**RADIOLYTIC HYDROGEN PRODUCTION ON NOACHIAN MARS.** J.D. Tarnas[1], J.F. Mustard[1], B. Sherwood Lollar[2], M.S. Bramble[1] [1]Brown University Department of Earth, Environmental, and Planetary Sciences (jesse_tarnas@brown.edu, 324 Brook Street, Box 1846, Providence RI, 02906), [2]University of Toronto Department of Earth Sciences, 22 Russell St., Toronto ON Canada M5S 3B1.

**Introduction:** Deep subsurface microbial communities on Earth are sustained by $H_2$ produced via water-rock reactions including radiolysis [1,2]. Radiolytic $H_2$ has previously been proposed as a key precursor to methane production on modern Mars [3] and could have been an energy source for a deep subsurface martian biosphere during the Noachian. Here we quantify radiolytic $H_2$ production on Noachian Mars.

Radiation from decay of K, Th, and U in Earth's crust breaks apart water molecules in rock pore spaces, releasing $H_2$ that either travels towards the surface in gas phase or is dissolved into groundwater. Molar $H_2$ concentrations in deep groundwaters [1,2,4] in Precambrian rocks provide an estimated radiolytic production rate of $[1.6\text{-}4.7] \times 10^{10}$ moles of $H_2$ per year in Precambrian rocks globally from the Earth's cratons [2]. Microorganisms can be sustained in dissolved $H_2$ concentrations >0.05-10 nM [5] depending on the favored redox reaction. Generated $H_2$ gas is trapped in the crust via groundwater dissolution, or gas build up beneath layers of impermeable rock or ice, or potentially in $H_2$ clathrates [6].

**Modeling:** $H_2$ production is modeled for the Noachian (Figure 3) by extrapolating *Mars Odyssey*'s GRS K and Th elemental maps [7] to Noachian concentrations (Figure 1), modeling the spatially resolved cryosphere depth based on models of Noachian surface temperature [8] and heat flux [9,10] (Figure 2), and modeling Mars porosity [11] using parameter values derived from GRAIL [12] considering martian gravity. The subsurface hydrogen of greatest potential biological use is produced between the cryosphere base and the megaregolith (highly fractured ejecta layer affected by impacts) base, where the majority of groundwater and aquifers would have likely existed during the Noachian, due to its higher estimated fracture aperture than underlying bedrock [13], and the majority of subcryospheric $H_2$ would have been produced due to higher porosities relative to underlying bedrock. $H_2$ could have been dissolved into these aquifers in concentrations sufficient for sustainment of microbial communities, depending on its diffusion rate through water, megaregolith rock, and ice, as well as its solubility in water under low temperature, high pressure conditions.

**Results:** We find the Noachian cryosphere and subcryosphere both produce the same order of magnitude total $H_2$ as the terrestrial Precambrian crust ($[0.72\text{-}2.40] \times 10^{10}$, $[2.63\text{-}6.23] \times 10^{10}$ moles per year, respectively). The region between the cryosphere and megaregolith bases contributes $[0.35\text{-}1.13] \times 10^{10}$ moles per year to the total

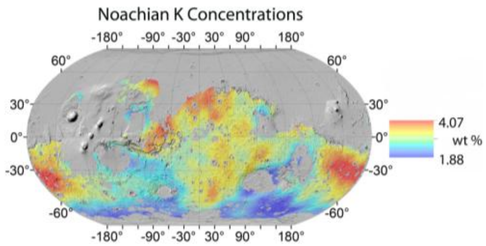


**Fig 1:** K concentrations in the Noachian extrapolated from GRS measurements of modern Mars [7], with only the Noachian aged terrains displayed. We also calculated Noachian values for the GRS Th map [6].

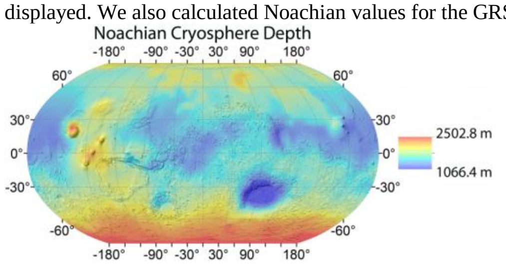


**Fig 2:** Modeled depth of cryosphere 4.1 Gya based on modeled surface temperature from [8] (1 bar $CO_2$ atmosphere, 25° obliquity) and heat flux from [10] (initial mantle temperature = 1650 K).

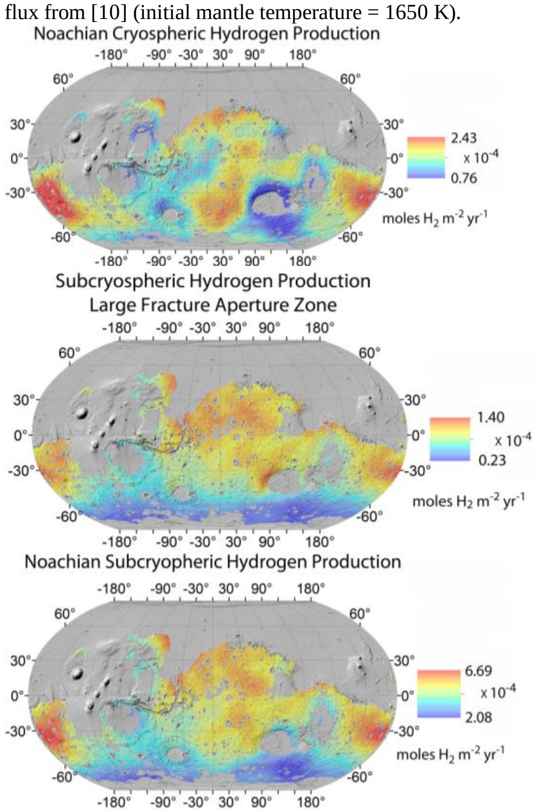


**Fig 3:** Modeled hydrogen production via radiolysis in the Noachian cryosphere (top), cryosphere base-megaregolith base fractured zone (middle), and subcryosphere (bottom) assuming 30% initial porosity.

