

Looking at reaction signatures of chemodenitrification through a multi-isotopic lens

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Over century long timescales, the climatic forcing of nitrous oxide (N₂O) is far larger than that of carbon dioxide. Although increasing atmospheric levels are linked to excess nitrogen loading, factors regulating emission of N₂O to the atmosphere remain difficult to predict. This challenge largely stems from disentangling the diversity of N₂O production pathways, especially in environments hosting dynamic redox conditions. Chemodenitrification, here referring to the abiotic reaction between Fe(II) and the reactive nitrogen intermediate nitrite (NO₂⁻), yields large amounts of N₂O, yet its environmental importance is not well understood. We present results from experiments designed to improve our understanding of the isotopic signatures of chemodenitrification-derived N₂O. We find that while NO₂⁻ reduction catalyzed by both aqueous and mineral associated Fe(II) imparts a range of kinetic isotope effects on NO₂⁻, the relationship between these N and O isotope effects (¹⁸ε:¹⁵ε) is consistently distinct from biological nitrite reduction. Further, the intramolecular ¹⁵N site preference of the product N₂O is also distinct from sources deriving from bacterial NO₂⁻ reduction. Although the complexity of natural systems presents numerous challenges, these results help refine our understanding of N₂O isotopic dynamics and high variability in fluxes, which may be in part be driven by heterogeneity in organic matter respiration and the redox cycling of iron.