

ON DETECTING BIOSPHERES FROM THERMODYNAMIC DISEQUILIBRIUM IN PLANETARY ATMOSPHERES. Joshua Krissansen-Totton¹, David S. Bergsman² and David C. Catling¹ ¹Department of Earth and Space Sciences/Astrobiology Program, University of Washington, ²Department of Chemical Engineering, Stanford University. Contact: joshkt@uw.edu

Introduction: Earth's atmospheric composition is profoundly altered by the biosphere. All the major constituents (except Ar) are cycled by biology [1], and the resultant mixture of gases is not in thermodynamic equilibrium. It has been argued that atmospheric disequilibrium is a generalized biosignature, potentially accessible to remote sensing [2, 3]. However, disequilibrium can also be maintained by abiotic processes such as photochemistry or volcanic outgassing, and so inferring life from disequilibrium is a question of degree and context. Since the atmospheric composition of terrestrial exoplanets can be inferred from future telescopic spectra, the question arises as to whether thermodynamic disequilibrium could be used to determine if exoplanets host life. Here, we quantify thermodynamic atmospheric disequilibrium for the Solar System planets and develop methodologies that could be applied to future observations of Earth-like exoplanets.

Methodology: For a closed system, chemical equilibrium is achieved when the Gibbs free energy of the system, $G_{(T,P)}$, is minimized:

$$G_{(T,P)} = \sum_i n_i \left(G_{i(T,P)}^\circ + RT \ln \left(P \gamma_{fi} n_i / n_{tot} \right) \right) \quad (1.1)$$

Here, n_i is the number of moles of species i , $G_{i(T,P)}^\circ$ is the standard Gibbs free energy of species i at some reference pressure P_r and temperature T , P is the pressure of the system, γ_{fi} is the fugacity coefficient of species i (corrects for non-ideality in high pressure atmospheres such as Venus), T is the temperature of the system, n_{tot} is the total number of moles of all species, and R is the universal gas constant. The equilibrium composition can be found by determining the molecular abundances, n_i , that minimize $G_{(T,P)}$ subject to atom conservation. The equilibrium state of a planetary atmosphere is thus found by solving a constrained, non-linear optimization problem (we used Matlab's *fmincon* function). For Earth, a purely gas phase approach is insufficient because the atmosphere is in contact with a surface ocean, which requires a multiphase calculation. Following [4], we constructed a Gibbs free energy minimization method to calculate equilibrium in Earth's atmosphere-ocean system.

For both gas phase and multiphase systems, to quantify disequilibrium, we calculate the difference in the Gibbs free energy between the observed state and calculated equilibrium state.

Results and Discussion: Fig. 1 shows the Gibbs free energy difference for each Solar System atmosphere. The large disequilibrium in Mars' atmosphere (136 J/mol) comes from the photochemically induced coexistence of CO and O₂. The purely gas phase disequilibrium of Earth's atmosphere (no ocean) is only 1.5 J/mol, which is not unusual compared to other Solar System atmospheres. However, the disequilibrium in Earth's atmosphere-ocean system, 2326 J/mol, is more than an order of magnitude larger than all other Solar System atmospheres. The largest contributor to this disequilibrium is the coexistence of O₂, N₂ and liquid water; in equilibrium these species react to form dissolved nitrate and H⁺ ions. This disequilibrium is maintained by life: O₂ is produced almost exclusively by oxygenic photosynthesis, and N₂ is modulated by microbial nitrification and denitrification.

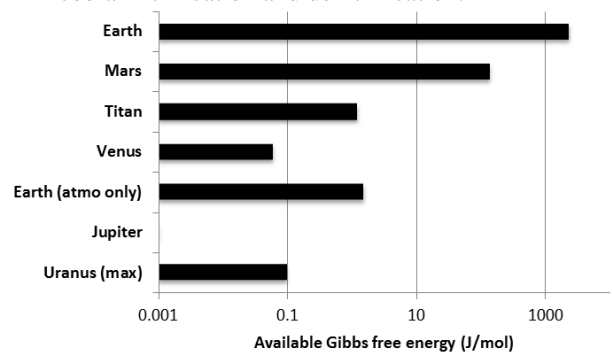


Fig. 1: Gibbs free energy (observed-equilibrium) for each planetary atmosphere, measured in joules per mole of atmosphere.

To calculate gas phase chemical equilibrium requires only bulk atmospheric abundances, surface temperature, and pressure, all of which are potentially accessible to future observations of exoplanets. In principle, multiphase calculations for atmosphere-ocean systems require knowledge of surface ocean volume, pH, and salinity, which is not accessible to remote observations. Fortunately, sensitivity analysis reveals that the disequilibrium in Earth's atmosphere-ocean system is mostly insensitive to these variables. We conclude that thermodynamic disequilibrium is a potentially valuable life detection metric for exoplanets.

Refs: [1] Catling D.C., Kasting J.F., in *Planets and Life: The Emerging Science of Astrobiology*, Sullivan, W., Baross, J., Eds. (Cambridge University Press, 2007), 91. [2] Lovelock J. E., Kaplan I. (1975) *Proc. R. Soc. B.* B189, 167. [3] Lederberg J. (1965) *Nature* 207, 9. [4] Karpov I. K. et al. (1997) *American Journal of Science* 297, 767.