane (lat. 36°37′11″, long. 138°32′06″) located in the central part of Honshu Island, Japan is an active stratovolcano. An active crater lake called Yugama is situated on the summit of the volcano (Fig. 1). Since the beginning of the 19th century, the style of eruption has been steam explosion and the eruptions have been limited to around the crater lakes. In 1976, a small-scale steam explosion occurred in a crater beside the Yugama crater. Five steam explosions were observed in Yugama in 1982 to 1983 (Soya *et al.*, 1983). The presence of fumarolic gases on the northern flank of the Kusatsu Shirane volcano were thought to have been caused by the leakage of the vapor phase in a hydrothermal reservoir (Ohba *et al.*, 2000). The hydrothermal reservoir is considerd as the source of steam explosive eruptions at Kusatsu Shirane (Fac. of Eng., Tokyo Inst. Tech. *et al.*, 1983). Before the eruption in 1976, Ossaka *et al.* (1980) detected an increase in SO_2/H_2S ratio of fumarolic gas. However, no increase in the SO_2/H_2S ratio was detected prior to the eruption of 1982/1983. The investigation of fumarolic gas could be a key to the prediction of an eruption. To make a prediction, we need to understand what is the cause of changes in the chemical and isotopic compositions of fumarolic gases.

The chemical components in fumarolic gases, such as H_2S and SO_2, have chemical reactivity, then the concentration will be altered during the ascension from the reservoir to the surface by chemical reaction and phase changes etc. In a

hydrothermal system, the isotopic compositions, such as δD of H_2 and H_2O, and $\delta^{13}C$ of CO_2 and CH_4, could be altered through chemical processes (Hoefs, 1980; Taylor, 1986). To the contrary, noble gases are chemically inert, and their concentrations in fumarolic gases are controlled by the concentrations in the sources and physical processes, such as the distribution between vapor and liquid phases. The data of the noble gas and major components and elemental ratios, if we are to take full advantage of both features, may give realistic constraints on the physical and chemical processes in hydrothermal systems. In this study, we propose a quantitative hydrothermal model for the Kusatsu Shirane volcano based on $^{36}Ar/H_2O$ and $^{18}O/^{16}O$ ratios of water vapor in fumarolic gases.

2. Sampling and Analytical Method

Fumarolic gases were sampled in a geothermal area situated on the northern flank of the Kusatsu Shirane volcano (Fig. 1). The fumarolic area is located at an elevation of around 2000 m and it was in this area that we carried out fumarolic gas sampling at 15 fumaroles (Fig. 1). The fumaroles show a variety in gas fluxes. They were classified into the following three groups based on the sound generated by the discharge and appearance of gas discharge: (1) Strong – a loud sound like a jet engine discernible over a distance of several hundred meters; (2) Medium – a quiet sound. The position of the fumarole can be confirmed even from far away; (3) Weak – no sound is discernible. Under the condition of low humidity, the Weak fumarolic gas is difficult to identify from far away. Among the fumaroles used for sampling, only the N10 fumarole was classified as being
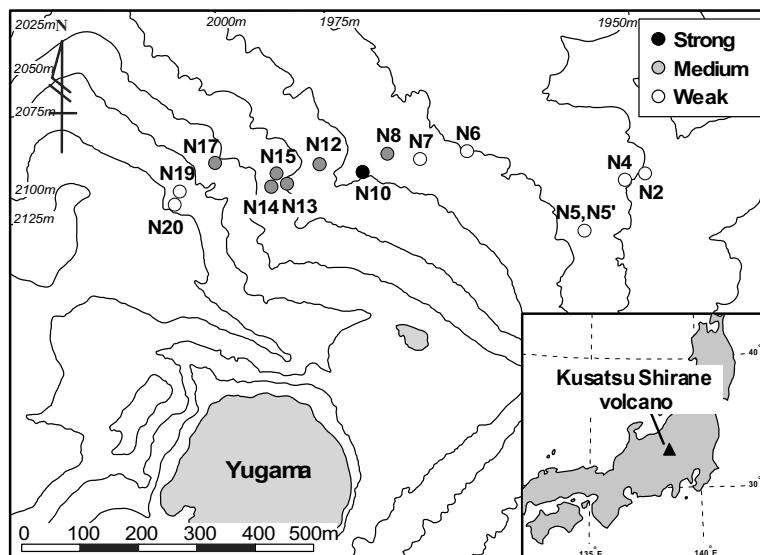
Fig. 1.   Distribution of fumaroles on the northern flank of the Kusatsu Shirane volcano, Japan. The Strong, Medium and Weak in the legend indicate a scale of gas discharge based on sound and appearance.

