

RESEARCH LETTER

10.1002/2016GL071766

Key Points:

- New ab initio and line-by-line calculations show that warming by H₂ in CO₂ atmospheres is far stronger than previously believed
- Contrary to previous research, we show that methane could also have been an effective greenhouse gas on early Mars
- Reducing atmospheres could have been produced transiently by a combination of aqueous alteration of Mars' crust and volcanic CO₂ outgassing

Supporting Information:

- Supporting Information S1

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Citation:

Wordsworth, R., Y. Kalugina, S. Lokshantov, A. Vigasin, B. Ehlmann, J. Head, C. Sanders, and H. Wang (2017), Transient reducing greenhouse warming on early Mars, *Geophys. Res. Lett.*, *44*, 665–671, doi:10.1002/2016GL071766.

Received 1 NOV 2016

Accepted 2 JAN 2017

Accepted article online 5 JAN 2017

Published online 21 JAN 2017

Transient reducing greenhouse warming on early Mars

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Abstract 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 CO₂–H₂ and CO₂–CH₄ 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 CO₂–CH₄ CIA in the critical 250–500 cm^{−1} spectral window region. In atmospheres of 0.5 bar CO₂ or more, percent levels of H₂ or CH₄ raise annual mean surface temperatures by tens of degrees, with temperatures reaching 273 K for pressures of 1.25–2 bars and 2–10% of H₂ and CH₄. Methane and hydrogen produced following aqueous alteration of Mars' crust could have combined with volcanically outgassed CO₂ 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, hyper-oxidizing 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 fluvio-lacustrine deposits [Fassett and Head, 2008a; Hynke 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 CO₂–H₂O 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 CO₂ 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 NH₃. However, a hydrogen-dominated atmosphere would be lost to space rapidly after formation and NH₃ is photolyzed 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 H₂ emitted from volcanoes into a CO₂-dominated atmosphere could have kept Mars in a “warm and wet” state for periods of tens of millions of years or longer. However, lacking CO₂–H₂ CIA data they used the same N₂–H₂ data as *Wordsworth and Pierrehumbert* [2013] 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 with either constraints on the total amount of CO₂ 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 CO₂–H₂ warming to be significantly more effective than predicted by *Ramirez et al.* [2014] 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. 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.

2. 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 [*Li et al.*, 2010]. 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 were acquired, the zeroth spectral moment for the system was calculated as

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

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 supporting information [*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 CO₂–H₂ and CO₂–CH₄ CIA coefficients we calculated with previously derived N₂–H₂ and N₂–CH₄ CIA data [*Borysow and Frommhold*, 1986; *Borysow and Tang*, 1993; *Richard et al.*, 2012]. Figure 1 shows that the peak values of the CO₂ CIA coefficients are significantly stronger than the previously calculated N₂ data. The difference can be explained by the higher electronegativity of oxygen than carbon, which leads to a more heterogenous electron density distribution for CO₂ than for N₂. This in turn leads to stronger multipole moments and a higher polarizability, which enhances CIA. For example, the quadrupole moment of CO₂ is approximately 3 times greater than that of N₂ [*Graham et al.*, 1998]. A significant portion of CIA scales with the square of the quadrupole moment, leading to a factor of ~9 increase (cf. the coefficients in Figure 1). The CO₂ 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 CO₂–H₂ data and (incorrectly) using

