Letter of intent for Pacific GEOTRACES collaborative proposal:

Casciotti, Karen: lead NO_3^-, NO_2^-, and N_2O isotopic measurements in seawater; seawater N_2O concentration and $\delta^{18}O_{H2O}$ measurements.

Altabet, Mark: N_2/Ar, $\delta^{15}N_{N2}$, $\delta^{18}O_{O2}$ measurements in seawater; NO_3^-, NO_2^- and N_2O isotopic measurements in seawater for intercalibration.

Hastings, Meredith: NO_3^- isotopic measurements in aerosols and rain water.

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 extreme NO_3^- isotopic signatures ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$). NO_3^- consumption leaves behind a pool elevated in ^{15}N and ^{18}O, which can be mixed throughout the ocean and globally impact $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ distributions. The $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ signals in regions such as the Peru 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. Additionally, the isotopic impact of atmospheric deposition in the region is unconstrained. While NO_3^- deposition in the South Pacific is expected to have much less of an impact on surface concentrations than in the Northwestern Pacific (e.g., Kim et al., 2011), the isotopic composition of atmospheric deposition can significantly perturb isotopic budgeting (e.g., Knapp et al., 2010; Wankel et al., 2010). The isotopes of NO_3^- can be used to understand the contributions of nitrate source and removal processes to nitrogen cycling and loss in ODZs. Our primary goal will be to collect and analyze seawater and atmospheric samples for $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ analyses. Casciotti will be the lead PI, Altabet plans to perform (seawater) NO_3^- isotopic analyses in this region on separate German-led process cruises (SFB 754) in 2013, and Hastings will analyze aerosol and rainwater $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ in samples collected as part of the cruise. Casciotti and Altabet will collaborate and exchange samples to facilitate intercalibration between the GEOTRACES and SFB 754 sections. Triplicate 100 mL samples (includes rinses) will be needed for $\delta^{15}N_{NO3}$ (and $\delta^{18}O_{NO3}$, measured simultaneously) analyses. Following the cruise, subsections of aerosol filters and rainwater collections will be required for the atmospheric analyses. (Note that the aerosol and rainwater collections are proposed to be lead by Ana Aguilar-Isles (U. of Alaska-Fairbanks) and will not require additional berth space for our study).

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^- isotopic analyses ($\delta^{15}N_{NO2}$ and $\delta^{18}O_{NO2}$), which will also be subject to intercalibration between Casciotti and Altabet. A single 100 mL sample (includes rinses) will provide the necessary sample volume for NO_2^- concentration and replicate isotopic analyses. 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_3^- and NO_2^- where they coexist. We will request a berth for a graduate student or postdoc from Casciotti's lab to collect and preserve these samples at sea. This person would also be available to assist with collection of samples from the ship's rosette for other groups. NO_2^- isotope samples will only be collected from ODZ stations and depths ($[O_2] < 2$ μM and $[NO_2^-] > 0.5$ μM)

We will also propose to collect and analyze samples for nitrous oxide (N_2O) concentration and isotopic composition ($\delta^{15}N$, $\delta^{18}O$, and isotopomer site preference, all obtained simultaneously; Casciotti), as well as N_2/Ar, $\delta^{15}N_{N2}$, and $\delta^{18}O_{O2}$ analyses (all obtained simultaneously; 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 ODZs, as well as the availability of trace elements such as Cu and Fe. The N_2O concentration and isotopic analyses may therefore provide useful constraints on the processes involved with N cycling in oxygen deficient zones and trace element availability, and as such were deemed to be an essential parameter for this section. The sample volumes required for these analyses (500 mL per sample x duplicate samples = 1 L; includes rinses) may require that they be collected only at super stations. 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 ODZs (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' NO_3^-; if anammox is responsible for N_2 production, the produced N_2 may differ from that expected from missing NO_3^-, reflecting production of N_2 from reduced forms (Devol et al., 2006). The sample volumes required for these analyses is 250 mL per sample x duplicate samples = 500 mL (includes rinses).

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 (seawater and atmosphere) 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 preservation in sediments. Furthermore, as all N-cycle processes involve metalloenzymes and micronutrients such as Cu and Fe, these measurements can provide insights into the connections between micronutrient availability, N isotopic fractionation, and the extent of nutrient uptake.

Summary:

Water budget:
NO_3^- isotopes: 300 mL (includes rinses) from entire section
NO_2^- isotopes: 100 mL (includes rinses) from ODZ stations and depths
N_2O concentration and isotopes: 1 L (includes rinses) from super stations
N_2/Ar, $\delta^{15}N_{N2}$, $\delta^{18}O_{O2}$: 500 mL (includes rinses) from entire section
Aerosols and rainwater (entire section): Aguilar-Islas/Landing aerosol collectors, if available
Particle $\delta^{15}N$ (entire section): in situ pumps, if available.
$\delta^{18}O_{H2O}$ (entire section): no additional water needed (can take from NO_3^- isotope sample).

Personnel:
1 berth for sample collection and preservation.