Measurement of nitrogen and oxygen isotope ratios in considerably low nitrate concentration ice core samples

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Nitrate (NO_3^-) concentration in polar regions is caused by relevant stratospheric sources[1)], related extraterrestrial fluxes of energetic particles, and solar irradiation. In the Talos Dome ice core (Antaractica), NO_3^- data exhibit highly significant agreement with cosmic ray flux reconstructions[2)]. Nitrogen and oxygen isotope ratios ($\delta^{15}N$ and $\delta^{18}O$) of NO_3^- in the polar ice core are expected to reflect the difference of isotope fractionations through photochemical reactions in the stratosphere caused by cosmic ray and solar irradiation. Our final object is to clarify the history of solar activity and cosmic events, on the basis of precise analyses of $\delta^{15}N$ and $\delta^{18}O$ in the ice core. However, it is difficult to measure the isotope ratios of $\delta^{15}N$ and $\delta^{18}O$ in NO_3^- in the Antarctic ice core, because NO_3^- concentrations are low (typically < 20 μg l^{-1}) and the sample volume is limited.

In this study, we examined the method of measuring$\delta^{15}N$ and $\delta^{18}O$ with high sensitivity for 11 ice core samples from Dome Fuji drilled in 2010, corresponding to relatively high NO_3^- concentration (average 22.3 μg l^{-1}) using the denitrifier method[4)] and we successfully obtained accurate data. In this method, 10 ml of each sample was used and NO_3^- in sample water was quantitatively converted to N_2O, utilizing denitrifying bacteria (*Pseudomonas aureofaciens*) that lack N_2O-reductase. The isotopic composition of N_2O is then measured using the mass spectrometer (IsoPrime100) in RIKEN. The results of the measurements of $\delta^{15}N$ and $\delta^{18}O$ are summarized in Fig.1. Each sample is referenced to the internationally recognized standard USGS32, USGS34 and USGS35. In Fig. 2, the blue frame indicates the maximum and minimum values in the measured 11 ice core samples. These standards were diluted with ice core water in which NO_2^- and NO_3^- were removed using the ion exchange resin for minimizing the effect of the exchange of oxygen atoms between the nitrogen oxide intermediates and water[3)]. We corrected the background N_2O associated with the medium for bacteria, atmosphere and ice core water used for dilution of standard. The error of the $\delta^{15}N$ and $\delta^{18}O$ in 11 samples were calculated by the propagation of errors including uncertainties in the background and in sample measurement. The maximum errors of the $\delta^{15}N$ and $\delta^{18}O$ were ± 0.75‰ and ± 0.34‰, respectively.

The $\delta^{15}N$ and $\delta^{18}O$ range from 201.7‰ to 258.5‰ and from 45.9‰ to 64.1‰, respectively (Fig.2). The variations of $\delta^{15}N$ and $\delta^{18}O$ show 24% and 34% for 20% NO_3^- change, respectively. $\delta^{15}N$ values are inside a certain range except for one sample (201.7‰). High positive $\delta^{15}N$ values may be attributed to the nitrate post-depositional effect because of low accumulation rate in Dome Fuji[4)]. NO_3^- and $\delta^{18}O$ show significant correlation ($r = -0.69$, $p < 0.05$), while there is no correlation between NO_3^- concentration and $\delta^{15}N$.

We have successfully established the method to measure $\delta^{15}N$ and $\delta^{18}O$ of NO_3^-. Further detailed measurements are expected to contribute to elucidate the origin of NO_3^- produced by photochemical reactions in the stratosphere.

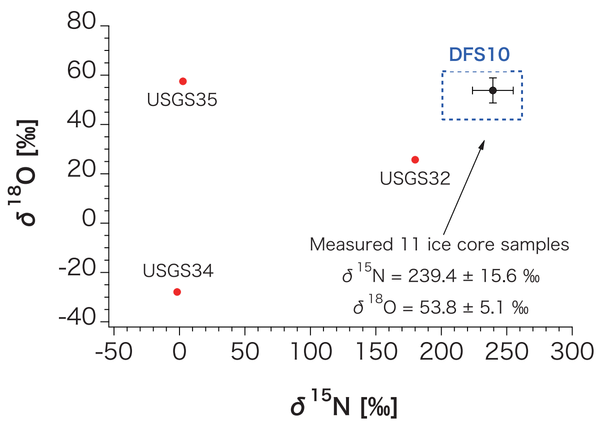

Fig. 1. The $\delta^{15}N$ and $\delta^{18}O$ of ice core samples and international standards USGS32, USGS34 and USGS35.

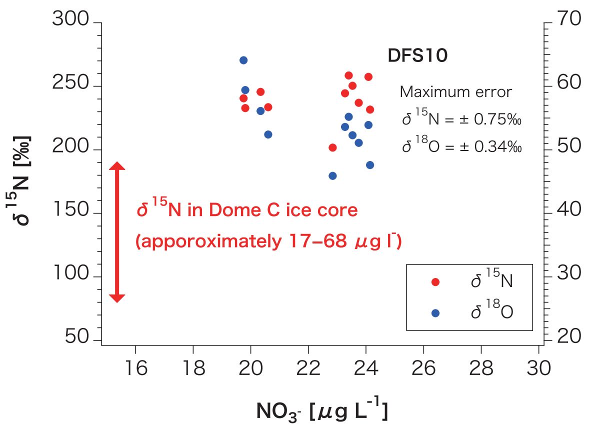

Fig. 2. NO_3^- concentration, $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- in Dome Fuji ice core. Red arrow indicates the range of $\delta^{15}N$ in Dome C ice core, inland Antarctica[5)]. The unit of NO_3^- concentration in Dome C converts assuming ice density 850 kg m^{-3}.

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