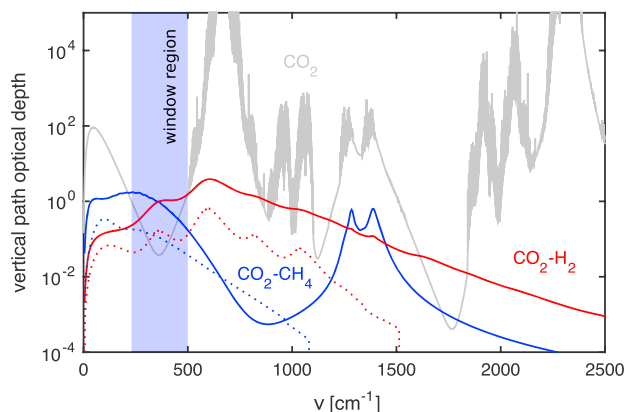


Figure 1. Total vertical path optical depth due to CO₂ (gray), CO₂-CH₄ CIA (blue) and CO₂-H₂ CIA (red) in the early Martian atmosphere, assuming a pressure of 1 bar, composition 94% CO₂, 3% CH₄, 3% H₂, and surface temperature of 250 K. Dotted lines show optical depth from CIA when the absorption coefficients of CO₂-H₂ and CO₂-CH₄ are replaced by those of N₂-H₂ and N₂-CH₄, respectively. Both the CO₂-H₂ and CO₂-CH₄ CIA are strong in a critical window region of the spectrum where absorption by pure CO₂ is weak.

N₂-H₂ as a substitute for CO₂-H₂. As can be seen, the difference is significant, with surface temperatures increasing by many tens of degrees for H₂ abundances greater than a few percent. Global mean temperatures exceed 273 K for H₂ molar concentrations from 2.5 to 10%, depending on the background CO₂ 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 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 CH₄ near-IR absorption, leading to a temperature inversion in the high atmosphere when CH₄ is present. Hence, although CH₄ near-IR absorption decreases planetary albedo, its net effect is to slightly decrease surface temperatures in the absence of other effects (Figure 2b).

Despite its antigreenhouse 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 CO₂-CH₄ CIA absorption

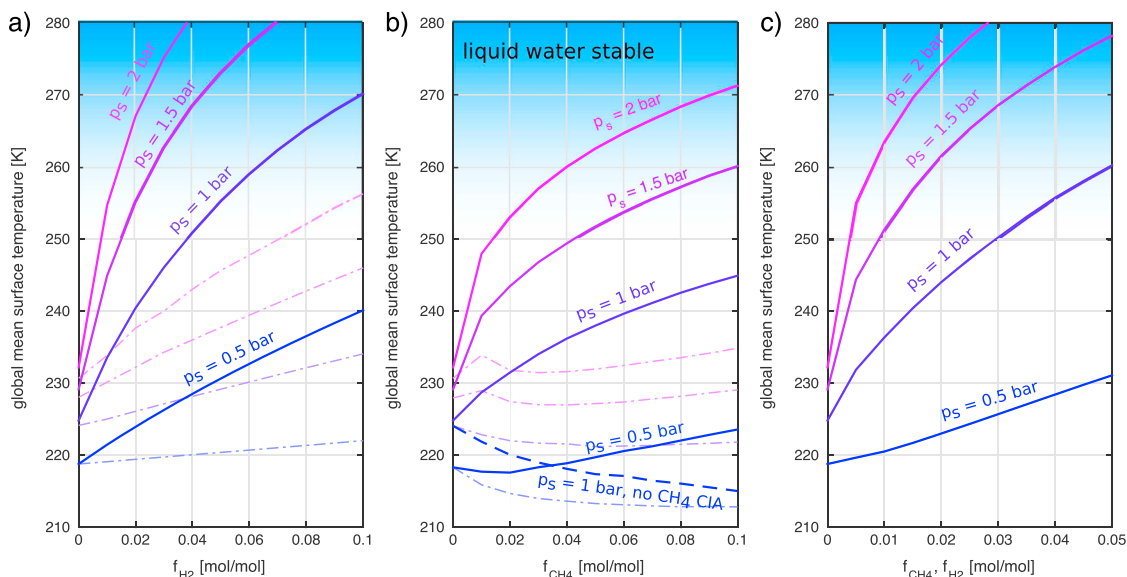


Figure 2. Surface temperature in CO₂-dominated atmospheres as a function of (a) H₂ and (b) CH₄ molar concentration for various surface pressures p_s . The solid lines show results calculated using our new CIA coefficients, while dash-dotted lines show results using N₂-H₂ and N₂-CH₄ CIA coefficients in place of the correct coefficients. In Figure 2b, the dashed line shows the case at 1 bar where CH₄ CIA is removed entirely, demonstrating that without it, methane actually has an antigreenhouse effect. (c) Both H₂ and CH₄ are present in equal amounts. Note the change of scale on the x axis compared to Figures 2a and 2b.

