AN INTEGRATIVE APPROACH TO ASSESSING HABITABILITY OF H2 METABOLISMS IN HYDROTHERMAL SPRINGS.

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Introduction: Geological settings dominated by hydrothermal activity are natural targets for astrobiological investigations. The rich geochemical diversity that characterize such sites provide abundant energy to support microbial life. Hydrogen oxidizers are of particular interest because H2-based metabolisms are widespread and deeply rooted throughout the phylogenetic tree of life, implying they may have emerged extremely early in the evolution, and possibly even the origin, of life on Earth and potentially any other rocky body bearing liquid water [e.g., 1, 2]. Dihydrogen (H2) can be lithogenically produced by the hydrolytic oxidation of the ferrous iron component in Fe-bearing minerals [3] as well as by radiolytic cleavage of water by α, β, or γ radiation produced during the decay of radioactive isotopes [4]. Initial work on lithogenic H2 production has focused on ultramafic serpentinization, as it is occurring on Earth, is known to have occurred on Mars, and is likely occurring on icy satellites such as Europa. Lithogenic H2 production mechanisms, however, can operate across a range of rock types thus increasing the diversity of potential habitats on planetary bodies. Here, we present results of an ongoing project that surveys H2 concentrations from springs sourced in rock types of varying silica content and in parallel investigate habitability numerically by coupling an equilibrium geochemical model of serpentinization with a single-cell bioenergetic model. Methanogenesis is the metabolism of focus.

Hydrogen Survey: In order to assess the potential importance of H2-based metabolisms in geologic environments other than serpentizing systems, a field sampling campaign was undertaken in 2013 to assess the variation in lithogenic H2 abundance across a range spring waters hosted in non-ultramafic rocks. Aqueous H2 concentrations were measured in spring waters across the western U.S. at sites including Yellowstone National Park, Lassen Volcanic National Park, Idaho Batholith, Oregon Cascades, and California's Long Valley Caldera. The springs at these sites are hosted in rocks ranging in composition from mixed alluvial sediments to rhyolite to andesite to basalt. Sampling of dissolved gases was accompanied by measurements of physicochemical parameters including pH, temperature, dissolved inorganic carbon, and major ion chemistry. These field measurements are used in the bioenergetic model to quantitatively assess the habitability index for the various sites. A plot of aqueous hydrogen concentration from this survey reveals that dissolved hydrogen concentration can vary across several orders of magnitude irrespective of host rock type, and absolute values overlap those found in serpentinizing ultramafic sytems (Figure 1). Thus, this initial survey suggests the possibility for supporting H2-based metabolisms in a range of geologic environments beyond ultramafics.

Bio-energetic Modeling: Assessment of Gibbs Free Energy change (ΔG) alone is not sufficient to robustly assess habitability. Microbes require a minimum maintenance energy - the energy spent by cells to fix what the environment damages - in addition to any excess energy for growth [5]. This maintenance energy requirement is expected to vary with environmental conditions, such as temperature and pH. From this, we define habitability index as the ratio of the catabolic energy yield available through metabolism (H2-consuming methanogenesis is considered in the present example) to the energy required for maintenance for the microbe and physicochemical environment in question [6]. As such, it is both the energy made available by geochemistry and the energy required for biochemistry that define habitability. To efficiently investigate a large array of environmental parameters and their effect on habitability, we numerically couple a geochemical model of water-rock interaction (e.g., serpentinization) with that of single-cell methanogenesis and compute a habitability index for the given environment. In particular, we investigate the control that temperature, rock composition, water composition and water to rock ratio (dilution) has on biological potential.

Two methanogenic metabolisms are investigated, one using neutral species, and the other using ionized species. These are investigated separately as species cross-membrane transport is different for ionic vs neutral species. For the metabolism $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$, the membrane is assumed to have no effect on transport because the small non-polar molecules CO_2, H_2, CH_4 and H_2O diffuse through the membrane with little resistance. However, cross-membrane transport is critical for a cell undertaking $HCO_3^- + 4H_2 + H^+ \rightarrow CH_4 + 3H_2O$, as the ionic species HCO_3^- and H^+ cross the membrane only through trans-membrane proteins (porins). We implement porins numerically by changing the diffusion coefficient of polarized species. Charge neutrality is maintained inside the cell by keeping track of the proton flux required to replace those utilized in the methane-producing metabolism, and the energy expenditure required to support that proton flux.

