AN INSUFFICIENT METHANE BUDGET FOR WARMING NOACHIAN AND HESPERIAN MARS. J.D. Tarnas[1], J.F. Mustard[1], B. Sherwood Lollar[2], K.M. Cannon[3], A.M. Palumbo[1], A.-C. Plesa[4], M.S. Bramble[1] [1]Brown University Department of Earth, Environmental and Planetary Sciences, [2]University of Toronto Department of Earth Sciences, [3]University of Central Florida Department of Physics, [4]German Aerospace Center Institute of Planetary Research.

Introduction: Mars is known to have warmed to above-freezing temperatures during the Noachian and Hesperian based on geomorphic evidence for fluvial channels [1] and paleolakes [2]. Wordsworth et al. [3] demonstrate that above-freezing temperatures can be achieved in the Noachian and Hesperian if there was a 1.25-2 bar CO_2 atmosphere with 2-10% CH_4 and H_2 due to the greenhouse and collision induced absorption effects of these molecules with the CO_2-rich atmosphere. These transient reducing greenhouse atmospheres (TRGAs) would last for 10^5-10^6 years, which is consistent with the expected timescales for delta formation and overall lack of chemical weathering that are observed on the surface [4]. Given the obliquity variations Mars is expected to have experienced throughout its history, release of CH_4 to the atmosphere through depressurization of CH_4 clathrate via latitudinal ice migration to form TRGAs during the Noachian and Hesperian is a hypothesis consistent with geomorphic observations [1,2], mineralogic observations [5], modeling results [4] and atmospheric paleopressure estimations [6-9]. Impacts and volcanism can also destabilize CH_4 clathrate in the Noachian cryosphere. Here we demonstrate that while CH_4 is thermodynamically stable throughout the Noachian crust, kinetic barriers to its formation via CO_2-reduction make it difficult to form sufficient CH_4 for a single TRGA given the expected amount of available H_2 from radiolysis [10] and serpentinization [11] and our current understanding of abiotic methane formation on Earth.

Methods: To estimate the amount of CH_4 that could be produced abiotically in the Noachian crust via the Sabatier reaction, we first quantify the thermodynamic stability of CH_4 with respect to depth in the crust using the CHNOSZ model [12], which uses the SUPCRT92 thermodynamic database [13]. Parameters fed into the thermodynamic database include the crustal temperature-vs-depth profile with a surface temperature boundary condition from climate models [14], the expected geothermal heat flux [15], and assuming heat transport by conduction [16], in addition to hydrostatic pressure, and dissolved H_2 concentrations [10].

CH_4 is thermodynamically stable throughout most of Earth's crust [17]. However, its formation via reduction of CO_2, the primary form of carbon input into the terrestrial crust, is kinetically inhibited, typically requiring metal catalysts on which H_2 and CO_2 can adsorb to facilitate the reaction. Awaruite [18] and chromite [19] are metal catalysts demonstrated to facilitate CH_4 formation in natural systems. Abiotic CH_4 formation on Noachian Mars may have occured in crustal regions that were rich in these metal alloys. On Earth, some serpentinites are mined for Ni due to the concentration of Ni in awaruite [20] formed in association with highly-reducing fluids involved in serpentinization reactions [18]. Lithologically similar crustal regions could have hosted abiotic CH_4-forming environments on Mars, in addition to chromite-rich igneous rocks.

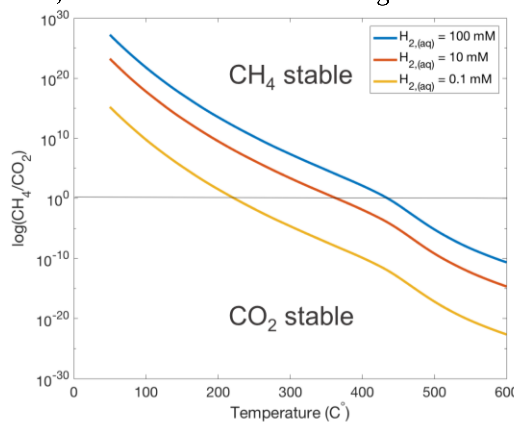

Figure 1 | Thermodynamic stability of CO_2 and CH_4 as a function of temperature and oxidation state ($H_{2,aq}$ content) expected in Earth's crust (adapted from [17]).

Oze et al. [21] integrate the results from 6 abiotic serpentinization experiments and 10 measurements from natural systems—containing biology—to show the range of expected H_2/CH_4 values for these two different environments. The highest conversion percentage of H_2 to CH_4 [21] is 2.4%. The average conversion percentage in abiotic serpentinization experiments is 0.04%. We use these values to constrain the amount of H_2 converted to CH_4 in the martian crust. We assume the entire crust is composed of serpentinite, meaning the value for total CH_4 production that we find is a high-CH_4 endmember scenario. We consider a mantle source for CH_4 as well. Experiments show the oxidizing nature of the martian mantle causes little to no CH_4 to be dissolved in magma that degasses via volcanism [22,23].

