# RF-065 Tracing atmospheric nitrate in water environments using the triple oxygen isotopes as tracers (Abstract of the Final Report)

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[Abstract]

We developed a rapid and sensitive analytical system to determine $\Delta^{17}O$ of $NO_3^-$ through the isotopic analysis of $N_2O$ which is quantitatively converted from $NO_3^-$. Besides $\delta^{15}N$ and $\delta^{18}O$, we can determine $\Delta^{17}O$ under the precision of 0.2 ‰ for a sample that contain more than 20 nmol of $NO_3^-$, through the continuous flow isotope ratio mass spectrometry for both $N_2O$ directly and $O_2$ produced from $N_2O$. Besides, we determined $\Delta^{17}O$ values of $NO_3^-$ in some natural water samples to quantify the fraction of depositional atmospheric $NO_3^-$ ($NO_3^-{}_{atm}$) within each $NO_3^-$ pool. The $NO_3^-{}_{atm}$ fraction was 10±2 % in oligotrophic freshwater at Lake Mashu, 9±4 % in groundwater at Rishiri Island, 0 % in deep seawater, from 3±2 % in surface seawater in and around subarctic North Pacific, 5±2 % and 25±5 % in coastal area at Tokyo Bay and Ishigaki Island, respectively. These values are consistent with the independent estimates based on direct observations on both the $NO_3^-{}_{atm}$ deposition rate and the new production rate in each area.

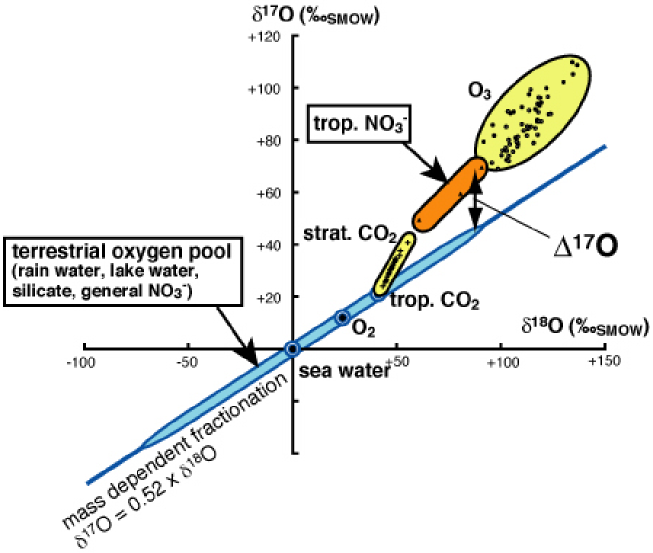

**Fig. 1** Triple oxygen isotope plot of atmospheric $NO_3^-$, as well as the other terrestrial oxygen compounds.

## 1. Introduction

Increased atmospheric deposition rate of fixed nitrogen species to both pelagic and coastal oceans could change phytoplankton activities qualitatively and quantitatively. Such changes result in significant variations in biogeochemical cycles, such as air-sea or air-land fluxes of climatically important gases and particles. The triple oxygen isotopic compositions ($^{18}O/^{16}O$ and $^{17}O/^{16}O$) of $NO_3^-$ in water environments can be a useful tracer to quantify the contribution of $NO_3^-{}_{atm}$ to total $NO_3^-$ in a water mass, because general $NO_3^-$, the oxygen atoms of which are derived from either terrestrial $O_2$ or $H_2O$ through the reactions such as nitrate remineralization or nitrification, shows mass-dependent relative variations in between $^{17}O$ and $^{18}O$, whereas $NO_3^-{}_{atm}$ displays an anomalous enrichment in $^{17}O$ (Michalski et al., 2003; **Fig. 1**). By using $\Delta^{17}O$ signature defined by the following equation, we can distinguish $NO_3^-{}_{atm}$ ($\Delta^{17}O > 0$) from the other $NO_3^-$ in general ($\Delta^{17}O = 0$).

$$\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$$

Besides, $\Delta^{17}O$ won't vary through mass-dependent isotope fractionation processes so that we can trace $NO_3^-{}_{atm}$ irrespective of assimilation reactions subsequent to deposition.

