A Methane Extension to the Classical Habitable Zone

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Abstract

The habitable zone (HZ) is the circumstellar region where standing bodies of liquid water could exist on the surface of a rocky planet. Conventional definitions assume that CO2 and H2O are the only greenhouse gases. The outer edge of this classical N2−CO2−H2O HZ extends out to nearly ∼1.7 au in our solar system, beyond which condensation and scattering by CO2 outstrip its greenhouse capacity. We use a single-column radiative-convective climate model to assess the greenhouse effect of CH4 (10−~100,000 ppm) on the classical HZ (N2−CO2−H2O) for main-sequence stars with stellar temperatures between 2600 and 10,000 K (∼A3 to M8). Assuming N2−CO2−H2O atmospheres, previous studies have shown that cooler stars heat terrestrial planets more effectively. However, we find that the addition of CH4 produces net greenhouse warming (tens of degrees) in planets orbiting stars hotter than a mid-K (∼4500 K), whereas a prominent anti-greenhouse effect is noted for planets around cooler stars. We show that 10% CH4 can increase the outer edge distance of the hottest stars \( T_{\text{Eff}} = 10,000 \) K by over 20%. In contrast, the CH4 anti-greenhouse can shrink the HZ for the coolest stars \( T_{\text{Eff}} = 2600 \) K by a similar percentage. We find that dense CO2−CH4 atmospheres near the outer edge of hotter stars may suggest inhabitance, highlighting the importance of including secondary greenhouse gases in alternative definitions of the HZ. We parameterize the limits of this N2−CO2−H2O–CH4 HZ and discuss implications in the search for extraterrestrial life.

Key words: astrobiology – planets and satellites: atmospheres – planets and satellites: terrestrial planets

1. Introduction

The habitable zone (HZ) is the circular region around one or multiple stars where standing bodies of liquid water could exist on a rocky planet’s surface (e.g., Kasting et al. 1993; Haghighipour & Kaltenegger 2013; Kaltenegger & Haghighipour 2013) and facilitate the detection of possible atmospheric biosignatures (see e.g., Kaltenegger 2017). Unlike earlier studies (e.g., Hart 1978) that computed a relatively narrow HZ, Kasting et al. (1993) showed that the carbonate-silicate cycle, which regulates the transfer of CO2 between the surface, atmosphere, and interior on the Earth, is what allows for a relatively wide (∼0.95–1.67 au in our solar system) region for the classical HZ, which is calculated using a single-column radiative-convective model.

The classical N2−CO2−H2O HZ is defined by the greenhouse effect of two gases: CO2 and H2O vapor. The inner edge corresponds to the distance where mean surface temperatures exceed the critical point of water (∼647 K, 220 bar), triggering a runaway greenhouse that leads to rapid water loss to space on very short timescales (see Kasting et al. 1993 for details). Toward the outer edge of the classical HZ, weathering rates decrease, allowing atmospheric CO2 concentrations to increase as stellar insolation decreases. At the outer edge, condensation and scattering by CO2 outstrip its greenhouse capacity, the so-called maximum greenhouse limit of CO2.

The inner edge of the classical HZ appears to be relatively robust to additions of secondary greenhouse gases, because trace gas absorption is outstripped by water vapor absorption in these extremely dense (>200 bar) water steam atmospheres (Ramirez & Kaltenegger 2017). In contrast, the outer-edge limit of the N2−CO2−H2O HZ can change significantly if other gases are added to the model. For example, if volcanic hydrogen is outgassed in sufficiently high amounts on a planet, it can increase the outer-edge distance of the classical HZ by well over 50%. In addition, adding a light gas like hydrogen to the atmosphere would improve the detectability of atmospheric features on outer-edge planets (Ramirez & Kaltenegger 2017), making super-Earths beyond the traditional HZ compelling observational targets as well. The accumulation of tens to hundreds of bars of primordial hydrogen in the atmosphere of a young planet can increase this distance even farther; however, the duration of habitable conditions within the classical HZ in this case is very short (see Pierrehumbert & Gaidos 2011).

Many studies have shown that the stellar energy distribution (SED) of a star (Figure 1) influences both the magnitude and location of atmospheric warming (e.g., Kasting et al. 1993; von Paris et al. 2010; Hu & Ding 2011; Wordsworth et al. 2011; Kopparapu et al. 2013; Ramirez & Kaltenegger 2014, 2016). In comparison with terrestrial planets around G stars, those around M stars absorb more stellar energy, whereas those around A and F stars absorb less. This is partly due to the effectiveness of Rayleigh scattering, which decreases at longer wavelengths. A second effect is the increase in near-IR absorption by H2O and CO2 as the star’s spectral peak shifts to these wavelengths. That means that the same integrated stellar flux that hits the top of a planet’s atmosphere from a cool red star warms a planet more efficiently than the same integrated flux from a hot blue star. However, these previous studies have only analyzed atmospheres consisting of N2, CO2 and H2O, with neither gas possessing near-infrared absorption features that are similar in strength to their dominant IR features in the temperature regime typically considered for habitable planets (∼150–300 K). In contrast, methane has several absorption bands in the near-IR that are comparable in strength to its IR absorption bands as
well as a scattering cross section 2.4 times that of air (Pavlov et al. 2000, Sutton & Driscoll 2004) (see Figure 2).

Plus, CH4 has been invoked to solve the faint young Sun problem on the early Earth (e.g., Pavlov et al. 2000; Haqq-Misra et al. 2008; Wolf & Toon 2013). Methane concentrations high enough to generate above-freezing surface temperatures in these N2–CO2–H2O–CH4 atmospheres may have been produced by methanogens. Likewise, it has been proposed that CH4 could have been a key greenhouse gas on early Mars (e.g., Ramirez 2017; Wordsworth et al. 2017). As a trace gas on the modern Earth, CH4 is notable because ~90% of the present-day atmospheric CH4 on our own planet has a biotic origin.

