O₂- and CO-rich Atmospheres for Potentially Habitable Environments on TRAPPIST-1 Planets

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Abstract

Small exoplanets of nearby M-dwarf stars present the possibility of finding and characterizing habitable worlds within the next decade. TRAPPIST-1, an ultracool M-dwarf star, was recently found to have seven Earth-sized planets of predominantly rocky composition. The planets e, f, and g could have a liquid water ocean on their surface given appropriate atmospheres of N₂ and CO₂. In particular, climate models have shown that the planets e and f can sustain a global liquid water ocean, for \( \geq 0.2 \) bar CO₂ plus 1 bar N₂, or \( \geq 2 \) bar CO₂, respectively. These atmospheres are irradiated by ultraviolet emission from the star’s moderately active chromosphere, and the consequence of this irradiation is unknown. Here we show that chemical reactions driven by the irradiation produce and maintain more than 0.2 bar O₂ and 0.05 bar CO if the CO₂ is \( \geq 0.1 \) bar. The abundance of O₂ and CO can rise to more than 1 bar under certain boundary conditions. Because of this O₂–CO runaway, habitable environments on the TRAPPIST-1 planets entail an O₂– and CO-rich atmosphere with coexisting O₃. The only process that would prevent runaway is direct recombination of O₂ and CO in the ocean, a reaction that is facilitated biologically. Our results indicate that O₂, O₃, and CO should be considered together with CO₂ as the primary molecules in the search for atmospheric signatures from temperate and rocky planets of TRAPPIST-1 and other M-dwarf stars.

Unified Astronomy Thesaurus concepts: Extrapolar rocky planets (511); Habitable planets (695); Super Earths (1655); Habitable zone (696); Exoplanet atmospheres (487); Astrobiology (74)

1. Introduction

The era of characterizing temperate and rocky exoplanets has begun. Ground-based surveys have found temperate planets hosted by M-dwarf stars like the TRAPPIST-1 planets and LHS 1140 b (Dittmann et al. 2017; Gillon et al. 2017). The K2 mission and the Transiting Exoplanet Survey Satellite (TESS) are finding a few tens transiting and temperate planets around nearby M stars (e.g., Sullivan et al. 2015). Orbiting small stars, these planets provide an accelerated path toward finding and characterizing potentially habitable worlds. The TRAPPIST-1 planets already have transmission spectra measured by Hubble (De Wit et al. 2018; Zhang et al. 2018). With \( > 7 \) times more collecting area and infrared instruments, the James Webb Space Telescope (JWST) will be capable of providing a more detailed look into the atmosphere of these cold exoplanets (Beichman et al. 2014).

A key factor that impacts the atmospheric compositions of rocky planets around M-dwarf stars is stellar ultraviolet (UV) irradiation. UV radiation dissociates CO₂ into CO and O, but the direct recombination of the two products is slow. Two O produced then combine to form O₂. In the solar system, the CO₂ atmosphere of Mars is stabilized principally by catalytical cycles of OH and HO₂ that recombine CO₂ and O₂ (McElroy & Donahue 1972; Nair et al. 1994), while that of Venus is additionally stabilized by chlorine species (McElroy et al. 1973). If the star is an M dwarf, its irradiation is strong in the far-UV (FUV) bandpass but weak in the near-UV (NUV) bandpass (France et al. 2013). Because FUV radiation dissociates CO₂ and NUV radiation amplifies the catalytical cycles of OH and HO₂, a liquid-water-ocean planet of an M dwarf is inclined to accumulate CO and O₂ in the atmosphere. Using the spectrum of the M dwarf GJ 876, atmospheric photochemistry models have predicted an O₂ mixing ratio up to 5% in an N₂-dominated atmosphere with 0.05 bar CO₂ (Domagal-Goldman et al. 2014; Tian et al. 2014; Harman et al. 2015). Atmospheric photochemistry models have also shown that massive O₂ and CO would be produced from CO₂-dominated atmospheres of desiccated—and hence uninhabitable—rocky planets of M-dwarf stars (Guo et al. 2015).

Climate models of the planets TRAPPIST-1 e, f, and g indicate that they need more than 0.05 bar CO₂ to sustain a global liquid water ocean, because the planets have lost their primordial hydrogen envelopes due to X-ray and extreme-UV irradiation (Bolmont et al. 2017; Bourrier et al. 2017). For an atmosphere with 1 bar N₂ and varied abundance of CO₂ on planet e, ice would cover 57% of the planet at 0.1 bar CO₂, and the coverage drops quickly to nearly zero at \( \geq 0.2 \) bar CO₂ (Wolf 2017). On the planet f, \( \geq 2 \) bar CO₂ are required (Wolf 2017; Turbet et al. 2018). Substituting CO₂ with CH₄ or NH₃ as the main greenhouse gas would be unlikely to sustain the habitability, because of their much weaker greenhouse effect and tendency to form photochemical hazes that cause an anti-greenhouse effect (Turbet et al. 2018). The photochemical lifetime of CH₄ could however be quite long on TRAPPIST-1 planets for weaker NUV radiation (e.g., Rugheimer et al. 2015).

To investigate the effect of stellar irradiation on this high CO₂ abundance, we use our photochemistry model (Hu et al. 2012, 2013) to determine the steady-state composition of the atmospheres under irradiation. The photochemistry model uses the atmospheric pressure–temperature profiles generated by the
3D climate model (Wolf 2017), which was calculated for varied partial pressures of CO₂. We find that more than 0.2 bar O₂ and 0.05 bar CO are produced in the steady state if the CO₂ partial pressure is ≥0.1 bar. The abundance of O₂ and CO can rise to more than 1 bar depending on their deposition velocities, which constitutes an “O₂–CO runaway.” The paper is organized as follows. We describe our models, including the 3D climate model in Section 2, present the conditions and the chemistry of the O₂–CO runaway in Section 3, discuss its climate implications, feedback, and geologic context in Section 4, and conclude in Section 5.

2. Methods

2.1. Photochemistry Model

The photochemistry model used in this study (Hu et al. 2012, 2013) has been validated by computing the atmospheric compositions of present-day Earth and Mars, as the outputs agreed with the observations of major trace gases in Earth’s and Mars’ atmospheres. The model has also been used to determine the photochemical oxygen buildup in abiotic atmospheres (Hu et al. 2012; James & Hu 2018). For the latter purpose, the model has been compared with other photochemistry models in detail, and we have found good agreement (Gao et al. 2015; Harman et al. 2018). The photochemistry model solves the one-dimensional chemical transport equation for 111 O, H, C, N, and S species including sulfur and sulfuric acid aerosols. The full species and reaction list can be found in Hu et al. (2012). The model seeks to balance product and loss terms from all chemical and photochemical reactions for each gas at each altitude level. We typically do not assume photochemical equilibrium for any gas; so, unless otherwise stated, all gases are included in the full chemical transport calculation. The system is considered as converged to a steady state if the minimum variation timescale is greater than, for instance, the age of the solar system (10^17 s).

In the models that feature the O₂–CO runaway, the ambient pressure changes in the simulation because the produced O₂ and CO meaningfully contribute to the pressure. Our photochemistry model self-consistently calculates the effect of the changing ambient pressure on the kinetic rates. Because the photochemistry model solved the continuity equation of number densities (Hu et al. 2012), the total number density of each layer is obtained by summing the number densities of all molecules in that layer. As such, the total number density, and thus the pressure, of each layer is updated after each time stepping. The changing pressure affects the rates of termolecular reactions, because they are proportional to the total number density of each layer. In particular, an important termolecular reaction is the direct combination between CO and O in the atmosphere, CO+O+M → CO₂+M, and its rate increases with the ambient pressure. This feedback loop eventually limits the size of the atmosphere when the O₂–CO runaway is strong.

We adopt the eddy diffusion coefficient derived from the number density profiles of trace gases on Earth (Massie & Hunten 1981). The eddy diffusion coefficient is characterized by a high value in the convective troposphere, a minimum corresponding to the tropopause, and an increasing value with smaller number densities in the nonconvective stratosphere.