Strong. The Weak fumaroles are distributed in the eastern and western ends of geothermal area.

The fumarolic gases were sampled through a titanium pipe and absorbed into a 5M KOH solution using the procedure of Ozawa (1968) and Giggenbach and Goguel (1989). In order to analyze the major components of the fumarolic gases, a glass syringe was filled with 20ml of 5M KOH before sampling. The water vapor condensed in the syringe and the acid components were dissolved in an alkaline solution. The increment in the volume of the KOH solution was attributed to the amount of H_2O vapor. The inert gases (e.g. noble gas, H_2, N_2, O_2, and CH_4) which do not react with the KOH solution, remained in the syringe as a gaseous phase so-called residual gas. The helium concentration in the residual gas was determined by a gas chromatograph with TCD. A fumarolic gas condensate (H_2O vapor) was collected with a water-cooled double tubing condenser. The D/H and $^{18}O/^{16}O$ ratios of condensate were determined using a stable isotope mass spectrometer (Thermo Quest, MAT 252) using zinc metal reduction (Coleman *et al.*, 1982) and the CO_2-H_2O equilibrium method (Epstein and Mayeda, 1953), respectively. For noble gas analysis, a fumarolic gas was sampled by an evacuated bottle equipped with a Teflon stopcock containing 20ml 5M KOH solution (Giggenbach and Goguel, 1989). The residual gas left in the headspace of the bottle was transferred to a glass ampoule with a breakable seal by a vacuum line and introduced into a purification system. The abundance and isotopes of noble gas were measured with a modified VG 5400 mass spectrometer. Details of the purification procedure and measurement for the noble gas have been described by Aka *et al.* (2001).

We have determined the abundance and isotope ratios of He, Ne, Ar, Kr and Xe in fumarolic gas. Argon showed the highest concentration among the five noble gases in fumarolic gas with a small analytical error. Although ^{40}Ar was the isotope with the highest abundance among the three stable Ar isotopes, we selected ^{36}Ar for discussion because it

receives no contribution from radiogenic and fissogenic components, and the magmatic ^{36}Ar is expected to be very small. The upper mantle (primordial magma) has been depleted in ^{36}Ar because volatiles were distributed into the atmosphere in the early stages of the Earth's evolution and the recycling of ^{36}Ar in the upper mantle by subduction of the plate is limited (Ozima and Podosek, 2002), suggesting a substantially limited magmatic ^{36}Ar relative to the atmospheric ^{36}Ar. The $^{36}Ar/H_2O$ ratio of the magmatic component can be approximated to be zero in comparison with that of meteoric component. As will be shown later, this assumption enables a simple modeling of hydrothermal system.

3.   Results

The concentration of H_2O and ^{36}Ar, δD_{SMOW} and $\delta^{18}O_{SMOW}$ of H_2O vapor of fumarolic gases are shown in Table 1 together with the outlet temperature of gas and the scale of gas discharge. The ^{36}Ar concentration was estimated from the $^{36}Ar/^4He$ ratio in the residual gas sampled by the evacuated bottle and the helium concentration in residual gas sampled using the glass syringe method. In this estimation, we assumed that the concentration of helium in the evacuated bottle is equal to that of helium in the glass syringe. The outlet temperature of N10 fumarole was higher than $100°C$, whereas temperatures of the other fumaroles were nearly $93°C$, which is the boiling point of pure water at the altitude of the fumarolic area. In all samples, H_2O was the major component with a concentration more than 980 000 μmol/mol, whereas noble gases were minor components. The amount of air contamination during the sampling was less than 5% relative to the residual gas with a few exceptions, the contamination of which was about 13%.