In this paper, we explore the effect of CH4 on the habitability of terrestrial planets and its effect on the limits of the classical N2–CO2–H2O HZ. We model the effects of CH4 on the temperature structure of various terrestrial atmospheres as a function of SED with a single-column radiative-convective climate model. We then calculate the N2–CO2–H2O–CH4 HZ limits for A–M stars (T\textsubscript{eff} = 2600–10,000 K) and parameterize these limits. Finally, we discuss the implications of life near the outer edge and its relevance to atmospheric detection and characterization. Our models are described in Section 2, Section 3 describes our results, and Section 4 discusses the implications of this work. We then summarize with concluding thoughts.

2. Methodology

As in previous studies of the classical HZ (e.g., Kopparapu et al. 2013; Ramirez & Kaltenegger 2014, 2016, 2017) we used a single-column radiative-convective climate model to compute HZ boundaries for stars of stellar effective temperatures, T\textsubscript{eff}, ranging from 2600 to 10,000 K (Ramirez & Kaltenegger 2016). The HZ limits we compute here (and in Ramirez & Kaltenegger 2016, 2017) include A-stars, with larger orbital separations of the HZ. We use spectra derived from BT-Settl data (Allard et al. 2003, 2007) and a standard Thekaekara solar spectrum for the Sun-like (G2) star (Thekaekara 1974).

The model uses correlated-k coefficients to parameterize absorption by H2O, CO2, and CH4 across 38 spectral intervals at solar wavelengths and 55 intervals in the infrared. The near-infrared (NIR) CH4 coefficients for wavelengths less than 1 \textmu m are derived from Karkoschka (1994). As in Ramirez (2017), we use HITRAN 4-term CH4 infrared absorption coefficients derived for eight pressures (1 × 10\textsuperscript{-5}–100 bar) and five temperatures (100, 200, 300, 400, and 600 K). We include new CO2–CH4 collision-induced absorption data (Wordsworth et al. 2017), which has been recently shown to greatly increase the efficacy of the CH4 greenhouse (Ramirez 2017; Wordsworth et al. 2017). Although we also included the most updated CH4–CH4, N2–CH4, and N2–N2 CIA (Richard et al. 2012), previous sensitivity studies showed that the additional forcing from these CIA is negligible for these atmospheres (Ramirez 2017). We also added Rayleigh scattering due to CH4, based on experimentally derived indices of refraction (Snee & Ubachs 2005).

In previous 1D radiative-convective climate modeling of the outer edge of the HZ, inverse calculations (e.g., Kasting et al. 1993) were typically used, in which a surface temperature is specified and the solar flux required to maintain it is computed. In those earlier computations, the surface and stratospheric temperatures were both fixed at 273 K and ~155 K, respectively (Kasting et al. 1993; Kopparapu et al. 2013) and the CO2 partial pressure was varied from 1 × 10\textsuperscript{-2} to 34.7 bar (the saturation CO2 partial pressure at 273 K). The effective fluxes incident on the planet (S\textsubscript{eff}) to sustain a surface temperature of 273 K are then computed for all spectral classes. For the inner edge the stratospheric temperature is 200 K and the surface temperature is gradually increased from a starting temperature of 200 K, which simulates pushing the planet closer and closer to the star until a runaway greenhouse is triggered, following Kasting et al. (1993) and Ramirez & Kaltenegger (2017). An Earth-like CO2 concentration of 330 ppm is assumed. A background of 1 bar N2 is assumed for all atmospheres (ibid).

However, assuming a constant stratospheric temperature profile for CH4 is inaccurate because significant absorption at solar wavelengths produces upper atmospheric temperature inversions (see Results). We instead employ the method of forward calculations for these CO2–CH4–H2O atmospheres (e.g., Kasting 1991). With this method, we specify a solar flux and compute the surface temperature once stratospheric fluxes are balanced and convergence is achieved.

We pick several representative stars from the A–M spectral classes (2600, 3400, 3800, 4400, 5000, 5800, 7200, and 10,000 K) and calculate the effective flux needed to converge to a mean surface temperature of 273 K, the freezing point of water, due to a gradual increase in pCO2. For pCO2 < 1 bar, we assume the following grid of atmospheric pCO2 levels (in bar) [1 × 10\textsuperscript{-3}, 5 × 10\textsuperscript{-3}, 1 × 10\textsuperscript{-2}, 5 × 10\textsuperscript{-2}, 1 × 10\textsuperscript{-1}, 5 × 10\textsuperscript{-1}]. At higher pCO2 levels, pressure is gradually increased by whole units. This is a much more time-intensive procedure than inverse calculations because a convergent solution must be obtained for each pCO2 level before the solution for the next one can be computed. If a mean surface temperature of 273 K is not obtained on a given initial stellar flux, the calculation must be repeated using a different estimate on the stellar flux for the entire suite of pCO2 levels.

We compute the resultant outer-edge effective stellar incident flux limits of the N2–CO2–H2O–CH4 HZ for A3–M8 stars (T\textsubscript{eff} = 2600–10,000 K) for 3 CH4 concentrations: 10 ppm, 10,000 ppm, and an upper limit equal to 10% of the CO2 abundance, above which photochemical hazes should form that cool the planet (Haqq-Misra et al. 2008). Although recent results suggest that haze formation may be inhibited on
HZ planets orbiting stars with high FUV fluxes (A and F spectral classes and active M stars) (Arney et al. 2017), this result will need to be verified with a more complex photochemical model that incorporates oxygen into the haze molecules (ibid). We nominally assume that hazes can form around such stars for this analysis. The 10,000 ppm (1% CH₄) case is a limit for Earth-like planets assuming terrestrial outgassing rates and diffusion-limited escape (Pavlov et al. 2000; Kharecha et al. 2005). For the inner edge, even the highest CH₄ concentration yields 33 ppm (~1/300 of a percent CH₄) for the dry (N₂ + CO₂) atmosphere. We verified that at such low CH₄ concentrations this inner edge calculation would be virtually indistinguishable from that predicted with the classical N₂−CO₂−H₂O HZ. Thus, we focus our work on the outer edge.

