

A PRELIMINARY STUDY OF ISOTOPE COMPOSITION OF NITROGEN IN FUMAROLIC AND  
GEOTHERMAL GASES, JAPAN

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Nitrogen gas is commonly observed in fumarolic and geothermal gases as one of the major constituents among uncondensable gases (so called residual gas or R-gas;  $N_2$ ,  $H_2$ ,  $CH_4$ , Ar...) which were passed through NaOH solution to remove  $H_2O$ ,  $H_2S$ ,  $SO_2$ ,  $CO_2$  and so on. A part of the nitrogen gas must come from air due to contamination during gas sampling from fumaroles and geothermal wells. In contrast, the  $N_2/O_2$  ratio is usually higher than that of air (3.7) and nitrogen gas is a still major component of fumarolic and geothermal gases after correction of the air contamination based on that oxygen gas should be trace in magmatic gas. This implies that nitrogen gas is of deep origin. Recently, Kiyosu (1985) indicated that  $N_2/Ar$  and  $He/Ar$  ratios of fumarolic gases in Japan fall along a simple mixing line of two end members, air dissolved in groundwater and magmatic gas. The ratios increase with increasing degree of contribution of magmatic gas.

The magmatic gas in Japan is thought to be enriched in deuterium (-20 to -30 ‰ vs SMOW) compared to juvenile water (eg. Kusakabe et al., 1977) and is also enriched in  $^{34}S$  (+4 to +6 ‰; Ueda and Sakai, 1984) against mantle sulphur. Recently, Ueda et al. (1987) reported more negative  $\delta D$  value (-180 ‰) for magmatic water in dacite magma of Hakkoda area, northeast Japan. These isotope characteristic are important to discuss the origin of magma itself as well as magmatic gas under the Japanese island arc system. In contrast, no systematic study of isotope composition of nitrogen in fumarolic and geothermal gases in the world has been done in comparison with other gas components such as water, sulphur and carbon. In the past few years, the data for nitrogen isotope composition of igneous rocks and the mantle increase and show a positive  $\delta^{15}N$  value (average +7.5 ‰; eg. Exley et al., 1986). In this work, nitrogen isotope composition of fumarolic and geothermal gases from several volcanic fields in Japan were analyzed in order to evaluate the isotope composition of the deep-seated magma under the Japanese island arc.

The residual gases studied in this work has been collected by us and members of Tokyo Institute of Technology from several fumarolic fields (Showa-Shinzan, Nasu, Satsuma-Iwojima ...) and from geothermal fields such as Onuma, Akita. The chemical composition of these residual gases has been partly reported elsewhere. However, we analyzed them again for the checking, because some of the gas samples were collected 10-years ago. The nitrogen isotope determination of gas samples were done as follows; An aliquote of residual gas was first determined for their chemical compositions by a gas chromatographic method. Another aliquote (5 to 20 ml STP depending on the nitrogen content) was passed twice through  $CuO$  at  $900^\circ C$  to remove  $CH_4$  and  $H_2$  and transferred into a gas storage using charcoal. The nitrogen isotope composition was then measured by a mass spectrometer (Finnigan Mat DELTA-E). As mentioned above, the fumarolic and geothermal gas samples generally contain a small amount of oxygen gas due to air contamination. Therefore, the observed nitrogen isotope composition should be also corrected on the assumption that air nitrogen incorporated has a  $\delta^{15}N$  value of 0 ‰.

The major components of the residual gases studied are  $N_2$ ,  $H_2$  and  $CH_4$  and the other gases are trace. They vary from sample to sample even in the same locality. So far, 20 gas samples has been analyzed for their chemical and nitrogen isotope compositions. The  $\delta^{15}N$  value are -0.5 to +8 ‰ (average 2 ‰) and increase scatteringly with increasing the  $N_2/Ar$  ratios (from 40 to 900). The former  $N_2/Ar$  ratio is similar to that of air dissolved in groundwater. These results mean that the isotope fractionation between  $N_2$  in air and  $N_2$  dissolved in groundwater is small (Klots and Benson (1963) reported the  $^{15}N$  enrichment in air by 0.9 ‰) and that the nitrogen isotope of magmatic gas underneath Japan is at least enriched in  $^{15}N$ . In conclusion, it is not clear whether  $N_2$  of magmatic gas in Japan is heterogeneous in the isotope composition or the  $N_2$  gas comes from different sources such as  $N_2$  in magma and in sedimentary rocks overlying the magma. This is a preliminary report of our results and more gas samples are analyzing now and the origin of the  $N_2$  gas in the Japanese geothermal areas will be discussed in details.

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