

POTENTIAL PRODUCTION OF NITROUS OXIDE WITH A UNIQUE ISOTOPIC SITE PREFERENCE ON THE EARLY EARTH FROM ABIOTIC REACTION OF NITRIC OXIDE AND FERROUS IRON.

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The Faint Young Sun paradox is central to questions of evolving habitability on Earth, and provides an important case study of the regulatory interactions that allow a planet to sustain a biosphere on long time-scales. Evidence for liquid water at Earth's surface, perhaps since the Hadean eon, despite vastly lower solar output is commonly attributed to high concentrations of the greenhouse gases CO₂ and CH₄ in the early atmosphere. The third most abundant greenhouse gas in the modern atmosphere, N₂O, has a global warming potential 300x that of CO₂ and 12x that of CH₄, and has previously been implicated in mid-Proterozoic warming [1]. However, Earth's earliest N₂O cycle, during the Hadean and Archean eons, has been less well-explored.

N₂O levels in the atmosphere are regulated by fluxes from the biosphere, abiotic reactions, and atmospheric oxidation state. Nitric oxide (NO) reduction to N₂O can occur via both enzymatic and chemical mechanisms. In both cases, Fe(II) supplies electrons for reduction of NO to N₂O; NO reductase enzymes contain Fe(II) in the heme cofactor at their active site, while NO reduction to N₂O with dissolved Fe(II) can also occur abiotically in anoxic environments.

In this study, we explored the rates and isotopic fractionation of abiotic NO reduction to N₂O in anoxic artificial seawater at circumneutral pH. The reaction occurred rapidly; in the presence of 75 μM Fe(II), 30% of the NO added was converted to N₂O within the first 24 hours of the experiment. Thus, at dissolved Fe(II) concentrations relevant for much of Precambrian time [2,3], abiotic production of N₂O from NO via Fe(II) would have been rapid and efficient. Moreover, the isotopic site preference (SP), the difference in δ¹⁵N between the two nitrogen atoms in N₂O, of N₂O produced from NO reduction by Fe(II) was +19‰. This SP is distinct from previous analyses of biological pathways (-10 to 0‰ for denitrification vs. +33-37‰ for hydroxylamine oxidation [4]) and is also different from the SP of abiotic N₂O produced by hydroxylamine oxidation by Fe(III) (33-35‰) [5]. Moreover, a kinetic isotope effect of +12.7‰ in δ¹⁸O_{NO/N2O} was observed during NO reduction to N₂O by Fe(II).

Based on these results, we propose that N₂O production from NO and Fe(II) may have been an important source of this potent greenhouse gas in the

ocean throughout Precambrian time, and perhaps even before the Great Oxidation Event. In the latter case, these abiotic reactions could have supplied a source of atmospheric N₂O before the evolution of NO reductase enzymes. The presence of abundant (~10⁻⁵ M) Fe(II) in the anoxic and ferruginous early ocean is well supported on theoretical and empirical grounds, but the origin of the requisite NO substrate is more debatable. We suggest that NO could have been produced by lightning discharge in volcanic clouds during Earth's earliest history, followed by enzymatic reduction of NO₂ to NO once biological pathways of nitrification and denitrification evolved. In any case, our results highlight an additional 'shunt' that links the oceanic iron and nitrogen cycles [7], with potential importance for both abiotic N₂O production and the modulation of ocean-atmosphere N₂O fluxes via enzymatic NO production during much of Earth's history.

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