As explained in Kasting et al. (1993), the effective flux S_eff, is the ratio of the net outgoing infrared radiation (Fₒ) over the net incoming solar radiation (Fₛ). An S_eff value of 1 is the normalized flux received at Earth’s orbit. Higher S_eff values correspond to distances closer to the star. Given S_eff, the stellar luminosity L normalized to the solar luminosity L_sun, and the outer and inner edge distances (d) in au can be determined using Equation (1):

\[
d(\text{au}) = \sqrt{\frac{L}{L_{\text{Sun}}} \cdot S_{\text{EFF}}}.
\]

All our atmospheres are fully saturated although a moist CO₂ adiabat is followed in the upper atmosphere. Six solar zenith angles are used in our calculations. We set the model surface albedo to 0.31, which reproduces the mean surface temperature for Earth (288 K) in our model. As with previous work on the HZ (Kasting et al. 1993; Kopparapu et al. 2013; Ramirez & Kaltenegger 2017), this value is higher than Earth’s surface albedo (~0.2) and is designed to account for the additional reflectivity as well as heating effect from clouds. Cloud effects continue to be poorly understood, however, particularly for atmospheres very different from the Earth’s. Thus, we do not vary cloud properties for our atmospheres (see e.g., Kasting et al. 1993; Zsom et al. 2012; Kopparapu et al. 2013; Kitzmann 2016). However, the planetary albedo is a sum of atmospheric and surface reflection, evolving as the atmospheric composition changes.

3. Results

3.1. Methane Heats or Cools a Planet Depending on the Host Star’s SED

The stellar radiation for three representative star types (F0, Sun, and M3) are shown in Figure 1. A significant portion of an M-star’s stellar radiation is emitted at near-infrared wavelengths, particularly between 1 and 3 µm. Figure 2 shows three different atmospheres with CO₂, CH₄ and H₂O concentrations representative of worlds near the outer edge of the HZ, where CO₂ dominates the atmospheric composition.

The NIR absorption cross-sections for CH₄ between ~1 and 4 µm are comparable to those in the IR near and around the 7.7 µm band (Figure 2) for the atmospheres shown Modeled. In contrast, the largest CO₂ and H₂O infrared absorption cross-sections are near the Planck function peak and are generally orders of magnitude larger than their NIR ones between ~1 and 2.5 µm. Moreover, H₂O vapor concentrations and its resulting absorption are relatively weak in dense CO₂ atmospheres near the outer edge (Figure 2).

We model the effect of the addition of methane on the temperature profiles of CO₂-rich atmospheres near the outer edge of the HZ of host stars with T_eff = 7200 K, 5800 K, and 3400 K (F0, Sun, and M3 spectral classes), respectively (Figure 3). For ease of comparison, the same stellar insolation value (S/S☉ = 0.33) and dry atmospheric (minus water vapor) composition (1 bar N₂ and 3 bar CO₂) and a 4 bar surface pressure is shown in Figure 3. We present results for (10,000 ppm) 1% CH₄ simulations to compare against those with no CH₄, which changes the surface pressure by about 0.4 bar between the two cases shown. Sensitivity studies (not shown) revealed the same general behavior to the addition of methane at both higher and lower CH₄ concentrations.

In the CH₄-free simulations, the surface temperature is greatest for the planet orbiting the M3 (3400 K) host star (279 K versus 201 K for the F0 planet) (dashed lines Figure 3) because its SED is shifted toward longer wavelengths where Rayleigh scattering is reduced (given that Rayleigh scattering is proportional to 1/λ⁴), lowering the overall planetary albedo.

The addition of 1% CH₄ to the model planet (Figure 3 solid lines) produces sufficient upper atmospheric heating to generate a temperature inversion in all three model planets. The surface temperature increases when 1% CH₄ is added for
atmosphere. The surface temperature increases when 1% CH4 is added for the planet orbiting the F0 solar analog, and (c) an M3 host star when adding 1% (10,000 ppm) CH4. A temperature inversion forms for all three model planets when CH4 is added to the atmosphere. The surface temperature increases when 1% CH4 is added for the planet orbiting the F0 (18 K) and solar analog (29 K), but decreases for the planet orbiting an M3 star (31 K).

Figure 3. Changes in temperature profiles for a 3 bar CO2 atmosphere (S/EFF = 0.33) for a model planet with a surface pressure of about 4 bar orbiting (a) an F0, (b) a solar analog, and (c) an M3 host star when adding 1% (10,000 ppm) CH4. A temperature inversion forms for all three model planets when CH4 is added to the atmosphere. The surface temperature increases when 1% CH4 is added for the planet orbiting the F0 (18 K) and solar analog (29 K), but decreases for the planet orbiting an M3 star (31 K).

Figure 4. Changes in net surface spectral fluxes for a 4-bar total surface pressure, 3-bar CO2 atmospheres around different host stars (temperature structures are shown in Figure 3). The addition of 1% (10,000 ppm) CH4 reduces the NIR net stellar radiation received at the surface for the F0, Sun and M3 by 12.1, 17.8, and 15 W m⁻², respectively, which is equivalent to decreases of 25% (F0), 34% (Sun), and 43% (M3).

