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A BIOENERGETIC PATH TO PREDICT THE HABITABILITY OF ENCELADUS: STARTING FROM ANALOG ENVIRONMENTS

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RESUMEN

La confirmación del agua líquida en el satélite de Saturno, Encélado, aunada a la detección de partículas de sílice e hidrógeno molecular ha apoyado la noción de un satélice helado habitable. Además, hay indicios de actividad hidrotermal en el Encélado actual. Los ambientes análogos conceden la oportunidad de evaluar si en este océano global puede prosperar la vida y en qué medida. Esta valoración es posible utilizando la expresión de Helmholtz-Gibbs de bioenergética, para determinar el rendimiento de energía bajo condiciones no estándar. En este contexto se registraron distintos parámetros (e.g., pH, temperatura y composición del fluido) de 570 puntos de muestreo para determinar el rendimiento de la energía libre de Gibbs no estándar y cuantificar la habitabilidad del océano de Encélado. El flujo de energía resultó en 9×10^{23} W, esto es al menos dos órdenes de magnitud mayor que estudios anteriores en los que no se consideraron condiciones no-estándar. Nuestros resultados sugieren un Encélado más habitable que lo pensado anteriormente.

ABSTRACT

The confirmation of liquid water in the Saturn's satellite Enceladus and the detection of silica grains and molecular hydrogen have supported the conjecture of a habitable icy satellite. In addition to this notion, there is an indication of ongoing hydrothermal activity on Enceladus. Analog environments provide the opportunity to test whether this global ocean may harbor life and to what extent. This examination is possible using bioenergetic principles, especially by Helmholtz-Gibbs' expression to determine energy yield under a non-standard state. Within this context, a series of environmental parameters (e.g., pH, temperature, and fluid composition) from 570 site studies were compiled to determine the non-standard Gibbs free energy yield and to quantify the habitability of Enceladus Ocean. The energy flux resulted in 9×10^{23} W, which is at least two orders of magnitude larger than previous studies where the non-standard condition was not considered. Our results suggest an Enceladus Ocean more habitable than previously thought.

Key Words: enceladus — habitable planets — icy bodies — methanogenesis

1. ENCELADUS

Among the Solar System bodies, Enceladus has become one of the most interesting targets for Astrobiology. This interest started from to the very beginning of Cassini flybys observations of Enceladus which resulted in the detection of extensive water plumes venting into the space from the south polar region. Moreover, geophysical data from the Cassini spacecraft describe a mean core radius of ∼192 km and a ∼60 km water layer which includes a mean global ocean thickness of ∼30 km (Hemingway et al. 2018). Several plume impurities have been detected such as silica nanoparticles, H_2, CH_4, N_2, NH_3, CO, CO_2, and a wide variety of organic compounds (Cable et al. 2020). Among them, remarkably, hydrogen (H_2) and silica nanoparticles because their presence and abundance can be rooted to active hydrothermal systems, therefore, enhance the favorability of life or "habitability" of Enceladus. This hydrothermal scenario is also sustained by the low-density interior of Enceladus, which implies a core composition dominated by mafic and ultramafic minerals (Mg-, Fe-, and Ca- bearing olivine).

2. HYDROTHERMAL ENVIRONMENTS

The interface ocean-core in Enceladus is likely to be an analogue of Earth peridotites, i.e., ultramafic rock composed by primary minerals such as olivine and pyroxene (Zandanel et al. 2021). Within the group of geochemical reactions commonly associated with hydrothermal environments, submarine and continental peridotite serpentinization stand out, see

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e.g., general equation (1) which depicts a redox reaction where water acts as an electron donor and the ultramafic basement (oliv=olivine; pyr=pyroxene; serp=serpentine; bruc=brucite; mag=magnetite) as the acceptor. These reactions commonly occur at oceanic spreading centers where water convection cells take place. This mineral alteration toward serpentinite, predominantly, occurs in a wide range of temperatures, including the low-temperature chimneys known as "white smokers" with a fluid temperature of $< 300°$ C (Herzig & Hannington 2006).

$$oliv + pyr + H_2O \rightleftharpoons serp + bruc + mag + H_2 \quad (1)$$

Serpentinization is especially relevant for astrobiology because hydrogen is highly reductant. On Earth, oxygen and other molecules are prone to oxidize H_2 releasing useful energy for some organisms over the reaction. Among the environments on Earth, white smokers are the most comparable hydrothermal vents on Enceladus and may help us to assess habitability on this satellite since serpentinization at low temperature has been claimed to be the most plausible geochemical processes to occur on Enceladus. This statement is supported on the geophysical approaches for heat power generated by tidal friction, i.e., mechanical energy that is converted into heat, which has been predicted to be $\sim$10 GW, implying a geothermal scenario of water upwelling with a temperature of 363 K (Choblet et al. 2017). Temperature and water residence time are determinant factors for the hydrothermal fluid chemical composition (Tivey 2016). Consequently, the understanding of hyperalkaline white smokers is a starting point to infer the habitability of Enceladus.

