Exploring Chemical Disequilibrium Biosignatures in Icy Moon Oceans with Antarctic Subglacial Lake Analogs

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Abstract

Chemical disequilibrium, or the long- term coexistence of two or more incompatible species, may be a useful metric for finding life. The presence of CH4 and O2 (that ought to react) in Earth's atmosphere is an example and indicates biogenic sources of these gases. It is reasonable to think that life on an exoplanet or an icy moon would influence chemical disequilibrium because terrestrial life influences chemical disequilibrium by cycling almost all the bulk atmospheric gases. A chemical disequilibrium biosignature is appealing because it does not make assumptions about underlying biochemistry, unlike a search for biomolecules (e.g. DNA). Krissansen-Totton et al. (2016) calculated the atmosphere or atmosphere-ocean chemical disequilibrium of several planets and moons in our solar system. The metric used was the Gibbs free energy released when all chemical species are reacted together to an equilibrium state. They found that Earth's atmosphere-ocean system has significantly more disequilibrium than any other planet due to biogenic fluxes. They propose high atmosphere-ocean chemical disequilibrium as a biosignature for exoplanets similar to the modern Earth, with photosynthetic biospheres. While disequilibrium is promising for detecting life on photosynthetic worlds, it remains to be determined how this metric applies to oceans in icy moons such as Europa and Enceladus. Indeed, an argument exists that purely chemosynthetic life will tend to destroy disequilibrium through its metabolism and produce anomalous equilibrium (Sholes et al., 2018). Thus, disequilibrium may have different interpretations: (1) High disequilibrium (uneaten food) on a dead world is an anti-biosignature. (2) High disequilibrium on a photosynthetic world would come from biogenic gases. (3) Low disequilibrium on a chemosynthetic world would be caused by biological consumption of chemical energy. We investigate the chemical disequilibrium biosignature for oceans on icy moons using analog environments: Antarctic subglacial lakes. First, we compute the disequilibrium in an observed "living" and modeled "dead" Antarctic subglacial lake. For a "living" subglacial lake, we use the aqueous composition of Subglacial Lake Whillans (SLW), located in Western Antarctica (Christner et al., 2014). For a "dead" subglacial lake, we model the steady-state chemistry of SLW if there was not life influencing chemical cycling. The disequilibrium calculation of both environments indicate that the "dead" lake has more available Gibbs energy than the "living" lake, suggesting that in purely chemosynthetic environments, anomalous chemical equilibrium is a sign of life, or inversely, that large chemical disequilibrium is an anti-biosignature. Our work on subglacial lakes can be considered within the context of measurements of Enceladus' plumes by the Cassini Spacecraft. Plume measurements indicate relatively high available Gibbs energy in Enceladus' ocean which may indicate low biomass, if life exists.

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1. INTRODUCTION

Chemical disequilibrium is the long-term coexistence of two or more incompatible molecules or atoms.

Example of chemical disequilibrium: coexistence of CH₄ and O_2 in Earth's atmosphere. They should react out of the atmosphere, but instead persist because of biological fluxes.

In dark environments (e.g. icy moon oceans) all life, as we know it, must get energy by consuming chemical disequilibria.

Chemical Disequilibrium = Microbial food = **Chemical Energy**

Relatively low chemical disequilibrium should be a biosignature for icy moon oceans because it is a sign that life is consuming the microbial food generated by abiotic processes (e.g. hydrothermal vents).

We explore this biosignature by calculating the chemical disequilibrium in

- 1. an environment analogous to icy moons: Antarctic Subglacial Lake Whillans (Figure 1).
- 2. Enceladus' ocean.



Figure 1: A map showing the location of Subglacial Lake Whillans.

2. METHODS

Chemical disequilibrium quantification: The available work, or Gibbs free energy, that is produced from reacting all chemical species to an equilibrium state. We do this calculation with a Gibbs minimization code. [1]

Disequilibrium = Available Gibbs energy = ΔG Subglacial Lake Whillans: **3 ΔG calculations**

- 1. Observed lake composition which is influenced by the life found in the lake. [2]
- 2. Modeled "dead" lake chemistry (i.e. lake composition if life was not influencing lake chemistry). See Figure 2.
- 3. Modeled lake composition if an aerobic heterotrophic ecosystem was energy limited (similar to Figure 3).
- Enceladus' Ocean: **2 ΔG calculations**
- 1. Observed ocean composition from Cassini measurements and Fifer et al. modeling (see poster 127-064).
- 2. Modeled ocean composition if a methanogenic ecosystem was present and was energy limited. See Figure 3.

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Relatively small amounts of chemical energy in icy moon oceans might be a biosignature because it is a sign that life is consuming the microbial food generated by geologic processes.

Enceladus' ocean likely has a lot of chemical energy which would indicate low biomass, if life exists, because life should consume this free lunch.

Air O ₂	O ₂ O	2	Space
Antarctic ice sheet	Melting ice flux	Bubbles carry O_2 through ice xes O_2 into lake $(\Phi_{in}(O_2))$	Enceladus' ice sh
Lake Whillans CH ₂ O CH ₂ O come from dead ancient microbes Bedrock	Abiotic reaction r $O_2 + CH_2O \rightarrow C$ Steady state "dead" Lake $\frac{d[O_2]}{dt} = 0$	ate R([O ₂]) [3] $O_2 + H_2O$ O ₂ concentration of the Whillans is given by solving $O = \Phi_{in}(O_2) - R([O_2])$	Enceladus' ocean Methanogens ea 30 kJ/mol is the the concentration energy limited ea [4] 30 kJ mol ⁻
Figure 2: Method for modeling the "Dead"			Figure 3: Me
Subglacial Lake Whillans.			methanogeni

 ΔG_r = Gibbs energy of reaction (J mol⁻¹ $R = \text{ideal gas constant } (\text{J mol}^{-1} \text{ K}^{-1})$ T =temperature (K) $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$ at H_2 until they obtain 30 kJ/mol from this reaction. energy requires to generate 1 mol of ATP. We find ns (e.g m_{CH4} in mol/kg H_2O) associated with this cosystem by solving for x in the following equation. $= \Delta G = \Delta G_{r} + RT \ln \left(\frac{(m_{CH4} + x)}{(m_{CO2} - x)(m_{H2} - 4x)^{4}} \right)$

ethod for modeling an energy limited methanogenic ecosystem in Enceladus' ocean.

Observed (living)





- that life isn't around to consume the available microbial food

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