The δD and $\delta^{18}O$ of fumarolic gas condensates show -134 to -49‰ and -20.6 to -4.1‰ to SMOW (Table 1), respectively. There is a linear trend between δD and $\delta^{18}O$ (Fig. 2). However, the trend is different from the meteoric water line ($\delta D = 8 \times \delta^{18}O + 16$) and also different from the mix-

Table 1. Chemical and isotopic compositions of fumarolic gases in Kusatsu Shirane volcano.

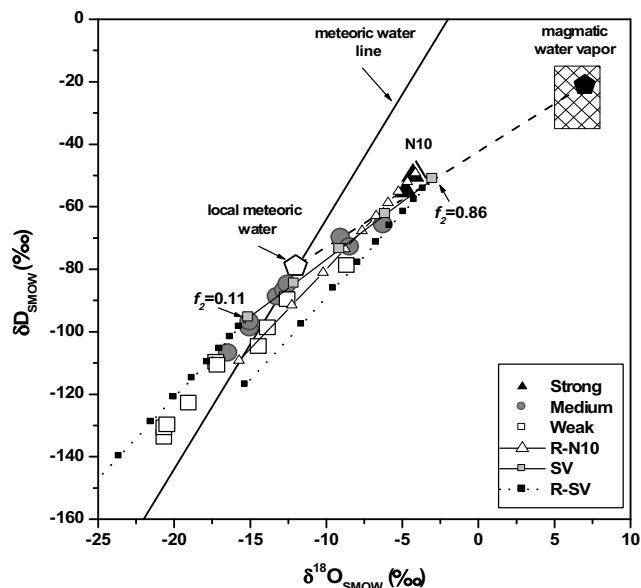| Name	Date	Temp.	H_2O	^{36}Ar	δD	$\delta^{18}O$	scale of gas
	mm/dd/yy	°C	μmol/mol		‰		discharge
N2	08/03/00	93.6	984401	1.64×10^{-3}	-110	-17.2	Weak
N4	07/27/00	93.6	987861	0.65×10^{-3}	-90	-12.5	Weak
N4	07/19/01	93.6	991026	0.51×10^{-3}	-79	-8.6	Weak
N5	10/26/01	93.7	991095	0.52×10^{-3}	-99	-13.8	Weak
N5'	10/26/01	93.6	989594	0.65×10^{-3}	-105	-14.4	Weak
N6	10/26/01	93.4	982853	0.78×10^{-3}	-123	-19.0	Weak
N7	08/04/00	93.3	986317	2.41×10^{-3}	-134	-20.6	Weak
N7	07/02/01	93.3	987053	1.16×10^{-3}	-131	-20.6	Weak
N8	07/27/00	93.6	990138	0.38×10^{-3}	-70	-9.0	Medium
N10	08/01/00	102.6	990132	0.39×10^{-3}	-55	-4.8	Strong
N10	05/22/01	105.2	990728	0.36×10^{-3}	-49	-4.1	Strong
N10	10/27/01	103.3	991736	0.43×10^{-3}	-50	-4.3	Strong
N12	08/01/00	93.4	989206	0.69×10^{-3}	-73	-8.4	Medium
N12	07/19/01	93.4	990379	0.48×10^{-3}	-66	-6.2	Medium
N13	08/01/00	93.3	986235	0.22×10^{-3}	-89	-13.2	Medium
N14	08/04/00	93.6	987782	0.33×10^{-3}	-99	-15.0	Medium
N14	07/24/01	93.6	989338	0.47×10^{-3}	-97	-15.0	Medium
N15	08/04/00	93.3	987664	0.60×10^{-3}	-107	-16.4	Medium
N17	09/19/00	93.3	986478	0.74×10^{-3}	-87	-12.7	Medium
N17	07/24/01	93.6	980996	0.53×10^{-3}	-85	-12.5	Medium
N19	07/24/01	93.1	988656	0.51×10^{-3}	-111	-17.1	Weak
N20	09/19/00	93.2	984552	0.97×10^{-3}	-130	-20.4	Weak

Fig. 2. Isotope ratio of H_2O vapor in fumarolic gas. The hatched area indicate the range of magmatic water vapor for volcanoes on the Japan Island arc, which is −15 to −35‰ for δD and +5 to +8‰ for $\delta^{18}O$ (Kusakabe and Matsubaya, 1986). The SV in the legend indicates the secondary vapor. The f_2 represents the mass fraction of the secondary vapor. R-N10 and R-SV represent the change in δD and $\delta^{18}O$ due to the partial removal of H_2O vapor by condensation at 93°C starting from the composition of N10 and the secondary vapor, respectively.

