MARS COULD HAVE BEEN WARMED BY ECCENTRICITY VARIATIONS OR A SUBSURFACE BIOSPHERE.

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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 CO_2 atmosphere with ~4-20% CH_4 and H_2. These transient reducing greenhouse atmospheres would last for 10^5-10^6 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 CH_4 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 H_2 from volcanism [15], but do not last sufficiently long to match expected warming timescales [6,16] due to the escape rate of H_2 [15] and the punctuated nature of volcanism predicted by expected effusion rates and total lava emplacement times [17]. If H_2 is instead formed in the crust via radiolysis and serpentinization and reduces CO_2 to form CH_4, the CH_4, CO_2, and some H_2 can be locked into clathrate hydrates and released due to catastrophic cryosphere destabilization [6,18].

Here we demonstrate that while CH_4 is thermodynamically stable throughout the Noachian martian 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 [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 CH_4 can be formed to generate TRGAs.

Methods: To estimate the amount of CH_4 that could be produced abiotically in the Noachian crust via Fischer-Tropsch Type (FTT) reactions, we first quantify the thermodynamic stability of CH_4 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 H_2 concentrations [18].

CH_4 is thermodynamically stable throughout most of Earth's crust [24]. However, its formation via reduction of CO_2, the primary form of carbon input into the terrestrial crust, is kinetically inhibited, requiring metal catalysts on which H_2 and CO_2 can adsorb to facilitate the reaction. Awaruite [25] and chromite [26] are metal catalysts demonstrated to cause CH_4 formation in natural systems, thus abiotic CH_4 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 CH_4-forming environments on Mars, in addition to chromite-rich igneous rocks.

Abiotic CH_4 formation via reduction of CO_2 by H_2 has been demonstrated to be sluggish by multitudinous experiments [28 and sources therein]. McCollom et al. 2016 [29] demonstrated that the small quantities of CH_4 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 CH_4. They found that conversion percentages of the H_2 to non-background-derived CH_4 ranged from 0.00041%-0.025%, with 0.025% CH_4 formed in an experiment with an H_2-rich vapor phase, simulating conditions in which awaruite is formed in serpentinite under highly reducing fluid conditions [30]. We use this range of H_2:CH_4 conversion percentage to estimate the amount of CH_4 that could be formed abiotically in Mars' crust.

We consider a mantle source for martian CH_4 as well. Experiments show that the martian mantle's oxidation 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 0.00002-0.00044% 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 ~10^4 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.

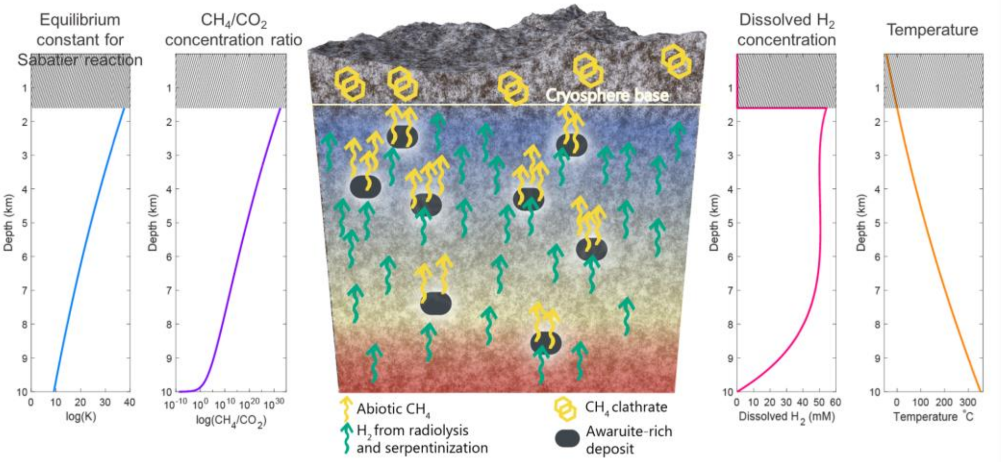

Figure 1 | Equilibrium constant for Sabatier reaction as a function of depth, which shows the reaction is thermodynamically favorable throughout the crust. CH_4/CO_2 concentration ratio as a function of depth, showing CH_4 is more thermodynamically favorable throughout the crust. Conceptual model for CH_4 formation process in ancient martian crust. Dissolved H_2 concentrations from radiolysis. Crustal temperature profile.

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