The planet orbiting the F0 host star (~18 K) and the solar analog (~29 K). However, the surface temperature decreases for the planet orbiting an M3 host star (~31 K) because the redshifted SED of its M3 star produces stronger upper atmospheric heating, which reduces the stellar energy available to heat the lower atmosphere and surface (Figure 4). In contrast, modeled planets orbiting the F0 host star and the Sun show less upper atmospheric heating from near-IR absorption (Figure 3) and smaller atmospheric temperature inversions. The upper atmospheric heating for planets orbiting a M3 host star cools their surfaces more efficiently than the increased Rayleigh scattering for planets orbiting an F0 star.

3.2. Methane Expands the Classical HZ Outward for Hot Host Stars but Reduces the HZ Width for Cool Host Stars

The effect of adding different amounts of CH4 to the classical N₂−CO₂−H₂O HZ are shown in Figure 5 for the whole HZ, and in Figure 6 for the outer edge. An alternative HZ limit that is not based on atmospheric models (like the classical HZ) but on empirical observations of our solar system is shown in both figures for comparison, the empirical HZ. The inner edge of the empirical HZ is defined by the stellar flux received by Venus when we can exclude the possibility that it had standing water on the surface (about 1 Gyr ago), equivalent to a stellar flux of S₁EFF = 1.77 (Kasting et al. 1993). The “early Mars” limit is based on observations, suggesting that the Martian surface may have supported standing bodies of water ~3.8 Gyr when the Sun was only 75% as bright as it is today. For our solar system, S₁EFF = 0.32 for this limit, corresponding to a distance of ~1.77 au (e.g., Kasting et al. 1993). The incident flux in both figures is normalized to that received by Earth’s orbit (~1360 W m⁻²), S₀.

Figure 5. The effect of adding methane to the outer edge of the classical HZ. Stellar effective temperature vs. incident stellar flux (S₁EFF) for the traditional (dashed); empirical (solid black) and CO₂−CH₄ HZ (solid blue); respectively, for mixing ratios of 10 ppm CH₄ (triangle), 1% CH₄ (square), and /CH₄ = 0.1 × /CO₂.

Figures 5 and 6 show that CH₄ decreases the insolation needed at the outer edge of the HZ for hotter stars (~>4500 K). Thus, the effect of CH₄ on the HZ depends on the host star’s SED with lower stellar effective temperatures resulting in a CH₄ anti-greenhouse effect. As a haze is expected to build up for CH₄/CO₂ ratios greater than ~0.1 (Haqq-Misra et al. 2008), we do not explore even higher CH₄ mixing ratios.

The addition of CH₄ has a substantial effect on the limits of the outer edge of the HZ in a solar system like our own,
decreasing $S_{\text{EFF}}$ from $\sim0.357$ at the classical maximum greenhouse limit to $\sim0.305$ for $f_{\text{CH}_4} = 0.1 \times f_{\text{CO}_2}$ ($\sim14.5\%$) (Figures 5–6), equivalent to moving the outer edge from $\sim1.67 \text{ au}$ to $1.81 \text{ au}$, beyond the empirical limit of the HZ. This lies just beyond the early Mars limit and is consistent with recent calculations suggesting that CO$_2$–CH$_4$ collision-induced absorption could have been significant on early Mars if CH$_4$ concentrations were sufficiently high (Ramírez 2017; Wordsworth et al. 2017).

For planetary systems around hotter stars than the Sun, the addition of $\sim10$ ppm CH$_4$ decreases the $S_{\text{EFF}}$ required to support the outer edge for the hottest star in our sample, an A-star ($T_{\text{eff}} = 10,000 \text{ K}$) by $\sim8\%$ from 0.598 to 0.552. Assuming $L/L_{\text{Sun}} = 20$, the orbital distance of the outer edge of the HZ moves from 5.78 to 6.01 au. For $f_{\text{CH}_4} = 0.1 \times f_{\text{CO}_2}$, $S_{\text{EFF}}$ decreases by as much as 31% (0.598–0.412) for the hottest sample star, moving the orbital distance of the outer edge of the HZ outward by over 1 au ($\sim21\%$), thus increasing the HZ width by 1.2 au.

For host stars cooler than about 5000 K, the addition of CH$_4$ leads to a net cooling. For the coldest star in our sample, an M8 star model at 2600 K, $S_{\text{EFF}}$ increases by $\sim3\%$ for a concentration of $\sim10$ ppm CH$_4$. Assuming $L/L_{\text{Sun}} \sim 0.0006$, the orbital distance of the outer edge of the HZ moves from 0.0519 to 0.0512 au. For CH$_4$ concentrations of $\sim1\%$, $S_{\text{EFF}}$ increases by as much as 46% (0.2265–0.3305) (Figures 5–6) for the coolest sample star, moving the orbital distance of the outer edge of the HZ inward by over 0.009 au ($\sim18\%$). As with the greenhouse effect in the hotter stars, this anti-greenhouse effect becomes more pronounced in cooler stars as CH$_4$ concentrations increase (Figures 5–6).

The addition of CH$_4$ reduces the CO$_2$ pressures required to achieve warm conditions. Whereas 8 bars of CO$_2$ are required at the outer edge of the solar system’s classical HZ (e.g., Kasting et al. 1993; Kopparapu et al. 2013), this decreases to only 5 bar here for the high CH$_4$ case. The corresponding CO$_2$ pressures for A (10,000 K), F (7200), and K-stars (5000 K) are 4.5, 5, and 6 bar, respectively. In comparison, the equivalent CO$_2$ pressures for the classical outer edge are $\sim5.5$, 6, and 8 bar.

Our calculations here replace the original CO$_2$–CH$_4$ HZ calculation in Ramírez (2014), which had used an older CO$_2$–CH$_4$ parameterization. Overall, the general trends in both sets of results are similar to one another although the outer-edge distance moves farther out for hotter stars in these new results.

