



Atmospheric Chemical Disequilibrium as a Biomarker

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Abstract

Most of the present researches focus on find molecules which can address the availability for life on other planets. Chemical disequilibrium of the Earth's atmospheric composition has long been seen as a consequence of widespread life on a planet [4]. While a biological explanation for the presence of some molecules may be plausible, it is also possible that their source are non-biological reactions.

The chemical disequilibrium can be recognized in the contemporaneous presence of usually reacting species, such as molecular oxygen, reduced gasses, reduced carbon in biota, and the reduced crust of the solid Earth. We demonstrate with a first order estimate that chemical disequilibrium in the atmosphere results primarily from photosynthetic activity. We start by describing the atmosphere as a closed thermodynamic system on suitable time scales, since its chemical activity is faster than matter inflows. Consequently, the atmosphere should be driven towards the thermodynamic equilibrium state by a number of chemical processes. In conclusion, we suggest that the extent of chemical disequilibrium is the most general biomarker to identify widespread life on other planetary systems, but that this biomarker is only suitable for detecting photosynthetic life..

1. Introduction

The great and long lasting debate on what is life has never found a complete answer. This lack weakens any proposal of molecular biomarkers. Most of the present research focuses on the presence of specified biomarkers, in order to recognize the availability for life. Several of the proposed molecules are also the product of other non-biological reactions. This is the case of chemotrophic activities, such as the ones producing CH_4 . The problem is then to find a marker specific for life, which can be seen in the high extent of some parameters.

Life fights for low entropy [6]; the study of Earth compartments in contact with the biosphere (atmosphere, geosphere) and their interactions can give information

on life dynamics and on its effect on Earth System. High entropic gradients can be addressed as important biomarkers. Life allowed the use of more degree of freedom associated to geological and atmospheric cycles, and so the generation of more free energy from the same initial energy sources; finally, it increases the net entropy production during time.

The presence of an high disequilibrium in the atmosphere is due to many inflows (Figure 1). Most of the chemical disequilibrium extent is expressed as the contemporaneous presence of usually reacting gasses, as O_2 and reduced gasses. We address the search for biomarkers as the measure of the distance of the Earth Atmosphere from its thermodynamic equilibrium.

The chemical disequilibrium in the Earth atmosphere is calculated as the net entropy production of the system, applying a simple, reduced atmospheric chemical model. The entropy production due to chemical reactions can be calculated by:

$$\left(\frac{1}{V}\right)\left(\frac{dS}{dt}\right) = \left(\frac{1}{V}\right)\left(\frac{A}{T}\right)\left(\frac{dz}{dt}\right) \quad (1)$$

where V is the total volume of the system, expressed in liters, A is the Chemical Affinity of each reaction. T is assumed at 300 K. For a simple step reaction, this can be written [3] as:

$$\left(\frac{1}{V}\right)\left(\frac{dS}{dt}\right) = R(R_f - R_r)\ln\left(\frac{R_f}{R_r}\right) \quad (2)$$

where R is the Boltzmann gas constant and reaction rates R_f , R_r can be deduced by each reaction formula. Atmospheric reaction were then selected from the most updated and widely used databases [2] [5]. Examined chemical compounds are shown in Table 1 with their actual concentration. Selected reactions were tested in a batch model [1]. Finally, the net entropy production of each reaction has been calculated, and integrated on different time scales.

2. Summary and Discussion

We have provided a first-order estimate of the chemical disequilibrium that drives the atmosphere far from

the Thermodynamic Equilibrium. The net entropy produced by atmospheric chemical reactions is in the order of magnitude of $\sim 10^6 \text{ J K}^{-1} \text{ m}^{-2}$, between 50 to 100 times higher than the photochemical and electrochemical power inflows in the atmosphere, and quite similar to the inflows due to biochemical activities. Due to the high entropy produced by oxygen chemistry, photosynthesis can be addressed to have been the higher and more durable source of large extent chemical disequilibrium in the atmosphere.

We conclude that our thermodynamic analysis of atmospheric disequilibrium provides a quantitative, holistic basis to understand the effects that life has on transforming the whole Earth system. The proposed approach should help us to better understand habitable conditions, allow us for possible remote detection of life on other planetary bodies, but also provides us a holistic framework to evaluate the effect of human activity on the natural disequilibrium of the Earth system.

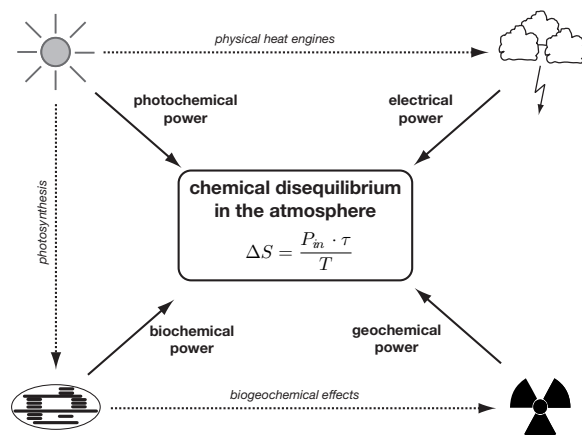


Figure 1: The most important power inflows driving chemical disequilibrium in the Atmosphere.

Table 1: Chemical compounds considered in our model.

Compound	Atmospheric Concentration / M
CO ₂	0.00032
H ₂ O	0.005
O ₃	$4 \cdot 10^{-8}$
NH ₃	$1 \cdot 10^{-8}$
NO _x	$3 \cdot 10^{-5}$
O ₂	0.2085
N ₂	0.78
CO	$1 \cdot 10^{-7}$
CH ₄	$2 \cdot 10^{-6}$
N ₂ O	$3 \cdot 10^{-4}$

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