The dissertation of Ramses M. Ramirez was reviewed and approved* by the following:

James F. Kasting  
Evan Pugh Professor of Geosciences  
Dissertation Advisor  
Chair of Committee

Christopher House  
Professor of Geosciences

Eugene E. Clothiaux  
Professor of Meteorology

Steinn Sigurdsson  
Professor of Astronomy

Chris Marone  
Professor of Geosciences  
Associate Head of Graduate Programs

*Signatures are on file in the Graduate School.
ABSTRACT

The CO$_2$-H$_2$O habitable zone is defined as the region around a star where liquid water is stable on a planetary surface. The inner edge is defined by the initiation of a wet stratosphere followed by escape of water to space, whereas the location of the outer edge is determined by the maximum greenhouse effect of CO$_2$. Previous calculations have shown that a conservative estimate of the habitable zone is relatively wide at ~0.95–1.67 AU (Kasting et al., 1993). A wide habitable zone facilitates the search for extraterrestrial life because the probability of finding potentially habitable planets increases, relaxing design specifications for observing telescopes. In our own solar system, the solar flux received by early Mars 3.8 Ga is only slightly less than that predicted at the outer edge, suggesting that the Red Planet may have once been habitable if it contained additional greenhouse gases in its atmosphere. In the case of Earth, our close proximity to the inner edge implies susceptibility to various climatic catastrophes at elevated temperatures. The calculations of Kasting et al. have become obsolete as line-by-line absorption databases are continually updated with newly discovered lines, leading to increased absorption for key greenhouse gases such as CO$_2$, H$_2$O, CH$_4$, and H$_2$. This suggests that current climate models may just be able to produce warm conditions for early Mars, although it also means that life on Earth may be more vulnerable than previously thought. The aim of this Thesis is to update the 1-D climate model of Kasting et al., derive updated habitable zone boundaries and use them to a) refine the telescopic search for life in exoplanetary systems, b) assess whether early Mars may have once manifested a warm and wet climate, and c) evaluate the implications for the habitability of the Earth as a result of continued increases in CO$_2$. With our new climate model we find: a) that these new absorption databases move the inner edge past the orbit of Earth, demonstrating the inadequacy of 1-D models, b) 5 – 20% H$_2$, along with 1.3 – 4 bar CO$_2$, generates above freezing mean temperatures for early Mars, and c) a runaway greenhouse cannot be triggered from increased fossil fuel emissions. All of these problems should be revisited using 3-D models.
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$A_p =$ planetary albedo
AU: Astronomical Unit
BPS: Baranov-Paynter-Serio
CH$_4$: Methane
CIA: collision-induced absorption
CO$_2$: carbon dioxide
$f_{CO_2}$: volume mixing ratio of CO$_2$
$f_{CH_4}$: volume mixing ratio of methane
$f_{H_2}$: volume mixing ratio of hydrogen
$f_{H_2O}$: volume mixing ratio of water
H$_2$O: water
F$_{IR}$: net outgoing infrared radiation
F$_s$: net incoming solar radiation
H$_2$: Hydrogen
HZ: habitable zone
IE: inner edge of the habitable zone
IR: infrared
LHS: left-hand side
LBL: line-by-line
OE: outer edge of the habitable zone
NIR: near-infrared
$p_{CO_2}$: partial pressure of CO$_2$
$p_{H_2O}$: partial pressure of water
HZ: habitable zone
RHS: right-hand side
SED: stellar energy distribution
$S_{eff}$: effective solar flux
$S_o$: total incident solar flux
$T_{eff}$: stellar effective temperature
$T_s$: surface temperature
TOA: top of the atmosphere
UV: ultraviolet
VIS: visible (wavelength)
I am especially indebted to my advisor, James F. Kasting, who has been both my mentor and friend throughout my 4+ year journey. I am not only blessed to be working in a field I love, but his mild-mannered and easygoing demeanor made it a real joy to come to work every day. I also thank my three committee members: Eugene Clothiaux for his upbeat personality and wisdom-filled discussions, not just on radiative transfer, but on life in general; Chris House for always asking tough questions; and Steinn Sigurdsson for his dry sense of humor and useful suggestions for testing my hypotheses. I also thank the Head of our Department, Lee Kump, for pointing out the utility of iron carbonyl, which we put to great effect in our early Mars paper!

Furthermore, I am grateful to have worked with a splendid group of colleagues and friends. Special thanks go to Ravi Kopparapu, Chester Harman, and Mike Zugger, who have been great collaborators and wonderful people to debate the most crucial questions in life, including Microsoft Word vs. LaTeX, Windows vs. LINUX, and Star Trek vs. Star Wars. I also thank David Crisp, David Paynter, and Itay Halevy for taking the time to answer my many radiative transfer questions, greatly improving the quality of my papers. I thank Vincent Eymet for both providing KSPECTRUM and addressing my installation and technical questions. I also appreciate all the technical help I received from the computer support staff, with special kudos to both Tom Canich and John Miley. Additionally, none of this work would have been made possible without high performance computing, both on campus and through the University of Washington. I am grateful to Vikki Meadows for her successful management of the Virtual Planetary Laboratory, which provides a regular venue for scientists interested in problems of astrobiological interest. Thanks go to both Tyler Robinson and Mike Mischna for taking the time to compare their radiative transfer models versus ours. I am also extremely grateful to the Sloan Scholars program, whose financial support enabled me to purchase important software programs and attend conferences I would not have otherwise attended.

And last, but not least, I would like to thank mom, dad, and my brother, who have been extremely supportive every step of the way; having the wherewithal to tolerate a crazy kid with lifelong dreams of getting abducted by aliens and whisked away to strange new worlds many light years away...
1. BACKGROUND

More than 800 extrasolar planetary systems have now been detected, and more than 3000 additional candidate systems, from the Kepler mission are waiting to be confirmed (Batalha et al 2013). One of the primary goals of the ongoing radial velocity (RV) and transit surveys is to identify a terrestrial mass planet (0.3 – 10M$_{\oplus}$) in the so-called Habitable Zone (HZ) around its parent star. The HZ is traditionally defined as the circumstellar region in which a terrestrial-mass planet with a CO$_2$-H$_2$O-N$_2$ atmosphere can sustain liquid water on its surface (Kasting et al 1993). Initial estimates suggest that there could be a total of ~ 22 billion habitable planets in our galaxy alone (Petigura et al 2013, Kasting & Harman 2013).

