

**NO<sub>x</sub> IN THE ATMOSPHERES OF AQUAPLANETS AS ELECTRON ACCEPTORS FOR LIFE.** Michael. L. Wong<sup>1</sup>, Yuk. L. Yung<sup>1</sup>, and Michael. J. Russell<sup>2</sup>, <sup>1</sup>California Institute of Technology (1200 E. California Blvd., Pasadena, CA 91125; mlwong@caltech.edu), <sup>2</sup>Jet Propulsion Laboratory.

**Introduction:** A high-potential electron acceptor is required for life's emergence at submarine alkaline hydrothermal vents. This molecule would drive the highly endergonic reactions at the entry points to the autotrophic metabolic pathways, helping "light up" the hydrothermal fuels hydrogen and methane [1]. On early Earth, the most attractive candidates for this role are nitrate (NO<sub>3</sub><sup>-</sup>) and nitrite (NO<sub>2</sub><sup>-</sup>) [2].

What is the provenance of nitrogen oxides (NO<sub>x</sub>) on early Earth? An atmosphere dominated by CO<sub>2</sub> and N<sub>2</sub> and shocked by lightning and impacts will produce nitric oxide (NO) [2, 3]. Photochemical reactions involving NO and H<sub>2</sub>O vapor will then produce acids such as HNO<sub>3</sub> and HNO<sub>2</sub> that rain into the ocean and dissociate into NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> [4].

Previous work suggests that 10<sup>18</sup> g of NO<sub>x</sub> can be produced in a million years or so, satisfying the need for micromolar concentrations of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> in the ocean [2]. But because this number is controversial, we present new calculations based on an atmosphere comprised of 10 bars of CO<sub>2</sub>, 2 bars of N<sub>2</sub>, and stepped concentrations of water vapor dependent on surface temperatures.

**Modeling:** We aim to quantify the amount of NO<sub>x</sub> available for the emergence of life by adapting the Caltech/JPL one-dimensional chemical transport model (Kinetics) to early Earth. The model's photochemical package has been tested on numerous planetary bodies, including present-day Earth, Mars, Jupiter, Saturn, Titan, and Pluto. Given starting parameters (atmospheric profiles of pressure, temperature, the eddy diffusion coefficient, initial concentrations, etc.), Kinetics solves the mass continuity equation to calculate the steady-state distribution of each chemical species as well as the flux of each species between altitudes [5]. Using Kinetics, we can assess the photochemical production rates and precipitation rates of NO<sub>x</sub> molecules in the Hadean atmosphere.

**Preliminary results:** We have completed a preliminary model of the early-Earth atmosphere. For the temperature profile, we use the moist adiabatic lapse rate until reaching the radiative, isothermal zone (taken to be 180 K, approximately Earth's present-day mesopause temperature). Water vapor follows its saturation vapor pressure until the tropopause, then takes on a constant mixing ratio. We vary the two most uncertain parameters: surface temperature and lightning-induced NO. We test surface temperatures ranging from 10–50 °C and NO fluxes of 1, 3, and 5 × 10<sup>8</sup> molecules cm<sup>-2</sup>

s<sup>-1</sup>. In the end, we tabulate the precipitation and flux of NO<sub>x</sub> species at the bottom of the atmosphere.

The results show that HNO<sub>3</sub> is the dominant source of NO<sub>x</sub> in the Hadean ocean; HNO<sub>3</sub> rainout alone contributes 10<sup>12</sup>–10<sup>13</sup> grams of NO<sub>3</sub><sup>-</sup> to the ocean per year. Over the ocean water recycling timescale (~1 My), NO<sub>3</sub><sup>-</sup> exceeds micromolar concentrations by 1–2 orders of magnitude [Fig. 4]. (We assume that the Hadean ocean was twice as massive as today's [6].)

**Discussion:** These initial results assure the hydrothermal vent hypothesis of a crucial component. Thanks to the forces of lightning and photochemistry in Earth's early atmosphere, high-potential electron acceptors are certain to have been ubiquitous and readily available to kickstart life.

This model still requires tuning. Immediate improvements include changing the solar flux from present-day to young Sun luminosity. We will also vary the bulk atmospheric composition to see how NO<sub>x</sub> production depends on the mixing ratios of CO<sub>2</sub> and N<sub>2</sub>, which may have varied during the tumultuous Hadean epoch.

Once completed, this model can be applied to any wet, rocky world. The next obvious choice is early Mars. With the recent confirmation of methane on Mars [7], the excitement about Martian life has never been higher. This model will be able to predict whether or not such life could have arisen at hydrothermal vents on early Mars, when the Red Planet was more tectonically active, had a significantly thicker CO<sub>2</sub> atmosphere, and flowed with liquid water.

**References:** [1] Russell, M. J. *et al.* (2014) *Astrobiology* 14(4), 308–343. [2] Ducluzeau, A-L. *et al.* (2008) *Trends in Biochemical Sciences* 34, 9–15. [3] Nna Mvondo, D. *et al.* (2001) *Adv. Space Res.* 27, 217–223. [4] Yung, Y. L. and McElroy, M. B. (1979) *Science* 203, 1002–1004. [5] Yung, Y. L. and DeMore, W. B. (1999). *Photochemistry of planetary atmospheres*. New York: Oxford University Press. [6] Bounama, C. *et al.* (2001) *Hydrology and Earth System Sciences* 5, 569–575. [7] Webster, C. R. *et al.* (2014) *Science* 347, 415–417.