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The oxygen isotope anomaly of nitrate as tracer of atmospheric nitrate in marine nitrogen cycling

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Nitrogen is an essential nutrient in marine ecosystem. While nitrate supplied from the depths beneath euphotic zone is the dominant source of new nitrogen in the ocean, atmospheric deposition of nitrate is recognized as an alternative important source of new nitrogen at ocean surface. Quantifying the contribution of the atmospheric input is one of the key factors to clarify the marine nitrogen cycle.

The triple oxygen isotopic compositions ($\Delta^{17}O \approx \delta^{17}O - 0.52 \times \delta^{18}O$) of oceanic nitrate can be an useful tracer to quantify the mixing ratios of depositional nitrate within total nitrate in a water mass, because atmospheric nitrate shows large ^{17}O anomaly ($\Delta^{17}O > 0$) due to the contribution of atmospheric ozone having large $\Delta^{17}O$ values, whereas re-mineralized nitrate produced biologically shows little ^{17}O anomaly ($\Delta^{17}O = 0$). Determination on the $\Delta^{17}O$ values of nitrate allows us to estimate the mixing ratios of depositional nitrate within total nitrate.

Here we determined the $\Delta^{17}O$ values of nitrate in surface seawater samples, which have been collected in sub-arctic area of the western North Pacific, where we can find high nitrate concentrations year-round. As a result, we found definite positive $\Delta^{17}O$ anomaly in seawater samples. The $\Delta^{17}O$ values were anti-correlated with their concentrations, ranged between 0 and +5.0 ‰ while most of samples were less than +0.6 ‰The surface waters contained atmospheric nitrate to some extent. We conclude that the mixing ratio of atmospheric nitrate within total nitrate in surface seawater was $1 \pm 1\%$ in the area.

We demonstrate that the coupled measurements of $\Delta^{17}O$ of nitrate in the euphotic zone and flux of depositional nitrate can estimate average "new production" without any cumbersome and time-consuming in situ incubation. The complementary measurements of $\Delta^{17}O$ values of nitrate indicate that spatial distributions of $\delta^{15}N$ and $\delta^{18}O$ of oceanic nitrate in surface waters were associated with not only assimilation but also input of depositional nitrate. The combination of $\delta^{15}N$, $\delta^{18}O$, and $\Delta^{17}O$ data can be useful tracers to understand the N-cycle in surface waters.