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Microbial denitrification: Isotopic clumping can clarify enzyme kinetics and nitrogen cycling

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Stable isotopes at natural abundance can elucidate aspects of nitrogen cycling in terrestrial and marine environments. A key uncertainty regarding interpretation of N and O isotope signals in nitrate is the origin of the observed linear relationship between $\delta^{15}N$ and $\delta^{18}O$, which differs between species and environments. We have applied density functional theory molecular modeling to investigate the enzymatic underpinnings of denitrification reactions and their isotope effects. Irreversible nitrate reduction is consistent with isotope signals observed in marine nitrate reduction and microbial cultures utilizing Nar enzyme. In contrast, observed isotope signals in terrestrial groundwater and Nap enzyme microbial cultures are consistent either with (1) partial reversibility prior to nitrite release or (2) a modified mechanism employing bidentate active site binding. Measurements of isotopic clumping ($\Delta^{15}N$-^{18}O and $\Delta^{18}O$-^{18}O) in intact NO_3^- using electrospray ionization Orbitrap mass spectrometry with base peak ($^{14}N^{16}O_3^-$) exclusion would be capable of distinguishing the two mechanisms. Anti-clumping (negative Δ) is predicted to develop during closed-system denitrification, but not in systems open to continuing nitrate supply, implying a clumping-based proxy which may be generalizable to quantifying system closure in other geochemical reactions. This work provides an example of the utility of molecular modeling to emerging isotope measurement capabilities applicable to geochemistry.