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^{15}N and ^{18}O Isotope Systematics of Anaerobic Abiotic Reduction of Nitrite by Iron (II)

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Evidence is mounting for the environmental importance of interactions between iron and nitrogen. While previous studies have shown that oxidation of Fe(II) by nitrate (NO_3-) and nitrite (NO_2-) - a reactive intermediate of both reductive and oxidative N cycling processes - the controls on these reactions in the environment remain poorly understood. Moreover, the N product of abiotic, anaerobic NO_2- reduction by Fe(II) can include nitrous oxide (N_2O), nitric oxide, ammonium or dinitrogen gas - yeilding a myriad of implications for the fate of N across all types of ecosystems. Furthermore, we posit that such reactions may represent an important control on the dual NO_3- and NO_2- isotopic composition in reducing environments low in organic carbon (e.g., aquifers). To date, however, the kinetic isotope effects ($^{15}\varepsilon$ and $^{18}\varepsilon$) of these processes remain uncharacterized and hence our ability to use the dual isotopic composition of these compounds as quantitative records of cycling processes remains limited.

Here we present the first investigation of the dual (^{15}N and ^{18}O) isotope systematics of abiotic nitrite reduction by Fe(II) minerals under a variety of environmentally relevant pH values (6 to 8) and reactant concentrations (200 µM nitrite; 1 to 10 mM Fe(II)). In our experiments, we observe rapid decreases in nitrite correlated with loss of Fe(II) and the precipitation of Fe minerals that were distinct among pH conditions. Further, we observed a distinct evolution in isotopic effect during experiments. During the early stages, nitrite reduction occurred with no isotope effect, while later isotope effects increased to 12-18‰ for both $^{15}\varepsilon$ and $^{18}\varepsilon$, apparently reflecting an evolving importance of heterogenous reactions with Fe(II) associated with minerals. Additionally, the degree of oxygen isotope exchange between water and nitrite also influenced results and was closely related to pH. Although no exchange occurred at pH 8, lower pH conditions slowed reaction rates and induced substantial exchange - effectively overprinting any kinetic isotope effect. Finally, although generally producing N_2, under certain conditions the reaction converted up to 40% of the nitrite to nitrous oxide - representing a potentially important abiotic source of this greenhouse gas under environmentally relevant conditions. As studies suggest the potential for anaerobic, abiotic nitrogen transformations coupled with iron cycling, the N and O isotope effects determined here will be helpful for using dual isotopes of nitrite (and nitrate) to decipher the biogeochemical fate of N in host of important environments including soils, sediments, wastewater treatment.