

REDUCING GREENHOUSE SOLUTIONS ON EARLY MARS.

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Introduction

Today Mars is cold and dry, but in the past a diverse array of geological evidence points to episodically warmer and wetter conditions. This evidence includes dendritic valley networks distributed over large regions of the equatorial and southern Noachian highlands, fluvial conglomerates, open-basin lakes, and fluvio-lacustrine deposits.

This evidence for surface aqueous modification is paradoxical, because the Sun's luminosity was only around 75-80% of its present-day value during the period 3-3.8 Ga when most of the erosion occurred. In combination with Mars' distant orbit, this implies cold surface conditions: even given a planetary albedo of zero, early Mars would have had an equilibrium temperature of only 210 K [1]. Carbon dioxide provides some greenhouse warming but not enough: climate models that assume pure CO₂-H₂O atmospheres consistently predict global mean temperatures of less than 240 K for any surface pressure [2]. Many alternative mechanisms to warm early Mars have subsequently been investigated, including CO₂ clouds [3], large meteorite impacts [4], sulfur dioxide emission from volcanoes [5], and local snowmelt due to diurnal forcing and/or obliquity and eccentricity variations [6]. However, all suffer shortcomings that render them unlikely as the main explanation [1].

Reducing greenhouse solutions for early Mars have also been considered previously. Sagan [7] argued that early Mars might have been warmed by a hydrogen-dominated atmosphere or by abundant NH₃. However, a hydrogen-dominated atmosphere would be lost to space rapidly after formation and NH₃ is photolysed rapidly by UV radiation and lacks a plausible martian source. Later, in a paper focused on the early Earth, [8] showed that hydrogen could act as an important greenhouse gas in terrestrial-type atmospheres even in abundances of a few percent, due to the strength of its collision-induced absorption in combination with heavier gases like nitrogen. [9] applied this mechanism to early Mars, where they argued that H₂ emitted from volcanoes into a CO₂-dominated atmosphere could have kept Mars in a 'warm and wet' state for periods of 10s of millions of years or

longer. However, lacking CO₂-H₂ CIA data they used the same N₂-H₂ data as [8] for their climate calculations. As a result, they found that > 5% H₂ in a 4 bar CO₂ atmosphere (20% H₂ in a 1.3 bar atmosphere) was required to raise annual mean surface temperatures to the melting point of liquid water: an amount that is not consistent either with constraints on the total amount of CO₂ present in the Noachian or estimates of the rate of hydrogen escape to space [9]. Hence the early martian faint young Sun paradox remains unresolved.

Here we describe new calculations that we have performed to assess the warming potential of reducing climates on early Mars. We find CO₂-H₂ warming to be significantly more effective than predicted by [9] due to the strong polarizability and multipole moments of CO₂. Furthermore, we show for the first time that methane (CH₄) could have been an effective warming agent on early Mars, due to the peak of CO₂-CH₄ CIA in a key spectral window region.

1 Methods

To calculate the collision-induced absorption spectra for CO₂-CH₄ and CO₂-H₂ pairs, we first acquired the potential energy surface (PES) and induced dipole surface (IDS) for the relevant molecular complex. The PES for CO₂-H₂ calculated at the coupled-cluster level was taken from the literature [10]. For the IDS for CO₂-H₂ and both the PES and IDS for CO₂-CH₄, we performed the *ab initio* calculations ourselves. Once the *ab initio* data was acquired, the zeroth spectral moment for the system was calculated and combined with spectral data for the known CO₂-CO₂, H₂-H₂ and CH₄-CH₄ systems to create new CO₂-CH₄ and CO₂-H₂ absorption coefficients. We assessed the climate effects of the new coefficients using a new iterative line-by-line spectral code [1]. Using this model allowed us to perform extremely high accuracy globally averaged calculations and span a wide range of atmospheric compositions.

