

Reaction kinetics and isotopic fractionation during NO_3^- reduction to NH_4^+ under hydrothermal conditions

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Hydrothermal vent systems exist in all ocean basins and are important in regulating ocean chemistry. While the transformation of many elements during the convective circulation of seawater through the oceanic lithosphere is well established, nitrogen cycling in these environments remains poorly understood. Although many studies report a substantial influence of microbial communities utilizing nitrogen (N) metabolisms on the abundance of N species in the vicinity of vents, investigations of abiotic N reactions are limited. Nitrate (NO_3^-) is typically abundant in bottom seawater, but its concentration is usually undetectable in high-temperature focused vent fluids. Accordingly, it is frequently assumed that NO_3^- is quantitatively reduced to ammonium (NH_4^+). However, concentrations of NH_4^+ in vent fluids rarely reflect such quantitative conversion — raising questions about the production and fate of NH_4^+ in these systems. We conducted a series redox-buffered laboratory hydrothermal experiments at 150 to 250°C and 350 bar to determine reaction products, kinetics, and N and O isotope fractionation during NO_3^- reduction. Results indicate that in the presence of a hematite-magnetite redox buffer, NO_3^- is quantitatively reduced to NH_4^+ . The N isotopic effect associated with nitrate reduction to NH_4^+ ($^{15}\epsilon$) ranged from -70 to -10‰ at 150 to 250°C. Such large isotope fractionation, especially at lower temperatures, implies that incomplete reduction could impart a large isotopic imprint on the product NH_4^+ and residual NO_3^- . This work adds to our understanding of the nature of NH_4^+ isotopic composition in both high-temperature vent fluids and low-temperature mixed fluids, allowing us to better understand the production and consumption of N species as seawater is hydrothermally circulated through the oceanic lithosphere.