peaks in the key 250 to 500 cm⁻¹ window region. We find that adding 5% CH₄ increases global mean temperatures by up to ~30 K, depending on the background CO₂ pressure (Figure 2). Finally, when CH₄ and H₂ 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 N₂ dominated atmosphere with CH₄ 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 Myr [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 CH₄ 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 10¹²–10¹⁴ molecules/cm²/s of CH₄ 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 CH₄ emission rate of 5 × 10¹⁰–10¹² molecules/cm²/s (Figure 3).

Volcanism is another source of reduced gases, particularly of H₂. 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 H₂ directly would outgas CO₂ 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 CH₄ and H₂ 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 CH₄ and H₂ on early Mars would have been chemical destruction of CH₄ and escape of H₂ 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 supporting information). Previous detailed photochemical modeling has shown that this limit is approached in CO₂-rich atmospheres when $f_{\text{CH}_4} > 0.1\text{--}1\%$ [Zahnle, 1986]. Using an estimate of the solar XUV flux at 3.8 Ga at Mars' semimajor 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 CH₄ becomes negligible [Chen and Wu, 2004], we calculate an upper limit CH₄ photodestruction rate of 2.5–3.2 × 10¹¹ molecules/cm²/s. This corresponds to a methane residence time of about 250,000 years starting from 5% CH₄ in a 1.25 bar CO₂ atmosphere. Note that this estimate ignores chemical recycling of dissociated CH₄ 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 CH₄ residence time.

The escape of H₂ to space on early Mars would most likely have been limited by diffusion through the homopause, with a characteristic rate of

$$\Phi_{\text{H}_2} \approx \frac{b_{\text{CO}_2-\text{H}_2}}{H_{\text{CO}_2}} f_{\text{H}_2} \quad (2)$$

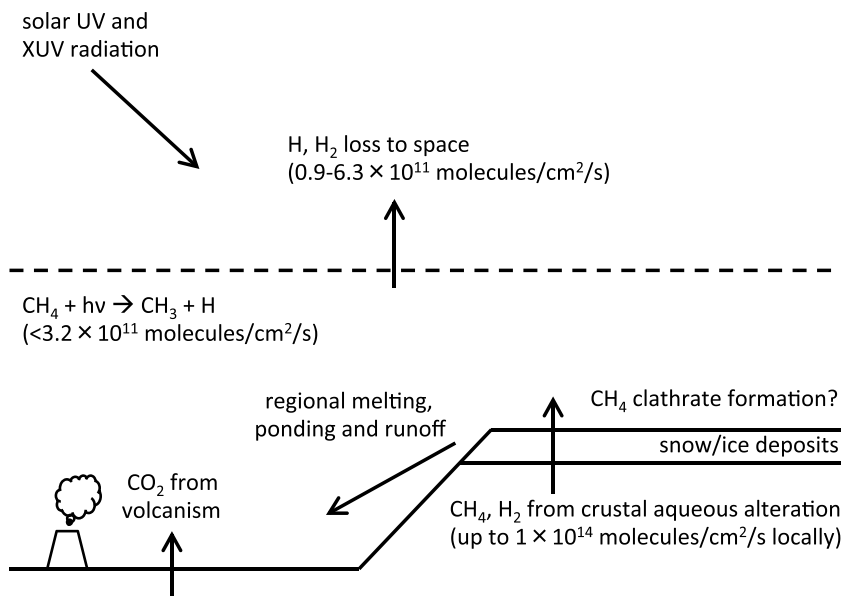


Figure 3. Schematic of key processes on early Mars in the transient reducing atmosphere scenario. Highland ice deposits created by adiabatic cooling under a denser CO₂ atmosphere are episodically melted by H₂/CH₄ warming, leading to runoff, lake formation and fluvial erosion.

