EVALUATING N_2O AS AN EXOPLANET BIOSIGNATURE: COMBINING BIOGEOCHEMICAL, PHOTOCHEMICAL AND SPECTRAL MODELS.
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Introduction: Recent studies demonstrating the possibility of 'false positives' for biotic O_2 [e.g., 1] and scenarios of low CH_4 and O_2 [2], as indicated for a billion or more years of Earth history, have increased the importance of fully characterizing alternative biosignature gases to support the search for life outside the solar system. Nitrous oxide (N_2O) has been proposed as an exoplanet biosignature because its abiotic sources on Earth are small and because it has potentially observable spectral features [3]. However, the absorption bands of N_2O are relatively weak, and no study has thus far examined the realistic limits of N_2O detectability assuming both chemically plausible fluxes and photochemistry. Here we present preliminary results from a novel approach coupling the ocean biochemistry model GENIE [2] with the NAI-VPL *Atmos* photochemical model [4] to predict the mixing ratio profiles of N_2O for a variety of oxygenation and flux conditions. We then model the spectral observability of these predicted N_2O concentrations in simulated emission and transmission spectra using the SMART radiative transfer code [5]. We describe the limiting scenario for an ocean biosphere below.

Scenario: N_2O production in the ocean is inhibited by oxygenation of the water column, but could have been substantially greater during parts of the Proterozoic Eon (2.5-0.8 Ga) after the advent of oxygenic photosynthesis, but before the surface ocean was fully oxygenated. However, N_2O is more effectively photolyzed with reduced O_2, which provides a shielding effect. A recent estimate for pO_2 during the Proterozoic is 0.1% PAL, but could have been as high as 2.5% PAL without significant oxygenation of the deep ocean and reduced N_2O generation [6]. An optimistic limit for the N_2O flux from the ocean is obtained by assuming that nitrate is the sole electron acceptor for carbon mineralization, and that complete reduction to N_2 was inhibited, perhaps by trace metal limitation, i.e., all primary production results in an N_2O flux. In this case, we obtain a global N_2O flux of 3.2×10^{13} mol/year.

Results: Inputting the above flux into the photochemical model results in a ground-level N_2O concentration of 126 ppb for pO_2 = 0.1% PAL, and 1,800 ppb for pO_2 = 2.5% PAL. We find that, for a Sun-like host star, ocean-atmosphere systems will tend to produce maximum steady state concentrations of ~2 ppm N_2O assuming Earth-like levels of primary productivity, or about 6X the modern N_2O concentration (~320 ppb), which is mostly derived from the terrestrial biosphere. Greater concentrations of N_2O would require large contributions from a terrestrial biosphere far exceeding that of modern day Earth. For contrast, an estimate for abiotic generation of N_2O from lightning is <1 ppb [7].

N_2O has significant spectral bands centered at 3.7, 4.5, 7.8, and 8.6 μm. Figure 1 shows the strength of the MIR bands as a function N_2O concentrations resulting from the limiting N_2O flux and pO_2 values described above. While N_2O has weak bands between 1.3 and 3.7 μm, we find they produce insignificant absorption for N_2O concentrations plausible from an ocean biosphere. This is potentially problematic because future space-based telescope concepts such as LUVOIR will likely not have access to wavelengths longer than 2.5 μm. Additionally, photochemical destruction at high altitudes will mute the transit transmission signatures of N_2O. In sum, we find that biogenic N_2O would only be detectable through direct infrared (> 3.7 μm) observation at levels plausible for an ocean-based biosphere.

References: [1] Harman et al. (2015) *ApJ,* 812:137. [2] Olson et al. (2016) *PNAS*, 113:11447–11452. [3] Sagan, et al. (1993) Nature 365:715–21. [4] Arney et al. (2016) Astrobiology 16(11):873-899. [5] Meadows & Crisp. (1996) JGR 101:4595–4622. [6] Reinhard et al. (2016) PNAS, 113:8933–8938 [7] Schumann & Huntrieser, H. (2007) *ACPD* 7:2623–2818.

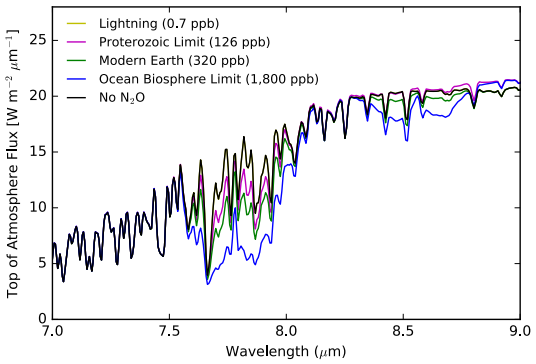

Figure 1 – Synthetic mid-infrared (7-9 μm) emission spectrum of an Earth-like planet with N_2O levels consistent with five scenarios: 1) No N_2O (black), 2) production from lightning only (yellow; 0.7 ppb), 3) the Proterozoic limit assuming pO_2 = 0.1% PAL (magenta, 126 ppb), 4) the modern Earth level (green, 320 ppb), 5) and the maximum limit for an ocean biosphere, assuming (3) except pO_2 = 2.5% PAL (blue, 1,800 ppb).