The HZ limits that were cited in many recent discoveries were obtained from 1-D radiative-convective, cloud-free climate model calculations by Kasting et al (1993). For our Sun, these authors estimated conservative boundaries of the HZ to be 0.95 AU for the inner edge and 1.67 AU for the outer edge.

For planets with Earth-like water inventories (~ 270 bar), a runaway greenhouse is initiated should the surface temperature exceed the critical temperature for water (647 K for pure H$_2$O). Alternatively, some authors (Rennó 1997, Goldblatt et al 2013) prefer to define the runaway greenhouse as a situation in which the absorbed solar flux exceeds the outgoing infrared flux. In practice, these two definitions are equivalent, because a sustained imbalance in the radiation budget inevitably leads to evaporation of the ocean. Moreover, a runaway greenhouse can also occur at surface temperatures below 647 K on a planet that has less water than Earth if its water inventory is less than the critical pressure (~ 220 bar).

The outer edge, in contrast, is defined by the maximum greenhouse effect of CO$_2$ (the distance at which the greenhouse effect is overwhelmed by the additional albedo from added CO$_2$). This limit is characterized by global condensation of CO$_2$ in a 1-D climate model or by polar condensation in a more realistic 3-D model. The solar flux at the empirical early Mars limit (1.77 AU) corresponds to the flux received by early Mars 3.8 billion years ago when the planet was inferred to have had a warm and wet climate. The computed location of the outer edge, just inside the early Mars limit, implies that a CO$_2$-H$_2$O greenhouse alone is almost, but not quite sufficient, to raise martian surface temperatures above freezing (Postawko & Kuhn 1986, Kasting et al 1993, Wordsworth et al 2010a, Wordsworth et al 2012, Forget et al 2012), suggesting additional greenhouse gases may be required.
A particularly promising secondary greenhouse gas turns out to be H₂, whose utility was first pointed out by Stevenson (1999). Pierrehumbert and Gaidos (2011) later showed that H₂ is capable of extending our solar system’s outer edge to ~10 AU for a planet with a dense (10’s of bar), nearly pure H₂ atmosphere. In these two papers, the H₂ atmospheres were primordial in origin and assumed to have been captured from the protoplanetary disk. However, more recent work has extended this concept to terrestrial planets with outgassed H₂ envelopes. Although Wordsworth and Pierrehumbert (2013a) claim concentrations as high as 10% H₂ for early Earth, such large accumulations would be difficult to attain because high pressures within Earth’s interior would have disproportionated Fe²⁺ into Fe⁰ and Fe³⁺, oxidizing the mantle (Tuff et al 2013) and causing H₂ to be only a minor component of volcanic gases. In fact, these voluminous atmospheric H₂ amounts may be able to accumulate more readily in smaller planets with reduced mantles, such as early Mars (Grott et al 2011). Furthermore, there is an additional complication in warming inhabited planets with such H₂-rich atmospheres. Evolving methanogens would have consumed the H₂, forming CH₄ instead (Pavlov et al 2000, Kharecha et al 2005, Wordsworth & Pierrehumbert 2013a).

A final habitability-related question for the Earth concerns the question of whether increased CO₂ levels from burning fossil fuels can trigger a runaway greenhouse. The runaway greenhouse problem for Earth has been previously studied by Kasting and Ackerman (1986), who found that Earth is stable against a runaway greenhouse, even with 100 bar of CO₂. However, in these previous calculations, the surface relative humidity was assumed to be constant as temperature rises, which probably underestimates tropospheric water vapor concentrations. Moreover, using updated absorption coefficients, a recent study suggests that a runaway greenhouse is possible to trigger in this manner (Goldblatt et al 2013)—a conclusion that is revisited here.

An additional motivation for this Thesis is that the 1-D climate model used in Kasting et al (1993) is outdated and needed to be updated for several reasons:

1. Kasting et al (1993) used ‘band models’ for H₂O and CO₂ absorption in the thermal-infrared. These coefficients were considered valid up to ~700 K and were later replaced (Mischna et al 2000) by coefficients generated using the correlated-k technique (Mlawer et al 1997, Kato et al 1999). A line-by-line (LBL) radiative transfer model, in this case LBLRTM (Clough & Iacono 1995), was used to generate detailed spectra for H₂O and CO₂ at a variety of different temperatures and pressures. Once the detailed spectra were calculated, separate broad-band k-coefficients for both H₂O and CO₂ were generated by R. Freedman using standard procedures. But these coefficients were only derived for temperatures less than 350 K and should therefore underestimate thermal-IR absorption in warm, moist greenhouse atmospheres. (This prediction was verified by direct experimentation with that model.) Furthermore, the coefficients adopted by and used in subsequent climate modeling studies by the Kasting research group (Mischna et al 2000,
Haqq-Misra et al (2008) were obtained using the HITRAN 1996 database (Rothman et al 1998) and had not been updated since then.

2. Recent studies (Halevy et al 2009, Wordsworth et al 2010a) have observed that the Kasting et al (1993) model may have significantly overestimated absorption of thermal-IR radiation by collision-induced absorption (CIA) bands of CO$_2$, which may affect the outer edge of the HZ.

3. The Kasting et al (1993) model used an older water vapor continuum which parameterizes absorption in the 8-12 micron window (Roberts et al 1976). However, this has been superseded by more modern parameterizations that also characterize the shortwave windows, which become influential in moist atmospheres.

4. Relative humidity distributions as a function of temperature are difficult to predict using 1-D climate models and thus fully-saturated atmospheres are often assumed for the Kasting et al (1993) model (for HZ calculations), or the fixed relative humidity profile of Manabe and Wetherald (1967) is prescribed for modern Earth. We argue below that surface relative humidity should increase as temperature rises; otherwise, the surface latent heat flux increases to unphysical values and the system runs out of energy.