ing line between the magmatic water vapor (Kusakabe and Matsubaya, 1986) and the local meteoric water around the Kusatsu Shirane volcano (Ohba *et al.*, 2000), the δD and $\delta^{18}O$ of which is −79‰ and −12‰, respectively. The $\delta^{18}O$ of magmatic water vapor for the Kusatsu Shirane volcano was assumed to be +7‰, because $\delta^{18}O$ of magmatic water was controlled by the $\delta^{18}O$ of magma. Although no $\delta^{18}O$ data for the lava from Kusatsu Shirane has been reported, the $\delta^{18}O$ of lava from the Asama and Yatsugatake volcanoes were +7.1‰ and +6.8‰, respectively (Matsuhisa, 1979; Matsuhisa and Kurasawa, 1983). As the two volcanoes are located close to Kusatsu Shirane, +7‰ was assumed to be the $\delta^{18}O$ of magma for the volcano. The δD of magmatic water vapor was assumed to be −21‰, which is consistent with the hydrothermal model of Ohba *et al.* (2000). The assumed δD and $\delta^{18}O$ of magmatic water vapor are in the same range of magmatic water vapors from other volcanoes in the Japan Island arc, which is −15 to −35‰ for δD and +5 to +8‰ for $\delta^{18}O$ (Kusakabe and Matsubaya, 1986). The N10 fumarole shows the δD and $\delta^{18}O$ to be higher than the local meteoric water, and it is plotted on the mixing line between magmatic water and local meteoric water. The other samples are plotted outside the mixing line, and are depleted of D and ^{18}O relative to N10. Especially, the depletion is significant for the Weak fumaroles, the δD and $\delta^{18}O$ of which are lower than the local meteoric water.

The $^{36}Ar/H_2O$ molar ratios of fumarolic gases were 2.2×10^{-10} to 2.4×10^{-9}. The fumarolic gases, except for the Weak fumaroles, show a $^{36}Ar/H_2O$ ratio lower than 7.4×10^{-10}, which is the $^{36}Ar/H_2O$ ratio of air-saturated water (ASW) calculated by using Henry's constants of Ar (Harvey and Sengers, 1990) at 10°C, the partial pressure of ^{36}Ar at the local atmospheric pressure (795 hPa) on fumarolic area, the Ar concentration (9340 ppm), and $^{40}Ar/^{36}Ar$ ratio (296.0) of the air (Ozima and Podosek, 2002).

4. Discussion
4.1 D/H and $^{18}O/^{16}O$ ratios of H_2O in fumarolic gases

As shown in Fig. 2, the isotope ratios of H_2O have a wide variation. The highest δD and $\delta^{18}O$ of N10 fumarole suggest a large magmatic contribution to N10 fumarole. Ohba *et al.* (2000) studied the lake water and hot spring waters of the Kusatsu Shirane volcano in terms of δD, $\delta^{18}O$ and Cl^- concentrations. They proposed a hydrothermal model in which a high temperature magmatic fluid is mixed with a low enthalpy meteoric water, and hydrothermal reservoir separated in vapor and liquid phases, is created at 200°C. According to the model, the fumarolic gas on the northern flank of Kusatsu Shirane is a leakage of the vapor phase from the reservoir. If N10 represents the compositions of the vapor phase, the variations in δD and $\delta^{18}O$ for other fumaroles might be explained by a H_2O vapor loss, because the temperatures of gases other than N10 fumarole are close to the local boiling point and the remaining water vapor should be depleted in D and ^{18}O if H_2O is lost by condensation. When the removal by condensation occurs in an open system, the isotope ratio of H_2O vapor follows the Rayleigh equation as

