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The evidence for abundant liquid water on early Mars despite the faint young Sun is a long-standing problem in planetary research. Here we present new *ab initio* spectroscopic and line-by-line climate calculations of the warming potential of reduced atmospheres on early Mars. We show that the strength of both CO_2-H_2 and CO_2-CH_4 collision-induced absorption (CIA) has previously been significantly underestimated. Contrary to previous expectations, methane could have acted as a powerful greenhouse gas on early Mars due to CO_2-CH_4 CIA in the critical 250-500 cm^{-1} spectral window region. In atmospheres of 0.5 bar CO_2 or more, percent levels of H_2 or CH_4 raise annual mean surface temperatures by tens of degrees, with temperatures reaching 273 K for pressures of 1.25-2 bar and 2-10% of H_2 and CH_4. Methane and hydrogen produced following aqueous alteration of Mars' crust could have combined with volcanically outgassed CO_2 to form transient atmospheres of this composition 4.5-3.5 Ga. Our results also suggest that inhabited exoplanets could retain surface liquid water at significant distances from their host stars.

1. Introduction

Today Mars is cold and dry, with annual mean surface temperatures of around -60° C and a mainly arid, hyperoxidising surface. In the past, however, 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 fluvolacustrine deposits [*Fassett and Head*, 2008a; *Hynek et al.*, 2010; *Grotzinger et al.*, 2015].

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 [*Wordsworth*, 2016]. 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 [*Kasting*, 1991; *Wordsworth et al.*, 2013]. Many alternative mechanisms to warm early Mars have subsequently been investigated, including CO_2 clouds [*Forget and Pierrehumbert*, 1997], large meteorite impacts [*Segura et al.*, 2002], sulfur dioxide emission from volcanos [*Postawko and Kuhn*, 1986; *Halevy and Head*, 2014], and local snowmelt due to diurnal forcing and/or obliquity and eccentricity variations [e.g., *Wordsworth et al.*, 2013]. However, all suffer shortcomings that render them unlikely as the main explanation [*Forget et al.*, 2013; *Ramirez et al.*, 2014; *Kerber et al.*, 2015; *Wordsworth*, 2016].

Reducing greenhouse solutions for early Mars have also been considered previously. *Sagan* [1977] argued that early Mars might have been warmed by a hydrogen-dominated atmosphere or by abundant NH_3. However, a hydrogen-dominated atmosphere would be lost to space rapidly after formation and NH_3 is photolysed rapidly by UV radiation and lacks a plausible martian source. Later, in a paper focused on the early Earth, *Wordsworth and Pierrehumbert* [2013] 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. *Ramirez et al.* [2014] applied this mechanism to early Mars, where they argued 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 *Wordsworth and Pierrehumbert* [2013] 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 [*Hu et al.*, 2015] or estimates of the rate of hydrogen escape to space [*Ramirez et al.*, 2014]. Hence the early martian faint young Sun paradox remains unresolved.

Here we describe new spectroscopic and one-dimensional line-by-line climate 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 predicted by *Ramirez et al.* [2014] due to the strong polarizability and multipole moments of CO_2. Furthermore, we show for the first time that methane (CH_4) 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. We propose that early Mars could have been transiently warmed by emission of these gases due to crustal aqueous alteration, volcanism and impact events. Our results also have implications for the habitability of exoplanets that orbit far from their host stars.

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2. 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. The PES for CO_2-H_2 calculated at the coupled-cluster level was taken from the literature [*Li et al.*, 2010]. For the IDS for CO_2-H_2 and both the PES and IDS for CO_2-CH_4, we performed the *ab initio* calculations ourselves. Once the *ab initio* data were acquired, the zeroth spectral moment for the system was calculated as

$$\tilde{\Gamma} = \frac{32\pi^4}{3hc}\int_0^\infty \int_\Omega \mu(R,\Omega)^2 \mathrm{e}^{-V(R,\Omega)/k_B T} R^2 \mathrm{d}R\mathrm{d}\Omega, \qquad (1)$$

where h is Planck's constant, c is the speed of light, R is the separation of the molecular centers of mass, Ω is solid angle, V is the PES, μ is the IDS, k_B is Boltzmann's constant and T is temperature [*Frommhold*, 2006].