where $b_{\text{CO}_2-\text{H}_2}$ is the CO₂–H₂ 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 $\Phi_{\text{H}_2} = 0.9\text{--}6.3 \times 10^{11}$ molecules/cm²/s: approximately the same magnitude as the maximum rate of CH₄ photolysis. Hence, a pulse of CH₄ emission into the early Martian atmosphere would result in a mixed CO₂–CH₄–H₂ composition that would last for a period of 100,000 years 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 $\sim 10^5$ years formation timescales are indeed sufficient to explain all Noachian fluvial geomorphology.

What mechanism could cause pulses in reduced gas outgassing rates 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 H₂ and CH₄ inventory. A third possibility is CH₄ clathration [Lasue *et al.*, 2015]. Due to adiabatic cooling of the surface under a denser CO₂ 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 CH₄ 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 H₂ would cause greenhouse warming, leading to a positive feedback that would destabilize the remaining ice.

Finally, transient CH₄/H₂ emissions also require CO₂ levels of 0.5 bar or greater to significantly impact surface temperature. From the late Noachian onward, atmospheric CO₂ levels were determined by a balance between volcanic outgassing, escape to space, and surface carbonate formation. During this period, coupled modeling of the ¹³C/¹²C isotope ratio has constrained Mars' maximum atmospheric pressure to between 1 and 1.8 bars [Hu *et al.*, 2015]. While the upper value is a hard limit, the CO₂ pressures we require to cause significant CH₄/H₂ warming are nonetheless within current evolutionary constraints.

A CO₂–CH₄ 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 CH₄ with oxygen from CO₂ photolysis could lead to increased stratospheric H₂O.

This would cause increased formation of high-altitude cirrus clouds, which would enhance warming [Urata and Toon, 2013], reducing the background CO₂ 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 CO₂, a few percent of H₂ and/or CH₄ 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 CO₂ and H₂/CH₄ abundance requirements further and deserve detailed investigation (probably with a 3-D climate model) in future.

Our CIA calculation methodology has been validated against existing data for N₂ – H₂ and N₂ – CH₄ pairs. Nonetheless, the complexity of CIA interactions involving CH₄ means that it may not capture all differences between the N₂–CH₄ and CO₂–CH₄ systems. For this reason we strongly encourage the experimental investigation of CO₂–CH₄ CIA in the future. Testing other aspects of the reducing atmosphere scenario for early Mars will require better constraints on the rate of crustal H₂/CH₄ 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 CO₂ or H₂ 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 CO₂–CH₄ CIA means that an uninhabited planet could potentially retain a stable climate at great distances from its host star.

Acknowledgments

R.W. acknowledges financial support from the Kavli Foundation and discussions with T. Robinson and F. Ding on line-by-line radiative calculations and K. Zahnle on atmospheric chemistry. S.L., Y.K., and A.V. gratefully acknowledge partial support of this work from RFBR grants 15-03-03302 and 15-05-00736 and the Russian Academy of Sciences Program 9. B.L.E. thanks B. Sherwood-Lollar and G. Etiope for discussion of H₂/CH₄ observed in terrestrial serpentinizing systems. The ab initio calculations were performed using the HPC resources of the FAS Research Computing Cluster (Harvard University) and the “Lomonosov” (Moscow State University) supercomputer. The CIA data produced from our spectroscopic calculations and the line-by-line and temperature data produced from our climate model are available from the lead author on request (rwordsworth@seas.harvard.edu).

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