$$\delta = (\delta_i + 1000) f^{\alpha-1} - 1000, \qquad (1)$$

where δ is the isotope ratio in delta notation for H_2O vapor, and f is the fraction of H_2O left in the vapor phase. The subscript i denotes the initial values of δ. Alpha is the fractionation factor for D/H or $^{18}O/^{16}O$ between liquid and vapor (Horita and Wesolowski, 1994). The temperature during this process is assumed to be 93°C, which is the boiling point of water at the altitude of the sampling site. The changes in δD and $\delta^{18}O$ by condensation from the composition of N10 are shown in Fig. 2 as the R-N10 line. Although some data are
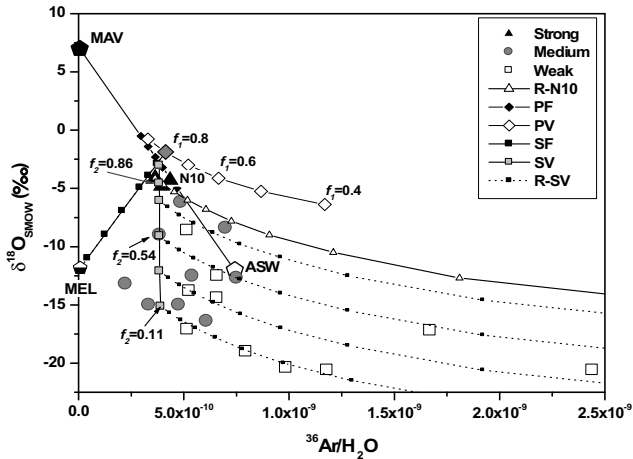
Fig. 3. The $\delta^{18}O$ and $^{36}Ar/H_2O$ ratio of fumarolic gases and modeled vapors. The f_1 and f_2 represent the mass fraction of the primary and secondary vapor, respectively. R-N10 and R-SV represent the change due to the partial removal of H_2O vapor by condensation starting from the compositions of N10 and the secondary vapor, respectively. PF, PV, SF and SV in the legend indicate the primary fluid, primary vapor, secondary fluid and secondary vapor, respectively.
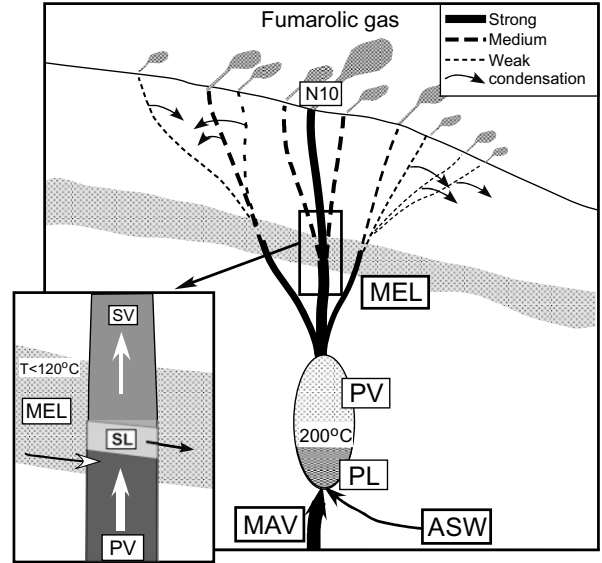

Fig. 4. The two-step mixing-separation model for the hydrothermal system on the northern flank of the Kusatsu Shirane volcano. MAV, ASW, PL, PV, SL, SV and MEL are magmatic vapor, air saturated meteoric water, primary liquid, primary vapor, secondary liquid, secondary vapor, and partially vaporized meteoric liquid water, respectively.

located close to the line, several data deviate from the line, suggesting the insufficiency of the hydrothermal model by Ohba *et al.* (2000).