We assessed the climate effects of the new CIA coefficients using a new iterative line-by-line spectral code [*Wordsworth*, 2016; *Schaefer et al.*, 2016]. Using this model allowed us to perform extremely high accuracy globally averaged calculations while spanning a wide range of atmospheric compositions. The code has been validated against a number of analytic results and previous radiative-convective calculations. Further details of our CIA and line-by-line climate calculations are given in the Auxiliary Online Material [*Cherepanov et al.*, 2016; *Boys and Bernardi*, 1970; *Knizia et al.*, 2009; *Cohen and Roothaan*, 1965; *Clough et al.*, 1992; *Rothman et al.*, 2013; *Murphy and Koop*, 2005; *Gruszka and Borysow*, 1997; *Baranov et al.*, 2004; *Wordsworth et al.*, 2010; *Pierrehumbert*, 2011; *Hansen and Travis*, 1974; *Claire et al.*, 2012; *Béguier et al.*, 2015; *Goldblatt et al.*, 2013; *Schaefer et al.*, 2016].

3. Results

First, we compared the CO_2-H_2 and CO_2-CH_4 CIA coefficients we calculated with previously derived N_2-H_2 and N_2-CH_4 CIA data [*Borysow and Frommhold*, 1986; *Borysow and Tang*, 1993; *Richard et al.*, 2012]. Figure 1 shows that the peak values of the CO_2 CIA coefficients are significantly stronger than the previously calculated N_2 data. The difference can be explained by the higher electronegativity of oxygen than carbon, which leads to a more heterogenous electron density distribution for CO_2 than for N_2. This in turn leads to stronger multipole moments and a higher polarizability, which enhances CIA. For example, the quadrupole moment of CO_2 is approximately 3 times greater than that of N_2 [*Graham et al.*, 1998]. A significant portion of CIA scales with the square of the quadrupole moment, leading to a factor of ~ 9 increase (c.f. the coefficients in Fig. 1). The CO_2 enhancement 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 [*Wordsworth*, 2016].

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 CO_2-H_2 data and (incorrectly) using N_2-H_2 as a substitute for CO_2-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 2.5 to 10%, depending on the background CO_2 pressure.

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 peak at 250-300 K to reduce the outgoing longwave radiation (OLR) significantly [*Ramirez et al.*, 2014; *Wordsworth*, 2016]. Methane also absorbs incoming solar radiation significantly in the near-infrared [*Brown et al.*, 2013]. We find strong CH_4 near-IR absorption, leading to a temperature inversion in the high atmosphere when CH_4 is present. 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 CO_2-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 up to $\sim$30 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 may be 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 (see e.g., *Wordsworth et al.* [2013]; *Kite et al.* [2013]; *Rosenberg and Head* [2015]).

4. Discussion

Our spectroscopic CIA and line-by-line climate calculations have shown that a combination of reducing gases in the early martian atmosphere could potentially solve the faint young Sun problem. But is such a solution physically and chemically plausible? While the abundances of methane and hydrogen on Mars today are extremely low [*Webster et al.*, 2015], highly reducing atmospheres are observed elsewhere in the solar system: Titan has a 1.5 bar N_2 dominated atmosphere with CH_4 levels of 4.9% (mole fraction) near the surface [*Niemann et al.*, 2005]. Titan's methane is destroyed by photochemistry on a timescale of order 10 My [*Lunine and Atreya*, 2008], and is most likely replenished episodically due to destabilization of methane clathrates in the subsurface [*Tobie et al.*, 2006].

Mars today has a highly oxidized surface and atmosphere due to hydrogen loss to space over geological time. However, early on methane and hydrogen may have been episodically released from the subsurface in quantities sufficient to raise surface temperatures. Serpentinization, a process in which mafic minerals such as olivine are hydrothermally altered to produce reducing gases, has been proposed as the ultimate origin of the CH_4 on Titan [*Tobie et al.*, 2006]. Serpentine deposits have been observed on the martian surface at Nili Fossae, Isidis Basin and in some southern highland impact craters [*Ehlmann et al.*, 2010]. Extensive serpentinization may also have occurred on early Mars in the deep olivine-rich crust [*Chassefière et al.*, 2013]. Study of terrestrial analogs suggests that low-temperature alteration of martian ultramafic rocks would be capable of producing of order $10^{12} - 10^{14}$ molecules/cm^2/s of CH_4 in local active regions [*Etiope et al.*, 2013]. If 5% of the early martian crust was rich enough in olivine for serpentinization, this translates to a global CH_4 emission rate of $5\times10^{10} - 10^{12}$ molecules/cm^2/s.