2 Results

First, we compared the $\text{CO}_2\text{-H}_2$ and $\text{CO}_2\text{-CH}_4$ CIA coefficients we calculated with previously derived $\text{N}_2\text{-H}_2$ and $\text{N}_2\text{-CH}_4$ CIA data [11]. Figure 1 shows that the peak values of the CO_2 coefficients are 5-10 times stronger than the previously calculated N_2 data. The difference can be explained by a combination of stronger multipole moments and a higher polarizability for CO_2 vs. N_2 . The effect is particularly significant for climate because both pairs absorb significantly between 250 and 500 cm^{-1} : a key spectral window region for the martian climate [1].

These increased opacities translate directly to higher surface temperatures in climate calculations. Figure 2a) shows the result of calculating surface temperature using both our new $\text{CO}_2\text{-H}_2$ data and (incorrectly) using $\text{N}_2\text{-H}_2$ as a substitute for $\text{CO}_2\text{-H}_2$. As can be seen, the difference is significant, with surface temperatures increasing by many tens of degrees for H_2 abundances greater than a few percent. Global mean temperatures exceed 273 K for H_2 molar concentrations from 3 to 10%, depending on the background CO_2 pressure.

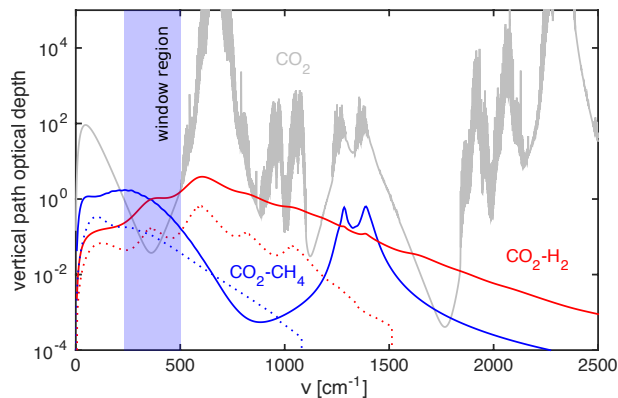


Figure 1: Total vertical path optical depth due to CO_2 (gray), $\text{CO}_2\text{-CH}_4$ CIA (blue) and $\text{CO}_2\text{-H}_2$ CIA (red) in the early martian atmosphere, assuming a pressure of 1 bar, composition 94% CO_2 , 3% CH_4 , 3% H_2 , and surface temperature of 250 K. Dotted lines show optical depth from CIA when the absorption coefficients of $\text{CO}_2\text{-H}_2$ and $\text{CO}_2\text{-CH}_4$ are replaced by those of $\text{N}_2\text{-H}_2$ and $\text{N}_2\text{-CH}_4$, respectively.

Next, we studied the effects of methane. In the past, methane has not been regarded as an effective early martian greenhouse gas because its first vibration-rotation absorption band peaks at 1300 cm^{-1} , too far from the blackbody emission spectrum at 250-300 K to reduce the outgoing longwave radiation (OLR) significantly [9, 1]. Methane also absorbs incoming solar radiation significantly in the near-infrared [12]. We find strong CH_4 near-IR absorption, leading to a temperature inversion in the high atmosphere in cases where the CH_4 abun-

dance is high. Hence although CH_4 near-IR absorption decreases planetary albedo, its net effect is to slightly *decrease* surface temperatures in the absence of other effects (Fig. 2b).

Despite its anti-greenhouse properties in the near-IR, we nonetheless find that at high abundance, methane can also act as an important greenhouse gas on early Mars. This occurs because the $\text{CO}_2\text{-CH}_4$ CIA absorption peaks in the key 250 to 500 cm^{-1} window region. We find that adding 5% CH_4 increases global mean temperatures by 20-45 K, depending on the background CO_2 pressure (Figure 2). Finally, when CH_4 and H_2 are combined in equal proportions, only 3.5% of each gas is required to achieve 273 K given a 1.5 bar atmosphere (Figure 2). Note that 273 K is likely an upper limit on the global mean temperature required to explain valley network formation due to the importance of local and seasonal effects in determining runoff [6].