5. The Kasting et al (1993) calculations spanned stellar effective temperatures from 7200 K to 3700 K, corresponding approximately to stellar classes F0 to M0. Stellar effective temperature affects the HZ boundaries because the radiation from F stars is bluer relative to that from the Sun, whereas the radiation from K and M stars is redder, and this affects calculated planetary albedos. The HZ limits from the Kasting et al (1993) model do not include M stars with effective temperatures lower than 3700 K. As pointed out above, such stars are promising candidates for current observational surveys because their HZs are closer to the star. Therefore, potential rocky planets in the HZs will have shorter orbital periods and higher transit probabilities.

This thesis updates the Kasting et al (1993) model by addressing the above mentioned five points. This updated model is then used to derive new habitable zone limits for F-M main sequence stars (Section 3). In Section 4, the question of whether early Mars could have been warm and wet is tested by assuming a dense CO$_2$ atmosphere complemented by secondary H$_2$. Section 5 answers if a runaway greenhouse can be triggered from the anthropogenic burning of fossil fuels. Finally, the appendices cover the following assortment of topics: radiative transfer flux comparisons against other models, H$_2$O continuum description, CIA data, description of the k-distribution technique, derivations of key physical formulae, an assessment of the Redlich-Kwong equation of state (Redlich & Kwong 1949), and a summary of useful LINUX commands.
2. CLIMATE MODEL DESCRIPTION AND UPDATES

2.1 Overall climate model description

The climate calculations described in this thesis were performed with a 1D (horizontally-averaged) radiative-convective climate model that has been recently updated (Kasting et al 1984, Kopparapu et al 2013, Ramirez et al 2013). In such a model, the planet is assumed to be flat, and the Sun is placed at a solar zenith angle of 60° from the vertical. Because \( \cos(60°) = 0.5 \), multiplying the resulting solar fluxes by another factor of 0.5 gives the planetary average incident solar flux of \( S/4 \) (= 340 W/m\(^2\)). The current version of the model divides the atmosphere into 100 unevenly spaced layers in log pressure extending from the ground to a pressure of \( 3 \times 10^{-5} \) bar. Radiative equilibrium is assumed for each layer in the stratosphere. At lower altitudes, if the radiative lapse rate within a layer exceeds the moist adiabatic lapse rate, then a convective adjustment is performed (Manabe & Wetherald 1967). At higher temperatures, the model relaxes to a moist H\(_2\)O pseudoadiabat (methodology explained in Appendix A of Kasting (1988)), which is an adiabat in which the condensed phase leaves the system immediately. Alternatively, when it is cold enough for CO\(_2\) to condense the model relaxes to a moist CO\(_2\) pseudoadiabat (Kasting 1991). This defines a convective troposphere near the surface. H\(_2\)O and CO\(_2\) clouds are neglected in the model, but the effect of the former is accounted for by increasing the surface albedo, as done in previous climate simulations by our group (Haqq-Misra et al 2008, Kasting et al 1984, Kopparapu et al 2013, Ramirez et al 2013). However, this methodology may tend to overestimate the greenhouse effect of dense early atmospheres because the clouds are effectively placed on the ground, producing errors in the energy balance (Goldblatt & Zahnle 2011). By contrast, our neglect of CO\(_2\) clouds may cause us to underestimate the greenhouse effect (Forget & Pierrehumbert 1997, Mischna et al 2000). Realistically determining the effect of clouds would probably require a 3-D climate model, and even then the cloud problem remains difficult. Unless otherwise specified, a surface albedo of 0.315 is assumed for all of our Earth and habitable zone calculations, whereas a value of 0.216 was used for Mars. These are the values that allow our model to reproduce the mean surface temperature of 288 K for Earth and 218 K for present Mars, respectively.

Incident solar radiation and outgoing thermal infrared radiation are both treated using a two-stream approximation (Toon et al 1989). In this approximation, integration over the upward and downward hemispheres is accomplished by choosing a single average zenith angle. In such a model, the stratosphere is assumed to be in radiative equilibrium, that is, the net emitted infrared flux is equal to the net absorbed solar flux in each layer.
2.2 KSPECTRUM program description

We have generated line-by-line (LBL) absorption cross sections using a radiative transfer code called KSPECTRUM. It is designed to produce spectra using the HITRAN 2008 (Rothman et al 2009) and HITEMP 2010 (Rothman et al 2010) linelists. As of December 2013, the source code and a detailed description of the program are available at http://code.google.com/p/kspectrum/.

2.3 K-distribution method overview

The \(k\)-distribution technique was then used to convert these LBL spectra to correlated-\(k\) coefficients for use in climate model calculations. (For a description of the \(k\)-distribution technique see Appendix D.) We used a double gauss quadrature scheme in place of a standard Gaussian scheme (Sykes 1953, Thomas & Stamnes 2002). In this formulation, half of the \(k\)-coefficients are chosen within the \(g\)-space interval 0.95–1.00 for improved resolution of the steeply rising portion of the cumulative distribution function. The other half of the \(k\)-coefficients then span the Lorentz-broadened line wings. Overlap between gases was computed by weighing the \(k\)-coefficients for each species within each broadband spectral interval.

2.4 Absorption coefficient description and updates

At solar wavelengths, the model parameterizes absorption by CO\(_2\), H\(_2\)O and CH\(_4\) across 38 spectral intervals ranging from 0.23 \(\mu\)m to 4.54 \(\mu\)m. In the solar, we currently use 8-term CO\(_2\) \(k\)-coefficients derived from HITRAN 2008 (Rothman et al 2009), whereas our 8-term H\(_2\)O coefficients utilize HITRAN 2008 (Rothman et al 2009) at low pressures and HITEMP 2010 (Rothman et al 2010) for pressures greater than or equal to 0.1 bar (Kopparapu et al 2013). The HITEMP 2010 linelist contains ~14 million lines, which is ~2000 times the number found in HITRAN 2008. Although the radiative effects of these extra lines are negligible in the modern atmosphere, their impact becomes significant in extremely warm and dense atmospheres (Goldblatt et al 2013). We justify using HITRAN at 0.1 bar and below because HITRAN and HITEMP become indistinguishable at the temperatures associated with these lower pressures (Section 3.7).