Following previous studies (e.g., Kopparapu et al. 2013; Ramírez & Kaltenegger 2017) we express a fourth-order polynomial curve fit for this methane HZ expansion (N$_2$–H$_2$O–CO$_2$–CH$_4$ atmospheric composition):

$$S_{\text{EFF}} = S_{\text{Sun}} + a \cdot T^* + b \cdot T^*^2 + c \cdot T^*^3 + d \cdot T^*^4,$$

where $T^* = (T_{\text{eff}} - 5780)$ and $S_{\text{Sun}}$ is the $S_{\text{EFF}}$ value in our solar system. The quantities $(a, b, c, d)$ are constants. We have tabulated the parameterization data for both the outer edge of the N$_2$–H$_2$O–CO$_2$–CH$_4$ HZ (Table 1) as well as for the classical and empirical HZ (Table 2). Our parameterizations are valid for a larger spectral range than that in previous work (e.g., Kopparapu et al. 2013), expanded to include A spectral classes ($T_{\text{eff}} = 2600–10,000 \text{ K}$).

### 4. Discussion

#### 4.1. Inverse Calculations Overestimate the Effect of Methane Heating—a Sensitivity Study

As effective as CH$_4$ is in increasing the width of the HZ for hotter stars (Figures 5–6), competing absorption at solar wavelengths reduces some of its effectiveness (Pierrehumbert 2010). We show the results derived from inverse calculations to assess what the effect on the N$_2$–H$_2$O–CO$_2$–CH$_4$ outer edge would be if a constant stratospheric temperature (155 K) were assumed (equivalent to the assumption that upper atmospheric absorption was inefficient) (Figure 7). Such a scenario would overestimate the effect of CH$_4$ absorption, reducing the $S_{\text{EFF}}$ in our solar system to 0.292 and 0.246, for 1% and $\sim0.1$ CH$_4$/CO$_2$, respectively. This would correspond to overestimated outer-edge distances of 1.86 and 2.02 au, respectively. These are increases of $\sim0.13$ au and 0.21 au ($\sim8\%$ and 12% error), accordingly, over the actual values computed from forward calculations. These calculations suggest that other gases that can significantly heat the upper atmosphere, like ozone, cannot be accurately modeled via inverse calculations. To improve the reliability of results, forward calculations should be used for atmospheres that contain such atmospheric constituents.
4.2. A-star Habitability

Our recent papers (Ramirez & Kaltenegger 2016, 2017) have expanded the stellar effective temperature range of stars relevant for the HZ from ~7200 to 10,000 K. This reflects the notion that life on Earth may have evolved as quickly as ~700 million years (Mojsis et al. 1997), which suggests that mid-late A-stars could be possible hosts for life (Danchi & Lopez 2013; Ramirez & Kaltenegger 2016).

4.3. M-star Outer Edge HZ’s Dependence on Methane Concentration

The width of the HZ narrows for M-star planets near the outer edge as atmospheric CH$_4$ concentrations increase (Figures 5–6). Therefore, planets with CH$_4$-rich atmospheres near the outer edge of the classic HZ of M stars should have frozen surfaces according to this study. Such conditions may not bode well for the habitability of these worlds. Nevertheless, our results predict a CH$_4$ partial pressure gradient toward the outer edge of M stars that can be tested by future observations observing atmospheres rich in both CO$_2$ and CH$_4$.

4.4. The Effect of CO$_2$–CH$_4$ Hazes

Our models assume CH$_4$ concentrations no higher than ~10% of the CO$_2$ concentration, above which cooling photochemical hazes form as discussed earlier. Even though the inner edge would be relatively robust to increases in CH$_4$ at the concentrations considered, at even higher concentrations, the cooling effect from these hazes may be effective in moving the inner edge inward (e.g., Arney et al. 2016). Future work could assess this possibility, studying the effects of hazes composed of different particle sizes and shapes, including fractals (e.g., Wolf & Toon 2010) in addition to coupling photochemical and climate modeling calculations. Nevertheless, any results would greatly depend on the assumed properties of the haze.

Our results here are unaffected even if hazes do not cool M-star planets (Arney et al. 2017). This is because the anti-greenhouse effect we find here for such stars is not due to haze and would occur anyway. Given the hypothesis that stars with high FUV fluxes may not produce haze (Arney et al. 2017), we performed a sensitivity study at a high CH$_4$ concentration (20%) for our A-star planet. The outer edge moves from 5.78 to 7.18 au in this case (~24% increase), as compared to a 21% increase for the $f_{CH_4} = 0.1/f_{CO_2}$ case (see Results).

4.5. Estimates of the Occurrence Rate of Other Earths “n$_{Earth}$”

The atmospheres considered here, suggest that the outer edges of hotter (~A–G spectral classes) stars may extend proportionately farther out than those around cooler (K–M) stars at a given CH$_4$ concentration. Our models show that the classical HZs around cooler stars can shrink if planetary atmospheres contain even small amounts (ppm levels) of CH$_4$. This suggests that estimates of “n$_{Earth}$,” which describes the fraction of terrestrial planets within the liquid water HZ, is both sensitive to the composition of the atmosphere of the planet as well as the host star’s SED.

4.6. The Plausibility of High CO$_2$–CH$_4$ Atmospheres and the Importance of Life

To assess the plausibility of our CO$_2$–CH$_4$ atmospheres, we evaluate the various atmospheric sources (volcanism, serpentinitization) and sinks (photolysis and H$_2$ escape) for CH$_4$ on a hypothetical Earth-sized planet with a 5.5 bar CO$_2$–CH$_4$ atmosphere (5 bar CO$_2$, 9% CH$_4$; neglecting the N$_2$) located near the outer edge (1.8 au) of a G2-star.

