Re-evaluating the isotope effect of phytoplankton nitrate assimilation through the lens of the Atlantic Southern Ocean

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The Southern Ocean is a key driver of global carbon and climate cycles, today and in the past. A large volume of the CO_2-rich ocean interior is ventilated in the Southern Ocean, and this region also has great potential for increased phytoplankton nitrate utilization (and thus CO_2 drawdown) due to its high-nitrate, low-chlorophyll condition. Indeed, more complete Southern Ocean nitrate consumption is a leading hypothesis for glacial/interglacial CO_2 changes. The nitrogen isotopic composition ($\delta^{15}N$) of microfossil-bound organic matter preserved in deep-sea sediments provides a means of reconstructing changes in Southern Ocean nutrient status over time, with a higher $\delta^{15}N$ for glacial sediments indicating more complete upper ocean nitrate utilization. However, such interpretations rely on the assumption that the isotope effect of nitrate assimilation (ε_{assim}) – the degree of isotope discrimination between nitrate and the biomass produced from it – has remained constant over time, which may not be the case. Previous nitrate isotope data from the summertime Pacific Southern Ocean (from the Subantarctic Zone (SAZ) to the Antarctic Zone (AZ)) show a strong positive correlation between ε_{assim} and surface mixed layer depth (MLD). This has been interpreted as indicative of the physiological response of phytoplankton to light limitation, with lower light availability (i.e., greater MLD) leading to increased intracellular nitrate efflux and thus a higher ε_{assim}.

These data are nominally measurements of the combined nitrate+nitrite pool; however, due to the method of sample preservation, it is possible that nitrite was (at least partially) removed from the samples prior to isotope analysis. Recent work from the late-summer Ross Sea Gyre has revealed the occurrence of a process of enzymatic interconversion between nitrate and nitrite in the mixed layer, which acts to increase nitrate $\delta^{15}N$ while decreasing nitrite $\delta^{15}N$, without altering the $\delta^{15}N$ of the combined nitrate+nitrite pool. The result is that if nitrate alone is considered (i.e., after nitrite removal), ε_{assim} is significantly higher than if nitrate+nitrite is used (8.2 ± 1.8‰ *vs.* 5.2 ± 0.8‰). Moreover, the nitrate-nitrite interconversion is likely catalyzed by light-inhibited nitrite oxidizing bacteria entrained from the subsurface into the deepening late-summer mixed layer. Thus, an alternate explanation for the correlation between ε_{assim} and MLD is enhanced nitrate-nitrite interconversion with deeper mixed layers due to more entrainment of nitrite-oxidizing organisms, which increases the $\delta^{15}N$ of nitrate-only. Here, we present nitrate+nitrite and nitrate-only isotope data from the mid-summer Atlantic Southern Ocean (SAZ to AZ), which suggest the occurrence of nitrate-nitrite interconversion, albeit to a lesser extent than in the late summer. Values of ε_{assim} for nitrate-only samples (6-8‰) are higher than those for nitrate+nitrite (4.5-5.5‰). Moreover, these data suggest that ε_{assim} for nitrate+nitrite bears no relationship to MLD, and is similar in the AZ and SAZ, in contrast to previous findings. Given that field estimates of ε_{assim} from the rest of the global ocean centre around 5‰, an implication of our findings for palaeo-reconstructions is that the value of ε_{assim} expressed in the environment may not vary as much as previously thought.