In the near-IR, the Karkoschka (1994) data were used to derive CH\(_4\) coefficients for wavelengths less than 1 \(\mu\)m, whereas those longward of 1 \(\mu\)m were derived from self-broadened \(k\)-distributions (Irwin et al 1996). These latter coefficients were interpolated between 188 K and 295 K (ibid).

In the thermal infrared, 8-term \(k\)-coefficients were used for CO\(_2\) and H\(_2\)O (Kopparapu et al 2013, Ramirez et al 2013) and new 4-term coefficients were derived for CH\(_4\) in 55 spectral intervals extending from 0 – 15,000 cm\(^{-1}\). HITRAN 2008 was used for all thermal infrared coefficients. These HITRAN 2008 H\(_2\)O IR coefficients replace earlier ones (Kopparapu et al
that had used HITTEMP 2010 for $P \geq 0.1$ bar after correcting an error with KSPECTRUM. However, as HITTEMP and HITRAN are indistinguishable at $T < \sim 350$ K (Section 3.7), and the atmosphere is opaque in the infrared above this temperature, the decision to not include the additional HITTEMP lines does not compromise our results. The coefficients for CO$_2$ and H$_2$O were calculated using line width truncations of 500 cm$^{-1}$ and 25 cm$^{-1}$, respectively, and were computed over 8 temperatures (100, 150, 200, 250, 300, 350, 400, 600 K) and 8 pressures ($10^{-5} - 100$ bar). A short truncation width was used for H$_2$O because the Lorentz line shape is known to underestimate absorption for H$_2$O in the far wings (Halevy et al 2009). To characterize this super-Lorentzian absorption, a water vapor continuum was overlain in the wings, as described below.

In climate studies of dense atmospheres, empirically-determined line shape parameterizations, called chi factors, are commonly used to characterize the pressure broadening of the far wings to spectral bands. For CO$_2$ far wing absorption, we have employed the 4.3 µm CO$_2$ chi factors of Perrin and Hartmann (1989) as a proxy for the 15 µm region. The far wing behavior for CH$_4$ is unknown, but we truncated the line wings for this gas at 35 cm$^{-1}$, following a previous study (Roe et al 2002). These CH$_4$ coefficients were computed at the same 8 pressures as were CO$_2$ and H$_2$O, although a slightly different temperature grid was used: 100, 200, 300, 400, 600 K.

These CO$_2$, CH$_4$, and H$_2$O coefficients replaced those used in previous studies (Mischna et al 2000, Haqq-Misra et al 2008, Tian et al 2010), as the older coefficients were derived for temperatures < 350 K and underestimate absorption in warm, moist atmospheres (Section 5). Furthermore, the coefficients adopted by Mischna et al (2000), and used in subsequent climate modeling studies by the Kasting research group, were obtained using the HITRAN 1996 database (Rothman et al 1998) and had not been updated since then. Our new model produces excellent agreement for various flux comparisons done for Earth, early Mars, and runaway atmospheres (Appendix A).

Although the correlated-$k$ method is very quick compared to line-by-line models like SMART (Meadows & Crisp 1996), combining too many gas species at once can become computationally expensive. Combining just the CO$_2$ and H$_2$O $k$-coefficients produces $8 \times 8 \times 55 = 3520$ separate thermal-IR radiative transfer calculations at each time step in the climate model. This number is multiplied by a factor of four when we include CH$_4$ in the model, and by another factor of six when we include C$_2$H$_6$. Thus, from a practical standpoint, the utility of this approach diminishes as the number of included greenhouse gases increases.
2.5 Model updates

The climate model has been further updated in the following ways:

1) We used the Baranov-Paynter-Serio (BPS) H\textsubscript{2}O continuum of Paynter and Ramaswamy (2011) and overlaid it over its entire range of validity (0 – ~17,000 cm\textsuperscript{-1}). This replaces the Roberts et al (1976) formalism which only parameterizes absorption in the 8-12 µm window, whereas the BPS continuum also characterizes the shortwave windows, which become influential in moist atmospheres (Paynter & Ramaswamy 2011). Although empirical measurements for the continuum do not exist above~19,000 cm\textsuperscript{-1} (D. Paynter, Princeton University, private communication), the continuum is thought to be proportional to the strength of the water vapor bands, which are weak at those shorter wavelengths (see Goldblatt et al (2013), Supp Info, Fig, 3); thus, its contribution to the overall solar absorption should be rather small (D. Paynter, Princeton University, private communication). This is confirmed by our excellent agreement (within 1%) with the Goldblatt et al (2013) solar fluxes (Section 5.3 and Appendix A5).

2) Both Haley et al (2009) and Wordsworth et al (2010a) have pointed out that our old climate model, which was derived from that of Kasting et al (1984), may have significantly overestimated absorption of thermal-IR radiation by CIA bands of CO\textsubscript{2}. Consequently, we replaced our old CO\textsubscript{2} CIA parameterization with the one described in Wordsworth et al (2010a). CO\textsubscript{2} CIA becomes significant at higher pressures and consists of two separate effects: 1) close collisions between CO\textsubscript{2} molecules that induce temporary dipoles, and 2) colliding molecules that form CO\textsubscript{2}-CO\textsubscript{2} dimers. These two phenomena result in the creation of new absorption bands (Gruszka & Borysow 1997, Borysow & Gruszka 1998, Baranov et al 2004). Our revised parameterization (hereafter, GBB after ref. 64 (Wordsworth et al 2010a)) computes the optical depth (τ\textsubscript{CO\textsubscript{2}}) from the following formula:

\[
\tau_{\text{CO}_2} = C_i \frac{n}{n_o} W_{\text{CO}_2} \tag{1}
\]

Here \(C_i\) is a constant (see below) with units of amagat\textsuperscript{-2} cm\textsuperscript{-1}, \(n\) is the number density, \(n_o\) is Loschmidt’s number (2.685x10\textsuperscript{19} molecules per cm\textsuperscript{3}-atm), and \(W_{\text{CO}_2}\) is the CO\textsubscript{2} pathlength in atm-cm. The quantity \(\frac{n}{n_o}\) is amagats.