Volcanism is another source of reduced gases, particularly of H_2. Hydrogen outgassing is highest if the oxygen fugacity of the early martian mantle was extremely low [*Ramirez et al.*, 2014; *Batalha et al.*, 2015]. An important problem with volcanism as the sole source of reduced gases, however, is that a mantle reducing enough to outgas sufficient H_2 directly would outgas CO_2 less efficiently, instead retaining large amounts of carbon in the melt [*Hirschmann and Withers*, 2008; *Wetzel et al.*, 2013]. A third potential reduced gas source is CH_4 and H_2 production due to atmospheric thermochemistry following large meteorite impacts. Because peak valley network formation occurs toward the end of the Noachian, a period of higher impact flux than today [*Fassett and Head*, 2008b, 2011], this mechanism deserves detailed investigation in future.

Once outgassed, the primary sinks for CH_4 and H_2 on early Mars would have been chemical destruction of CH_4 and escape of H_2 to space. The lifetime of methane in an atmosphere in which it is abundant is controlled by photodissociation, which is primarily powered by Lyman-α photons (see Auxiliary Online Material). Previous detailed photochemical modeling has shown that this limit is approached in CO_2-rich atmospheres when $f_{CH_4} > 0.1 - 1\%$ [*Zahnle*, 1986]. Using an estimate of the solar XUV flux at 3.8 Ga at Mars' semi-major axis as in *Wordsworth and Pierrehumbert* [2013] and integrating the solar flux up to 160 nm, the wavelength above which the absorption cross-section of CH_4 becomes negligible [*Chen and Wu*, 2004], we calculate an upper limit CH_4 photodestruction rate of $2.5 - 3.2 \times 10^{11}$ molecules/cm^2/s. This corresponds to a methane residence time of about 250,000 y starting from 5% CH_4 in a 1.25 bar CO_2 atmosphere. Note that this estimate ignores chemical recycling of dissociated CH_4 in the atmosphere and the decrease in XUV flux due to absorption by escaping hydrogen higher up in the atmosphere, both of which would increase the CH_4 residence time.

The escape of H_2 to space on early Mars would most likely have been limited by diffusion through the homopause, with a characteristic rate of

$$\Phi_{H_2} \approx \frac{b_{CO_2-H_2}}{H_{CO_2}} f_{H_2} \tag{2}$$

where $b_{CO_2-H_2}$ is the CO_2-H_2 binary collision coefficient, H_{CO_2} is the atmospheric scale height, and f_{H_2} is the hydrogen molar mixing ratio at the homopause. For hydrogen levels of 1-5% and a homopause temperature range of 150 to 500 K, we find $\Phi_{H_2} = 0.9 - 6.3 \times 10^{11}$ molecules/cm^2/s: approximately the same magnitude as the maximum rate of CH_4 photolysis. Hence a pulse of CH_4 emission into the early martian atmosphere would result in a mixed $CO_2-CH_4-H_2$ composition that would last for a period of 100,000 y or more. This timescale is more than sufficient to account for the formation of deposits in Gale crater, given the uncertainty range in sedimentation rates [*Grotzinger et al.*, 2015]. It is lower than some timescales estimated for valley network formation based on numerical runoff/erosion modeling [*Hoke et al.*, 2011], but is consistent with others [*Rosenberg and Head*, 2015], at least if a high discharge frequency is assumed. Coupled climate and landform evolution modelling in future will be necessary to test whether $\sim 10^5$ y formation timescales are indeed sufficient to explain all Noachian fluvial geomorphology.

