Nitrogen Isotopes

Statement of Interest for Pacific GEOTRACES

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The Peru to Tahiti Pacific section will cross the Peru oxygen deficient zone (ODZ), a major oceanic sink for nitrate (NO_3^-) (Codispoti and Christensen, 1985) with likely extreme NO_3^- isotopic signatures. NO_3^- consumption leaves behind a pool elevated in $\delta^{15}N$ and $\delta^{18}O$, which can be mixed throughout the ocean and globally impact $\delta^{15}N_{NO3}$. The $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ signals in regions such as the Peru oxygen deficient zone (ODZ) are thought to result from a combination of nitrate removal processes, including denitrification and anammox, and nitrate regeneration processes. However, the rates of these processes and the coupling between them remain poorly characterized, and NO_3^- (and NO_2^-) isotopes can be used to understand the contributions of these processes to nitrogen cycling and loss in ODZs. Our primary goal will be to collect and analyze samples for $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ analysis. Casciotti would be the lead GEOTRACES PI, whereas Altabet plans to perform NO_3^- isotopic analyses in this region on separate German-led process cruises (SFB 754) in 2013. We have agreed to collaborate and exchange samples to facilitate intercalibration between the GEOTRACES and SFB 754 sections.

Recent work suggests that the isotopic composition of the intermediate nitrite (NO_2^-) is critical for interpreting $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ variations in ODZs (Casciotti 2009). Therefore, a secondary goal of this project will be to collect and analyze samples for NO_2^- $\delta^{15}N$ and $\delta^{18}O$ analyses, which will also be subject to intercalibration. A berth at sea will be required to successfully carry out these goals, as rigorous sample preservation techniques (Casciotti et al., 2007) are needed to accurately preserve the isotopic composition of NO_2^-, and of NO_3^- where they coexist.

If the water budget allows, we will also collect and analyze samples for nitrous oxide (N_2O) concentration and isotopic composition ($\delta^{15}N$, $\delta^{18}O$, and isotopomer site preference; Casciotti), as well as N_2/Ar, $\delta^{15}N_{N2}$, and $\delta^{18}O_{O2}$ analyses (Altabet). N_2O is both produced and consumed by the denitrification process (Codispoti and Christensen, 1985), and the variations in N_2O concentration and isotopic composition may be closely coupled to NO_3^- isotope variations in ODZ's. The N_2O concentration and isotopic analyses may therefore provide useful constraints on the processes involved with N cycling in oxygen deficient zones. The N_2/Ar and $\delta^{15}N_{N2}$ measurements are also directly linked to nitrogen isotope budgets and the mass balance of N in and around ODZ's (Brandes et al., 1998). Deficits in 'fixed N' (NO_3^-, NO_2^-, and NH_4^+) produced by denitrification and/or anammox can be compared against the concentration and $\delta^{15}N$ of dissolved N_2 gas to better understand N loss pathways. Where denitrification is dominant, the amount and $\delta^{15}N$ of produced N_2 should closely match the 'missing' N; if anammox is responsible for N_2 production, the produced N_2 may differ from that expected from the missing N, reflecting production of N_2 also from reduced forms (Devol et al., 2006).

The work described herein most directly addresses objectives 1 and 3 in the GEOTRACES Science plan. Specifically, NO_3^- (and NO_2^-) isotope measurements from the South Pacific transect would allow better characterization of source regions for NO_3^- isotope enrichment and the processes generating those signals, as well as their propagation into the Pacific Ocean basin.

In addition, NO_3^- isotopic data for the productive waters overlying the Peru ODZ could allow better understanding of isotopic fractionation during nutrient uptake, and the connections between micronutrient availability, N isotopic fractionation, and the extent of nutrient uptake.