The new CO\textsubscript{2}-CO\textsubscript{2} collision-induced absorption coefficients, \(C_i\), used in eq. (1) are tabulated in Appendix C. Within the 0-495 cm\textsuperscript{-1} spectral region we replaced the calculated values at 150 K with those at 200 K. We did this because the model of Gruszka and
Borysow (1997) may be unreliable below ~200 K. However, because the pressures associated with such temperatures are very small for the planets we work on, such as early Mars, collisions should be very infrequent. Thus, CIA is unimportant at these lower temperatures and our results are insensitive to the absorption coefficient values at \( T = 150 \) K.

3) We also incorporated near-IR CO\(_2\) CIA from the 1.2 \( \mu \)m, 1.73 \( \mu \)m, and 2.3 \( \mu \)m regions using tabulated values from previous Venusian studies (Brodbeck et al 1991, Pollack et al 1993, De Bergh et al 1995, Tsang et al 2008). The temperature dependence of near-IR CO\(_2\) CIA is difficult to measure experimentally and the values are poorly known. However, as the resultant optical depths were of order \( 10^{-4} \) to \( 10^{-3} \), these bands had only a small effect on our simulations.

4) The Shomate Equation (http://www.vscht.cz/fch/cz/pomucky/fchab/Shomate.html) was used to calculate new heat capacity relationships for CO\(_2\), H\(_2\), and H\(_2\)O. Notably, at low temperatures, \( c_p \) for CO\(_2\) decreased by ~30% relative to values in our previous model. This increased the dry adiabatic lapse rate, \( g/c_p \), by an equivalent amount but had surprisingly little effect on computed surface temperatures, apparently because the steeper lapse rate in the upper troposphere was largely compensated by a decrease in tropopause height. (As mentioned earlier, our model assumes a moist adiabatic lapse rate, but this relaxes to a dry adiabat in regions where CO\(_2\) is not condensing and where H\(_2\)O is scarce.)

5) Previous 1-D calculations (Kasting & Ackerman 1986, Kasting 1988, Kasting et al 1993) had assumed that H\(_2\)O scattered as well as terrestrial air does because scattering cross sections for H\(_2\)O were not yet available. However, recent work (von Paris et al 2010, Kopparapu et al 2013, Goldblatt et al 2013) have utilized new data demonstrating that water only scatters about 80% as well as that of air (Edlén 1966, Bucholtz 1995, von Paris et al 2010). Thus, any significant differences here would impact solar absorption as well. We adopted the following expression for H\(_2\)O Rayleigh scattering cross sections (Vardavas & Carver 1984, Allen & Cox 2000, von Paris et al 2010):

\[
\sigma(\lambda) = 4.577 \times 10^{-21} \left( \frac{6+3D}{6-7D} \right) \frac{r^2}{\lambda^4} \text{cm}^2
\]  

Here, \( D \) is the depolarization ratio (0.17 for H\(_2\)O from Marshall and Smith (1990)); \( r \) is the wavelength (\( \lambda \))-dependent refractive index, calculated as \( r = 0.85 r_{\text{dryair}} \) from Edlén (1966); \( r_{\text{dryair}} \) is obtained from eq.(4) of Bucholtz (1995); and \( \lambda \) is in microns.

For planets like Earth or Mars, updating the Rayleigh scattering in this manner has a negligible effect because H\(_2\)O is always a minor constituent in these calculations. But the
effect of this change on a warm, moist atmosphere would be significant, as the coefficient for H₂O is about 80% that of air as mentioned above.

6) The method by which volume mixing ratios are specified in the model has been completely redone. Now, the non-condensable species (i.e., N₂, O₂, Ar, and CH₄) are treated separately from the condensable ones (CO₂ and H₂O) so that the mixing ratios of all gases always add up to 1. The true volume mixing ratio of any noncondensable (F_{dry}) can then be computed by F_{dry} = (1 - F_{con})f_{dry}. Here, f_{dry} is species volume mixing ratio of the noncondensable species with respect to the remaining noncondensables and F_{con} is the true condensable volume mixing ratio. This allows the model to treat mixing ratios correctly for a wide spectrum of atmospheric compositions ranging from CO₂-rich to H₂O-rich planets.

7) Our new model now incorporates the decrease of gravity with altitude, which tends to slightly decrease thermal infrared emission, because as the gravity decreases, the optical depth from the surface to a given pressure level increases. This effect is more pronounced for smaller planets such as Mars (Ramirez et al 2013).
3. HABITABLE ZONES AROUND MAIN SEQUENCE STARS: NEW ESTIMATES

3.1 Summary of Ph.D. candidate contributions to Kopparapu et al. (2013)

The first author (Ravi kumar Kopparapu) and I contributed equally to the work in Kopparapu et al. (2013). Ravi initiated the project, installed KSPECTRUM, helped me debug the climate model, and wrote the paper while I performed the background research, wrote a program that produces the \( k \)-coefficients, suggested new ideas, implemented over half of the climate model updates, and, with Ravi, produced that paper’s results, figures, and tables. Together we also generated the CO\(_2\) and H\(_2\)O spectra upon which our model’s \( k \)-coefficients are currently based. Because of both my high involvement in this paper and its high relevance to my two other first-authored papers, the work in Kopparapu et al. (2013) is appropriate for inclusion into my Ph.D. thesis.

