Letter of intent for the US Arctic GEOTRACES
Collaborative proposal: Characterization of the isotopic composition of atmospheric and dissolved nitrogen species on the Arctic Ocean GEOTRACES cruise

Julie Granger (lead): Dissolved nitrate (NO$_3^-$) $\delta^{15}$N and $\delta^{18}$O
Mark Altabet: Ammonium (NH$_4^+$) and nitrite (NO$_2^-$) $\delta^{15}$N, N$_2$/Ar, $\delta^{18}$O of dissolved oxygen (O$_2$), and N$_2$O concentration and isotopomer composition ($\delta^{15}$N, $\delta^{18}$O, isotopologue site preference).
Angela Knapp: Water column dissolved organic nitrogen (DON) concentration and $d^{15}$N
Meredith Hastings: Aerosol nitrate (NO$_3^-$) $\delta^{15}$N and $\delta^{18}$O

Scientific objectives: Define the geographic variations and oceanographic controls on nitrate $\delta^{15}$N and $\delta^{18}$O in the western basin of the Arctic Ocean, to obtain a first order understanding of the contribution water masses, rivers and atmospheric deposition to the regional N budget, and to diagnose important biological N transformations that occur in the basin.

- Measure the natural abundance $\delta^{15}$N and $\delta^{18}$O of NO$_3^-$ along the cruise line
- Survey the $\delta^{15}$N$_{NH_4}$ of NH$_4^+$ (and NO$_2^-$, if present) at continental shelf stations
- Measure the N$_2$/Ar gas ratio and the $\delta^{18}$O of dissolved O$_2$ along the cruise line
- Measure nitrous oxide (N$_2$O) concentrations and its $\delta^{15}$N and $\delta^{18}$O at continental shelf stations
- Measure the natural abundance $d^{15}$N of DON along the hydrographic cruise line
- Measure the natural abundance $\delta^{15}$N and $\delta^{18}$O of atmospheric particulate NO$_3^-$

Types of analyses planned
- $\delta^{15}$N and $\delta^{18}$O of NO$_3^-$ with the ‘denitrifier’ method (Sigman et al., 2001; Casciotti et al., 2002)
- $\delta^{15}$N of NH$_4^+$ and NO$_2^-$ by hypobromite oxidation and azide methods, respectively (McIlvin & Altabet, 2005; Zhang et al., 2007)
- Simultaneous analysis of the dissolved N$_2$/Ar gas ratio and the O$_2$/Ar and $\delta^{18}$O$_{O_2}$ of O$_2$ by continuous flow IRMS
- N$_2$O concentration and $\delta^{15}$N$_{N_2O}$ and $\delta^{18}$O$_{N_2O}$ (as well as isotopologue ‘site preference’) analyses on a PT-IRMS
- DON $\delta^{15}$N by persulfate oxidation and denitrifier method (Knapp et al., 2005)

Number of berths required: one

Sampling can be done by a super tech: yes

Nature and amount of sample required
- NO$_3^-$ isotopes (seawater): 2 x 100 mL including rinses, from the entire section; samples stored frozen at -10 to -20°C in 60 mL square PP bottles
- NH$_4^+$ (and NO$_2^-$) isotopes: 100 mL including rinses, from continental shelf stations
- N$_2$/Ar and $\delta^{18}$O$_{O_2}$: 600 mL including rinses, from all sections; stored in glass serum bottles
- [N$_2$O] and its isotopes: 600 mL including rinses, from continental shelf stations; stored glass serum bottles
- NO$_3^-$ isotopes (aerosol): Cuts of filters collected daily during the cruise; samples stored frozen in pre-cleaned bottles.
- Particle $\delta^{15}$N from in situ pumps form entire section, if available
- All dissolved analyte samples are collected from standard Niskin bottles

Granger and Altabet
The hydrographic survey of the western Arctic will traverse the very productive Chukchi continental shelf and the western flank of the Beaufort Gyre. The fertility of the western Arctic, in light of decreasing ice cover, is then largely dependent on the fixed N mixed from shallow halocline to surface, given the limited concentration of DIN relative to P with reference to algal requirements. The measurements of nitrate isotopes and accompanying TEI's proposed here will provide important insights into N cycling in the western Arctic in a number of regards: First, the proposed measurements will provide constraints on end-member compositions of Pacific waters entering the Arctic at Bering Strait. Second, they will provide a record of the biological transformation of N species across the productive Chukchi shelf. As recently evidenced by analogous measurements on the Bering Sea shelf (Granger et al., 2011; Granger et al., 2013), we anticipate that the DIN isotopologues in shelf waters will show evidence of the relative importance of benthic denitrification and remineralization of N on the shelf. The substantial N-deficit in subsurface and waters of the western Basin also highlights the importance of labile DON from the catchment as a potential assimilative N source. Benthic N cycling will further be evidenced in the water column by N2O and its isotope isotopic composition, and by the δ18O of oxygen - from which the relative contribution of benthic to pelagic respiration can be assessed. Below the wind mixed surface on the shelf and into the Arctic basin, N2/Ar ratios constitute an additional and direct measure of the fixed N lost to denitrification on the continental shelves. Additionally, the nitrate isotope ratio measurements in the deeper basin will provide a means of discerning the entrainment of nitrate from Pacific waters throughout the surface western Arctic, as evidenced by recent measurements in the Beaufort Gyre from the Canada GEOTRACES cruise (Granger & Sigman, 2012). Finally, the atmospheric measurements will provide constraint on the implication of N deposition on the isotopic budget. Recent studies at coastal Arctic sites show large, negative δ15N values in atmospheric nitrate as a result of the flux of reactive N species from photolyzed snow. The impact of this on the oceanic budget has not yet been explored. Together, the proposed measurements will provide a comprehensive view of N cycling in the western Arctic.

References


Granger and Altabet