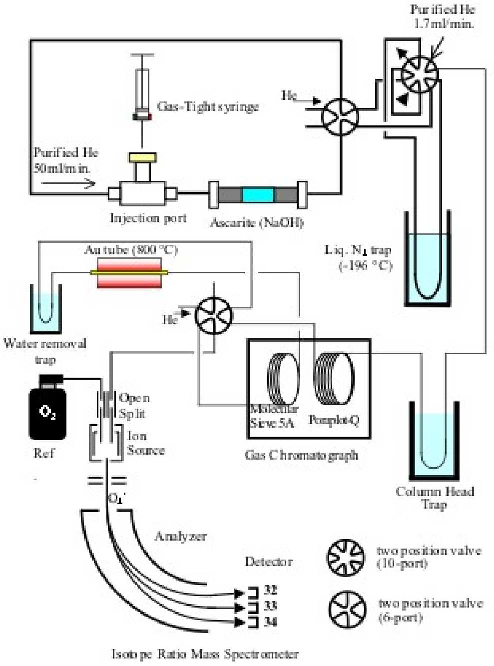

**Fig. 2** Schematic diagram of the system developed in this study for the triple oxygen isotope analysis of $N_2O$.

## 2. Research Objective

In this study, we will develop a rapid and sensitive analytical system to determine $\Delta^{17}O$ of $NO_3^-$ in nmol quantities. The major points can be classified into the following two parts: (1) quantitative conversion of $NO_3^-$ to $N_2O$ (Tsunogai et al., 2008), and (2) $\Delta^{17}O$ analysis of $N_2O$ using continuous-flow IRMS (CF-IRMS) (Tsunogai et al., 2002; Kawagucci et al., 2005; Komatsu et al., 2008). The simple reactions using spongy cadmium and sodium azide in an acetic acid buffer (McIlvine and Altabet, 2005) are adopted for the basic reaction to convert $NO_3^-$ to $N_2O$. The $\Delta^{17}O$ values of $N_2O$ are determined through the isotopic analysis of $O_2$ at the masses 32, 33, and 34, which is quantitatively produced from $N_2O$ in a gold tube (Kaiser et al., 2007; **Fig. 2**), in addition to the direct $N_2O$ isotopic analysis at the masses 44, 45, and 46.

Besides the development of the analytical system, we also determine $\Delta^{17}O$ values of $NO_3^-$ in some natural water samples in and around Japanese islands to clarify that $\Delta^{17}O$ tracer is useful for quantifying the fraction of depositional atmospheric $NO_3^-$ ($NO_3^-{}_{atm}$) within each $NO_3^-$ pool.

## 3. Results and discussion

### 3.1 Analytical precision

For the samples that contain more than 4 nmol $NO_3^-$, precisions are always better than ±0.12 ‰ and ±0.25 ‰ (1σ) for both $\delta^{15}N$ and $\delta^{18}O$. Besides, the $\delta^{15}N$ and $\delta^{18}O$ values of produced $N_2O$ exhibit linear correlations with their original values in $NO_3^-$ with the slope of 0.5 for $\delta^{15}N$ and close to 1 for $\delta^{18}O$, suggesting that half of N atoms within the produced $N_2O$ must be derived from original $NO_3^-$, while the rest are derived from $N_3H$ reagent. It is also suggested that all of O atoms within the produced $N_2O$ must be derived from original $NO_3^-$, while some kinetic isotope fractionations occur during the $N_3H$ reduction. Through the corrections for the produced $N_2O$ using the calibration lines, we can estimate accurate $\delta^{15}N$, $\delta^{18}O$ and thus $\Delta^{17}O$ of the original $NO_3^-$.

We measured the variation in the $\Delta^{17}O$ values of the same $N_2O$ as a function of introduced sample size. While they were found to be accurate and precise for the sizes larger than 5 nmol, the uncertainty of the measured $\Delta^{17}O$ increased with decreasing sample size less than 5 nmol. This is likely to be due to isotope exchange of the produced $O_2$ with an unidentified O reservoir. In conclusion, 20 nmol of $NO_3^-$ give a 1 σ uncertainty of 0.2 ‰ for $\Delta^{17}O$. Future identification and removal of the O reservoir will reduce the size drastically for $\Delta^{17}O$ measurement.