3.2 Individual author contributions to Kopparapu et al. (2013)

Ravi kumar Kopparapu initiated the project after discussions with Suvrath Mahadevan, Rohit Desphonde, and Ryan Terrien. Jim Kasting and Ramses Ramirez (with the help of a summer student) updated the model to allow for the averaging of multiple solar zenith angles. Jim Kasting, Ramses Ramirez, and Ravi Kopparapu reformulated how mixing ratios are treated in the climate model. Ramses Ramirez investigated the available line-by-line (LBL) absorption spectra programs and suggested using KSPECTRUM, which was provided by Vincent Eymet. Ravi kumar Kopparapu installed KSPECTRUM on the Penn State High Performance Cluster. After researching the pros and cons between mixed and separate \( k \)-coefficients, Ramses Ramirez opted for the use of separate coefficients. Ramses Ramirez and Ravi kumar Kopparapu updated the climate model with water vapor Rayleigh scattering. Ramses Ramirez used the Shomate Equation to update the heat capacity relationships of CO\(_2\) and H\(_2\)O as used in the climate model. Ramses Ramirez and Ravi kumar Kopparapu used KSPECTRUM to generate LBL spectra for CO\(_2\) and H\(_2\)O. Ramses Ramirez learned the \( k \)-distribution method and wrote a \( k \)-distribution program that converts the LBL spectra into \( k \)-coefficients. Using this program, Ramses Ramirez employed a 0.95 double gaussian integration scheme and converted the LBL spectra into \( k \)-coefficients. Ramses Ramirez added the \( k \)-coefficients to the climate model, with Ravi kumar Kopparapu and Ramses Ramirez debugging. Ramses Ramirez reprocessed the BT_SETTL data to our climate model resolution and updated the climate model with stellar spectra for F-M main-sequence stars. Ramses Ramirez read the current literature on the water vapor continuum and compared various parameterizations (BPS, MT-CKD, and Roberts et al., 1976), before inputting BPS into the climate model. Ramses Ramirez and
Tyler Robinson co-lead and co-organized the flux comparisons of our climate model with SMART. Ramses Ramirez updated the climate model with an altitude dependence on gravity. Ramses Ramirez fixed bugs with the model, including recomputing the CO$_2$ absorption cross sections after finding and correcting a bug with KSPECTRUM. Ramses Ramirez and Ravi kumar Kopparapu computed the inner and outer edge boundaries and produced the main plots for the paper. Ravi kumar Kopparapu derived the S$_{\text{eff}}$ parameterizations for F-M main-sequence stars. Ravi kumar Kopparapu wrote the paper. Jim Kasting provided overall guidance on the project. All authors contributed to both analyzing the data and proof-reading the various iterations of the paper.

3.3 About Chapter 3 and Kopparapu et al. (2013)

Although the material presented in this chapter is based on the work in Kopparapu et al. (2013), I have rewritten that paper and incorporated the latest scientific developments, updated all of the original calculations, clarified some aspects, and presented completely new calculations that were not described in Kopparapu et al. (2013).

3.4 Introduction

The habitable zone (HZ) is the circumstellar region around a star in which liquid water can remain stable on a planetary surface (Kasting et al 1993). The bounds of the HZ are calculated based on assumptions of Earth’s atmospheric composition, its position in the solar system, and the amount of radiant energy it receives from the Sun. Due to the importance of liquid H$_2$O for both the emergence and maintenance of life on Earth, the HZ is believed to be vital in guiding the design of telescopes capable of detecting extraterrestrial life on extrasolar planets.

The HZ limits were originally computed using 1-D radiative-convective, cloud-free climate model calculations by Kasting et al (1993). For our Sun, these authors estimated the boundaries of the HZ to be 0.95 AU for the inner edge (IE) and 1.67 AU for the outer edge (OE). These values represent the “water loss” and “maximum greenhouse” limits, respectively. Other, less conservative limits for the IE are the “runaway greenhouse (0.84 AU)” and “recent Venus limits (0.72 AU).” The latter estimate is empirical, based on the inference that Venus has not had liquid water on its surface for at least 1 billion years (Solomon & Head 1991). The OE, in contrast, is defined by the maximum greenhouse effect of CO$_2$. This limit is characterized by global condensation of CO$_2$ in a 1-D climate model or by polar condensation in a more realistic 3-D model. As mentioned in Section 1, the solar flux at the empirical early Mars limit (1.77 AU)$^1$, corresponds to the flux received

$^1$ All of these limits are computed using the following expression relating distance (d), effective solar flux ($S_{\text{eff}}$), and the ratio of stellar to solar luminosities ($L/L_\odot$): $d (\text{in AU}) = \sqrt{\frac{L}{L_\odot}} \sqrt{\frac{S_{\text{eff}}}{S_\odot}}$
by Mars 3.8 billion years ago, when the planet is inferred to have had a warm and wet climate. Furthermore, the first CO$_2$ condensation limit, as originally defined in Kasting et al (1993), can now be safely disregarded as it has been determined that CO$_2$ ice clouds generally warm the climate (Forget & Pierrehumbert 1997, Forget et al 2012).

The *Kepler* spacecraft, launched by NASA on March 7, 2009, was the first space observatory designed to discover Earth-like planets orbiting other stars. In its mission, the telescope has been a resounding success. As of July 2013, *Kepler* had found 134 confirmed exoplanets in 76 stellar systems, along with a further 3,277 unconfirmed planet candidates (Wall 2013, Batalha et al 2013). (“Confirmed” means that the existence of the planet has been verified by ground-based radial velocity (RV) measurements.)

One of the primary goals of Kepler is to determine $\eta_\oplus$, which is a fraction between 0 and 1, is the frequency of Earth-like$^2$ planets in and near the HZ of solar-type stars (Lunine et al 2008, Borucki et al 2011). Typically, both RV and *Kepler* data are used for $\eta_\oplus$ estimates (Bonfils et al 2011, Dressing & Charbonneau 2013). Other studies have attempted to estimate the occurrence of rocky terrestrial planets and determined that planetary frequency increases towards smaller, less massive planets (Howard et al 2010, Mayor et al 2011, Howard et al 2012, Swift et al 2012). In order to estimate $\eta_\oplus$, one must know the boundaries of the HZ. However, differences in HZ boundary definitions can give inaccurate values of $\eta_\oplus$. Recently, Dressing and Charbonneau (2013) calculated a value for $\eta_\oplus = 0.15^{+0.13}_{-0.06}$ for M-stars from the first year and a half of *Kepler* data (where the +/- values represent the error bars). However, as pointed out by our group (Kopparapu 2013, Kasting et al 2013), their analysis used the Kasting et al (1993) moist greenhouse and the first condensation limits of CO$_2$, the latter as discussed earlier, is no longer valid. Moreover, only planets up to 1.4 Earth radii were included in their analysis, although planets as large as 2 Earth radii can be potentially rocky. Using the same dataset, Kopparapu (2013) repeated the Dressing and Charbonneau (2013) analysis but instead applied the new HZ limits (Kopparapu et al 2013), and depending on the assumptions used, $\eta_\oplus$ ranged from $0.48^{+0.12}_{-0.24}$ to $0.61^{+0.07}_{-0.15}$. Other estimates also seem to converge on values of $\eta_\oplus$ of $\approx 0.4$ - 0.5 for M-stars (Bonfils et al 2013).