We use the following weathering rate parameterization from Berner & Kothavala (2001) to estimate volcanic outgassing rates, assuming that weathering and volcanic outgassing rates are equal at steady state:

$$\frac{W}{W_{Earth}} = \left(\frac{pCO_2}{pCO_2_{Earth}}\right)^{2.5} \times \left[1 + k_{run}(T_{surf} - 288)\right]^{0.55}$$

Here, W is the weathering rate, $k_{act}$ is an activation energy, $T_{surf}$ is surface temperature, $k_{run}$ is a runoff efficiency factor, $\beta$ is the dependence of pCO$_2$ on W. $W_{Earth}$ and $P_{Earth}$ are the soil-weathering rates and soil pCO$_2$ values, respectively, for the Earth.

This parameterization assumes that weathering/volcanic outgassing rates scales with pressure, as predicted for planets that have an operational carbonate-silicate cycle near the outer edge (e.g., Bean et al. 2017). Following Ramirez (2017), we assume $\beta = 0.4$, which is consistent with experimental measurements for silicate rocks (Lasaga 1984; Schwartzman & Volk 1989; Asolekar et al. 1991). We assume that soil pCO$_2$ is ~30 times that of atmospheric pCO$_2$, which assumes that life, particularly vascular planets, are present (Batalha et al. 2016). Although such high CO$_2$–CH$_4$ atmospheres are likely to be photochemically unstable as CH$_4$ slowly converts into CO (e.g., Zahnle 1986; Kharecha et al. 2005), if such planets are inhabited, CO would have likely been consumed by microorganisms and converted back to CH$_4$ and CO$_2$ (e.g., Kharecha et al. 2005). If we assume a relatively low mean surface temperature of 275 K, the CO$_2$ outgassing rate to support this atmosphere is ~2.72 × 10$^{15}$ g yr$^{-1}$, which is ~6.9 times that computed for Earth (3.3 × 10$^{14}$ g yr$^{-1}$; Holland 1984). The corresponding CH$_4$ production rate is ~2.5 × 10$^{11}$ g yr$^{-1}$, which may be produced abiotically and/or biotically (see below). Assuming no atmospheric mixing, these numbers are equivalent to CO$_2$ and CH$_4$ global production rates of 2.5 × 10$^{11}$ and 5.8 × 10$^{10}$ molecules cm$^{-2}$ s$^{-1}$, respectively.

If we neglect sinks, such production rates can produce 1 bar of
CO₂ and 0.1 bar of CH₄ in ~2 million years. This volcanic CO₂ would be further supplemented by that retained from the primordial inventory. Earth, for instance, may have accumulated ~60 bars equivalent from accretion (e.g., Walker 1985). Hydrodynamic escape rates during the early days of the stellar system for a planet located at 1.8 au would be ~1/3 that at 1 au, suggesting larger CO₂ inventories than Earth’s may be possible for our planets. Moreover, hydrodynamic escape rates would be lowest for outer-edge planets orbiting F- and A-stars because of their increased orbital distance and lower pre-main-sequence stellar luminosities as compared to their main-sequence values (e.g., Ramirez & Kaltenegger 2014). Nevertheless, such high CO₂ outgassing rates would require an oxidized mantle, which is predicted for larger terrestrial planets like Earth shortly after they form (e.g., Wade & Wood 2005; Hamano et al. 2013). Although this may suggest low CH₄ volcanic outgassing rates (e.g., Kasting & Catling 2003), CH₄ may be produced through a few other ways. CH₄ may be generated via serpen tinization, which is a process by which Fe-rich waters produce H₂ via oxidation of basaltic crust (e.g., Chassefière et al. 2013). On Earth, the methane flux produced by this process can be bounded by comparing it with the rate at which seafloor is oxidized by this process, resulting in the following equation (Shaw 2014):

$$\text{CO}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{CH}_4 + 2\text{O}_2.$$ (4)

Serpentinization of seafloor on Earth produces ~2 × 10¹¹ moles yr⁻¹ of O₂ (Sleep 2005). If we assume that serpen tinization produces only CH₄ (not H₂) an upper bound of 1 × 10¹¹ moles of CH₄ or 4 × 10⁶ molecules cm⁻² s⁻¹ are produced on the Earth according to the above equation. However, CH₄ production rates from serpen tinization can be potentially much higher if such rocks have an ultra-mafic composition (e.g., Batalha et al. 2015). For example, if serpen tinization occurs on present Mars, Etiope et al. (2013) estimated that CH₄ production rates within localized regions could be ~4.4 × 10¹²–4.4 × 10¹³ molecules cm⁻² s⁻¹. At such production rates, serpen tinization would only need to occur on ~0.13%–1.3% of the planet’s surface area to produce the above-mentioned CH₄ production rates.

Other potential abiogenic sources for CH₄ include impacts, although resultant atmospheric chemistries are highly dependent on impactor composition (e.g., Schaefer & Fegley 2010). Moreover, impacts could add or remove atmospheric mass depending on impactor and planetary properties (e.g., Melosh & Vickery 1989). M-star HZ planets may be particularly susceptible to atmospheric erosion because tightly packed orbits produce more energetic impactors (Lissauer 2007), suggesting that HZ planets orbiting hotter stars may be able to accumulate atmospheric mass more efficiently in this manner. CH₄ may also be produced through hydrothermal activity (e.g., Shaw 2008).

