Measurements of nitrogen isotope ratios in samples with very low nitrate concentrations from the Dome Fuji ice core (Antarctica) drilled in 2010

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Nitrate (NO_3^-) in ice core samples is known to provide a variety of information on past and present atmospheric conditions. For instance, NO_3^- data for samples from the Talos Dome ice core (Antarctica) exhibited a highly significant relationship with cosmic ray fluxes.[1] In addition, several research groups[2),3)] have measured the $\delta^{15}N$ of NO_3^- in surface snow in Antarctica to quantify the extent of isotopic fractionation due to photolytic processes after precipitation. However, there is little information available about the depth profiles of the $\delta^{15}N$ of NO_3^- in ice core samples from Antarctica.

Our goal was to precisely analyze the $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- in ice cores to clarify the history of solar activity and cosmic events. However, it is difficult to measure the $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- in Antarctic ice cores because the NO_3^- concentrations are low (typically <0.4 μmol/L), and the available sample volume is limited. In this study, as a feasibility study, we used a denitrifier method[4] to perform highly sensitive measurements of the $\delta^{15}N$ of NO_3^- in samples from the DFS10 ice core, which was drilled in 2010, 7 km south of Dome Fuji Station (DFS), to obtain a profile of the $\delta^{15}N$ of NO_3^-. The NO_3^- concentration in the core was approximately 0.35 μmol/L. In what follows, we will introduce the outline of the results for 70 samples collected from the ice core of depths of Dome Fuji at 3.3–7.6 m. The sampling procedure was the same as that described by Motizuki *et al.* (2014)[5] for the ice core drilled at Dome Fuji in 2001. We assume that these samples correspond to approximately the time interval from AD 1900 to 1960. Each sample segment cut from the ice core corresponds to a time interval of approximately 0.7–1.0 year. A 10 mL aliquot of each sample was used; NO_3^- in the sample water was quantitatively converted to N_2O by the denitrifying bacteria, *Pseudomonas aureofaciens*, which lack N_2O reductase. The isotopic composition of the N_2O gas produced by the bacteria was measured using a mass spectrometer (IsoPrime100) with a purge-and-trap introduction system. The isotope ratios were referenced to the internationally recognized standards USGS32, USGS34, and USGS35 provided by IAEA (International Atomic Energy Agency). Nitrate concentrations were analyzed by ion chromatography (ICS2000) with error limits of 2 or 3%. The amount of nitrogen used for the analysis ranged from 2.1 to 4.8 nmol. $\delta^{15}N$ ranged from 144.8 to 332.0‰ and the maximum error was ± 2.5‰. The high, positive $\delta^{15}N$ values obtained in the study were therefore attributed to a post-depositional effect on NO_3^-. Figure 1 shows the depth profiles of NO_3^- concentrations and $\delta^{15}N$ values. Despite the lack of any correlation between NO_3^- concentrations and $\delta^{15}N$ values, their depth profiles appear to be related for several depth intervals. For example, both profiles are convex in the depth intervals 3.3–4.0 and 5.5–6.0 m. It has been reported that NO_3^- concentration decreases as $\delta^{15}N$ values increases near the surface of snow because of photolysis in the surface snow (vide supra).[2] There was no negative correlation between NO_3^- concentration and $\delta^{15}N$ values for our ice core samples, which indicates that the variations of $\delta^{15}N$ and NO_3^- concentration in ice core samples below 3 m do not reflect post-depositional fractionation of nitrogen isotopes. Instead, the depth profiles of $\delta^{15}N$ and NO_3^- concentration likely preserve the corresponding variations in the original precipitation.

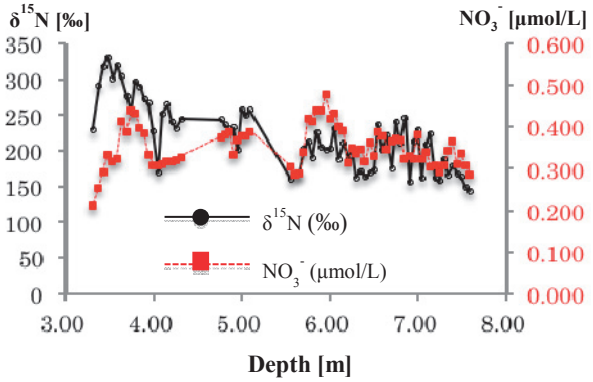

Fig. 1 The depth profiles of $\delta^{15}N$ and NO_3^- concentration.

We intend to continue the measurements of nitrogen and oxygen isotopes in NO_3^- for samples collected from deeper in the ice core. We expect that the depth profiles of nitrogen and oxygen isotopes will reflect the variations in the chemical and physical characteristics of past precipitation, indicate the origin of the NO_3^- production in the stratosphere, and provide important information that will help elucidate the history of solar activity and cosmic events.

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