### 3.2 Field results

### 3.2.1 atmospheric $NO_3^-$ ($NO_{3\ atm}^-$)

To define $\Delta^{17}O$ of atmospheric $NO_3^-$, rainwater samples had been taken at Sapporo (n=12) and Alaska (n=5) at least once every month from 2006 to 2007. The atmospheric $NO_3^-$ exhibited clear $^{17}O$ anomalies (**Fig. 3**). The average $\Delta^{17}O$ value is +24.8 ‰ with a 1 σ dispersion of ±2.8 ‰ and is in the same range as those previously reported for $NO_3^-$ in atmospheric aerosol (Michalski et al., 2003; Kaiser et al., 2007), and those expected from the model tracing $NO_x$ oxidation pathways (Michalski et al., 2003).

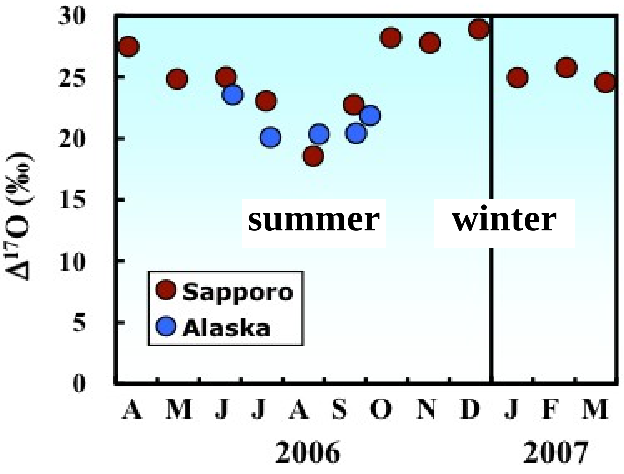

**Fig. 3** Temporal variations of $\Delta^{17}O_{NO3}$ in rainwater taken at Sapporo (red) and Alaska (blue).

### 3.2.2 $NO_3^-$ in oligotrophic lake (Lake Mashu)

We applied the $\Delta^{17}O$ tracer method to determine $NO_{3\ atm}^-$/ $NO_{3\ total}^-$ ratios in Lake Mashu, so as to clarify the N-cycles within the lake. Lake Mashu is a oligotrophic subalpine crater lake, located in the eastern part of Hokkaido, Japan. The lake has no streams either entering or outflowing, so that the water is extremely clear. It undergoes overturn twice a year, in spring and autumn. Lake water was taken at June and August, 2007 as a part of GEMS/Water project, at the central part of the lake for every 20-50 m depth.

Lake Mashu $NO_3^-$ exhibits clear $^{17}O$ anomaly ($\Delta^{17}O$ = +2.5 ± 0.5 ‰) in June (**Fig. 4**). Assuming that the $\Delta^{17}O$ value is +24.8 ± 2.8 ‰ for $NO_{3\ atm}^-$, the $NO_{3\ atm}^-$ fraction is estimated to be 10±2 % in the lake water, and the rest (ca. 90 %) must be remineralized $NO_3^-$, derived from remineralization in and around the lake. The vertically homogeneous distribution of both $NO_3^-$ concentrations and $\Delta^{17}O$ values irrespective to the sampling depths in June 2007 suggest that most of the $NO_3^-$

remineralization from organic nitrogen, as well as the $NO_3^-{}_{atm}$ deposition, seems to have been processed prior to the latest overturn in the lake.