Results: Preliminary results show that clinopyroxene content and water-rock ratio are the key controllers of the equilibrium fluid pH resulting from the serpentinization of an ultramafic rock (Figure 2). The pH of the fluid is important because it controls the speciation of the dissolved carbon species and thus whether CO_2 is available for microbial use. Clinopyroxene dissolution controls the concentrations of calcium cations released by the hydration of the rock and contained in the reacting fluid. Whereas Mg can scavenge the hydroxide generated by silicate hydration via formation of brucite, no comparable mineral buffer exists for Ca-OH except at very high pH. Thus, high Ca content in parent rocks can lead hyperalkaline fluids, especially when the reacting fluids are initially low in Mg (e.g, in fresh vs. saline waters) and thus very low CO_2 concentration. Increasing water to rock ratio causes a decrease in pH and thus an increase in CO_2/HCO_3^- concentrations, accompanied by a decrease in H_2 concentrations. Thus, a zone of “maximum habitability” exists for methanogens that use the products of the serpentinization reaction as reactants for their metabolisms.

Due to the challenge of pH and carbon speciation in serpentinizing systems, other geologic environments may offer comparably favorable habitability despite producing lower concentrations of hydrogen. Continuing work applies this bio-energetic model to asses habitability in the range of geologic environments that host available H2 beyond serpentinizing ultramafic systems.

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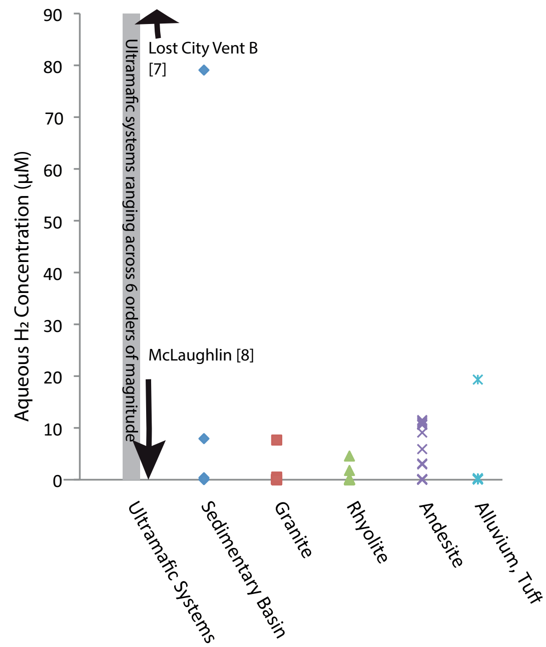

Figure 1. Aqueous H2 concentration in uM across a range of host rock compositions based on 2013 field measurements. Hydrogen is found in comparable concentrations across a range of rock types.

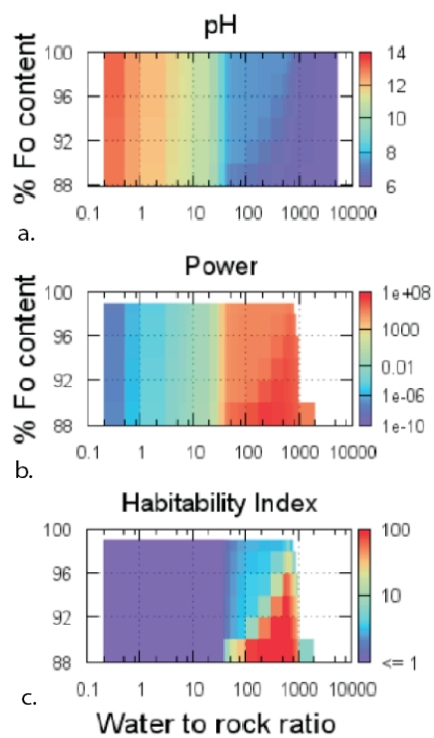

Figure 2. **a.** pH of equilibrium serpentinized fluid. **b.** biological power production: energy released by the production of methane (x10^15 kJ/d). **c.** Habitability Index, where HI = Power/ME (Maintenance Energy).