

NITROGEN OXIDE CONCENTRATIONS IN NATURAL WATERS ON EARLY EARTH. Sukrit Ranjan^{1,*}, Zoe R. Todd², Paul B. Rimmer^{3,4}, Dimitar D. Sasselov² and Andrew R. Babbin¹, ¹MIT, 77 Massachusetts Avenue, Cambridge, MA 02139; sukrit@mit.edu, ²Harvard University, 60 Garden Street, Cambridge, MA 02138, ³MRC Laboratory of Molecular Biology, Francis Crick Avenue, Cambridge CB2 0QH, UK, ⁴University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0HE, UK, *SCOL Postdoctoral Fellow.

Introduction: A key challenge in origin-of-life studies is determining the environmental conditions on early Earth under which abiogenesis occurred [1]. While some constraints do exist (e.g. zircon evidence for surface liquid water), relatively few constraints exist on the abundances of trace chemical species, which are relevant to assessing the plausibility and guiding the development of postulated prebiotic chemical pathways which depend on these molecules.

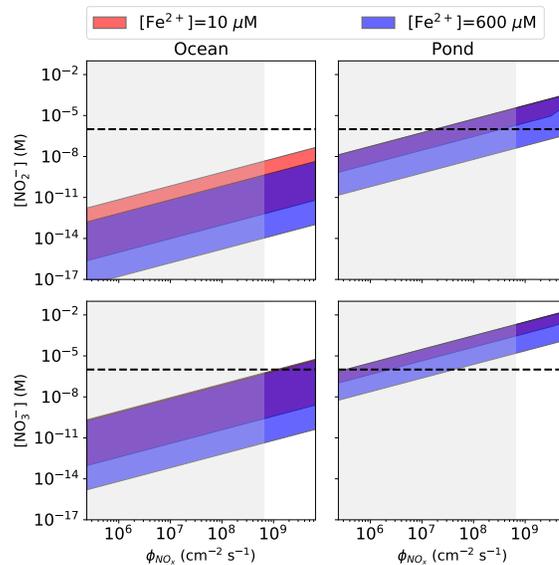
Nitrogen oxide anions (NO_x^- ; NO_2^- , NO_3^-) are chemical species of special importance. NO_x^- are invoked in diverse prebiotic chemistries, from the origin of protometabolism to the oligomerization of nucleotides [2,3]. More fundamentally, NO_x^- has long been proposed as a general source of fixed nitrogen for prebiotic and early biological chemosynthesis, based on the observation that lightning and precipitation in the N_2 - CO_2 atmosphere of early Earth should rain out NO_x^- into surficial aqueous reservoirs [4].

Past work has proposed that prebiotic NO_x^- levels were high, reaching concentrations of up to 10 mM in the bulk ocean [5,6]. We show that these conclusions rest on the key assumption that NO_x^- was stable in prebiotic natural waters unless processed at a hydrothermal vent. However, the reducing environment of early Earth had other sinks of NO_x^- , including reactions with Fe^{2+} and UV photolysis. We show that including these sinks suppresses $[\text{NO}_x^-]$ in the bulk ocean to sub-micromolar concentrations [7]. NO_x^- might have built up to prebiotically-relevant concentrations in favorable terrestrial environments, i.e. very shallow ponds with large drainage ratios. We explore the implications for prebiotic chemistry.

Methods: We calculate the kinetic steady-state concentration of NO_x^- by comparing its sinks to its source from lightning synthesis and subsequent rain-out to the surface. To calculate its source flux, we follow past work in using a photochemical model, largely reproducing past results. We extend past work by considering reduction by Fe^{2+} (known to have been present in the early oceans from banded iron formations) and photolysis from UV light (known to have been abundant on early Earth due to lack of biogenic ozone and from sulfur mass-independent fractionation) in addition to processing at hydrothermal vents. In calculating the sink due to UV, we include

the fact that UV photolysis would not have occurred below the photic depths of these molecules.

Results: We find that the sinks due to Fe^{2+} and UV are orders of magnitude stronger than the sink due to vents. Inclusion of the effects of these sinks suppresses $[\text{NO}_x^-] < 1 \mu\text{M}$ in the bulk ocean over the vast majority of the plausible parameter space. Oceanic NO_x^- -dependent prebiotic chemistries must identify mechanisms to concentrate local $[\text{NO}_x^-]$ above the oceanic mean. However, $[\text{NO}_x^-]$ could have reached prebiotically-relevant concentrations ($\geq 1 \mu\text{M}$) in favorable surficial aqueous environments, i.e. very shallow ponds with high drainage ratios. This is because such environments would have concentrated atmospherically-delivered NO_x^- from an area exceeding their surface area, and diluted it over a much shallower column than in the ocean. Such environments were likely present but not necessarily abundant on early Earth, meaning that they must be explicitly invoked by NO_x^- -dependent abiogenesis scenarios. Most NO_x^- was present as NO_3^- due to its higher stability, implying NO_3^- is a more plausible prebiotic reagent than NO_2^- . Intriguingly, our prediction that prebiotic pond environments should have had higher $[\text{NO}_x^-]$ than oceanic environments appears consistent with recent nitrogen isotopic studies of 3.2 Ga kerogens [8].



Range of concentrations of NO_2^- and NO_3^- as a function of atmospheric NO_x^- flux in ocean and pond environments for various $[\text{Fe}^{2+}]$. The

range of plausible atmospheric NO_x fluxes is shaded in grey. Micromolar concentrations, the boundary for prebiotic relevance, are demarcated by a dashed line.

References: [1] Ruiz-Mirazo K., Briones C., and de la Escosura A. (2014) *Chem. Rev.*, 114, 285–366. [2] Ducluzeau A.-L. et al. (2009), *Trends in Biochemical Sciences.*, 34, 9-15. [3] Mariani A. et al. (2018) *JACS*, 140, 8657-61. [4] Mancinelli R. L. and McKay C. P. (1988) *OLEB.*, 18, 311-325. [5] Wong M. L. et al. (2017) *Astrobiology* 17, 975-983. [6] Laneuville M., Kameya M., and Cleaves H. J. (2018) *Astrobiolog.* 18, 897-914. [7] Ranjan S. et al. (2019) *Geochemistry, Geophysics, Geosystems* 20, 2021-2039. [8] Homann M. et al. (2018) *Nat. Geosci.* 11, 665-671.