subcryospheric hydrogen production, assuming a 3 km depth megaregolith base. Local $H_2$ production rates range from [0.76-2.43] × $10^{-4}$ moles $m^{-2}$ $yr^{-1}$ in the cryosphere, [2.08-6.69] × $10^{-4}$ moles $m^{-2}$ $yr^{-1}$ in the subcryosphere, and [0.23-1.40] × $10^{-4}$ moles $m^{-2}$ $yr^{-1}$ in the region between the cryosphere and megaregolith bases. Using the alternative porosity model of [13] results in even higher $H_2$ production, as does assuming brine filled pore space [14,15]. A brine filled pore space would reduce the cryosphere depth, which results in greater volumes of biologically useful subcryospheric hydrogen production.

**Discussion:** Whether this $H_2$ was sufficiently concentrated to sustain microbial communities depends on the total volume and distribution of Noachian groundwater, as well as $H_2$ solubility under the low temperature and high pressure conditions immediately beneath the cryosphere, and the diffusion rate of $H_2$ through groundwater, megaregolith rock, and ice. Crustal permeability and fracture aperture is highest towards the surface [13], as fracture closure due to overhead pressure is limited. $H_2$ gas and groundwater flow through fractures is therefore greatest at these depths, which also correspond to the layer of highest subcryospheric $H_2$ production due to its higher porosity relative to the underlying crust.

Dissolution of $H_2$ into groundwater was therefore likely highest within the zone between the base of the megaregolith, estimated to be 1-3 km thick [13 & references therein], and the cryosphere base. $H_2$ gas produced beneath this layer may still diffuse towards the surface and dissolve into groundwater in this layer, but it could also be consumed via subsurface redox reactions and adsorption onto minerals. The regions of highest subsurface biological potential from radiolytic $H_2$ production during the Noachian would therefore be where radioactive element concentrations are highest and the distance between the cryosphere and megaregolith bases is minimized, as this would equate to higher $H_2$ concentrations in the aquifer.

*Relation to serpentinization:* There is considerable discussion about the production of $H_2$ (and methane) during serpentinization at low temperatures [16]. Serpentinization has been shown to produce gaseous $H_2$ at ~15 ppm concentrations during alteration at 30° C [17], but lower temperature experiments have yet to be performed. If serpentinization does not proceed at lower temperatures, it will primarily produce $H_2$ only where temperatures >30° C are reached above the megaregolith base, where the majority of groundwater would reside. Alternatively, if it still proceeds at temperatures close to 0° C, radiolytic $H_2$ production and serpentinization would both contribute to dissolved $H_2$ concentrations in groundwater and aquifers immediately below the cryosphere base.

*Climatic implications:* Atmospheric $CO_2$, $CH_4$, and $H_2$ concentrations required for Noachian temperatures to exceed melting have been found to be lower than previously estimated [18]. Still, radiolytically produced $H_2$ represents ~0.1-2% of the $H_2$ that can be produced via photodissociation of $CH_4$ formed by serpentinization of 5% of the martian crust [19], therefore episodic $CH_4$ release from clathrates [20] is likely a more powerful climatic influence than radiolytic $H_2$ production. Loss of water due to radiolysis can only account for 1-2 m of the Mars water budget.

**Conclusions:** Radiolysis of pore water in the martian crust produced $H_2$ in volumes potentially sufficient to support subsurface microbial communities during the Noachian, depending on $H_2$ diffusion rates and solubility under the low temperature, high pressure conditions between the cryosphere and megaregolith bases, in which the majority of groundwater likely existed. Future work to constrain these factors is planned. Furthermore, mechanisms for trapping gaseous $H_2$ in the subsurface, such as highly impermeable cap layers or clathrates, must be assessed, both in the context of serpentinization and radiolytic $H_2$ production. If serpentinization is found to proceed at near-freezing temperatures, both of these $H_2$ production mechanisms may have provided energy sources for extinct microbial communities that resided in aquifers immediately beneath the cryosphere base. If serpentinization reactions cannot proceed at temperatures <30° C, or if brine-filled pore space caused the cryosphere to melt at below freezing temperatures, then radiolysis would have been the only local $H_2$ production mechanism in these aquifers. Still, depending on the diffusion timescale and solubility of $H_2$, sufficient concentrations to support microbial communities may have developed in groundwater systems. Though it has received limited attention from the community, this post-production $H_2$ behavior is equally essential when considering serpentinization derived $H_2$. Since we have demonstrated that radiolysis produced $H_2$ in biologically significant quantities, a realistic subsurface $H_2$ availability model for the Noachian must include $H_2$ derived from both radiolysis and serpentinization, as well as characterization of post-production behavior.

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