Results: We find the amount of CH_4 produced abiotically in the crust via the reduction of CO_2 by H_2 derived from radiolysis [10] and serpentinization [11] is insufficient to introduce the necessary quantities of CH_4 into the atmosphere to increase temperatures above 273 K during the TRGA phase [3], even in the most optimistic scenario in which the H_2:CH_4 ratio is 2.4% and 100% of the crust is assumed to be serpentinite. This scenario produces 2 to 41% of the CH_4 required to generate one TRGA, assuming a 1:1 H_2:CH_4 ratio in the atmosphere. Using the average H_2:CH_4 value from abiotic serpentinization experiments (0.04%), the Sabatier reaction produces 0.0008-0.014% of the CH_4 required to generate a single TRGA

Taking H_2:CH_4 ratio values from biologically-active natural serpentinizing systems compiled in Oze et al. [21] (3-1000%), ~0.06-17 TRGAs can be generated during the Noachian and Hesperian via reduction of CO_2 by H_2 generated by radiolysis [10] and serpentinization [11]. Assuming 10% of the crust was composed of serpentinite, ~0.006-1.7 TRGAs can be generated during the Noachian and Hesperian by this process. The key differences between natural serpentinizing systems and abiotic serpentinization experiments are 1) the timescales involved in the reaction, which are longer in natural systems than in experiments, and 2) biological processes contributing the CH_4 formation in natural systems [21].

Implications & Conclusions: CO_2-H_2-CH_4 atmospheres have been invoked as a self-consistent explanation for warming a largely cold and icy Noachian and Hesperian Mars to generate the fluvial channels, paleolakes, and lack of chemical weathering features in fluvial channels that is observed on the surface today [4]. In this study we demonstrate that the current state of knowledge regarding H_2 abundances in the martian crust and abiotic CH_4 formation suggest the latter process can produce only 0.0008-41% of the CH_4 required for a single TRGA. These numbers also assume that 100% of the martian crust is composed of serpentinite, which is not realistic. If we assume that only 10% of the crust is composed of serpentinite, then abiotic CH_4 formation is only capable of forming 0.00008-0.041% of the CH_4 required to produce a single TRGA.

Based on our results it does not seem possible for TRGAs [3] from abiotic CH_4 to cause warming on early Mars [4]. Such warming from CH_4 could only occur if there is a yet uncharacterized source that generates ~100-1000 times more H_2 than radiolysis [10] and serpentinization [11] combined during the Noachian and Hesperian. [21]. Alternatively this analysis may underestimate CH_4 formation from H_2. For instance, if abiotic CH_4 formation is more prevalent in natural systems than suggested by necessarily short-timescale experimental studies; or if biological processes contributed to CH_4 formation on Noachian and Hesperian Mars.

It is worth noting that the TRGA proposed by Wordsworth et al. [3] produces above-freezing temperatures in an atmosphere devoid of CH_4, with purely H_2 and CO_2 contributing to warming. However, there exists no mechanism for H_2 to remain trapped in the crust for instantaneous catastrophic release. Pure H_2 clathrate is likely not stable in the Noachian cryosphere [26], thus H_2 concentrations in the cryosphere could not build up to sufficient levels for warming upon release. Rather, it will diffuse through the crust into the atmosphere, then from the atmosphere into space.

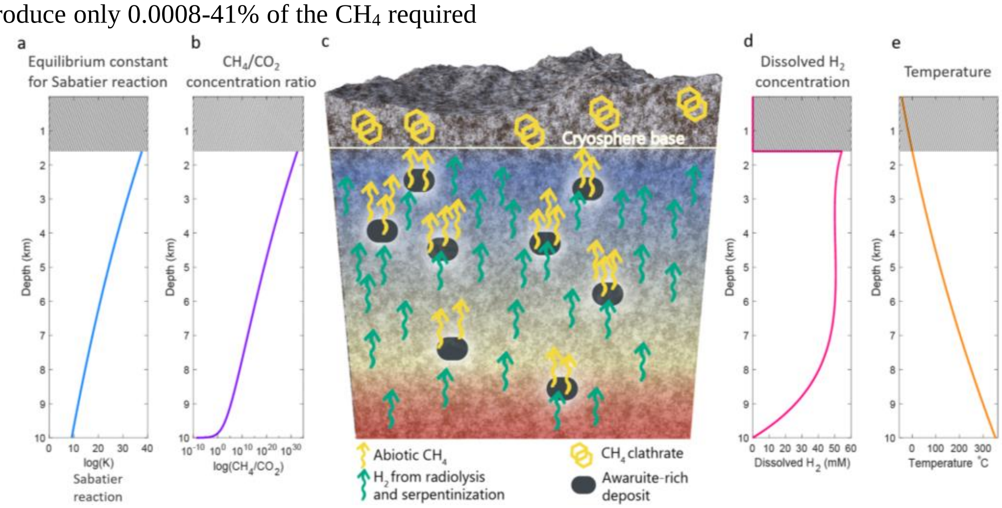

Figure 2 | a) Equilibrium constant for Sabatier reaction as a function of depth, showing the reaction is thermodynamically favorable throughout the crust. b) CH_4/CO_2 concentration ratio as a function of depth, showing CH_4 is thermodynamically favorable throughout the crust. c) Conceptual model for CH_4 formation process in ancient martian crust. d) Dissolved H_2 concentrations from radiolysis. e) Crustal temperature profile.

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