4.2 A model for the hydrothermal system

The $^{36}Ar/H_2O$ ratio of fumarolic gas should change as well as the isotope ratio by mixing and condensation processes. Figure 3 shows the relation between the $\delta^{18}O$ and the $^{36}Ar/H_2O$ ratios of fumarolic gases, together with two possible end members: (1) magmatic vapor (MAV), and (2) air saturated meteoric water (ASW). The $^{36}Ar/H_2O$ ratio of the magmatic end member (MAV) can be estimated by the abundance of ^{36}Ar and the content of H_2O in the magma. We used the data obtained for the Unzen volcano (Shimabara peninsula, Japan), because the ^{36}Ar and H_2O content of Kusatsu Shirane's magmas have not been estimated, whereas Unzen is the only volcano in the Japanese Island arc where ^{36}Ar and H_2O concentrations have been estimated or directly measured. The concentration of non-atmospheric ^{36}Ar trapped in phenocrysts of lava from the Unzen volcano is 0.414×10^{-9} cm³ STP/g (Hanyu and Kaneoka, 1997). The concentration is in the same range of concentration as for MORB (0.053×10^{-9} to 0.66×10^{-9} cm³ STP/g; Ozima and Zashu, 1983; Sarda and Graham, 1990; Hiyagon *et al.*, 1992; Niedermann *et al.*, 1997). The concentration of H_2O in the magma of the Unzen volcano has been estimated to be 6 wt% (Kusakabe *et al.*, 1999). Combining these values, the $^{36}Ar/H_2O$ ratio in magma is estimated to 5.6×10^{-12}. This value is significantly lower than the ASW value (7.4×10^{-10}). We employ the $^{36}Ar/H_2O$ ratio of the Unzen volcano (5.6×10^{-12}) for the magmatic vapor (MAV) of Kusatsu Shirane.

If the removal of H_2O vapor takes place in the fumarolic gas of N10, the change in $^{36}Ar/H_2O$ ratio is expressed as

$$^{36}Ar/H_2O = (^{36}Ar/H_2O)_i f^{\beta-1}, \qquad (2)$$

where β is the distribution coefficient for Ar between liquid and vapor calculated by Henry's constant (Harvey and

Sengers, 1990). The changes in the $\delta^{18}O$ and $^{36}Ar/H_2O$ ratios by condensation are shown in Fig. 3 as the R-N10 line. The trend is quite different from the distribution of observed fumarolic gases. Although N10 is close to the mixing line between MAV and ASW, other fumarolic gases are plotted below that line. If the fumarolic gases, except for N10 fumarole, suffer a partial condensation under an open system, $\delta^{18}O$ and $^{36}Ar/H_2O$ ratios should be distributed on the right side of the mixing line. The distribution of gases also suggests that a simple mixing between MAV and ASW and a subsequent partial condensation is insufficient to explain the observed data.

For the construction of a quantitative hydrothermal model, we assume that the magmatic vapor (MAV) has an enthalpy equivalent to that of H_2O vapor at 900°C at 1 bar. The temperature was assumed to be a representative temperature of andesitic magma. The enthalpy of the local meteoric water (ASW) is assumed to be the enthalpy of water at 10°C at 1 bar. Here, we define a fluid for mixture of MAV and ASW as 'the primary fluid'. We also assume that the primary fluid separates to vapor and liquid phases at 200°C (Ohba *et al.*, 2000) and that the bulk enthalpy of fluids is preserved during both mixing and separation. This process is schematically shown in Fig. 4. The enthalpy of the primary fluid is calculated using the following equation:

$$H_{PF} = H_{MAV}F_1 + H_{ASW}(1 - F_1), \qquad (3)$$

where H and F_1 denote the enthalpy and the mass fraction of MAV, respectively. The subscript PF indicates the primary fluid. We define 'the primary vapor and liquid' to be the vapor and liquid phases produced by the separation, respectively. The enthalpy of the primary vapor and liquid phases created by separation obey the following equation:

$$H_{PF} = H_{PV}f_1 + H_{PL}(1 - f_1), \qquad (4)$$

where f_1 is the mass fraction of the primary vapor. The subscript PV and PL represent the primary vapor and liquid, respectively. The H_{PV} and H_{PL} are assumed to be the enthalpy of saturated H$_2$O vapor and liquid at 200°C, respectively. Combining Eqs. (3) and (4), f_1 can be obtained as a function of F_1. The preservation in terms of δ^{18}O and ^{36}Ar during the mixing and separation is expressed as

$$\delta^{18}\text{O}_{PF} = \delta^{18}\text{O}_{MAV}F_1 + \delta^{18}\text{O}_{ASW}(1 - F_1), \quad (5)$$

$$\delta^{18}\text{O}_{PF} = \delta^{18}\text{O}_{PV}f_1 + \delta^{18}\text{O}_{PL}(1 - f_1), \quad (6)$$

$$(^{36}\text{Ar/H}_2\text{O})_{PF} = (^{36}\text{Ar/H}_2\text{O})_{MAV}F_1$$
$$+ (^{36}\text{Ar/H}_2\text{O})_{ASW}(1 - F_1), \quad (7)$$

$$(^{36}\text{Ar/H}_2\text{O})_{PF} = (^{36}\text{Ar/H}_2\text{O})_{PV}f_1$$
$$+ (^{36}\text{Ar/H}_2\text{O})_{PL}(1 - f_1). \quad (8)$$

