# Anomalous triple oxygen isotopic compositions in oceanic nitrate

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While general remineralized nitrate ($NO_3^-$) shows mass-dependent relative variations in both $^{17}O$ and $^{18}O$ ($d^{17}O = 0.52d^{18}O$), atmospheric $NO_3^-$ displays an anomalous enrichment in $^{17}O$ (Michalski et al., 2003). Thus, the triple oxygen isotopic compositions ($D^{17}O = d^{17}O - 0.52d^{18}O$) of $NO_3^-$ in a water mass can be a useful tracer to quantify the contribution of depositional atmospheric $NO_3^-$ to total $NO_3^-$ in the water mass, because oxygen isotope exchange reaction is minimum at the range of pH and $NO_3^-$ concentration in natural water environment. In this study, we applied the $D^{17}O$ tracer method to determine $NO_3^-$ cycles in western marginal area of north Pacific. Surface (mixed layer) seawater (0-10 m) are taken at open ocean area on Okhotsk sea, Bering sea, and western North Pacific, on Sep. 2006, using R/V Mirai (JAMSTEC). Both sub-surface seawater (30-50m) and deep seawater are taken as well in the area for comparison.

To determine $D^{17}O$ in oceanic nitrate, we developed a rapid and sensitive online analytical system to determine the triple oxygen isotopic compositions of $NO_3^-$ in nmol quantities using continuous-flow IRMS (CF-IRMS) without the cumbersome and time-consuming pretreatments. The system is based on the isotopic analysis of $N_2O$, which is quantitatively converted from $NO_3^-$ using the simple reactions using spongy cadmium and sodium azide in an acetic acid buffer, and then purified by PoraPLOT capillary column. Addition to the direct $N_2O$ isotopic analysis at the masses 44, 45, and 46, we determine the isotopic composition of $O_2$ which is quantitatively produced in a gold tube at 780 degree C to determine $d^{15}N$, $d^{18}O$ and $d^{17}O$ for $NO_3^-$. By using the method, 20 nmol of $NO_3^-$ give a 1 sigma uncertainty of 0.1 per mil for $d^{18}O$ and 0.1-0.3 per mil for $D^{17}O$.

Most of the deep water samples exhibit little anomaly in $D^{17}O$. The absence of a significant $^{17}O$ anomaly in the deep waters suggests that a minor contribution of atmospheric $NO_3^-$ inputs in the deep sea environments, in line with general understandings that most $NO_3^-$ in deep sea water have been remineralized from sinking organic nitrogen. On the other hand, surface seawater in both Okhotsk sea and Bering sea exhibit small but definite $^{17}O$ anomaly up to +1.2 per mil. The average $D^{17}O$ is +0.9 per mil in the area, except for the upwelling region in Bering sea, where $D^{17}O$ is less than +0.5 per mil in usual. Assuming that the $D^{17}O$ value is +25 per mil for $NO_3^-_{atm}$, the we estimate that $NO_3^-$atm fraction is ca. 4 % in the area. These values are basically consistent with the independent estimates on their nitrogen budgets. By determining the distribution of more $D^{17}O$ values of $NO_3^-$ in ocean surface, as well as precise $NO_3^-$ assimilation rates (= primary production rates), we can estimate more precise deposition rates of $NO_3^-_{atm}$, as well as their temporal variations.