When the ambient pressure increases, the eddy diffusion coefficient as a function of altitude is unchanged. This ensures vigorous transport in the atmosphere and preserves the sensitivity of the eddy diffusion coefficient to the convective nature of the atmosphere. There could be additional effects of the changing pressure on the eddy diffusion coefficient, and we thus caution that the results may be dependent on the assumption of the eddy diffusion.

To simulate the effect of lightning, we adopt the terrestrial production rate of NO from lightning, 6 × 10^8 cm⁻²s⁻¹ (Schumann & Huntrieser 2007), which is already greater than the majority of the parameter space explored previously for N₂–CO₂–H₂O atmospheres (Wong et al. 2017; Harman et al. 2018). In addition, it is found that in an atmosphere O₂ richer than Earth’s atmosphere, the NO production rate from lightning can be higher, up to ~10^9 cm⁻²s⁻¹ (Harman et al. 2018). We also consider this higher production rate in a sensitivity study.

The stellar spectrum of TRAPPIST-1 has not been measured in UV. Therefore, we use the UV spectrum of GJ 876 obtained by the MUSCLES project as the proxy (France et al. 2016). The survey uses Hubble observations in the UV to reconstruct intrinsic stellar Lyα emissions. The visible spectrum is obtained from ground-based observations, and the infrared spectrum is from the PHOENIX stellar atmosphere models. GJ 876, an M5V star of T eff ~ 3100 K, is one of the closest stars to TRAPPIST-1 (T eff ~ 2600 K) in the MUSCLES sample. As shown in Figure 1, we scale the spectrum in the UV wavelength (<300 nm) by the measured Lyα flux of TRAPPIST-1 (Bourrier et al. 2017, a factor of 0.135 with respect to GJ 876, Youngblood et al. 2016) and that in the visible wavelength (>300 nm) by the measured bolometric luminosity of TRAPPIST-1 (Van Grootel et al. 2018, a factor of 0.0428 with respect to GJ 876, Von Braun et al. 2014). In addition, we explore in a sensitivity study a spectral shape in the UV as AD Leo, an active M4.5V star. Figure 1 shows that the spectral shape of AD Leo has a larger FUV/NUV ratio, but the FUV flux may be inaccurate as Lyα reconstruction was not performed.
Table 1
Starting Scenarios of This Study and Their Key Climate Characteristics Based on the 3D Model of Wolf (2017)

| Planet | $N_2$ | $CO_2$ | $T$ Surf Glob (K) | Ice Fraction | Initial Mixing Ratio of $H_2O$ at Surface | Top of Atmosphere Altitude (km) |
|--------|-------|--------|------------------|--------------|------------------------------------------|-------------------------------|
| TRAPPIST-1 e | 1 bar | None | 227 | 86% | 0.0018 | 88 |
| TRAPPIST-1 e | 1 bar | 0.0004 bar | 241 | 80% | 0.0037 | 84 |
| TRAPPIST-1 e | 0.01 bar | 0.5 bar | 254 | 73% | 0.0056 | 84 |
| TRAPPIST-1 e | 0.2 bar | 0.5 bar | 274 | 57% | 0.0138 | 82 |
| TRAPPIST-1 e | 0.4 bar | 0.5 bar | 285 | 18% | 0.0213 | 82 |
| TRAPPIST-1 e | 1 bar | 0.5 bar | 303 | 0% | 0.0407 | 71 |
| TRAPPIST-1 f | None | 1 bar | 333 | 0% | 0.1001 | 73 |
| TRAPPIST-1 f | 2 bar | 0.5 bar | 289 | 2% | 0.0067 | 59 |
| TRAPPIST-1 f | 5 bar | 0.5 bar | 335 | 0% | 0.0444 | 66 |

Last but not least, our model ensures the redox flux balance of the atmosphere and the ocean. The convergence of the photochemistry model itself ensures the balance of the redox budget of the atmosphere. However, this does not ensure that the results are realistic on planets, as there is no known abiotic way to deposit reducing species at the bottom of the ocean. We therefore enforce the balance of the redox budget of the ocean by requiring the net transfer of the redox flux between the atmosphere and the ocean to be zero (Domagal-Goldman et al. 2014; Harman et al. 2015; James & Hu 2018). In practice, this balance is achieved by including a pseudo return flux of hydrogen. If we find a net transfer of the redox flux from the atmosphere to the ocean in a converged solution, we include this net flux as a return flux of hydrogen from the ocean to the atmosphere and relaunch the simulation. We repeat the process until the imbalance is no larger than 1% of the outgassing redox flux. This way, our results satisfy the redox balance for both the atmosphere and the ocean.

2.2. Outgassing and Deposition

We use the volcanic activity rate of present-day Earth and the per-mass outgassing rate calculated for mid-ocean ridge basalts (Gaillard & Scaillet 2014) to calculate the gas outgassing rate. The outgassing rate is $1.5 \times 10^{10} \text{cm}^2 \text{s}^{-1}$ for CO, H$_2$, and SO$_2$, and $1.5 \times 10^{10} \text{cm}^2 \text{s}^{-1}$ for H$_2$S (see James & Hu 2018 for details). TRAPPIST-1 e may have a tidal heating flux corresponding to $1 \times 10^{10}$ times the geothermal heat flux (Luger et al. 2017; Papaloizou et al. 2017). We have performed an additional set of simulations assuming a 10 times higher volcanic outgassing rate and found no noticeable difference in the $O_2$ or CO partial pressure. The model has a full sulfur chemistry network (Hu et al. 2013), and we find that the outgassed H$_2$S and SO$_2$ is either rained out directly or oxidized to H$_2$SO$_4$. The H$_2$SO$_4$ is then rained out. The outgassing rate, even at the 10 times level, is not high enough to produce a H$_2$SO$_4$ aerosol layer in the atmosphere.

The standard model assumes a deposition velocity of zero for $O_2$ and includes a deposition velocity of either zero or $10^{-8} \text{ cm} \text{s}^{-1}$ for CO. The nonzero value for CO comes from assuming the aqueous formation of formate ($CO + OH^- \rightarrow COO^-H^+$) as the rate-limiting step to remove CO (Kharecha et al. 2005). Other reactions acting as a rate-limiting step would lead to even lower deposition velocities (Harman et al. 2015), and thus the zero value for CO is included as another end-member scenario. We find that the exact abundance of $O_2$ versus CO in the O$_2$–CO runaway scenarios is quite sensitive to the choice of deposition velocity of CO (Section 3.1).

In addition to the standard model, we have performed additional simulations to evaluate the effect of potential sinks for $O_2$ in the ocean. (1) A deposition velocity of $10^{-8} \text{ cm} \text{s}^{-1}$ for $O_2$ would be possible for the potential recombination of $O_2$ and CO in hydrothermal flow through the mid-ocean ridges (Harman et al. 2015). We observed no noticeable changes in the results when adopting this deposition velocity. (2) A second potential sink of $O_2$ is $Fe^{2+}$ input in the ocean from crust formation. We describe the test to include this sink in Section 3.1. (3) As a limiting scenario, we consider the possibility that direct recombination of $O_2$ and CO occurs rapidly in the surface ocean. This would enable the rapid deposition of both $O_2$ and CO, and we also describe its impact on the result in Section 3.1.