In a rigorous meaning, F_1 and f_1 should be the fraction of H$_2$O. However, in practice, F_1 and f_1 can be the fraction of each fluid, because the amount of ^{36}Ar is much smaller than H$_2$O. The equilibrium between the liquid and vapor phases are expressed as

$$\alpha_1 = \frac{\delta^{18}\text{O}_{PL} + 1000}{\delta^{18}\text{O}_{PV} + 1000}, \quad (9)$$

$$\beta_1 = \frac{(^{36}\text{Ar/H}_2\text{O})_{PL}}{(^{36}\text{Ar/H}_2\text{O})_{PV}}, \quad (10)$$

where α_1 and β_1 is the fractionation factor and the distribution factor between liquid and vapor at 200°C, respectively. Solving Eqs. (5), (6) and (9), and solving Eqs. (7), (8) and (10), the δ^{18}O and ^{36}Ar/H$_2$O ratios can be obtained for the primary vapor, respectively, with the parameter F_1 or f_1, the fraction of the magmatic vapor or primary vapor. The δ^{18}O and ^{36}Ar/H$_2$O ratios of the primary vapor are drawn as a curve in Fig. 3. The distribution of fumarolic gases is inconsistent with the primary vapor curve, even if a subsequent partial condensation takes place. The contribution of the unknown end member seems to be necessary to explain the δ^{18}O and ^{36}Ar/H$_2$O ratios of fumarolic gases. The δ^{18}O and ^{36}Ar/H$_2$O ratios of the unknown end member should be lower than that of the primary vapor.

For the unknown end member, we propose a partially vaporized ASW. Because of the low solubility of noble gas in the liquid phase, most of the fraction of the noble gas dissolved in ASW should escape to a vapor phase during the partial vaporization. According to Kagiyama *et al.* (1992), a radiative heat discharge has been observed in the geothermal area of the Kusatsu Shirane volcano. Thus, a groundwater of meteoric origin would be heated and partially vaporized. According to calculations, 0.2 to 0.4% of vaporization at a temperature of between 93°C (local boiling point) and 200°C (temperature of primary reservoir) expels about 99% of ^{36}Ar in ASW under open system conditions. We define the liquid phase of partial vaporized local meteoric water as MEL (MEteoric Liquid water). Here we propose a secondary process, as shown in Fig. 4, where the primary vapor goes through the layer of MEL and mixes with it. We define the mixture as a 'secondary fluid', which is separated to a 'secondary vapor and liquid'. The temperature of MEL is unknown, although, it should be higher than the local boiling

point (93°C) and lower than 200°C, because MEL would be distributed at a depth shallower than the primary fluid. Here, the temperature of MEL and the secondary fluid is temporarily set to be 110°C, which is slightly higher than N10. Assuming an isenthalpic rising for the primary vapor, the mixing and separation processes are described as

$$H_{SF} = H_{PV}F_2 + H_{MEL}(1 - F_2), \quad (11)$$

$$H_{SF} = H_{SV}f_2 + H_{SL}(1 - f_2), \quad (12)$$

where F_2 and f_2 are the fraction of the primary vapor and the fraction of the secondary vapor, respectively. The subscripts SF, SV and SL represent the secondary fluid, vapor, and liquid, respectively. The preservation in terms of δ^{18}O and ^{36}Ar/H$_2$O ratio are described as

$$\delta^{18}\text{O}_{SF} = \delta^{18}\text{O}_{PV}F_2 + \delta^{18}\text{O}_{MEL}(1 - F_2), \quad (13)$$

$$\delta^{18}\text{O}_{SF} = \delta^{18}\text{O}_{SV}f_2 + \delta^{18}\text{O}_{SL}(1 - f_2), \quad (14)$$

$$(^{36}\text{Ar/H}_2\text{O})_{SF} = (^{36}\text{Ar/H}_2\text{O})_{PV}F_2$$
$$+ (^{36}\text{Ar/H}_2\text{O})_{MEL}(1 - F_2), \quad (15)$$

$$(^{36}\text{Ar/H}_2\text{O})_{SF} = (^{36}\text{Ar/H}_2\text{O})_{SV}f_2$$
$$+ (^{36}\text{Ar/H}_2\text{O})_{SL}(1 - f_2). \quad (16)$$

