

Amino acid nitrogen isotopic composition of marine sediments: A new approach for studies of the marine nitrogen cycle

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The nitrogen (N) isotopic composition of total sedimentary N ($\delta^{15}\text{N}_{\text{bulk}}$) is a common tool used to reconstruct past oceanic N cycling (e.g., natural fluctuations in the $\delta^{15}\text{N}$ of surface nutrient N). Analyses of $\delta^{15}\text{N}_{\text{bulk}}$ represents a mixture of multiple N sources with selective removal or preservation of N-containing compounds. Compound specific $\delta^{15}\text{N}$ analysis of individual amino acids ($\delta^{15}\text{N}_{\text{AA}}$) has the potential to simultaneously reconstruct changes in nutrient N $\delta^{15}\text{N}$ and changes in ecosystem trophic dynamics, and therefore provide more specific process information than $\delta^{15}\text{N}_{\text{bulk}}$. As a first test of $\delta^{15}\text{N}_{\text{AA}}$ in marine sedimentary applications, we compared $\delta^{15}\text{N}_{\text{AA}}$ signatures of surface and sinking POM with those in surface sediments from the Santa Barbara Basin (SBB), a depositional environment with excellent organic matter preservation.

Sedimentary $\delta^{15}\text{N}_{\text{AA}}$ signatures show excellent preservation of planktonic biomass and sinking POM $\delta^{15}\text{N}_{\text{AA}}$. However, an unexpected inverse correlation between the $\delta^{15}\text{N}$ of Phenylalanine (the best AA proxy for $\delta^{15}\text{N}$ at the base of the food web) and trophic position (TP) was observed. A $\delta^{15}\text{N}$ mass balance model for the AA pool confirms that TP dependence is in fact expected for $\delta^{15}\text{N}_{\text{AA}}$ values. While this result may appear incongruent with current applications of $\delta^{15}\text{N}_{\text{AA}}$ in individual organisms, it is consistent with expectations that paleoarchives integrate the sinking flux of N over much longer timescales. We propose that for paleoceanographic applications, key $\delta^{15}\text{N}_{\text{AA}}$ parameters are ecosystem TP (determining the relative partitioning of ^{15}N into source vs. trophic AA pools), and the integrated $\delta^{15}\text{N}_{\text{AA}}$ of all common protein AA ($\delta^{15}\text{N}_{\text{THAA}}$), a proxy for nutrient N $\delta^{15}\text{N}$. Together, these provide a picture of regime shifts in planktonic ecosystem structure and $\delta^{15}\text{N}$ at the base of food webs. The SBB sedimentary record of these new parameters ($\delta^{15}\text{N}_{\text{THAA}}$, TP) correspond well with recent shifts in the PDO.