For scenarios with substantial $O_2$ buildup, $O_3$ has a substantial mixing ratio at the surface and therefore can have a substantial deposition flux onto the surface. This would make the model results sensitive to the choice of the deposition velocity of $O_3$. Some of the previous studies assume $O_3$ to be the short-lived species in photochemical equilibrium (Harman et al. 2015, 2018), thus removing the need to specify a deposition velocity. On Earth, the deposition velocity of $O_3$ is very different between the land and the ocean. As a slightly soluble gas, $O_3$’s deposition velocity over the ocean is limited by the mass transfer rate in the liquid phase (Broecker & Peng 1982). Using the typical mass transfer coefficient and the Henry’s law coefficient for $O_3$, the deposition velocity is approximately $10^{-3} \text{ cm} \text{s}^{-1}$, and this value is consistent with the measurements over Earth’s ocean (Hardacre et al. 2015). The surface resistance of $O_3$ is considerably smaller over Earth’s land, and the measured deposition velocity is typically on the order of 0.3 cm s$^{-1}$. While this value is also valid for deserts (Hardacre et al. 2015), the lower resistance is most likely due to the prevalence of biosphere on Earth. We therefore adopt the value of $10^{-3} \text{ cm} \text{s}^{-1}$ in the standard model and explore a value of 0.1 cm s$^{-1}$ in a sensitivity study. The standard value is the same as that used in Tian et al. (2014).

2.3. Climate Modeling and Temperature–Pressure Profiles

To initialize the photochemical model, we use the substellar hemisphere mean vertical profile generated by the 3D climate model (Wolf 2017) in this study. The scenarios used in this study are summarized in Table 1. We fix the number density of water vapor at the bottom of the atmosphere according to the
3D model and allow water vapor to condense out as the temperature drops with altitude. The top of the atmosphere is assumed to be 0.1 Pa, corresponding to the different altitudes between the scenarios due to different temperatures and mean molecular weights. The mass and the radius of each planet are the measured values from Grimm et al. (2018).

When O₂–CO runaway occurs, O₂ and CO contribute meaningfully to the total atmospheric pressure. New for this work, we have conducted several additional 3D climate model simulations to test the climate effects of this increased atmospheric pressure. The radiative effects of O₂ and CO are primarily felt indirectly through their contribution to the total atmospheric pressure and subsequent pressure broadening of CO₂ absorption features, which can have a significant warming effect on climate (Goldblatt et al. 2009). As presently configured, our 3D model handles only N₂, H₂O, and CO₂, and therefore, we have substituted N₂ as the broadening gas in these simulations. While this substitution in the 3D model introduces some uncertainty, still, we can gain a useful estimate of the climate consequences of adding significant amounts of a radiatively inactive broadening gas. We discuss the climate feedback in Section 4.2.

3. Results

3.1. The O₂–CO Runaway

The steady-state abundance of O₂ jumps by seven to eight orders of magnitude to 0.2–2 bar on TRAPPIST-1 e when the CO₂ abundance increases from 0.01 to 0.1 bar (Figure 2, thick lines). The abundance of CO also increases by four to five orders of magnitude to >0.05 bar. The spread of the resultant abundances of O₂ and CO is caused by the uncertainties in their deposition velocities. As we start the calculation from 1 bar N₂ and 0.1 to ~1 bar CO₂, the steady-state atmosphere has O₂ and CO as main components, as well as a substantial abundance of O₃. We thus call this phenomenon “the O₂–CO runaway.” The abundance of O₂ continues to gradually increase with more CO₂, but the runaway is partially stabilized by the fact that a higher atmospheric pressure makes the direct recombination reaction between CO and O faster. For TRAPPIST-1 e, the condition for the O₂ runaway coincides with the condition for a global ocean, indicating that a habitable environment on the planet necessarily entails an O₂- and CO-rich atmosphere. For TRAPPIST-1 f and g, more CO₂ is required, and thus the same result applies qualitatively.

Figures 3 and 4 and Table 2 show the vertical profiles of key molecules and the redox fluxes of the scenarios before and after the O₂–CO runaway. The redox balances of the atmosphere and the ocean are well balanced for the models before and after the O₂–CO runaway, and the remaining imbalances are due to a subtle difference between the H₂ mixing ratio on the ground and that at the homopause. The water vapor profile calculated by the 1D photochemistry model agrees well with the mean water vapor profile calculated by the 3D climate model (see Section 4.2). After the O₂–CO runaway, O₂ is essentially well mixed in the atmosphere, and the mixing ratio of O₃ peaks at ~1 mbar (Figure 3). After the O₂–CO runaway, most of the HOₓ (OH and HO₂) species combine to form the “reservoir” molecule H₂O₂, and the abundance of the free radical OH is extremely low (Figure 4). This explains the inability of the OH–HO₂ catalytic cycle to recombine CO and O₂. Figure 4 also shows that after the O₂–CO runaway, most of the reactive nitrogen species combine to form HO₂NO₂ above the pressure level of 0.1 bar, the reservoir species for nitrogen. We will discuss the behaviors of nitrogen photochemistry in Section 3.2.

One might ask whether the O₂–CO runaway depends on the assumptions of the boundary conditions, particularly the lack of rapid surface sinks for O₂ and CO. We have explored the impacts of geochemical sinks of O₂ and CO on their atmospheric abundances, and the O₂–CO runaway. The geochemical sinks are expressed in the photochemistry model as the values for the deposition velocity. Conceptually, the transfer flux from the atmosphere to the surface is

\[ \phi = v_{\text{dep max}}(n_0 - \frac{M_0}{\alpha C}) = v_{\text{dep}}n_0, \]

where \( v_{\text{dep max}} \) and \( v_{\text{dep}} \) are the maximum and effective deposition velocities of the gas, \( n_0 \) is the gas’s number density at the surface, \( M_0 \) is the moality in the surface ocean, \( \alpha \) is the Henry’s law coefficient, and \( C \) is a unit conversion constant. The effective deposition velocity thus depends on how quickly the ocean can process the deposited molecule and drive \( M_0 \) away from the equilibrium value.

A major potential sink for O₂ is the Fe²⁺ input to the ocean from crustal formation. The O₂ can oxidize Fe²⁺ in the ocean and cause banded iron formation (BIF; 6 FeO+O₂ → 2 Fe₂O₃). On Earth, the estimated rate of iron output during the Hammersley BIFs in the late Archean is ~3 × 10⁻¹⁵ mol yr⁻¹, or 1.1 × 10⁻³ cm⁻² s⁻¹ (Holland 2006). Assuming this entire output of iron is oxidized to Fe₂O₃ in the ocean by O₂, it has two effects: (1) this would correspond to an additional 8 × 10⁻¹⁷ cm⁻² s⁻¹ equivalent H influx to the atmosphere, doubling the H₂ mixing ratio according to the redox balance; (2) this would be a sink of \( \phi_{\text{max}} = 2 \times 10^{-9} \text{cm}^{-2} \text{s}^{-1} \) for O₂. How should this limiting sink be implemented in the photochemistry model? For O₂ under typical conditions, the maximum deposition velocity \( v_{\text{dep max}} = 1.4 \times 10^{-4} \text{cm s}^{-1} \). This \( v_{\text{dep max}} \) is determined by the two-film model of mass transfer between the atmosphere and the ocean (Broecker & Peng 1982) and is related to the piston velocity and is sensitive to the solubility of the gas, the wind speed, and the temperature (Domagal-Goldman et al. 2014; Harman et al. 2015). Therefore, when the surface number density \( n_0 \) is small, the rate of deposition is smaller than the limiting sink due to BIF, and \( v_{\text{dep}} \) should be close to \( v_{\text{dep max}} \). When \( n_0 \) is large, the deposition flux is limited by \( \phi_{\text{max}} \). We therefore implement the lower boundary condition for O₂ due to BIF as follows: if \( v_{\text{dep max}}n_0 < \phi_{\text{max}} \), iron oxidation effectively removes O₂ in the ocean, and then \( v_{\text{dep}} = v_{\text{dep max}} \); if \( v_{\text{dep max}}n_0 > \phi_{\text{max}} \), the deposition velocity is limited by the rate of BIF, or \( v_{\text{dep}} = \phi_{\text{max}}/n_0 \).

