MARS COULD HAVE BEEN WARMED BY ECCENTRICITY VARIATIONS OR A SUBSURFACE BIOSPHERE. J.D. Tarnas1, J.F. Mustard1, B. Sherwood Lollar2, K.M. Cannon3, A.M. Palumbo1, A.-C. Plesa4, M.S. Bramble1 1Brown University Department of Earth, Environmental and Planetary Sciences, 2University of Toronto Department of Earth Sciences, 3University of Central Florida Department of Physics, 4German Aerospace Center Institute of Planetary Research.

Introduction: Mars is known to have warmed to above the freezing point of water during the Noachian and Hesperian based on geomorphic evidence for fluvial channels [1] and paleolakes [2]. Kite et al 2019 [3] demonstrated that transient fluvial activity continued to occur <1 Ga. Wordsworth et al. 2017 [4] and Turbet et al. 2019 [5] showed that seasonally above-freezing temperatures (255 K mean annual temperature) can be achieved from 4.5-3.5 Gyr ago in a 1-2 bar CO2 atmosphere with ~4-20% CH4 and H2. These transient reducing greenhouse atmospheres would last for 10^7-10^8 years, which is consistent with the expected timescales for delta formation and chemical weathering that are observed on the surface [6]. Given the obliquity variations Mars is expected to have experienced throughout its history, depressurization of CH4 clathrate via latitudinal ice migration to form transient reducing greenhouse atmospheres (TRGAs) during the Noachian and Hesperian is a hypothesis consistent with geomorphic observations [1,2], mineralogic observations [7], modeling results [6] and atmospheric paleopressure estimations [8-11].

Seasonal warming due to orbital eccentricity variations can also form the fluvial features seen on the martian surface [12]. The expected length of these transient warming periods has not been calculated from orbital dynamics. Eccentricity variations are likely based on the chaotic nature of orbital resonances [13] and events such as the divergent migration of Jupiter and Saturn [14]. TRGAs can be generated via H2 from volcanism [15], but do not last sufficiently long to match expected warming timescales [6,16] due to the escape rate of H2 [15] and the punctuated nature of volcanism predicted by expected effusion rates and total lava emplacement times [17]. If H2 is instead formed in the crust via radiolysis and serpentinization and reduces CO2 to form CH4, the CH4, CO2, and some H2 can be locked into clathrate hydrates and released due to catastrophic cryospheric destabilization [6,18].

Here we demonstrate that while CH4 is thermodynamically stable throughout the Noachian martian crust, kinetic barriers to its formation via CO2-reduction make it difficult to form sufficient CH4 for a single TRGA given the expected amount of available H2 from radiolysis [18] and serpentinization [19] and our current understanding of abiotic methane formation on Earth. However, if biological methanogenesis is invoked in the martian subsurface, sufficient CH4 can be formed to generate TRGAs.

Methods: To estimate the amount of CH4 that could be produced abiotically in the Noachian crust via Fischer-Tropsch Type (FTT) reactions, we first quantify the thermodynamic stability of CH4 with respect to depth in the crust using CHNOSZ [20], which uses the SUPCRT92 thermodynamic database [21]. Parameters fed into the thermodynamic database include the crustal temperature-vs-depth profile derived from surface temperatures expected from climate models [12], the expected geothermal heat flux [22], and assuming heat transport by conduction [23], in addition to hydrostatic pressure, and dissolved H2 concentrations [18].

CH4 is thermodynamically stable throughout most of Earth’s crust [24]. However, its formation via reduction of CO2, the primary form of carbon input into the terrestrial crust, is kinetically inhibited, requiring metal catalysts on which H2 and CO2 can adsorb to facilitate the reaction. Awaruite [25] and chromite [26] are metal catalysts demonstrated to cause CH4 formation in natural systems, thus abiotic CH4 formation on Noachian Mars might occur in rare crustal regions that are rich in these metal alloys or minerals (Fig. 1). On Earth, serpentinites are mined for Ni, which is highly concentrated in awaruite [27] formed due to highly-reducing fluids involved in the serpentinization reaction [25]. Lithologically similar crustal regions might have hosted abiotic CH4-forming environments on Mars, in addition to chromite-rich igneous rocks.

Abiotic CH4 formation via reduction of CO2 by H2 has been demonstrated to be sluggish by multitudinous experiments [28 and sources therein]. McCollom et al. 2016 [29] demonstrated that the small quantities of CH4 generated in these experiments primarily came from contaminant background sources. These authors conducted their own experiments and used isotope labelling to trace the origin of detected CH4. They found that conversion percentages of the H2 to non-background-derived CH4 ranged from 0.00041%-0.025%, with 0.025% CH4 formed in an experiment with an H2-rich vapor phase, simulating conditions in which awaruite is formed in serpentinite under highly reducing fluid conditions [30]. We use this range of H2:CH4 conversion percentage to estimate the amount of CH4 that could be formed abiotically in Mars’ crust.

We consider a mantle source for martian CH4 as well. Experiments show that the martian mantle’s oxi-
rotation state causes little to no CH$_4$ to be dissolved in magma that degasses via volcanism [31,32].

**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 [18] and serpentinization [19] is insufficient to produce a single TRGA [4,5], even in the most optimistic scenario in which the H$_2$:CH$_4$ ratio is 0.025% and 100% of the crust is assumed to be serpentinite. This scenario produces 0.0002-0.0044% of the CH$_4$ required to generate one TRGA, assuming 50% mixing of H$_2$ and CH$_4$ in the atmosphere.

Taking H$_2$:CH$_4$ ratio values from biologically-influenced natural serpentinizing systems compiled in Oze et al. 2012 [29] (3-1000%), ~0.024-10 TRGAs can be generated during the Noachian and Hesperian via reduction of CO$_2$ by H$_2$ generated by radiolysis [18] and serpentinization [19]. Assuming 10% of the martian crust was composed of serpentinite, ~0.0024-1.0 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 [28]. Tarnas et al. 2018 [18] demonstrated that a long-lived habitable subsurface environment fueled by radiolytic H$_2$ likely existed on Mars during the Noachian. It is theoretically possible that TRGA-forming CH$_4$ could have been generated via biological methanogenesis in this subsurface environment.

**Implications & Conclusions:** While 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 [6], the current state of knowledge regarding H$_2$ abundances in the martian crust and abiotic CH$_4$ formation demonstrates that abiotic CH$_4$ formation can produce only 0.0002-0.0044% 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 10% of the martian crust is composed of serpentinite, then abiotic CH$_4$ formation is only capable of forming 0.00002-0.0044% of the CH$_4$ required to produce a single TRGA.

Our results imply that at least one of the following options must be true, though it is possible that more than one (up to three) of them are true: 1) There is an uncharacterized source that generates $\sim10^4$ times more H$_2$ in the crust than radiolysis [18] and serpentinization [19] combined during the Noachian and Hesperian. 2) Transient reducing greenhouse atmospheres [4,5] from abiotic CH$_4$ did not cause warming on early Mars, though it is self-consistent with observational evidence [6]. 3) Biological processes contributed to CH$_4$ formation on Noachian and Hesperian Mars.


**Figure 1** | Equilibrium constant for Sabatier reaction as a function of depth, which shows the reaction is thermodynamically favorable throughout the crust. CH$_4$/CO$_2$ concentration ratio as a function of depth, showing CH$_4$ is more thermodynamically favorable throughout the crust. Conceptual model for CH$_4$ formation process in ancient martian crust. Dissolved H$_2$ concentrations from radiolysis. Crustal temperature profile.

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