The equilibrium between the vapor and liquid phases is expressed as

$$\alpha_2 = \frac{\delta^{18}\text{O}_{SL} + 1000}{\delta^{18}\text{O}_{SV} + 1000}, \quad (17)$$

$$\beta_2 = \frac{(^{36}\text{Ar/H}_2\text{O})_{SL}}{(^{36}\text{Ar/H}_2\text{O})_{SV}}, \quad (18)$$

where α_2 and β_2 are fractionation and distribution factors at 110°C. The δ^{18}O of ASW can be used for the δ^{18}O of MEL, because if the vaporization is limited, the change in δ^{18}O is negligible. For example, 0.3% vaporization at 110°C produces a 0.01% decrease in δ^{18}O of ASW. The ^{36}Ar/H$_2$O ratio of MEL can be approximated to be zero because only 0.3% vaporization at 110°C reduces the ^{36}Ar/H$_2$O ratio below 9.19×10^{-13}, which is only 0.12% of ASW.

The δ^{18}O and ^{36}Ar/H$_2$O ratios of the secondary vapor are drawn as a curve in Fig. 3. The position of the secondary vapor (SV) curve can be moved by changing F_1 or f_1. If N10 represents the secondary vapor, namely, the SV curve overlaps N10, F_1, f_1, F_2, and f_2 are evaluated to be 0.56, 0.80, 0.80, and 0.86, respectively. The difference in the δ^{18}O of the secondary vapor is mainly produced by the difference in the mixing ratio between the primary vapor and MEL. The observed ^{36}Ar/H$_2$O ratios for fumarolic gases other than N10 are higher than the secondary vapor curve, except two fumarolic gases. The discrepancy can be explained by a partial vapor removal from the secondary vapor by condensation. The changes in the δ^{18}O and ^{36}Ar/H$_2$O ratios by the condensation are obtained by Eqs. (1) and (2), respectively, and expressed as curves in Fig. 3. Half of the Weak fumaroles are distributed rightward, relative to the Strong and Medium fumaroles, suggesting that the degree of vapor loss for the Weak fumaroles is generally higher than the Strong and Medium fumaroles. The SV curve in Fig. 3 was obtained assuming 110°C to be the temperature of MEL. If

the temperature of MEL increases, the SV curve shifts rightward and upwards. When the temperature exceeds 120°C, some fumarolic gases were located on the left side of the SV curve or located below the condensation curve, suggesting that 120°C is the upper limit of the temperature for MEL and secondary fluid.

The proposed two-step mixing-separation model was also consistent with the observed δD of H_2O vapor in fumarolic gas. Instead of drawing a figure similar to that in Fig. 3, the δD and $\delta^{18}O$ of secondary vapor with a partial condensation are plotted in Fig. 2. The observed data are included in the range of the partially condensed secondary vapor line in Fig. 2.

5. Conclusions

The variation in $\delta^{18}O$ of H_2O vapor in fumarolic gases from the Kusatsu Shirane volcano was −20.6 to −4.1‰ to SMOW. The $^{36}Ar/H_2O$ ratios of fumarolic gases were 2.2×10^{-10} to 2.4×10^{-9}, respectively. In order to explain the variation, a quantitative hydrothermal model was proposed. In the model, the fumarolic gas was generated from a magmatic vapor and meteoric water through two-step mixing-separation processes and subsequent condensation (Fig. 4). The first step is the mixing of a magmatic vapor (MAV) with local meteoric water saturated with air (ASW), and a subsequent separation to primary vapor and liquid phases. In the second step, the primary vapor mixes with a partial vaporized local meteoric water (MEL) whose $^{36}Ar/H_2O$ ratio is much lower than the ratio of ASW. The mixture subsequently separates into a secondary vapor and liquid. The secondary vapor discharges as fumarolic gas. However, the secondary vapor suffers a partial H_2O vapor removal by condensation, the degree of which is significant for a weakly discharging fumarolic gas.

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