After implementing this boundary condition and performing another set of simulations, we find that the former condition is met before the O₂–CO runaway, and the latter condition is met after the O₂–CO runaway. In the cases after the O₂–CO runaway, the inclusion of BIF leads to a decrease of the O₂ column abundance by <10%. We therefore conclude that BIF does not substantially impact the onset of the O₂–CO runaway. We note that the rate of iron production during the early Archean (and presumably on a terrestrial exoplanet) may be 20-fold higher than the Hammersley BIFs (Kasting 2013). Here we consider its impact. The 0.1 bar CO₂ case (i.e., the onset of the O₂–CO runaway) has an O₂ number density of 5.5 × 10¹⁶ cm⁻³ at the bottom, the full deposition of which would have a flux of 7.7 × 10¹⁰ cm⁻² s⁻¹, about 4 × 10⁷ larger than the flux in the Holland (2006) estimate. Therefore, a 20-fold increase, even if it occurs, would not materially change our results.
Additionally, we consider a limiting scenario with direct recombination of \( \text{O}_2 \) and \( \text{CO} \) occurring rapidly in the surface ocean. In this case, the effective deposition velocities of \( \text{O}_2 \) and \( \text{CO} \) approach their \( v_{\text{dep}, \text{max}} \), which are mainly controlled by solubilities in the ocean (\( 1.2 \times 10^{-4} \text{ cm s}^{-1} \) for \( \text{CO} \) and \( 1.4 \times 10^{-4} \text{ cm s}^{-1} \) for \( \text{O}_2 \); Domagal-Goldman et al. 2014). The \( \text{O}_2-\text{CO} \) runaway is prevented in this case, and their abundances max out at \( 10^{-3} - 10^{-4} \) bar (Figure 1, thin lines). This reaction is performed by aerobic \( \text{CO} \)-oxidizing bacteria on Earth (King & Weber 2007) and is thus conceivable on an exoplanet with liquid water and abundant \( \text{O}_2 \) and \( \text{CO} \) on the surface.

In addition to the sink of \( \text{O}_2 \), the photochemistry model takes other input parameters such as the \( \text{NO} \) production rate from lightning, the stellar spectrum, and the deposition velocity of \( \text{O}_3 \). One might ask whether these parameters significantly bear upon the \( \text{O}_2-\text{CO} \) runaway. We have tested the sensitivity of the model on these parameters using TRAPPIST-1 e as the test case (Figure 5). First, we find that including a terrestrial rate of \( \text{NO} \) production by lightning reduces the resulting \( \text{O}_2 \) partial pressure by only a factor of \( \sim 2 \) in some cases, and the exact value of the lightning production rate near the terrestrial rate has little impact (Figure 5, panel a). This lack of sensitivity has to do the nitrogen photochemistry, which will be discussed in Section 3.2. Second, we find that the onset of the \( \text{O}_2-\text{CO} \) runaway is mildly sensitive to the stellar spectral shape. There is little difference between the standard model and the model using the GJ 876 spectrum. When using the AD Leo spectrum, however, the \( \text{O}_2-\text{CO} \) runaway requires a higher partial pressure of \( \text{CO}_2 \), \( \sim 0.2 \) bar (Figure 5, panel b). This sensitivity reaffirms the point that the \( \text{O}_2-\text{CO} \) runaway is driven by the high FUV/NUV ratio of the irradiation of late M dwarfs. The AD Leo spectrum has a lower FUV/NUV ratio compared to the GJ 876 spectrum or the assumed TRAPPIST-1 spectrum, and therefore it is less able to drive the \( \text{O}_2-\text{CO} \) runaway. Third, changing the \( \text{O}_3 \) deposition velocity from the standard value (\( 10^{-3} \text{ cm s}^{-1} \)) to a higher value (\( 10^{-1} \text{ cm s}^{-1} \)) only has some impact on the case of 0.1 bar \( \text{CO}_2 \), and overall, it does not affect the onset of the \( \text{O}_2-\text{CO} \) runaway. In sum, the \( \text{O}_2-\text{CO} \) runaway appears to be robust against reasonable uncertainties in the lightning rate, stellar spectrum, and deposition velocities.

3.2. Nitrogen Photochemistry on M Dwarfs’ Planets

Our photochemistry models show that nitrogen chemistry in the atmosphere initiated by lightning cannot prevent the \( \text{O}_2-\text{CO} \) runaway. Lightning mainly produces \( \text{NO} \) in an \( \text{N}_2-\text{CO}_2-\text{O}_2 \) atmosphere (Rimmer & Helling 2016; Wong et al. 2017; Harman et al. 2018). Reactive nitrogen species facilitate cycles of \( \text{OH} \) and \( \text{HO}_2 \) in Earth’s stratosphere and

\[\text{Figure 2. Modeled ice fraction and column-integrated abundances of } \text{O}_2, \text{CO}, \text{and } \text{O}_3 \text{ vs. the abundance of } \text{CO}_2. \text{ Thick lines are the standard models that include known surface sinks of } \text{O}_2 \text{ and } \text{CO}, \text{ and the shaded areas between the thick lines denote the spread of the results, due to the deposition velocity of } \text{CO} \text{ ranging from zero to } 10^{-8} \text{ cm s}^{-1}. \text{ The nonzero deposition velocity of } \text{CO} \text{ leads to a higher abundance of } \text{O}_2 \text{ and lower abundance of } \text{CO} \text{ than the zero deposition velocity. Thin lines are the models that additionally assume a direct recombination reaction of } \text{O}_2 \text{ and } \text{CO} \text{ in the ocean. } \text{O}_2 \text{ and } \text{CO} \text{ become main components of the atmosphere when } p_{\text{CO}_2} \text{ is } \geq 0.1 \text{ bar; for TRAPPIST-1 e, this jump is roughly coincident with the requirement of a global liquid water ocean.} \]
have been suggested to reduce the abundance of accumulated O\(_2\) in CO\(_2\)-rich planetary atmospheres by many orders of magnitude (Harman et al. 2018). A main catalytic cycle enabled by reactive nitrogen species is

\[
\text{NO + HO}_2 \rightarrow \text{NO}_2 + \text{OH},
\]
\[
\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O},
\]

which is followed by

\[
\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}.
\]

Our model indicates that the effect of lightning, however, is limited to within a factor of \(\sim 2\). This is because most of the reactive species is locked in the reservoir molecules HO\(_2\)NO\(_2\) and N\(_2\)O\(_5\) (Figure 4), and thus cannot participate in the catalytic cycles. These reservoir molecules are photodissociated by NUV irradiation in Earth’s stratosphere, but this photodissociation is severely limited on an M dwarf’s planet. HO\(_2\)NO\(_2\) also dissociates thermally in the troposphere, but the dissociation in the stratosphere appears to be more important for enabling the catalytic cycles. Our model includes photodissociation of HO\(_2\)NO\(_2\) via overtune and combination bands in the near-infrared (Roehl et al. 2002) where an M dwarf’s emission is strong, but finds that the total photodissociation rate at the top of the atmosphere is still more than an order of magnitude less.
than that around a Sun-like star. Additionally, the reservoir molecules are efficiently rained out from the atmosphere. If we do not include HO2NO2 or N2O5 in the model, we would reproduce the orders-of-magnitude effect by lightning. The detail of nitrogen photochemistry is described in the following.

Harman et al. (2018) found that the steady-state abundance of O2 would be reduced by many orders of magnitude by including lightning production of NO. Harman et al. (2018), however, did not have HO2NO2 or N2O5 in their chemical network. Here we perform a set of models with 1 bar N2 and 0.05 bar CO2, the same as Harman et al. (2018), with one model using our chemical network and the other without HO2NO2 or N2O5. The results are compared in Figure 6. To be comparable, the models here are for a hypothetical 1-Earth-radius and 1-Earth-mass planet in the habitable zone of GJ 876. The boundary conditions are the same as the standard models previously described. Because the results are insensitive to the spectral shape changing from the assumed TRAPPIST-1 to GJ 876, the models presented in Figure 6 can also be interpreted in the context of the TRAPPIST-1 models (Figures 2–5) as a case in the middle of the O2–CO runaway.

