NO LAUGHING MATTER: NITROUS OXIDE PRODUCTION BY CHEMODENITRIFICATION IN THE FERRUGINOUS PROTEROZOIC OCEAN. C. L. Stanton1, C. T. Reinhard1, J. F. Kasting2, T. W. Lyons3, J. B. Glass4*, 1School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA, 2Department of Geosciences, Pennsylvania State University, University Park, PA, USA, 3Department of Earth Sciences, University of California, Riverside, CA, USA, *Correspondence to jennifer.glass@eas.gatech.edu

Introduction: Due to dimmer solar luminosity, a modern greenhouse effect would not have melted water prior to ~2 Ga [1], although evidence for liquid water throughout Earth’s history is incontrovertible. Solutions to this “Faint Young Sun Problem” are often attributed to elevated carbon dioxide (CO2) and methane (CH4). Nitrous oxide (N2O) is ~300x more potent than CO2 and ~10x than CH4 on a 100 year timescale [2], but its contribution to the early greenhouse has largely been dismissed because it would have photodissociated in the anoxic Archean atmosphere.

Nitrous Oxide in the Proterozoic: N2O may have become an important greenhouse gas when oxygen (O2) levels rose to 0.0001-0.1x present atmospheric levels (PAL) following the Great Oxidation Event (~2.4 Ga) [3]. We hypothesize that chemodenitrification, the abiotic reduction of dissolved oxidized nitrogen to gaseous forms, was an important source of N2O during the Proterozoic. For this study, we focused on the reduction of nitric oxide (NO) by ferrous iron (Fe2+) shown below.

\[2 \text{NO} + 2 \text{Fe}^{2+} + 3 \text{H}_2\text{O} = \text{N}_2\text{O} + 2 \text{a-FeOOH} + 4 \text{H}^+\]

\[\Delta G_{\text{rxn}} = -148 \text{ kJ/mol}\]

Ancient Ocean Chemistry: Despite the increase in atmospheric O2, the deep ocean remained anoxic for much of the Proterozoic, serving as a large reservoir of Fe3+ [4]. New calculations based on iron mineral phase precipitation kinetics estimate that Proterozoic Fe3+ concentrations could have been 3 mM or higher [5].

The nitrogen species involved, NO, readily oxidizes in the presence of O2 and would also have been sustained in an anoxic marine environment. Additionally, the final step in microbial denitrification, reducing N2O to N2, would have been inhibited during the Proterozoic due to low copper concentrations [6].

We suggest that N2O production was promoted due to the chemical composition of the Proterozoic ocean.

Photochemical Modeling: In the Proterozoic, 1 ppmv N2O (roughly 3x modern) is needed to support surface temperatures above the freezing point with near-modern CO2 and CH4 [7]. A photochemical model was used to determine steady-state atmospheric N2O as a function of O2 and surface-atmosphere fluxes. To achieve 1 ppmv N2O at 0.001-0.1 PAL O2 levels, an upward flux 10-50x more the modern is needed.

Reaction Kinetics: Rates of N2O production were measured with Fe2+, nitrite (NO2-), nitrate (NO3-), or synthesized NO. Sterile artificial seawater experiments, conducted in an anoxic chamber, were sampled across regular time intervals on a gas chromatograph. Minimal N2O was produced with Fe2+ or NO alone, nor from 1 mM NO3 and Fe2+ in combination. Less than 0.01% of 1 mM NO3 was converted to N2O with 1 mM Fe2+. Increasing NO from 13 to 44 µM led to 2.9x higher N2O yield (Fig. 1A). Increasing Fe2+ from 10 to 500 µM led to 4.5x higher N2O yield (Fig. 1B). Preliminary calculations yield rate orders of 0.7 and 0.3 with respect to NO and Fe2+, respectively.

Implications: After the Proterozoic, ocean oxygenation would have decreased marine Fe3+ and NO, largely inhibiting chemodenitrification. However, our findings suggest that chemodenitrification could have contributed to solving the “Faint Young Sun Problem” in the Proterozoic when the conditions were optimal.


Acknowledgements: This material is based upon work supported by the National Aeronautics and Space Administration through the NASA Astrobiology Institute under Cooperative Agreement No. NNA15BB03A issued through the Science Mission Directorate.