In contrast, the major CH₄ sinks are chemical destruction via photolysis and hydrogen escape to space. If we assume that escape is limited by its diffusion through the homopause, which is the fastest possible escape rate at these concentrations, then

$$\phi = \frac{b}{H_a} f_{\text{H}_2},$$ (5)

where $f_{\text{H}_2}$ is the total H₂ mixing ratio at the homopause, $H_a$ is the atmospheric scale height, and $b$ is a constant that describes diffusion of H₂ in a CO₂-dominated atmosphere (Zahnle et al. 1988). We assume a H₂ concentration of 1/2%. Given high CO₂ cooling rates (Wordsworth & Pierrehumbert 2013), homopause temperatures for CO₂-dominated atmospheres should be low (300–500 K), suggesting a nominal H₂ escape rates of ~(5.5–8.5) × 10¹⁰ molecules cm⁻² s⁻¹. This calculation assumes that H₂ escape is dominated by CH₄ produced by the presence of life, increasing the escape rate by a factor of 2 (e.g., Pavlov et al. 2000). However, the diffusion-limited escape rate may overestimate the actual one because if the exobase is cold, as expected in a low-O₂ high CO₂ atmosphere, escape rates may follow the slower energy limit (e.g., Pavlov et al. 2001). Moreover, spherical geometry effects could decrease escape rates by a factor of four (Stone & Proga 2009). Magnetic fields may further reduce H₂ losses (e.g., Stone & Proga 2009; Ramirez et al. 2014), although we ignore such effects here. We only apply the geometric correction, calculating final H₂ escape rates of ~(1.4–2.1) × 10¹⁰ molecules cm⁻² s⁻¹.
The second major loss process for atmospheres rich in methane is photolysis (e.g., Zahnle 1986). An estimate for the maximum photodissociation rate of CH₄ for a planet located at Mars’s distance from the present-day Sun is \( \sim (5-9) \times 10^{10} \) molecules cm\(^{-2}\) s\(^{-1}\) (Wordsworth et al. 2017). The maximum CH₄ photodissociation rate at 1.8 au should then be \( \sim (3.6-6.4) \times 10^{10} \) molecules cm\(^{-2}\) s\(^{-1}\). Assuming no other sources or sinks, the CH₄ would be completely removed in \( \sim 6-12 \) million years. However, these photolysis rates neglect reformation of dissociated CH₄ and absorption of escaping H₂, both of which would reduce CH₄ destruction rates below these numbers. Also, at the high CH₄ concentrations considered here, photolysis is driven primarily by Lyα photons (e.g., Zahnle 1986; Pavlov et al. 2001). The latter suggests that photolysis rates should be considerably lower for planets orbiting stars hotter than the Sun, not only because of increased semimajor axis distances, but because Lyα emission seems to generally decrease with an increase in stellar effective temperature (e.g., Bohm-Vitense & Woods 1983; Landsman & Simon 1993). For example, an outer-edge HZ planet located at 3.5 au orbiting an F0 star would only need Lyα emission strength to be \( \sim 40\% \) that of the Sun for the aforementioned photolysis rates to decrease by an order of magnitude.

Overall, the total loss rates (photolysis plus H₂ escape) for CH₄ are of the same order as that of our computed volcanic outgassing rates for our solar case (although such loss rates may be lower for planets orbiting hotter stars). In the absence of life, these global production rates would decrease by a factor of \( \sim 4 \), although this would be partially offset by lower H₂ escape rates in that scenario. Moreover, serpentinization could potentially complement volcanism by increasing CH₄ yields by a comparable (if not greater) amount. Moreover, simply increasing the surface temperature of our hypothetical planet by 10 K (to 285 K), would increase CO₂ and CH₄ outgassing rates by nearly a factor of four, possibly bringing the atmosphere back into balance. However, all of these factors ignore perhaps the most important one: life. On Earth, well over 90% of the CH₄ produced has a biological origin. The enormous biological input of methanogens would greatly increase CH₄ production rates. As discussed, CO₂ outgassing rates may not need to be so high either, as microbes can convert CO into CO₂ (and CH₂) as well. Nevertheless, although our atmospheres can be maintained for some amount of time without life, especially around stars even hotter than the Sun, such planets still need relatively large atmospheric sources of CH₄ to compensate for the significant losses. Thus, finding relatively dense CO₂–CH₄ atmospheres near the outer edge of the HZ of hotter stars could potentially signal inhabitance. Indeed, a new study found this link between CO₂–CH₄ atmospheres and inhabitance for the early Earth (Krissansen-Totton et al. 2018), as we have discovered here. If we find a CO₂–CH₄ rich world near the outer edge of the HZ of a hot star, it should be further explored.

4.7. DaisyWorld: Methane Can Stabilize the Climate of Planets Near the Outer Edge of the HZ

We propose a stabilizing feedback loop suggested for the Archean Earth (Domagal-Goldman et al. 2008), which may also occur for habitable planets near the outer edges of hotter stars. Our scenario is essentially the “DaisyWorld hypothesis” (Watson & Lovelock 1983), although the axes of the plots are reversed, with surface temperature exhibiting a parabolic response to increases in atmospheric CH₄/CO₂ ratio, whereas CH₄/CO₂ exhibits linear responses to increases in surface temperature (Figure 8). At low CH₄/CO₂ ratios, increases in CH₄ lead to increases in surface temperature because of the greenhouse effect of CH₄. This positive feedback explains why points on the left half of the curve (e.g., P₁) are unstable. Such a positive feedback may operate if methanogens could evolve on these planets, assuming that methane productivity increases with temperature (Domagal-Goldman et al. 2008). The resultant methanogenesis yields the following reaction, assuming some atmospheric H₂ is available:

\[
4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}.
\]  

(6)

However, once CH₄/CO₂ ratios exceed \( \sim 0.1 \), photochemical hazes form and the surface cools until a stable warm point (P₂) just past the apex is reached. This point is stable because the slope of the line in the right half of the curve is negative. Further increases in surface temperature would lead to an increase in the CH₄/CO₂ ratio, thickening the haze and offsetting the warming with cooling (and returning the point leftward).

In contrast, the stabilizing feedback described would not operate on planets orbiting stars cooler than about 4500 K. This is because methanogenesis would lead to further increases in atmospheric CH₄, producing an anti-greenhouse effect on the planets orbiting these cooler stars, which would trigger a positive feedback and cooling until conditions could become too cold for surface life to exist (assuming life had arisen in the first place).

