TRANSIENT REDUCING ATMOSPHERES ON EARLY MARS AS A SOLUTION TO THE FAINT YOUNG SUN PARADOX.

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Introduction: Today Mars is cold and dry, but in the past a range of geological evidence points to episodically warmer conditions. This evidence includes dendritic valley networks distributed over large regions of the equatorial and southern highlands, fluvial conglomerates, open-basin lakes, and fluvolacustrine deposits [1-3].

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 [4]. Carbon dioxide provides some greenhouse warming but not enough: climate models that assume pure CO_2-H_2O atmospheres consistently predict global mean temperatures of less than 240 K for any surface pressure [5-7]. Many alternative mechanisms to warm early Mars have subsequently been investigated, but all suffer shortcomings that render them unlikely as the main explanation.

In 2013, in a paper focused on the early Earth, we [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. This mechanism was subsequently applied to early Mars by Ramirez et al. (2014) [9], who suggested that H_2 emitted from volcanoes into a CO_2-dominated atmosphere could have kept Mars in a warm and wet state for periods of 10s of millions of years or longer. However, lacking CO_2-H_2 CIA data they used the same N_2-H_2 data as [4] for their climate calculations. As a result, they found that > 5% H_2 in a 4 bar CO_2 atmosphere (20% H_2 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 CO_2 present in the Noachian or estimates of the rate of hydrogen escape to space. 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 CO_2-H_2 warming to be significantly more effective than estimated previously due to the strong polarizability and multipole moments of CO_2. Furthermore, we show for the first time that methane could have been an effective warming agent on early Mars, due to the peak of CO_2-CH_4 CIA in a key spectral window region. Our results, which are described in detail in Wordsworth et al. (2017) [10], also have important implications for the habitability of exoplanets that orbit far from their host stars.

Methods: To calculate the collision-induced absorption spectra for CO_2-CH_4 and CO_2-H_2 pairs, we first acquired the potential energy surface (PES) and induced dipole surface (IDS) for the relevant molecular complex. Once the *ab initio* data was acquired, the zeroth spectral moment for the far infrared rototranslation band was calculated and combined with spectral data for the known CO_2-CO_2, H_2-H_2 and CH_4-CH_4 systems to create the absorption coefficients. We assessed the climate effects of the new coefficients using a new iterative line-by-line spectral code. This model allowed us to perform extremely high accuracy globally averaged calculations and span a wide range of atmospheric compositions.

Results: We find that at high abundance, methane can act as a strong greenhouse gas on early Mars. This occurs because the CO_2-CH_4 CIA absorption peaks in the key 250 to 500 cm^{-1} window region (Figure 3). In the past, methane has not been regarded as an effective early martian greenhouse gas because its strong near-IR absorption leads to upper atmosphere inversion and an anti-greenhouse effect. However, previous studies did not account for the strong collision-induced absorption of CH_4 with CO_2 [4,9]. For hydrogen warming, we also find significant warming increases vs. previous calculations. In our results, gobal mean temperatures exceed 273 K for H_2 molar concentrations from 3 to 10%, depending on the background CO_2 pressure.

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, and then analyze how such atmospheres could have been produced. We show that methane and hydrogen outgassing following aqueous alteration of Mars' basaltic crust [11] could have led to transient warm episodes of 100-250,000 y duration, limited by the photolysis of CH_4 by XUV radiation and diffusion rate of hydrogen through the martian homopause (Figure 3). 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 transient reducing scenario for the late Noachian fits the weight of evidence indicating that early Mars was intermittently warm, rather than permanently warm and wet [4]. We will argue it is also amenable to additional testing by future geological investigations of the martian surface. For young planets that orbit reasonably far from their host stars, reducing atmospheres should be common in general. Our results therefore also have implications for the habitability and climate evolution of low-mass exoplanets.

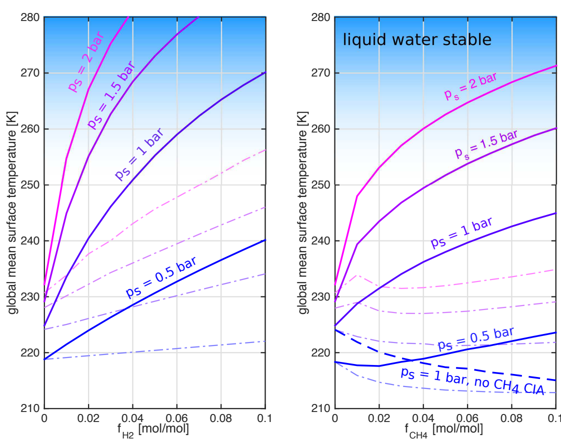

Figure 3: Surface temperature in CO_2-dominated atmospheres as a function of a) H_2 and b) CH_4 molar concentration for various surface pressures. The solid lines show results calculated using our new CIA coefficients, while dash-dot lines show results using N_2-H_2 and N_2-CH_4 CIA coefficients in place 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 antigreenhouse effect.

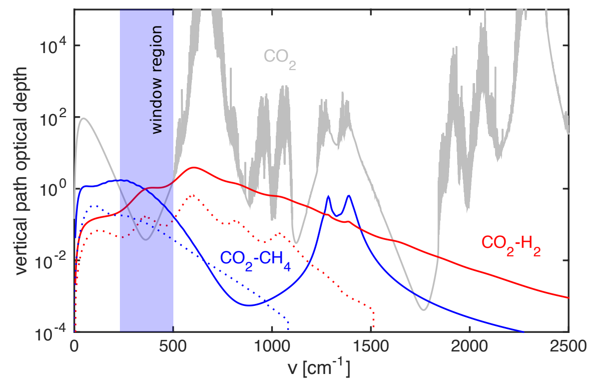

Figure 1: Total vertical path optical depth due to CO_2 (gray), CO_2-CH_4 CIA (blue) and CO_2-H_2 CIA (red) in the early martian atmosphere, assuming a pressure of 1 bar, composition 94% CO_2, 3% CH_4, 3% H_2, and surface temperature of 250 K. Dotted lines show optical depth from CIA when the absorption coefficients of CO_2-H_2 and CO_2-CH_4 are replaced by those of N_2-H_2 and N_2-CH_4, respectively.

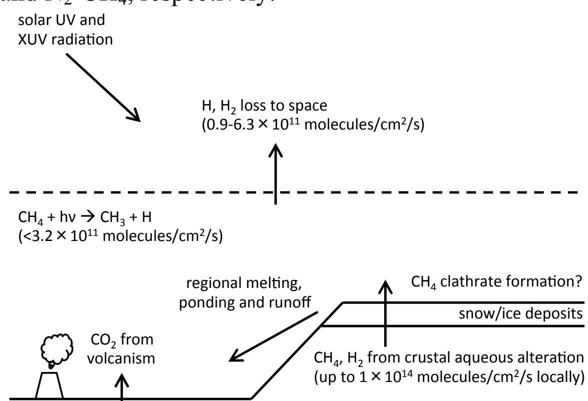

Figure 2: Schematic of key processes on early Mars in the transient reducing atmosphere scenario. Highland ice deposits created by adiabatic cooling under a denser CO_2 atmosphere [5,6] are episodically melted by H_2/CH_4 warming, leading to runoff, lake formation and fluvial erosion.

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