In November 2013, Petigura et al (2013) computed $\eta_\oplus$ to be $\approx 0.22$ for Sun-like stars. With roughly 100 billion stars in our galaxy, there could be as many as 22 billion other Earth-like planets within the Milky Way (Kasting & Harman 2013). However, as with the

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$^2$Here, we define *Earth-like* as a rocky planet (0.3 – 10 M$_\oplus$) located within the HZ, that has a substantial water inventory, including vast oceans, with an atmospheric composition predominantly consisting of N$_2$, with CO$_2$ and H$_2$O as the main greenhouse gases.
Dressing and Charbonneau (2013) analysis, Petigura et al (2013) redefined the HZ limits as extending from 0.5 – 2 AU around a Sun-type star. The 0.5 AU inner edge limit was obtained by averaging the recent Venus limit of Kopparapu et al (2013) with the 0.38 AU determined by Zsom et al (2013), which is demonstrably incorrect due to surface energy balance issues (Kasting et al 2013). Thus, the true inner edge of the HZ must lie farther out. The best theoretical estimate may come from a new paper by Leconte et al (2013). These authors used a 3D GCM (general circulation model) to compute an inner edge value for our solar system of 0.95 AU. Fortuitously, their estimate agrees with the moist greenhouse limit originally obtained by Kasting et al (1993). More importantly, if correct, this HZ boundary dramatically decreases the size of the Petigura et al (2013) HZ and should roughly halve their estimate of $\eta_\oplus$ from 0.22 to 0.1 (Kasting & Harman 2013). As the $\eta_\oplus$ story continues to evolve, it will become increasingly important to refine the HZ boundaries for future missions attempting to discover potentially habitable planets around other stars.

This section updates the HZ boundaries for F-M main sequence stars originally computed in Kopparapu et al. (2013) in two major ways. 1) An error in how KSPECTRUM generated the thermal infrared H$_2$O coefficients has been corrected. This correction increases water vapor absorption slightly, which moves the previously computed inner edge limits slightly farther away from their stars. 2) The original analysis averaged their calculations over 6 solar zenith angles (11°, 25.3°, 39.6°, 54°, 68.4°, ad 82.8°) to increase accuracy in terrestrial wavelengths, resulting in slightly increased solar absorption. However, the thesis author now believes it was inconsistent to use extra zenith angles at solar wavelengths without implementing the same approach in the thermal infrared. Thus, for consistency, these new HZ calculations have been computed with just one zenith angle across all wavelengths. The decision to do so, however, did not have a large impact on the computed HZ boundaries.

3.5 Methods

For a detailed description of the climate model see Section 2. Following similar calculations done by our group (Kasting et al 1993; Kopparapu et al 2013), we assumed an Earth-mass planet with either a CO$_2$-dominated (OE) or H$_2$O-dominated (IE) atmosphere for all of our calculations. As was done in Kasting et al (1993), the atmospheric composition of our Earth analogue is 1 bar of N$_2$ with 330 ppm CO$_2$. In our model, 330 ppm equates to an isolated CO$_2$ pressure of 5x10$^{-4}$ bar (Appendix E1). (One has to be careful because Dalton’s law assumes that total atmospheric pressure is the sum of the individual partial pressures. In reality, the partial pressure of any individual atmospheric gas depends on the pressures of the remaining gases.) Unless otherwise specified, our
computations use the inverse calculation procedure of Kasting et al (1993), which computes the solar flux required to maintain a specified surface temperature. A specific temperature-pressure profile was assumed for the 100 layer atmosphere. For the IE, the moist pseudoadiabat extended from the surface up to an isothermal 200 K stratospheric temperature. At temperatures above the critical point, this moist convective region was underlain by a dry adiabat. The surface temperature was gradually incremented (average step size: 200 K) from 200 K to 2200 K, which simulates pushing the planet closer and closer to its star.

For the OE, the surface temperature was fixed at 273 K and the CO$_2$ partial pressure was varied from 1x10$^{-2}$ bar to 37.8 bar (the saturation CO$_2$ partial pressure at 273 K). The stratospheric temperature was chosen by determining the altitude where the ratio of saturation vapor pressure to ambient pressure is equal to unity for a model Mars atmosphere representative of an OE planet. That height marks the onset of CO$_2$ condensation and the associated temperature was computed to be 154 K. The temperature profile above that altitude was replaced with a constant temperature of 154 K. This then allows the computation of the solar flux required to maintain a global mean surface temperature of 273 K. A moist CO$_2$ adiabat was followed in the upper troposphere when condensation occurred, following Appendix B of Kasting (1991). The effective fluxes incident on the planet ($S_{eff}$) are calculated for the stellar effective temperature ($T_{eff}$) in steps of 200 K from 2600 K to 7200 K. For both sets of calculations, the surface albedo was tuned to 0.315 for present Earth (see Section 2).

We have also included the following updates in addition to those described in Section 2:

We used the Bt_Settl class of models as input high resolution stellar spectra into our climate model (Allard et al 2003, Allard et al 2007), using appropriate solar abundances (Asplund et al 2009). Solar gravity and metallicity were also assumed for all stars. These data span the appropriate range of stellar effective temperatures (2600 K $\leq T_{eff} \leq$ 7200 K), corresponding approximately to stellar classes F0 to M9. This wide $T_{eff}$ range addresses the criticism that the Kasting et al. (1993) model did not include M stars with effective temperatures lower than 3700 K (Section 1). Stellar effective temperature affects the HZ boundaries because the radiation from F stars is bluer relative to that from the Sun, whereas the radiation from K and M stars is redder, and this alters calculated planetary albedos.

