Nitrogen Isotope Exchange Between Nitrate and Nitrite in the Fall Mixed Layer of the Antarctic Ocean

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In the Southern Ocean, the nitrogen (N) and oxygen (O) isotopes of nitrate (NO_3^-) have previously been used to investigate modern and past N cycling during summertime phytoplankton growth [1]. However, recent studies indicate the significance of processes in other seasons for producing the annual cycle of N isotope changes [2]. We explore the impact of fall conditions on the $^{15}N/^{14}N$ ($\delta^{15}N$) and $^{18}O/^{16}O$ ($\delta^{18}O$) of NO_3^- and nitrite (NO_2^-) in the Pacific Antarctic Zone of the Southern Ocean using eight depth profiles collected across the Ross Gyre in late March and early April 2014. In the mixed layer, the $\delta^{15}N$ and $\delta^{18}O$ of NO_3^-+NO_2^- increase roughly equally, as expected from phytoplankton NO_3^- assimilation; however, the $\delta^{15}N$ of NO_3^--only (measured after NO_2^--removal) increases significantly more than does its $\delta^{18}O$. Differencing the measurements indicates that NO_2^- has an extremely low $\delta^{15}N$, often less than -70‰ vs. air. These observations are consistent with the expression of a N equilibrium isotope effect between NO_3^- and NO_2^-, likely catalyzed by the nitrite oxidoreductase (NXR) enzyme of nitrite-oxidizing microorganisms that have been entrained into shallow waters from the subsurface as the mixed layer deepens during the fall. Although existing data suggest that the signal of this process is destroyed in winter and is thus not retained in the NO_3^- available for consumption the following spring, further investigation of the isotopic consequences is warranted. Moreover, a related NXR-catalyzed isotope exchange process may explain recent evidence of NO_2^- oxidation in oceanic oxygen-deficient zones, which is difficult to reconcile with the lack of appopriate oxidants.

[1] Sigman *et al.* (2009), *Deep Sea Research Part I* **56**, 1419-1439. [2] Smart *et al.* (2015), *GBC* **29**, 427-445.