If N2O5 and HO2NO2 (sometimes called HNO4) are not included in the chemical network, the mixing ratio of O2 would indeed be reduced by many orders of magnitude (Figure 6, Figure 4).
Table 2
Redox Fluxes of Representative Atmospheric Models for TRAPPIST-1 e

| Model       | $v_{dep}(CO) = 1E-8$ cm s$^{-1}$ | $v_{dep}(O_2) = 0$ | $v_{dep}(CO) = 1.2E-4$ cm s$^{-1}$ | $v_{dep}(O_2) = 1.4E-4$ cm s$^{-1}$ | $v_{dep}(CO) = 0$ | $v_{dep}(O_2) = 0$ |
|-------------|---------------------------------|-------------------|---------------------------------|---------------------------------|-----------------|-----------------|
| CO$_2$      | 0.01 bar                        | 0.1 bar           | 0.01 bar                         | 0.1 bar                         | 0.01 bar        | 0.1 bar         |
|             | **Escape**                      |                   |                                 |                                 |                 |                 |
| H           | $-3.1E+8$                       | $-2.9E+9$         | $-3.1E+8$                       | $-7.1E+8$                       | $-3.1E+8$       | $-1.5E+9$       |
| H$_2$       | $-5.4E+9$                       | $-2.8E+9$         | $-5.4E+9$                       | $-5.0E+9$                       | $-5.4E+9$       | $-4.2E+9$       |
| Total       | $-5.7E+9$                       | $-5.7E+9$         | $-5.7E+9$                       | $-5.7E+9$                       | $-5.7E+9$       | $-5.7E+9$       |
|             | **Outgassing**                  |                   |                                 |                                 |                 |                 |
| H$_2$       | 3.0E+9                          | 3.0E+9            | 3.0E+9                          | 3.0E+9                          | 3.0E+9          | 3.0E+9          |
| CO          | 3.0E+9                          | 3.0E+9            | 3.0E+9                          | 3.0E+9                          | 3.0E+9          | 3.0E+9          |
| H$_2$S      | 9.0E+8                          | 9.0E+8            | 9.0E+8                          | 9.0E+8                          | 9.0E+8          | 9.0E+8          |
| NO$_b$      | $-1.2E+9$                       | $-1.2E+9$         | $-1.2E+9$                       | $-1.2E+9$                       | $-1.2E+9$       | $-1.2E+9$       |
| Total       | 5.7E+9                          | 5.7E+9            | 5.7E+9                          | 5.7E+9                          | 5.7E+9          | 5.7E+9          |

**Dry and Wet Deposition**

| Species   | Flux $\pm 10$% | Flux $\pm 10$% | Flux $\pm 10$% | Flux $\pm 10$% | Flux $\pm 10$% | Flux $\pm 10$% |
|-----------|----------------|----------------|----------------|----------------|----------------|----------------|
| O$_2$     | ...            | ...            | ...            | ...            | ...            | ...            |
| O$_3$     | ...            | ...            | ...            | ...            | ...            | ...            |
| HO$_2$    | ...            | ...            | ...            | ...            | ...            | ...            |
| H$_2$O    | ...            | ...            | ...            | ...            | ...            | ...            |
| CO        | $-2.0E+6$      | $-9.1E+9$      | $-9.1E+9$      | $-8.1E+11$     | ...            | ...            |
| CH$_3$O   | $-2.8E+6$      | ...            | $-7.8E+5$      | ...            | $-2.8E+6$      | ...            |
| CH$_2$O   | $-2.4E+6$      | ...            | ...            | ...            | $-2.4E+6$      | ...            |
| H$_2$S    | $-1.1E+8$      | $-9.0E+18$     | $-1.1E+8$      | $-3.7E+8$      | $-1.1E+8$      | $-8.5E+8$      |
| H$_2$SO$_4$ | 1.0E+7        | 1.7E+7        | 9.9E+6         | 1.0E+7         | ...            | ...            |
| NO        | 1.1E+8         | 1.6E+8        | ...            | ...            | 1.1E+8         | ...            |
| NO$_2$    | 1.7E+6         | 4.0E+8        | 2.7E+6         | 1.9E+7         | 1.7E+6         | 1.8E+8         |
| NO$_3$    | ...            | 1.3E+9        | ...            | 5.4E+6         | ...            | 2.4E+7         |
| N$_2$O$_5$ | ...            | 1.2E+9        | ...            | 2.4E+5         | ...            | 1.3E+7         |
| HNO       | 5.1E+8         | ...            | 4.5E+8         | ...            | 5.1E+8         | ...            |
| HNO$_2$   | 2.6E+7         | 1.3E+8        | 5.8E+7         | 1.8E+9         | 2.6E+7         | 1.6E+9         |
| HNO$_3$   | 3.6E+6         | 1.1E+5        | 9.7E+6         | 1.4E+7         | 3.6E+6         | 5.0E+4         |
| HNO$_4$   | ...            | 2.2E+6        | 1.7E+7         | ...            | 3.0E+7         | ...            |
| Total     | 5.4E+8         | $-5.0E+9$     | $-8.5E+9$      | $-4.1E+9$      | $5.5E+8$       | $6.0E+9$       |

**Return H$_2$ Flux**

| H$_2$     | 5.0E+9         | 8.5E+9         | 4.1E+9         | $-5.5E+8$      | $-6.1E+9$      |

**Overall Flux Balance**

| 1.0E+4     | 1.1E+6        | 1.1E+7        | $-7.9E+6$      | 8.6E+5         | $-4.5E+6$      |

Notes.

a The redox flux is expressed as the equivalent of unit H influx to the atmosphere and has a unit of cm$^{-2}$ s$^{-1}$. H$_2$O, CO$_2$, N$_2$, and SO$_2$ are defined as redox neutral. For example, deposition of a CO molecule would create a redox flux of $-2$, and deposition of an O$_3$ molecule would create a redox flux of +6.

b The NO flux is included to simulate lightning production of NO.

dashed lines). The O$_3$ would be almost completely removed. This result is consistent with Harman et al. (2018) in terms of the effect of the NO and NO$_2$ cycle and in general with the basic understanding of terrestrial atmospheric chemistry, that the NO and NO$_2$ cycle help reduce O$_3$. Note that the amount of O$_2$ near the surface is still much higher than that in Harman et al. (2018), which may be due to different choices of species in photochemical equilibrium and different boundary conditions assumed (Section 4.1). When N$_2$O$_3$ and HO$_2$NO$_2$ are included in the chemical network, the results are dramatically different. We see that (1) most of the nitrogen other than N$_2$ or N$_2$O are locked in the form of HO$_2$NO$_2$ in the stratosphere, and the N$_2$O$_3$ reservoir is also significant (Figure 6, solid lines, also in Figure 4, dashed lines); (2) summing the reactive nitrogen species (nitrogen species other than N$_2$ or N$_2$O), the mixing ratio is smaller than the case without N$_2$O$_3$ or HO$_2$NO$_2$; and (3) the mixing ratio of O$_3$ remains constant throughout the atmosphere rather than being reduced by many orders of magnitude.

Why does including N$_2$O$_3$ and HO$_2$NO$_2$ in the chemical network have such a large effect? In the stratosphere, HO$_2$NO$_2$ is formed by the following combination reaction:

$$\text{HO}_2 + \text{NO}_2 + M \rightarrow \text{HO}_2\text{NO}_2 + M$$

and destroyed by photolysis:

$$\text{HO}_2\text{NO}_2 + hv \rightarrow \text{HO}_2 + \text{NO}_3$$

$$\text{HO}_2\text{NO}_2 + hv \rightarrow \text{HO} + \text{NO}_3$$
and reaction with OH

$$\text{HO}_2\text{NO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2.$$  

Similarly, for $\text{N}_2\text{O}_5$, its formation is by combination of NO$_2$ and NO$_4$, and its depletion is by photolysis.

