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Trial of measuring hydrogen isotopic ratios of water vapor in fumarolic gas collected in a gas bag

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1. Introduction

Isotopic ratio of water vapor in fumarolic gas reflects geothermal structures where magmatic water is mixed with meteoric water, and it is one of the indicators which represent the state of volcanic activity. We are evaluating the method to collect volcanic gas with gas bag in order to develop the gas-collecting method using mobile vehicles such as an Unmanned Aerial Vehicle. Because the amount of water collected in a gas bag is little, we applied "Zn shot method"(Coleman et al., 1982) to reduce the water into H_2. However, the percentage of success of the reduction was low, so we reviewed the factor of our failure.

2. Fumarolic gas samples

We collected condensed water and gas samples from Kengamine fumarole in Mt.Mihara, Izu-Oshima. The samples are 100 mL water condensed from the fumarolic gas by iced-water, and gas collected in 10 L gas bag just above the fumarole (Bag 1, 2, 3), gas collected in 10 L gas bag about 10 m above the fumarole along slope (Bag 4, 5, 6) .The 2 micro L of the condensed water measured with microcyringe was packed into a reduction glass tube with Zn shots using a glass-line. Water samples in gas bags were also extracted and packed into the reduction tube in the same way. The maximum amount of water in the gas bag was estimated to be 10 micro L.

3. Experimental method

The reduction tube containing Zn shots and water was set into a mantle heater whose temperature was set to 490 to 495 deg C to reduce the water. The reduction time was set to 30 minutes. After reduction, Zn metal re-condensed on inside the tube like mirror. We judged the end of the reduction by appearance of the mirror. Hydrogen isotopic ratio of samples was measured on a mass spectrometer of Sercon, Geo20-20.

4. Results

Three samples of the condensed water were succeeded in reduction, and their hydrogen isotopic ratio were delta D_{SMOW}=-69 permil. This value is consistent with the result of Ohba(2007). The reduction of the sample of Bag 2 had not finished for 30 minutes heating. The reduction of the samples of Bag 5 and 6 also had not finished for 30 minutes heating, therefore the duration of reduction was extended for another 30 minutes. The isotopic ratio of Bag 5 sample is delta D_{SMOW}=-78 permil and that of the Bag 6 is -141 permil. There is wide difference between the isotopic values of 2 samples, though they had been collected in the same site.

5. Discussion

The results show that there were some problems in the processes of Zn shot method. The reduction processes have 3 steps, evaporation of Zn, diffusion of Zn vapor, and reduction of water. Every step can be hindered by excess water vapor pressure. We have estimated the influence of initial water content on the diffusion and reduction steps.The diffusion profile of Zn vapor was calculated for the two initial water contents; 2 micro L (proper amount), and 20 micro L (excess amount). We derived diffusion coefficients D of Zn from its mean free path for two cases. Using these D values, we calculated the profile of Zn vapor contents in the reduction tube by the finite difference method. The result shows there is little difference in the Zn content profiles between these two cases.Next, we estimated the equilibrium constant of the reduction at 500 degC, and calculated hydrogen partial pressure in equilibrium state for 2 and 20 micro L of water content. The result indicated that in both cases, hydrogen partial pressure nearly equals to total pressure.The results of our calculations suggest that, as far as Zn vapor is supplied from solid Zn, Zn vapor spread sufficiently within the tube, and all the water is reduced to be hydrogen. The remaining cause of failure in case of excess amount of initial water would be inhibition of Zn evaporation. When oxidation speed of Zn is faster than its evaporation speed, the surface of Zn liquid might be immediately covered with the film of ZnO.

Keywords: Zn shot method, water vapor, hydrogen isotope, fumarolic gas