3 Discussion

We have produced the first physically realistic calculations of reducing greenhouse warming on early Mars. Our results suggest that with just over 1 bar of atmospheric CO_2 , a few percent of H_2 and/or CH_4 would have raised surface temperatures to the point where the hydrological cycle would have been vigorous enough to explain the geological observations. In this presentation, we will discuss the methodology of our calculation and results in detail, before discussing whether such atmospheres are physically plausible. We will argue that methane and hydrogen outgassing following aqueous alteration of Mars' basaltic crust could have led to transient warm episodes of 100-250,000 y duration, limited by the photolysis rate of CH_4 and diffusion rate of hydrogen through the martian homopause. Pulses in CH_4 outgassing rates could have been caused by local variations in the geothermal heat flux or destabilization of clathrate deposits via impacts or obliquity changes. This reducing scenario for the late Noachian is amenable to testing by future geological investigations of the martian surface.

4 Preprint

Further details on this work, which is currently under review, are available at <https://arxiv.org/abs/1610.09697>.

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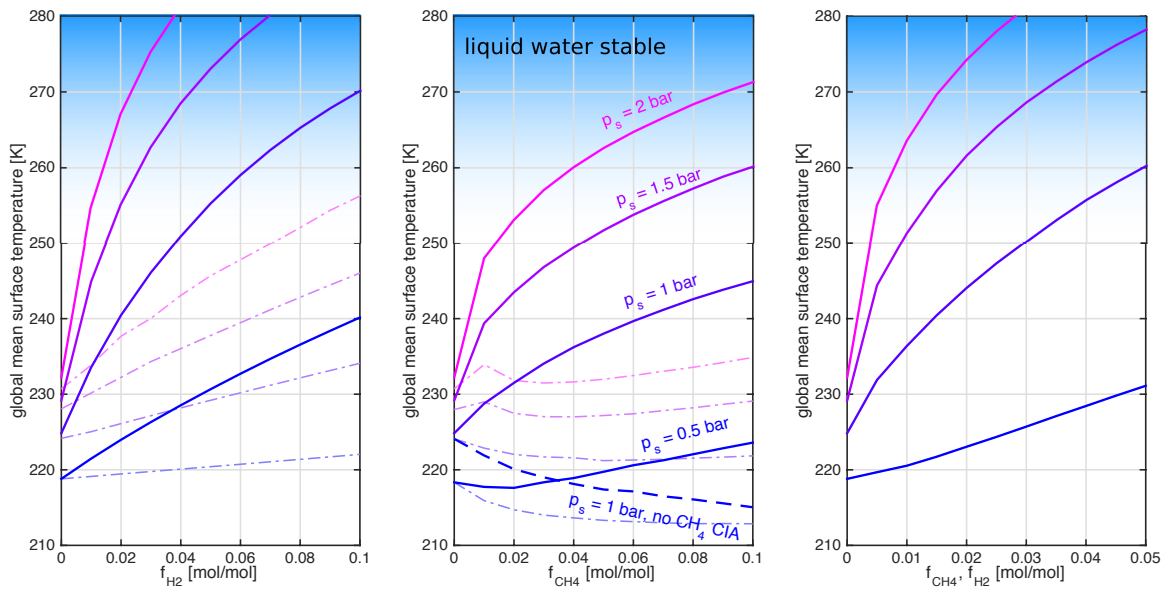


Figure 2: Surface temperature in CO_2 -dominated atmospheres as a function of a) H_2 and b) CH_4 molar concentration for various surface pressures p_s . The solid lines show results calculated using our new CIA coefficients, while dash-dot lines show results using N_2 - H_2 and N_2 - CH_4 CIA coefficients in place of the correct coefficients. In b), the dashed line shows the case at 1 bar where CH_4 CIA is removed entirely, demonstrating that without it, methane actually has an anti-greenhouse effect. Figure c) shows the case where both H_2 and CH_4 are present in equal amounts. Note the change of scale on the x -axis compared to a) and b).