HO$_2$NO$_2$ and N$_2$O$_5$ are important species in Earth’s atmosphere but they do not overtake NO or NO$_2$ as the main reactive nitrogen species. Under the conditions that correspond to present-day Earth’s midlatitude, our model predicted mixing ratio profiles of NO, NO$_2$, N$_2$O$_5$, HNO$_3$, and HO$_2$NO$_2$ in the middle atmosphere that are fully consistent with measurements from balloons (Sen et al. 1998; Hu 2013). On a terrestrial planet of M-dwarf stars, however, the UV irradiation flux that drives the photolysis of HO$_2$NO$_2$ and N$_2$O$_5$ is more than one order of magnitude lower (Table 3), and therefore, these species can accumulate to a higher abundance, overtaking NO or NO$_2$ as the main reactive nitrogen reservoir. This is what we see in the solid lines of Figure 6. We have included the photodissociation of HO$_2$NO$_2$ via overtone and combination bands in the near-infrared (Roehl et al. 2002) in our calculations, because the near-infrared irradiation on a planet in the habitable zone of M-dwarf stars is comparable to that of Sun-like stars. Table 3 indicates that while the near-infrared dissociation contributes dominantly to the total dissociation rate, the total dissociation rate is still more than one order of magnitude less than the value for Sun-like stars.

Additionally, more nitrogen in HO$_2$NO$_2$ and N$_2$O$_5$ leads to more rapid removal of reactive nitrogen from the atmosphere. Without these species, the only effective removal pathway of reactive nitrogen is the deposition and rain out of HNO, HNO$_2$, and HNO$_3$. It is well known that HO$_2$NO$_2$ and N$_2$O$_5$ are highly soluble or reactive in water and rain out very efficiently. Also, heterogeneous reactions of N$_2$O$_5$ on and within atmospheric aerosols or cloud droplets further facilitate rain out (Wang et al. 2017). Therefore, the formation of these species leads to more rapid removal and reduction of the total reactive nitrogen mixing ratio, as we see in Figure 6.

Finally, we point out that the atmosphere has a substantial amount (1 ppb) of N$_2$O produced abiotically. The production path is

$$\text{N}_2 + \text{O}(^1\text{D}) + \text{M} \rightarrow \text{N}_2\text{O} + \text{M}.$$  

The kinetic rate of this reaction was measured recently (Estupinán et al. 2002), and this reaction is not typically included in photochemistry models of planetary atmospheres. Again because of the low NUV irradiation, this abiotic N$_2$O can accumulate to 1 ppb in the atmospheres of TRAPPIST-1 planets. The longer lifetime of N$_2$O in planetary atmospheres around M stars has been suggested previously (Segura et al. 2005). Notably, this N$_2$O is the source of NO and NO$_2$ in the upper atmosphere (Figure 6), via

$$\text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow \text{NO} + \text{NO}.$$  

This source of NO exists without any lightning events. It is therefore necessary to also include N$_2$O in the photochemical model of rocky and potentially habitable planets around M-dwarf stars.

4. Discussion

4.1. Comparison with Prior Studies

To further confirm that the O$_2$ and CO buildup we found is not a model artifact, we compare with two prior studies that studied N$_2$–CO$_2$ atmospheres of terrestrial planets in the habitable zone of M-dwarf stars (Tian et al. 2014; Harman et al. 2015). The two studies built models for a hypothetical 1-Earth-radius and 1-Earth-mass planet, having 1 bar N$_2$ atmosphere with 0.05 bar CO$_2$. Note that the level of CO$_2$ they assumed is less than the level of CO$_2$ required for global habitability on TRAPPIST-1 e. Both studies used the habitable zone of GJ 876 as the representative case, and applied the same method to maintain the redox balance of both the atmosphere and the ocean (i.e., the pseudo H$_2$ flux). For comparison, we set up a model of a 1-Earth-radius and 1-Earth-mass planet, having 1 bar N$_2$ atmosphere with 0.05 bar CO$_2$, at the 0.21 au orbital distance from the M star GJ 876. We set up the same pressure–temperature profile as Tian et al. (2014), i.e., the surface temperature of 288 K and the stratosphere temperature of 180 K. We use the same profile of the eddy diffusion coefficient from terrestrial measurements, adopted by Tian et al. (2014). While these factors are not explicitly stated, we suspect that they are treated the same way as in Harman et al. (2015). We use the same emission rates as these works: the emission rate of H$_2$ is $10^{10}$ cm$^{-2}$ s$^{-1}$, and that of other gases is zero. Note that our models have a more expanded chemical network including HO$_2$NO$_2$ and N$_2$O$_5$, and the choices of species in photochemical
equilibrium are typically different between photochemical models. The main difference between Tian et al. (2014) and Harman et al. (2015) is in the deposition velocities. We adopt the deposition velocities that each work used. In Tian et al. (2014), the deposition velocities of CO and O$_2$ are $10^{-6}$ cm$^2$ s$^{-1}$, and O$_3$ as a long-lived species has a deposition velocity of $10^{-3}$ cm$^2$ s$^{-1}$. Figure 7 shows our results in this case.

Table 3

| Reaction                        | $J$ Earth (s$^{-1}$) | $J$ TRAPPIST-1 e (s$^{-1}$) | Of Which Caused by Near-infrared Irradiation |
|--------------------------------|----------------------|-----------------------------|--------------------------------------------|
| HO$_2$NO$_2$ + hv -> HO$_2$ + NO$_2$ | $1.83 \times 10^{-4}$ | $9.66 \times 10^{-6}$     | $6.28 \times 10^{-6}$                     |
| HO$_2$NO$_2$ + hv -> HO + NO$_2$  | $4.89 \times 10^{-5}$ | $8.90 \times 10^{-7}$     | 0                                          |
| N$_2$O$_5$ + hv -> NO$_3$ + NO$_2$ | $4.82 \times 10^{-5}$ | $6.56 \times 10^{-7}$     | 0                                          |
| N$_2$O$_3$ + hv -> NO$_3$ + NO + O  | $1.45 \times 10^{-4}$ | $2.52 \times 10^{-6}$     | 0                                          |

Note. The contribution from the overtone and combination bands of HO$_2$NO$_2$ in the near-infrared to the $J$ values for TRAPPIST-1 e is also shown.
results are sufficiently consistent with Tian et al. (2014) in terms of the mixing ratios of CO and O₂, as well as the peak mixing ratio of O₃.

Harman et al. (2015) assumed a deposition velocity of \(10^{-8}\) cm s\(^{-1}\) for CO, and zero for O₂, and assumed O₃ to be a short-lived species. The amount of O₂ in our result is consistent with Harman et al. (2015); however, the amount of CO in our result is a factor of a few greater (Figure 8). The difference may be due to the fact that the model of Harman et al. (2015) had 15 species assumed to be in photochemical equilibrium, while our model does not have any.

Note that the O₂ column abundance in both cases, assuming 0.05 bar CO₂, falls between the value for 0.01 bar CO₂ and 0.1 bar CO₂ in our TRAPPIST-1 e models (Figure 2). This comparison shows that the 0.05 bar CO₂ case that the previous studies have assumed happens to be in the transition into the O₂–CO runaway. A small increase in the CO₂ partial pressure will lead to a large increase in the accumulation of photochemical O₂. Comparing Figures 7 and 8, we find that assuming O₃ to be one of the species in photochemical equilibrium, or not, introduces substantial variation to the model results. O₃ may have substantial abundance at the
surface, and its deposition may contribute to the overall redox balance of the atmosphere (Table 2).