What mechanism could cause pulses in reduced gas outgassing rates? One possibility is simply local variations in the geothermal heat flux, which would alter the rate of subsurface aqueous alteration. Another is the contribution of impactors to the atmospheric H_2 and CH_4 inventory. A third possibility is CH_4 clathration [*Lasue et al.*, 2015]. Due to adiabatic cooling of the surface under a denser CO_2 atmosphere, most of Mars' surface ice would have stabilized in the southern highlands [*Wordsworth et al.*, 2013], in the regions where most serpentine has been detected from orbit [*Ehlmann et al.*, 2010]. Hence a substantial portion of outgassed methane could have become trapped as clathrate in the cryosphere. Episodic CH_4 release following large perturbations due to volcanism, impacts or obliquity changes would have destabilized clathrates by altering thermal forcing and by sublimation/melting of the overlying ice. Once released, methane and H_2 would cause greenhouse warming, leading to a positive feedback that would destabilize the remaining ice.

Finally, transient CH_4/H_2 emissions also require CO_2 levels of 0.5 bar or greater to significantly impact surface temperature. From the late Noachian onward, atmospheric CO_2 levels were determined by a balance between volcanic outgassing, escape to space and surface carbonate formation. During this period, coupled modeling of the $^{13}C/^{12}C$ isotope ratio has constrained Mars' maximum atmospheric pressure to between 1 and 1.8 bar [*Hu et al.*, 2015]. While the upper value is a hard limit, the CO_2 pressures we require to cause significant CH_4/H_2 warming are nonetheless within current evolutionary constraints.

A CO_2-CH_4 atmosphere on early Mars would not develop a thick haze as on Titan because organic aerosol formation is strongly inhibited for C/O ratios of 0.6 or lower [*Zahnle*, 1986; *Trainer et al.*, 2006]. However, reaction of atmospheric CH_4 with oxygen from CO_2 photolysis could lead to increased stratospheric H_2O. This would cause increased formation of high-altitude cirrus clouds, which would enhance warming [*Urata and Toon*, 2013], reducing the background CO_2 requirements beyond the baseline calculations shown here. We plan to investigate this possibility in detail in future work.

5. Conclusion

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. Other effects, particularly the contribution of methane photolysis to cirrus cloud formation, may lower these CO_2 and H_2/CH_4 abundance requirements further and deserve detailed investigation (probably with a 3D climate model) in future.

Our CIA calculation methodology has been validated against existing data for N_2-H_2 and N_2-CH_4 pairs. Nonetheless, the complexity of CIA interactions involving CH_4 means that it may not capture all differences between the N_2-CH_4 and CO_2-CH_4 systems. For this reason we strongly encourage the experimental investigation of CO_2-CH_4 CIA in the future. Testing other aspects of the reducing atmosphere scenario for early Mars will require better constraints on the rate of crustal H_2/CH_4 production during the Noachian and the nature of the early water cycle. Future investigation of the detailed chemical composition of the martian crust and mantle, along with a continued search for serpentine and other hydrated minerals, will be important to make further progress.

Besides early Mars, our results have implications for exoplanet habitability and the search for biosignatures. Current definitions of the outer edge of the habitable zone rely on either CO_2 or H_2 and assume that a biosphere would have a detrimental effect on habitability via methanogenic consumption of these gases [e.g., *Pierrehumbert and Gaidos*, 2011]. However, the apparent strength of CO_2-CH_4 CIA means that an inhabited planet could potentially retain a stable climate at great distances from its host star.

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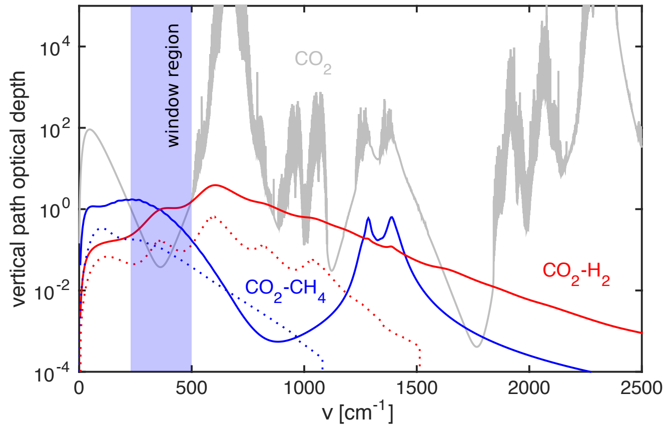

Figure 1. Total vertical path optical depth due to CO_2 (gray), CO_2-CH_4 CIA (blue) and CO_2-H_2 CIA (red) in the early martian atmosphere, assuming a pressure of 1 bar, composition 94% CO_2, 3% CH_4, 3% H_2, and surface temperature of 250 K. Dotted lines show optical depth from CIA when the absorption 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. Both the CO_2-H_2 and CO_2-CH_4 CIA are strong in a critical window region of the spectrum where absorption by pure CO_2 is weak.

