Development and Application of Foraminifera Shell-Bound Nitrogen Isotopes as a Paleoceanographic Tool to Reconstruct Past History of the Marine Nitrogen Cycle

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Nitrogen (N) and phosphorus are the two nutrients required in large quantity by phytoplankton in the ocean, and together they limit productivity throughout most of the tropical, subtropical, and temperate ocean. Both the cycling of N and its input/output budget have been argued to control the fertility of the ocean and the ocean's role in setting atmospheric CO_2. The two stable isotopes of N (^{14}N and ^{15}N) and their fractionation by natural processes provide a mechanism for studying the cycle and budget of oceanic fixed N in the past. In environments of high sedimentary organic matter preservation, bulk sedimentary N appears to suffice for paleoceanographic N isotope studies. However, across most of the open ocean, the $\delta^{15}N$ of N exported from the surface ocean is altered as it sinks through the water column and is buried in deep sea sediments; it can also be contaminated with allochthonous (e.g., terrestrial) N. To reconstruct N isotope changes in the ocean, we have developed a protocol for the isotopic analysis of foraminiferal shell-bound N, which is 100 times more sensitive than traditional method, allowing for rapid progress with a N isotope archive that was previously not feasible to measure. Measurements on surface sediments and downcore record from the global ocean show the promise of foraminifera-bound $\delta^{15}N$ (FB-$\delta^{15}N$) to provide both a robust N isotope archive for paleoceanography, and one with a unique potential of richness, given the existence of multiple foraminiferal species with different depth habitats and behaviors. In this talk, I will present two case studies using this new proxy to reconstruct past changes in the input/output budget of oceanic fixed N and its potential to change ocean fertility and atmospheric CO_2.

Marine nitrogen fixation, which produces most of the ocean's fixed nitrogen, is thought to be affected by multiple factors, including ocean temperature and the availability of iron and phosphorus. The past glacial-interglacial cycles are the natural experimental laboratory for testing and identifying the drivers for changing marine nitrogen fixation. Applications of foraminifera-bound nitrogen in several tropical/subtropical open ocean sediment cores have yielded the first evidence for reduced nitrogen fixation in the surface nutrient-depleted regions during the glacials. These work, when compared with reconstructions of ice age denitrification, provides perhaps the strongest direct evidence to date for a longstanding hypothesis of a feedback between denitrification and nitrogen fixation across the global ocean that stabilizes the size of the ocean nitrogen reservoir.

Iron fertilization has previously been suggested as a possible cause of the lower CO_2 levels that occur during ice ages. We analyzed fossils found in deep sea sediment — deposited during the last ice age in the Subantarctic region and central equatorial

Pacific — with the goal of reconstructing past changes in the nitrate concentration of surface waters and combining the results with side-by-side measurements of dust-borne iron and productivity. We found that in the Subantarctic region, nitrate concentrations indeed declined during the cold periods when iron deposition and productivity rose, in a manner consistent with the dust-borne iron fertilization theory, however, higher iron deposition in the equatorial Pacific did not lead to any apparent increase in productivity or nutrient uptake. The results suggest that while iron fertilization in the ice age Southern Ocean may contribute to the CO_2 drawdown, depletion in the Southern Ocean nutrient (i.e. N, P) concentration may reduce the potential impact of iron fertilization in other parts of the ocean.