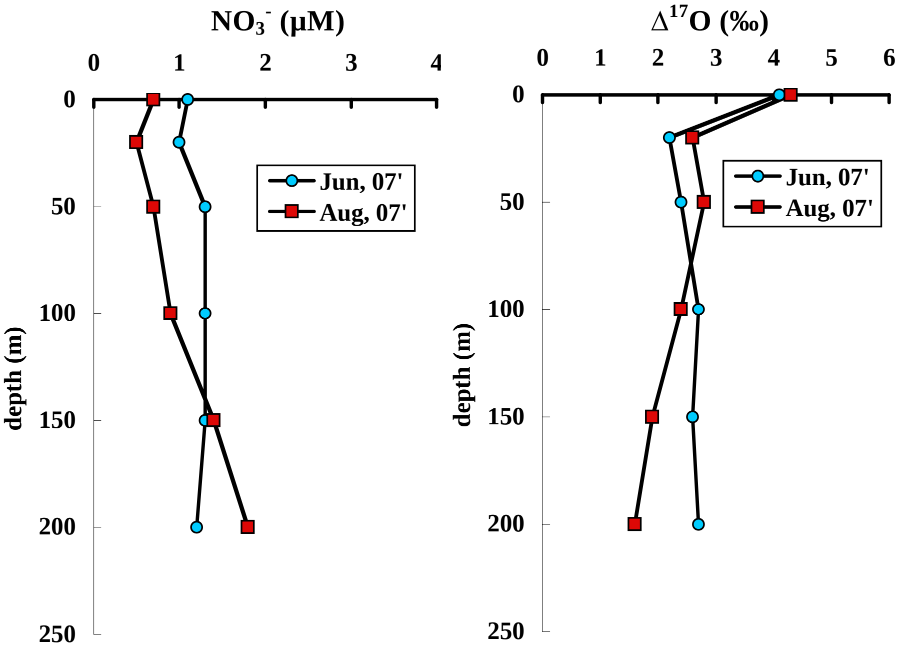

**Fig. 4** Vertical profiles of $NO_3^-$ and $\Delta^{17}O_{NO3}$ in Lake Mashu taken at June (blue circle) and August (red square).

On the other hand, $NO_3^-$ concentration in August can be characterized by both $NO_3^-$ depletion at surface 0 - 100 m and enrichment at 200 m depth in comparison with those in June, probably because the $NO_3^-$ assimilation rate is faster than the remineralization rate at surface 0 – 100 m while the remineralization rate is faster than the $NO_3^-$ assimilation rate at the deeper part. To quantify the absolute rates, we used the $\Delta^{17}O$ tracer because the $\Delta^{17}O$ values won't vary through mass-dependent isotope fractionation processes such as assimilation reactions. In conclusion, the depletion of $NO_3^-$ concentration at the lake surface on August relative to those in June is mostly due to assimilation of $NO_3^-$ by phytoplankton at the surface. On the other hand, the enrichment of $NO_3^-$ concentration at the 200 m depth on August relative to those in June is mostly due to remineralization of $NO_3^-$.

### 3.2.2 $NO_3^-$ in ground water (Rishiri Island)

We applied the $\Delta^{17}O$ tracer method to determine $NO_3^-{}_{atm}$/ $NO_3^-{}_{total}$ ratios within the groundwater system at Rishiri Island, a conical volcanic Island having a diameter of 8 km, located in the northern offshore of Hokkaido, Japan. The island has no major streams on surface, so that most portions of rain water run through into the groundwater system in the island and seep in and around the shore area as springs.

All the spring waters in Rishiri exhibit clear $^{17}O$ anomaly ($\Delta^{17}O = +2.5 \pm 0.8$ ‰). Assuming that the $\Delta^{17}O$ value is $+24.8 \pm 2.8$ ‰ for $NO_3^-{}_{atm}$, the $NO_3^-{}_{atm}$ fraction is estimated to be 9±5 % in the spring water $NO_3^-{}_{total}$. While the total $NO_3^-$ contents in the spring water coincide well with those in rain water at Rishiri, about 90 % of deposited $NO_3^-{}_{atm}$ had been substituted by $NO_3^-{}_{re}$ during the flow through the ground, from recharge on higher altitude until seepage around the shore. Most of the deposited $NO_3^-{}_{atm}$ is assimilated quickly into the biogeochemical N-cycle in the island.

Furthermore, the N-cycle in the island attain steady state, thus it discharge almost the same quantity of $NO_3^-$ with the influx.