3. BIOENERGETICS OF METHANOGENESIS

The Lost City hydrothermal field was discovered in 2000, since then, the exploration of low-temperature systems has grown expansively. As a result, the prediction of their geochemical characteristics is rapidly evolving from the initial descriptive works. Therefore, the debate about habitability prediction and its quantification on Enceladus can now be addressed. To quantify habitability two main aspects are needed: an analog environment (low-temperature hydrothermal systems), and a bioenergetically viable dissimilatory metabolism, i.e., an exergonic redox reaction, described by the general equation (2).

$$aA + bB = cC + dD \quad (2)$$

Regarding the metabolism, a plausible reaction is hydrogenotrophic methanogenesis, i.e., uses the inorganic serpentinizing product H_2 as electron donor, see equation (3), with the molecules chemically speciated (the equation is not balanced). Besides, CO_2 and H_2 have been detected in Enceladus plumes and have been used as an evidence for hydrothermal processes. The methanogenesis viability on Enceladus Ocean has been suggested earlier (Waite et al. 2017).

$$HCO_3^- + CO_3^{2-} + CO_{2(aq)} + H^+ \rightleftharpoons CH_{4(aq)} + H_2O \quad (3)$$

To approach the standard Gibbs free energy of reaction (3) it was applied the equation (4). In order to modify this resultant ΔG_r° value to 363 K, i.e. the fluid temperature on Enceladus according to tidal heating (Choblet et al. 2017), standard Gibbs free energy was adjusted by interpolation in accordance with previous assessments (Amend & Shock 2001).

$$\Delta G_r^\circ = \Sigma(n_i \Delta G_{fi})_{CD} - \Sigma(n_i \Delta G_{fi})_{AB} \quad (4)$$

Additionally, there are 570 measurements at site points available. They were compiled from ophiolite sites geothermally active, such as H_2, CH_4, and CO_2 concentration, and pH. These values obtained from the fluid were taken as the environmental analogs of the Enceladus hydrothermal systems. Typical examples of these sites are the Lost City hydrothermal field, Mid-Atlantic Ridge, and the peridotite aquifer location Samail Ophiolite, Oman. From each of these elements, the mean was calculated and, assuming normality, a confidence interval at 95% was obtained, which provides bounds for the central values and allows to avoid the effect of outliers. These mean values were used as input data in the Gibbs-Helmholtz equation (3) to modify the Gibbs free energy value at 363 K and resulted in a ΔG_r value for methanogenesis at conditions with more resemblance to the satellite than the standard one (Amend & Shock 2001). Physical-chemical values of ΔG_r were calculated using equation (5) (LaRowe & Amend 2014):

$$\Delta G_r = \Delta G_r^\circ + RTln\frac{Kr}{Qr} \quad (5)$$

Where R represents the gas constant, T the temperature, Qr the reaction quotient and Kr the equilibrium constant which, together with speciation in the aqueous solution, was inferred using *The Geochemists Workbench v.15.0* (Bethke 2007) based on the mean pH, temperature and previous osmolarity predictions (Glein et al. 2018) with Na^+ and HCO_3^- as major cation and anion, respectively. Pressure was not considered because between 1 and 1 kbar its effect is much less than the effect of the other variables, particularly pH and temperature within an

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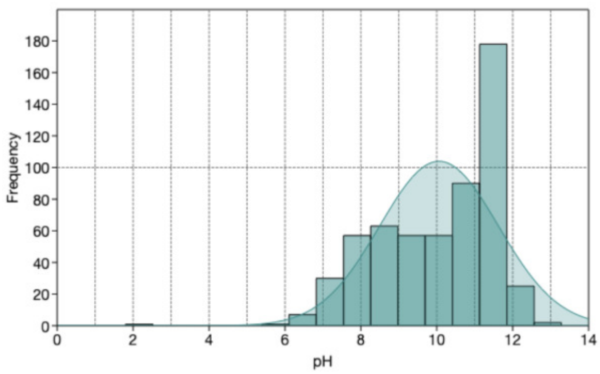

Fig. 1. Histogram of 570 pH values from analog environments for the Enceladus hydrothermal systems. Central values are described in section no. 3. The graph was elaborated using *PAST v.404* (Hammer et al. 2001).

interval of 0 and 100° C (Amend & LaRowe 2019). Therefore, under a pressure $\geq$ 10 MPa (Hemingway et al. 2018) differences in Gibbs free energy are negligible.

4. HABITABILITY

Habitability implies whether an environment can provide what life, as we know it, requires. However, there is a more accurate concept: quantitative habitability searches to solve to what extent life is plausible. The latter concept better describes the present study and is the ratio between the energy supply along time or "power supplied" (PS) by a dissimilatory metabolism (the flux of geochemical energy available for methanogenesis in the present study) and the energy demand along time required for microbial growth, i.e., "power demand" (PD) (Shock & Holland 2007). PS varies with environmental factors because the Gibbs free energy provided by any dissimilatory reaction, such as methanogenesis, is dependent on temperature, osmolarity, pH, etc. (Amend & LaRowe 2019). PD is generally expressed as "maintenance energy" (ME), i.e., the minimum energetic flux that is necessary to maintain cellular activity (Valentine 2007). To ascertain ME, only specific values for methanogens were examined, and a ME of 10^{-9} W cell^{-1} for methanogenesis at 363 K was taken from Higgins & Cockwell (2020).

5. RESULTS AND CONCLUSIONS

The outcome of using the specific values (non-standard conditions) from analog environments to approach Gibbs free energy yield resulted in a $\Delta G_r = -354.4$ kJ mol^{-1}. This value is higher than the Gibbs free energy under standard conditions, i.e., 1 *bar*, pH 7, 298.15 K, reactants and products at 1 M, and zero as ionic strength (Canfield et al. 2005), $\Delta G_r^{\circ} = -229.9$ kJ mol^{-1}. Relying on this reaction energy yield and a global hydrothermal flux of 10^{11} g yr^{-1} (Choblet et al. 2017), the global energy flux available for methanogenic organisms led to 9×10^{23} W, which implies an energy flux two orders of magnitude higher than the energy flux that resulted when using the H_2 production rate of 3×10^{15} mol yr^{-1} estimated by Vance (2018) and treated with the ME described above. This comparison underlines the convenience of using local environmental analogs to obtain simulations more reliable bioenergetically, and in the long-term to develop a better understanding of habitability of other worlds.

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