4.2. Climate Feedback of the O₂–CO Runaway

As photochemically produced O₂ and CO become main constituents in the atmosphere, they contribute meaningfully to the total pressure. O₂ has no strong infrared absorption bands, and CO absorption occurs only at the shoulders of the planetary thermal emission spectra. Their primary contribution to radiation is through the pressure broadening of CO₂ absorption lines and Rayleigh scattering, with the pressure broadening effect being the dominant of the two (Goldblatt et al. 2009). Several additional 3D climate model simulations are conducted newly for this work to test the effects of increased broadening gas partial pressures on the climate of TRAPPIST-1 e, summarized in Table 4. Three-dimensional simulations are conducted for TRAPPIST-1 e with 0.1 bar and 0.2 bar CO₂, and with broadening gas partial pressures of 1.5, 2, and 4 bar, respectively.

The results of the 3D climate models with increased atmospheric pressure are shown in Figure 9. Using a 3D climate model, we can self-consistently incorporate the effects of pressure broadening and Rayleigh scattering, along with resultant climatological feedbacks. Increasing the background pressure by up to 4 folds yields increases to the global mean surface temperature by a few tens of Kelvin; even though significant, this does not change the general assessment regarding habitability for atmospheres with ≤0.2 bar CO₂. However, for higher background pressures produced by larger CO₂ amounts, the combined effects may cause TRAPPIST-1 e to become too hot to be reasonably habitable. In addition, O₃ is a greenhouse gas with an absorption band in the middle of the planetary thermal emission spectra (9.6 μm). At expected concentrations, however, its contribution to the greenhouse effect is dwarfed by that of CO₂ and H₂O (Kiehl & Trenberth 1997), and thus would not significantly raise the surface temperature. Given the O₂ runaway and the climate models, we conclude that for TRAPPIST-1 e to remain globally habitable, it must have pCO₂ in a somewhat narrow range between 0.01 and 0.2 bar.

One might wonder if substituting O₂/CO with N₂ in the climate model is reasonable. O₂/CO and N₂ have mean molecular weights within ~15%, specific heats within ~10%, and neither have strong absorption bands in the planetary thermal emission spectra. Both O₂ and N₂ are diatomic molecules and thus do not have vibrational or rotational absorption modes, and thus are not conventional greenhouse gases. The absorption feature of CO at ~100 μm is swamped by H₂O rotational-vibration absorption bands. The feature of CO at ~5 μm may show through both CO₂ and H₂O, but this spectral region is located where both thermal emitted and incident stellar radiation are relatively small. In addition, in sufficiently dense atmospheres each molecular pair features collision-induced absorption (CIA) in the infrared, which can affect climate. But, in moist atmospheres, as modeled here, O₂–O₂ CIA at 6.4 μm is swamped by the H₂O feature in this same spectral region (Hopfner et al. 2012), and N₂–N₂ CIA, which affects wavelengths longward of ~30 μm, is swamped by H₂O rotational-vibration absorption bands (Wordsworth & Pierrehumbert 2013). In total, the radiative effects of O₂, CO, and N₂ are primarily felt indirectly through their contribution to the total atmospheric pressure and in the subsequent pressure broadening of CO₂ absorption features, which can have a significant warming effect on climate (Goldblatt et al. 2009). Collisions between molecules shift absorption from line centers toward the wings, with the end result being more total radiation being absorbed.

Increasing the total pressure of the atmosphere also increases Rayleigh scattering, which would act to cool the planet, countering the above discussed effect of pressure broadening. However, the increase in greenhouse forcing from enhanced pressure broadening dominates over the increase in reflection due to enhanced Rayleigh scatterings (Goldblatt et al. 2009). Note that the Rayleigh scattering cross sections for O₂, CO, and N₂ are also quite close (Thalman et al. 2014). CO has an absorption band at ~2.3 μm, and this band contributes to near-infrared absorption of stellar radiation from TRAPPIST-1. However, the near-infrared absorption of CO₂ and H₂O will be more significant. Thus, substituting N₂ for O₂ and CO in our model should not give rise to a large error in thermal or stellar forcings.

Our atmospheric chemistry model also predicts that the O₂-rich atmospheres on TRAPPIST-1 planets should have a significant O₃ layer (Figure 3), and this is consistent with previous models of O₂-rich planets found around M-dwarf stars (Segura et al. 2005; Meadows et al. 2018). That O₃ is also absent from our 3D climate model. However, note that because M-dwarf stars emit several orders of magnitude less radiation in the NUV region (λ ≥ 200 nm), a stratospheric O₃ layer would

| Table 4 |
| --- |
| New Climate Scenarios Modeled for This Study and Their Key Climate Characteristics |
| Planet | N₂ | CO₂ | T Surf Globe (K) | Ice Fraction |
| TRAPPIST-1 e | 1 bar | 0.1 bar | 274 | 57% |
| TRAPPIST-1 e | 1.5 bar | 0.1 bar | 286 | 12% |
| TRAPPIST-1 e | 2 bar | 0.1 bar | 291 | 0.3% |
| TRAPPIST-1 e | 4 bar | 0.1 bar | 320 | 0% |
| TRAPPIST-1 e | 1 bar | 0.2 bar | 285 | 18% |
| TRAPPIST-1 e | 1.5 bar | 0.2 bar | 297 | 0% |
| TRAPPIST-1 e | 2 bar | 0.2 bar | 308 | 0% |
| TRAPPIST-1 e | 4 bar | 0.2 bar | 332 | 0% |

Figure 9. Global mean surface temperature of TRAPPIST-1 e vs. the abundance of CO₂ (x-axis) and the broadening gas amount (legend). The temperature is calculated in 3D climate model simulations, with the H₂O abundance and the cloud feedback self-consistently modeled (Wolf 2017). We consider increases to the total pressure by increasing the N₂ background amount, rather than including O₂ or CO explicitly in the climate model. Increasing the background pressure results in meaningful increases in the mean surface temperature.
have little radiation to absorb and would not form a stratospheric inversion. Indeed, simulations of O2-rich planets around M-dwarf stars indicate that the stratospheric temperatures would remain cold (Segura et al. 2005; Meadows et al. 2018). While O3 is a greenhouse gas, with an absorption band at 9.6 μm, at expected concentrations its contribution to the greenhouse effect is dwarfed by those of CO2 and H2O (Kiehl & Trenberth 1997), and thus is not a significant driver of climate change. Based on the above discussions, we feel that substituting N2 for O2 and CO will not radically alter the resultant climates in our 3D model, and provides useful estimates for climate change for TRAPPIST-1 e under thicker atmospheres.

Finally, we briefly discuss “the feedback of the feedback:” the effect of the changed temperature profile after the O2–CO runaway onto the atmospheric photochemistry itself. Figure 10 shows the mean pressure–temperature and water profiles from the 3D climate models assuming varied partial pressure of N2. The similarity of these profiles is striking: the stratosphere’s temperature and water vapor abundance stay low, and only the lowest layers of the atmosphere experience higher temperatures after the O2–CO runaway. As such, even though new photochemical simulations were not performed with the new climate studies, the change in the temperature profile and its impact on the atmospheric chemistry is likely limited to the bottom layers of the atmosphere, and thus unlikely to significantly affect the O2–CO runaway.

4.3. Geologic Context for the O2–CO Runaway

Silicate weathering, if it occurs on a rocky planet, helps keep pCO2 in a desirable range that is consistent with a liquid water ocean (Walker et al. 1981). The O2–CO runaway, together with the enhanced warming due to pressure broadening, increases the sensitivity of the surface temperature on pCO2. This increased sensitivity would allow silicate weathering to maintain pCO2 in the required narrow range.
implied CO₂ outgassing rate does not necessarily come from the interior of the planet as “new” CO₂; instead, the very recombination process in hydrothermal flows that consumes O₂ will produce CO₂. The O₂–CO runaway state would therefore be sustainable via cycling through the deep ocean. Lastly, when the surface-ocean recombination of CO and O₂ is assumed, the O₂–CO runaway does not occur (Figure 2), but a large “outgassing rate” is still required for pCO₂ > 0.1 bar. This outgassing rate can be sustained by the product of the recombination itself. In all, the O₂–CO runaway appears to be sustainable from a geochemical point of view, and the sustainability may involve replenishment of CO₂ from the planetary interior, or cycling of CO, O₂, and CO₂ through the deep ocean.