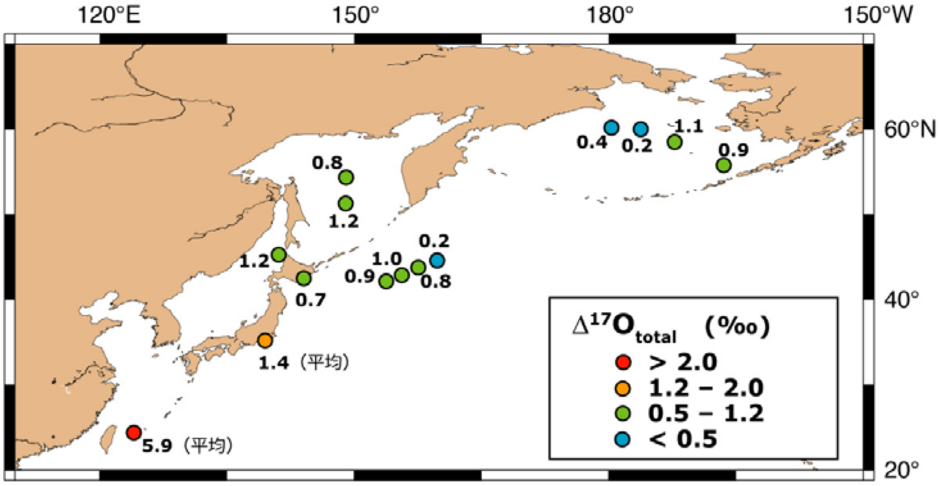

**Fig. 5** Schematic diagram showing the distribution of $\Delta^{17}O_{NO3}$ in ocean surface.

### 3.2.3 Oceanic $NO_3^-$ (in and around subarctic North Pacific)

We also applied the $\Delta^{17}O$ tracer method to determine the distribution of $NO_3^-{}_{atm}$/ $NO_3^-{}_{total}$ ratios in and around the subarctic North Pacific. In comparison with the other open ocean area, the area that can be characterized by enrichment of nitrate even at the surface due to active upwelling of deeper water. In Sep. 2006, surface (mixed layer) seawater samples were taken at the area of open ocean (n=5), Okhotsk sea (n=2), and Bering sea (n=4) at the depths of 0 - 10 m, using R/V Mirai (JAMSTEC). Besides, sub-surface seawater samples until bottom were taken at 3 of the surface sampling stations.

The absence of a significant $^{17}O$ anomaly in the deep waters more than 400 m depth suggests a minor contribution of $NO_3^-{}_{atm}$ in the deep sea environments, in line with general understandings that most $NO_3^-$ in deep sea water has been remineralized from sinking organic nitrogen. On the other hand, all the surface seawater samples exhibit small but definite $^{17}O$ anomaly (**Fig. 5**). While the samples taken at the active upwelling region of the off Kamchatka area that can be characterized by annual average nitrate concentration more than 10 μM exhibit relatively small $\Delta^{17}O$ values of 0.3 ± 0.1 ‰, the other area exhibit almost uniform $\Delta^{17}O$ values of +0.9±0.3 ‰. Assuming that the $\Delta^{17}O$ value is +24.8 ±2.8 ‰ for $NO_3^-{}_{atm}$, these average $\Delta^{17}O$ values corresponds to $NO_3^-{}_{atm}$ fraction of 1.2 ±0.5 % and 3.6 ±1.3 %, respectively. These values are basically consistent with the independent estimates based on direct observations on both the $NO_3^-{}_{atm}$ deposition rate and the new production rate in each area. By determining the $\Delta^{17}O$ values of $NO_3^-$ in ocean surface, as well as the new production rates, we can estimate deposition rates of $NO_3^-{}_{atm}$ even in oceanic area, including their temporal variations.

### 3.2.4 Oceanic $NO_3^-$ (coastal ocean)

We also applied the $\Delta^{17}O$ tracer method to determine $NO_3^-{}_{atm}$/ $NO_3^-{}_{total}$ ratios in coastal surface ocean water at Tokyo Bay (summer) and off Ishigaki Island. They exhibit $NO_3^-{}_{atm}$ enrichment up to 7 % (5 % on average) and 30 % (25 % on average), respectively. While the sites are located in coastal area, both area can be characterized by nitrate depletion relative to the subarctic North Pacific area during the sampling periods. Besides, both area located close to $NO_3^-{}_{atm}$ source on land area. Both the relatively small $NO_3^-{}_{re}$ contribution from sub-surface depths due to vertical stratification of water masses and high depositional flux of $NO_3^-{}_{atm}$ results in the observed $NO_3^-{}_{atm}$ enrichment at surface.

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## Major Publications

1) Tsunogai, U., T. Kido, A. Hirota, S.B. Ohkubo, D.D. Komatsu, F. Nakagawa : *Rapid Communications in Mass Spectrometry*, 22: 345-354 (2008)
"Sensitive determinations of stable nitrogen isotopic composition of organic nitrogen through chemical conversion to $N_2O$."

2) Komatsu, D.D., T. Ishimura, F. Nakagawa, and U. Tsunogai : *Rapid Communications in Mass Spectrometry*, 22, 1587-1596 (2008)
"Determination of the $^{15}N/^{14}N$, $^{17}O/^{16}O$, and $^{18}O/^{16}O$ ratios of nitrous oxide by using continuous-flow isotope ratio mass spectrometry."

3) Sasakawa, M., U. Tsunogai, S. Kameyama, F. Nakagawa, Y. Nojiri, A. Tsuda : *Journal of Geophysical Research*, 113, C03012, doi: 10.1029/2007JC004217 (2008)
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