

## ON THE CHEMICAL AND ISOTOPIC COMPOSITION OF FUMAROLIC GASES FROM KUJU VOLCANO, JAPAN

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### Introduction

Kuju volcano is one of the active volcanoes distributed on the volcanic belt crossing the northern Kyushu island of Japan. Kuju volcano is a complex of volcanic peaks. All of the peaks are the domes of andesitic lava except one peak of olivine-basalt. On the northern to eastern flank of Hosshou peak a persistent geothermal activity is present. Although the outlet temperature of a fumarole at the geothermal area increased up to 508°C in the 1960's, the recent fumarolic temperature is less than 350°C. Mizutani et al. (1986) investigated the chemical and isotopic composition of fumarolic gases from the geothermal area. According to their study, the <sup>18</sup>O/<sup>16</sup>O ratio of water vapor in the fumarolic gases was +10.6‰ to SMOW during the 1960's and it decreased in 1980's. The fumarolic gas with high <sup>18</sup>O/<sup>16</sup>O ratio during 1960's, contained CO gas with high concentration, indicating a high temperature at the source of gas.

### Eruption in 1995

On October 1995, a phreatic eruption took place on the eastern flank of Hosshou peak after 257 years of quiescent. Several fumarolic vents were created at the eruption, with sub linear arrangement suggesting the potential of a fault structure. At the eruption no significant crater-like topography was formed around the vents. At the initial stage of eruption in 1995, volcanic ash was involved in the fumarolic gases from new vents, although most part of the ejected ash was composed of altered rock debris and clay minerals. In the ash, small amounts of juvenile material, fresh glassy fragments were recognized, showing a direct contribution of magma. The gas sampling was only carried out at one vent "b", because the dynamic pressure of gas from other

vents were too strong to keep safety. The gas sampling from the b-vent was carried out periodically to investigate the change in the chemistry of gas and to evaluate the volcanic activity.

### Gas Chemistry

The volcanic gases from the b vent has the chemical composition significantly different from the gases from the old geothermal area. The HCl and SO<sub>2</sub> concentration is much low in the gas from new vent and a high concentration in CO. The outlet temperature of gas from b vent was low, about 130°C at just after the eruption, and it increased gradually until March 1998, when the maximum temperature, 272°C was recorded. During the above period no significant change was recognized in the D/H and <sup>18</sup>O/<sup>16</sup>O ratios of water vapor in gas. Then the increase in temperature would not be due to the change in the mixing ratio between a high temperature magmatic gas and cold meteoric water, and it would be due to the heating up of gas channel which was newly created at the eruption in 1995.

The <sup>13</sup>C/<sup>12</sup>C ratio of CO in the gas from b-vent is much lower than the ratio of CO<sub>2</sub>. The apparent equilibrium temperature for the <sup>13</sup>C exchange reaction between CO<sub>2</sub> and CO is given to be 780~1060°C based on the fractionation factor by Richet et al.(1997), suggesting a high temperature at the source of gas.

The gases from new vent shows a large variation in CO<sub>2</sub>/H<sub>2</sub>O ratio with a limited variation in the D/H or <sup>18</sup>O/<sup>16</sup>O ratio of water vapor. These features can be modeled to be a partial condensation of water vapor in the gas from new vent. The condensation is the result of conductive cooling by a cold wall of gas channel.

The depletion of HCl and SO<sub>2</sub> in the gas from b-vent will be brought by the distribution to a liquid phase. For HCl, a simple dissolution reaction,

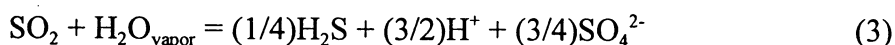


is responsible to the distribution. However the distribution factor obtained by Simonson and Palmer (1993) prevents the liquid phase from the higher molality of HCl relative to vapor phase over 250°C. The reduction of H<sup>+</sup> in liquid phase increases the Cl<sup>-</sup> distribution to liquid phase, therefore a subsequent interaction of liquid phase, which is acidic because of the HCl uptake, with minerals in rock is necessary for the depletion of HCl in gas.

For the depletion of SO<sub>2</sub> in the gas from b vent, two reactions may be responsible. One is the deposition of native sulfur, described as



The above reaction depends on the temperature and the total pressure of gas. The gases from b-vent before 1997 require a pressure less than 100 bar at the outlet temperature for the saturation in terms of native sulfur. However the pressure increases over a reasonable value for the gases after 1997. For the gases after 1997, the hydrolysis of SO<sub>2</sub> gas,



will be responsible to the depletion. The molality of SO<sub>4</sub><sup>2-</sup> should exceed the molality of (SO<sub>2</sub> + H<sub>2</sub>S) in gas phase at the outlet temperature in order to reduce SO<sub>2</sub> from gas phase. The high H<sup>+</sup> activity in liquid phase prevents the efficient SO<sub>2</sub> transfer to liquid phase, therefore an interaction of the acidic liquid phase with minerals in rock is also necessary for the depletion of SO<sub>2</sub> gas. An estimation based on a thermochemical data base shows that the pH of liquid phase should be higher than 5 in order to obtain enough SO<sub>4</sub><sup>2-</sup> molality in liquid phase. The application of SO<sub>2</sub> hydrolysis is also valid for the gases before 1997. For the gases before 1997, the limitation in pH of liquid phase is loosened to 3.

### References

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