As such, the O₂– and CO-rich atmosphere modeled here does not require any planetary outgassing outside of typical geological regimes; neither does it require a highly oxidized or dried upper mantle, presumably produced by loss of hydrogen into space over a long active period of the M dwarfs (Luger & Barnes 2015; Tian & Ida 2015; Bolmont et al. 2017). The atmosphere modeled here has O₂ and CO coexisting at large abundances, different from the predicted massive O₂ atmospheres from accumulative hydrogen loss that would have little CO (Bolmont et al. 2017; Lincowski et al. 2018).

5. Conclusion

We use an atmospheric photochemistry model to study the effect of stellar UV radiation on the varied abundance of CO₂ on the rocky planets in the habitable zone of the late M dwarf TRAPPIST-1. Our models show that for a small abundance of CO₂, an atmosphere with O₂ and CO as the main components would be the steady state. This “O₂–CO runaway” is robust against the nitrogen catalytical cycles from lightning, reasonable uncertainties in the stellar spectrum, as well as various geochemical sinks for O₂ and CO, including the BIF. For the planets TRAPPIST-1 e, f, and g, because they require sizable biochemistry.

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References

Beichman, C. A., Benneke, B., Knutson, H., et al. 2014, PASP, 126, 1134
Bolmont, E., Selsis, F., Owen, J. E., et al. 2017, MNRAS, 464, 3728
Bourrier, V., Ehrenreich, D., Wheatley, P. J., et al. 2017, A&A, 599, L3
Broecker, W. S., & Peng, T. H. 1982. Tracers in the Sea (Palisades, NY: Lamont-Doherty Geological Observatory)
De Wit, J., Wakeford, H. R., Lewis, N. K., et al. 2018, NatAs, 2, 214
Dittmann, J. A., Irwin, J. M., Charbonneau, D., et al. 2017, Natur, 544, 333
Domagal-Goldman, S. D., Segura, A., Claire, M., Robinson, T. D., & Meadows, V. S. 2014, ApJ, 792, 90
Estupiñán, E. G., Nicovich, J. M., Li, J., Cunoldo, D. M., & Wine, P. H. 2002, JPCA, 106, 5880
France, K., Crongin, C., Linsky, J. L., et al. 2013, ApJ, 763, 149
France, K., Loyd, R. P., Youngblood, A., et al. 2016, ApJ, 820, 89
Gaillard, F., & Scallen, B. 2014, E&PSL, 403, 307
Gao, P., Hu, R., Robinson, T. D., Li, C., & Yung, Y. L. 2015, ApJ, 806, 249
Gillon, M., Traia, A. H., Demory, B. O., et al. 2017, Natur, 542, 456
Goldblatt, C., Claire, M. W., Lenton, T. M., et al. 2009, NatGe, 2, 891
Grimm, S. L., Demory, B. O., Gillon, M., et al. 2018, A&A, 613, A68
Hardacre, C., Wild, O., & Emerson, L. 2015, ACP, 15, 6419
Harman, C. E., Felton, R., Hu, et al. 2018, ApJ, 866, 56
Harman, C. E., Schwieterman, E. W., Schottelkotte, J. C., & Kasting, J. F. 2015, ApJ, 812, 137
Holland, H. D. 2006, RJSTP, 361, 903
Hopfner, M., Milz, M., Buehler, S., Orphal, J., & Stilg, G. 2012, GeoRL, 39, L07076
Hu, R. 2013, Doctoral dissertation, MIT
Hu, R., Seager, S., & Bains, W. 2012, ApJ, 761, 166
Hu, R., Seager, S., & Bains, W. 2013, ApJ, 769, 6
James, T. S., & Hu, R. 2018, ApJ, 867, 17
Kasting, J. F. 2013, ChGeos, 362, 13
Kharecha, P., Kasting, J., & Siefer, J. 2005, Geobiology, 3, 53
Kiehl, J. T., & Trenberth, K. E. 1997, Earth’s Annual Global Mean Energy Budget. Bull. Amer. Meteo. Soc, 78, 197
King, G. M., & Weber, C. F. 2007, Nature Reviews Microbiology, 5, 107
Lincowski, A. P., Meadows, V. S., Crisp, D., et al. 2018, ApJ, 867, 76
Lovis, C., Snellen, I., Mouillet, D., et al. 2017, A&A, 599, A16
Loyd, R. P., France, K., Youngblood, A., et al. 2016, ApJ, 824, 102
Luger, R., & Barnes, R. 2015, AsBio, 15, 119
Luger, R., Sestovic, M., Kruse, E., et al. 2017, NatAs, 1, 0129
Massie, S. T., & Hunten, D. M. 1981, JGR, 86, 9859
McElroy, M. B., Dak Sze, N., & Ling Yung, Y. 1973, JAtS, 30, 1437
Meibom, R. M., & Donahue, T. M. 1972, Sci, 177, 986
Meadows, V. S., Arney, G. N., Schwieterman, E. W., et al. 2018, AsBio, 18, 133
Misra, A., Meadows, V., Claire, M., & Crisp, D. 2014, AsBio, 14, 67
Nair, H., Allen, M. A., Anbar, A. D., Yung, Y. L., & Clancy, R. T. 1994, Icar, 111, 124
Papaloizou, J. C., Szuszkiewicz, E., & Terquem, C. 2017, MNRAS, 476, 5032
Rimmer, P. B., & Helling, C. 2016, ApJS, 224, 9
Roehl, C. M., Nizkorodov, S. A., Zhang, H., Blake, G. A., & Wennberg, P. O. 2002, JPCA, 106, 3766
Rugheimer, S., Kaltenegger, L., Segura, A., Linsky, J., & Mohanty, S. 2015, ApJ, 809, 57
Schumann, U., & Huntrieser, H. 2007, ACP, 7, 3823
Segura, A., Kasting, J. F., Meadows, V., et al. 2005, AsBio, 5, 706
Sen, B., Toon, G. C., Osterman, G. B., et al. 1998, JGRD, 103, 5571

Hu, Peterson, & Wolf
Sleep, N. H., & Zahnle, K. 2001, JGRE, 106, 1373
Snellen, I. A., De Kok, R. J., De Mooij, E. J., & Albrecht, S. 2010, Natur, 465, 1049
Sullivan, P. W., Winn, J. N., Berta-Thompson, Z. K., et al. 2015, ApJ, 809, 77
Thalman, R., Zarzana, K. J., Tolbert, M. A., & Volkamer, R. 2014, JQSRT, 147, 171
Tian, F., France, K., Linsky, J. L., Mauas, P. J., & Vieytes, M. C. 2014, E&PSL, 385, 22
Tian, F., & Ida, S. 2015, NatGe, 8, 177
Turbet, M., Bolmont, E., Leconte, J., et al. 2018, A&A, 612, A86
Van Grootel, V., Fernandes, C. S., Gillon, M., et al. 2018, ApJ, 853, 15
Von Braun, K., Boyajian, T. S., van Belle, G. T., et al. 2014, MNRAS, 438, 2413
Walker, J. C., Hays, P. B., & Kasting, J. F. 1981, JGRC, 86, 9776
Wang, Z., Wang, W., Tham, Y. L., et al. 2017, ACP, 17, 12361
Wolf, E. T. 2017, ApJL, 839, L1, [Erratum: Wolf, E. T. 2018, ApJL, 855, L14]
Wong, M. L., Charnay, B. D., Gao, P., Yung, Y. L., & Russell, M. J. 2017, AsBio, 17, 975
Wordsworth, R., & Pierrehumbert, R. 2013, Sci, 339, 64
Youngblood, A., France, K., Loyd, R. P., et al. 2016, ApJ, 824, 101
Zhang, Z., Zhou, Y., Rackham, B. V., & Apai, D. 2018, AJ, 156, 178