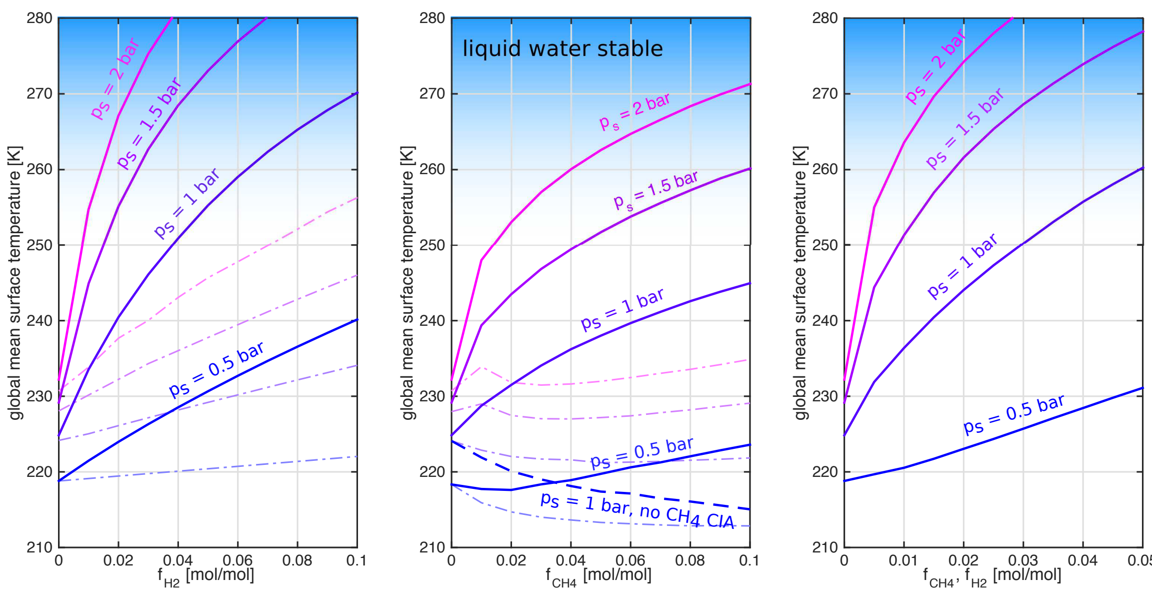

Figure 2. Surface temperature in CO_2-dominated atmospheres as a function of a) H_2 and b) CH_4 molar concentration for various surface pressures p_s. The solid lines show results calculated using our new CIA coefficients, while dash-dot lines show results using N_2-H_2 and N_2-CH_4 CIA coefficients 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).

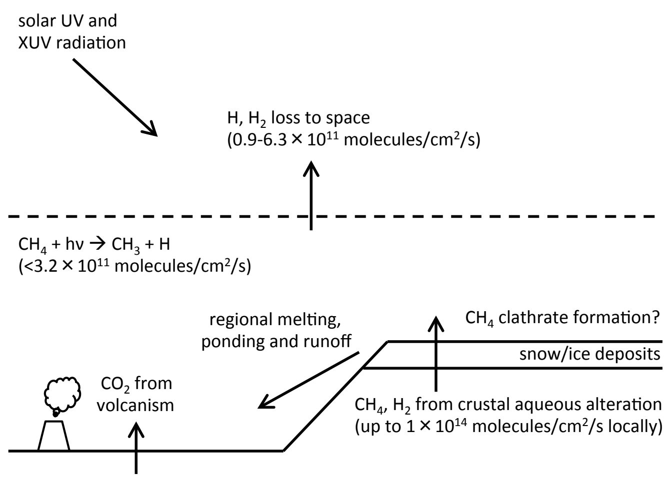

Figure 3. Schematic of key processes on early Mars in the transient reducing atmosphere scenario. Highland ice deposits created by adiabatic cooling under a denser CO_2 atmosphere are episodically melted by H_2/CH_4 warming, leading to runoff, lake formation and fluvial erosion.