ATMOSPHERIC DISEQUILIBRIUM BIOSIGNATURES ON EARTH THROUGH TIME

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Introduction: Waste gases from life may modify the atmospheric composition of inhabited planets. Consequently, atmospheric chemical disequilibrium caused by such gases has been proposed as a possible biosignature for exoplanets [1]. In previous work, we developed a quantiative metric for thermodynamic atmospheric disequilibrium and applied it to Solar System atmospheres [2]. We found that when the entire atmosphere-ocean reservoir is considered, Earth has the largest thermodynamic disequilibrium compared to other Solar System atmospheres. This disequilibrium is biogenic, and mostly attributable to the coexistence of O_2, N_2, and liquid water. In the absence of oxygenic photosynthesis and biological denitrification these disequilibrium species would not persist; they would react to form nitric acid in the ocean. This disequilibrium is also potentially detectable on exoplanets since both O_2 and N_2 have spectroscopic features [3,4], and techniques have been proposed to detect surface oceans [5]. However, Earth's atmosphere has possessed a ~20% oxygen atmosphere for only 1/8th of history. Here, we explore whether remotely detectable disequilibrium biosignatures were present in Earth's atmosphere at earlier times in its evolution.

Methods: We compiled plausible ranges for Earth's atmospheric and ocean composition through the Archean, Proterozoic, and Phanerozoic. Using these compositions we calculated the thermodynamic disequilibrium in Earth's atmosphere-ocean system using the methodology of [2]. In short, we calculate the equilibrium state of the atmosphere-ocean system using multiphase Gibbs energy minimization. We quantify disequilibrium as the difference in Gibbs free energy between the true ("observed") state and the equilibrium state. The larger this available Gibbs energy, the larger the untapped free energy in the atmosphere-ocean system, and greater the disequilibrium. The Gibbs energy calculation also reveals the degree to which each species contributes to disequilibrium.

Results: Fig. 1 shows a preliminary calculation of the evolution of Earth's atmosphere-ocean disequilibrium since 3.5 Ga. There is considerable uncertainty about the magnitude of the Archean and Proterozoic disequilibria due to inexact knowledge of past atmospheric composition. However, we calculate a step-wise increase in Earth's atmosphere-ocean disequilibrium that parallels the rise of oxygen. In the Proterozoic, the disequilibrium is mostly attributable to the coexistence of O_2, N_2, and liquid water, as is the case for the Phanerozoic. However, in the Archean, the largest contributor to the disequilibrium is the coexistence of CO_2, CH_4, N_2, and liquid water – these species should react to form ammonium and bicarbonate in the ocean.

Discussion: The disequilibrium in the Proterozoic and Phanerozoic is clearly biogenic. The disequilibriaum in the Archean is also biogenic since methanogenesis is replenishing CH_4. We conclude that Earth's atmosphere-ocean system has been in disequilibrium throughout its history due to the presence of biology. The detectability of these disequilibria and potential false positives will be discussed.

References: [1] Lovelock, J. E. (1975), *Proc. R. Soc. Lond., B, Biol. Sci.* 189(1095), 167-181. [2] Krissansen-Totton J., Bergsman, D. and Catling D. C. (2016), *Astrobiology,* 16(1), 39-67. [3] Schwieterman, E. et al. (2015) *ApJ.*, 810, 1. [4] Sagan, C. et al (1993), *Nature* 365(6448), 715-721. [5] Robinson, T. D., Meadows, V. S. and Crsip, D. (2010) *ApJ. 721*, 1.

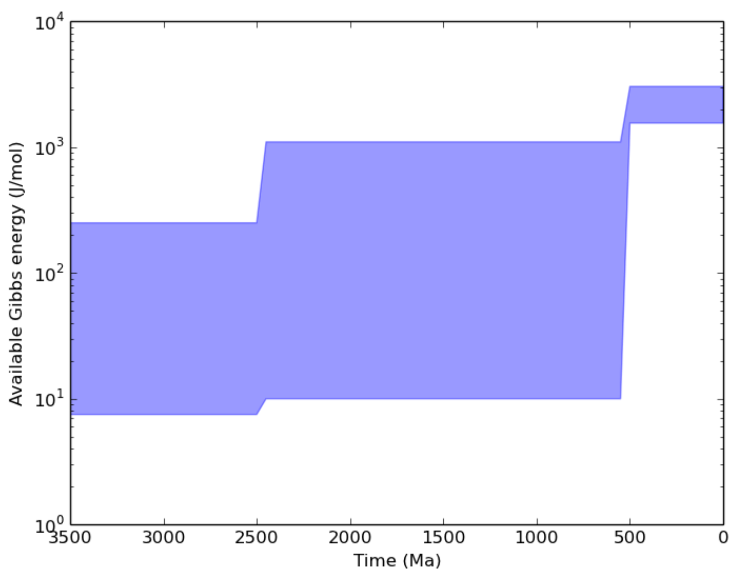

Fig. 1: Earth's atmosphere-ocean disequilibrium since 3500 Ma. The broad range of Gibbs energies in the Proterozoic and Archean are attributable to the large uncertainty in atmospheric and ocean compositions. Estimates for the composition of the atmosphere and ocean through time were sourced from a variety of proxies and theoretical calculations.