4.8. Comparison of Classical and CO₂–CH₄ HZ

As had been shown previously (Ramirez 2014; Ramirez & Kaltenegger 2017) and in this work, secondary greenhouse gases are important to consider in HZ calculations. The percent changes to the outer-edge distance from the addition of CH₄ are quite substantial (\( \sim 20 \) to \( >20\% \)).

Moreover, the addition of CH₄ can significantly reduce the CO₂ pressures required to achieve warm conditions as compared with the classical HZ (see the Results section), potentially relaxing the requirements that models need to satisfy to achieve warm mean surface temperatures. Our results

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Figure 8. Proposed “DaisyWorld” scenario for planets at the outer edge of the methane HZ with CH₄ in their atmospheres orbiting hotter (\( \sim \)A–G class) stars. The curved lines illustrate the effect that the CH₄/CO₂ ratio has on surface temperature, whereas the straight lines depict the effect that temperature has on the CH₄/CO₂ ratio (adapted from Domagal-Goldman et al. 2008).
here are consistent with previous ones that found that the addition of H₂ also reduces the CO₂ pressures required to support warm outer-edge atmospheres (Ramirez & Kaltenegger 2017). This implies that carbonate-silicate cycle predictions suggesting that CO₂ pressures on potentially habitable planets should increase toward the outer edge (Kasting et al. 1993; Bean et al. 2017) may be complicated by the contribution of secondary greenhouse gases. Significant nonlinearities could be introduced that could thwart a straightforward relationship between CO₂ pressure and orbital distance.

Ramirez & Kaltenegger (2017) show that the empirical outer-edge limit (i.e., early Mars) distance can be exceeded by modest increases in secondary greenhouse gas concentrations (Figures 5–6). At 1.81 au, our computed outer edge for our solar system is still 0.04 au greater than the corresponding empirical early Mars limit distance (1.77 au) (Figures 5–6). Moreover, much larger margins are calculated for A- and F-stars. For example, the early Mars limit would be exceeded by ~0.68 au (~11%) in our A-star case (see Results). We also point out that if hazes do not form around F- to A-stars (Arney et al. 2017) (see Methodology), then even higher CH₄ concentrations than what we consider here might be possible, which would extend the outer edge of our CO₂–CH₄ HZ for those stars even farther out than what we considered here. Plus, the early Mars limit distance can be exceeded by well over 40% using H₂ as a secondary greenhouse gas (Ramirez & Kaltenegger 2017). All of this suggests that the optimistic outer-edge limit for the classical HZ is still a lower bound on the outer-edge distance. Thus, the continued exploration of different greenhouse gas combinations will show which scenarios can extend the HZ outer edge (Pierrehumbert & Gaidos 2011; Ramirez 2014; Ramirez & Kaltenegger 2017; Wordsworth et al. 2017; Ramirez et al. 2018). This may also help solve the faint young Sun problem for outer-edge planets like Mars (e.g., Ramirez et al. 2014; Ramirez 2017).

4.9. Effects of Clouds and Planetary Rotation Rates
Although we cannot assess multi-dimensional effects, like clouds and rotation rate variations, self-consistently using only our 1-D climate model, we have recently assessed the effects of rotation rate on ocean worlds near the outer edge using a combination of our 1D and latitudinally-dependent energy balance climate models (Ramirez & Levi 2018). We also note that such effects have also been assessed for the inner edge of the classical HZ using 3-D models (e.g. Kopparapu et al. 2017). If the results of such studies are any indication, rotation rates and clouds may also influence the extent of our CO₂–CH₄ HZ.

5. Conclusion
We show that adding methane to a terrestrial planet’s atmosphere heats or cools it depending on the host star’s spectral energy distribution because upper atmospheric absorption competes with that from the greenhouse effect. We assess the greenhouse effect of CH₄ (10~100,000 ppm) on the outer edge of the HZ (N₂–CO₂–H₂O–CH₄) for main-sequence host stars for stellar temperatures of 2600–10,000 K (A3 to M8). Adding CH₄ to the classical HZ (N₂–CO₂–H₂O) produces net greenhouse warming for planets orbiting stars hotter than about 4500 K (~K3), whereas CH₄ absorption produces an anti-greenhouse effect for planets around cooler stars. We parameterize the outer-edge limits of this methane HZ (atmospheric composition N₂–CO₂–H₂O–CH₄).

Methane expands the classical HZ outward for host stars with effective temperatures above about 4500 K, but reduces the HZ width for cooler host stars. We show CH₄ concentrations that are 10% that of CO₂ can increase the width of the HZ of the hottest stars in our model grid (10,000 K) by over 20%. In contrast, that same CH₄ concentration can shrink the HZ for the coolest stars in our model grid (2600 K) by a similar percentage. The classical empirical outer-edge limit is also exceeded for G–M planetary systems. Lower required CO₂ pressures also relax requirements that models need to satisfy to simulate warm conditions.

We find that dense CO₂–CH₄ atmospheres found near the outer edge of the HZ of hotter stars could suggest inhabitation, although we cannot completely rule out that abiotic processes, such as high volcanic outgassing and/or serpentinization rates, cannot also produce similar atmospheres. Moreover, lower H₂ escape rates for outer-edge planets and potentially lower photolysis rates for worlds orbiting stars hotter than the Sun, could favor CH₄ buildup, even in the absence of life.

We also propose a stabilizing feedback loop for inhabited planets on the outer edge of the HZ for planets orbiting host stars with effective temperatures above ~4500 K.

These results highlight the importance of including secondary greenhouse gases, complementing CO₂ and H₂O, in alternate definitions of the HZ in our search for habitable worlds.

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