Our model includes CH$_4$-CH$_4$ and N$_2$-N$_2$ CIA (Richard et al 2012). Unlike the CO$_2$-CO$_2$ and N$_2$-H$_2$ CIA described in Chapter 4, the forcing from these two CIA mechanisms is

http://perso.ens-lyon.fr/france.allard/
negligible. Their corresponding optical depth expressions take the same form as the $H_2-H_2$ CIA in Section 4.7.

### 3.6 Gliese 581d comparison against previous studies

Before calculating the revised HZ limits we first compare our model’s CO$_2$-H$_2$O absorption against that of recent calculations by other groups for a dense CO$_2$-H$_2$O exoplanetary atmosphere. Gliese 581d is chosen for this comparison because several studies have claimed it to be the first exoplanet in the habitable zone (Wordsworth et al 2010b, von Paris et al 2010, Wordsworth et al 2011, Kaltenegger et al 2011, Hu & Ding 2011). Here, we compare our 1-D fully-saturated results against those of Wordsworth et al (2010b) because their simulation spans the low- to high-temperature regime. Following Wordsworth et al (2010b) we used a surface albedo of 0.2, a surface gravity of 20 m/s$^2$, and a globally-averaged stellar flux ($S_o$) of 381.4 W/m$^2$ incident at the location of Gliese 581d. Gliese 581d has a highly eccentric orbit ($e = 0.38$), which increases the global- and orbital-averaged flux from 95.4 W/m$^2$ ($S_o/4$) to 103.1 W/m$^2$ (~30.3% that received by Earth), computed from the following expression by Williams and Pollard (2002):

$$S_m = \frac{S_o}{4\sqrt{1-e^2}}$$

Here, $S_m$ is the global- and orbital-averaged flux for an eccentric orbit. We used an original Gliese 581d spectrum ($T_{\text{eff}} = 3480$ K) provided by Lucianne Walkowicz from Princeton University. In this model simulation, the CO$_2$ partial pressure ($p_{CO_2}$) was raised incrementally from 0.001 bar to 20 bar (Fig. 3.1). Both models require ~ 5.6 bar of CO$_2$ to reach the freezing point of water. Overall, the agreement between the two models is very good up to ~8 bar. As predicted in Wordsworth et al (2010b), their neglect of the effects of moist condensation on the lapse rate will cause surface temperatures to be overestimated at the highest pressures. This lends confidence in our model, which computes somewhat lower temperatures for P > ~8 bar. Surface temperatures should be lower at those highest pressures because the net flux absorbed decreases as the lapse rate decreases, as can be demonstrated mathematically through the integral form of Schwarzschild’s equation (Appendix E3). In any case, a freezing point $p_{CO_2}$ value of 5.6 bar is considerably lower than the ~7 bar computed in previous studies (Hu & Ding 2011, Kaltenegger et al 2011). These studies employed a previous version of our climate model with older CO$_2$ coefficients (HITRAN 1996) derived at short truncation distances (Rothman et al 2009). Wordsworth et al (2010a) show that paleoclimate studies that assume shorter CO$_2$ line truncation distances (i.e. < 25 cm$^{-1}$) underestimate the greenhouse effect at elevated pressures. Moreover, Kaltenegger et al (2011) used a spectrum with a higher effective temperature (3600 K) than that of other investigations, which would have
resulted in a higher planetary albedo and lower mean surface temperature. Radiative flux comparisons versus our model for a wide range of atmospheric compositions are given in Appendix A.

**Figure 3.1:** Surface temperature as a function of surface pressure for Gliese 581d ($S/S_0 = 0.303$) comparing our model (blue solid line) versus that of Wordsworth et al (2010b) for a fully-saturated CO$_2$ atmosphere. The assumed surface albedo is 0.2.
3.7 The inner edge of the habitable zone for our solar system

The inner edge (IE) computation is akin to pushing the planet closer and closer to its star until temperatures become too warm, triggering either a moist or runaway greenhouse (explained below). The inverse calculations used to calculate the IE are described in Section 3.5.

The calculated net radiative top-of-atmosphere (TOA) fluxes versus surface temperature for our Earth analogue are given in Figure 3.2. As surface temperatures increase, so does atmospheric H₂O, which causes an initial rise in both the net outgoing infrared flux (F_{IR}) and net absorbed solar flux at the TOA (F_{S})(Figure 3.2). Above surface temperatures exceeding ~ 400 K, F_{IR} converges to an asymptotic limit of ~280 W/m² and the atmosphere becomes opaque at infrared wavelengths (Kasting 1988, Nakajima et al. 1992, Kasting et al. 1993). This value of 280 W/m² is 11 W/m² lower than that computed in Kopparapu et al. (2013) due to an error found in our LBL spectra. This is also 2 W/m² lower than that computed by Goldblatt et al. (2013), who assumed a higher solar flux (1372 W/m²), resulting in slightly higher emission. As shown in Chapter 5, we obtain the Goldblatt et al. (2013) value when the higher solar flux is used.
Figure 3.2: Net absorbed solar ($F_S$) and net outgoing infrared ($F_{IR}$) fluxes at the top of the atmosphere (TOA) versus surface temperature for an Earth-like planet around the Sun. The water-loss (moist greenhouse) and runaway greenhouse limits are computed to be at 1.01 AU and 0.99 AU, respectively. The corresponding estimates from the Kasting et al (1993) climate model are 0.84 AU and 0.95 AU, respectively.

The atmosphere remains opaque until about 1500 K, above which $F_{IR}$ increases again because the underlying dry adiabat achieves high enough altitudes that emission in spectral regions (< 4 $\mu$m) where the water vapor opacity is low becomes substantial (Figs. 3.3-3.4). The relatively high emission at ~ 10 $\mu$m for the 300 K case is due to the high mole fraction of $N_2$, a very weak greenhouse gas. At higher surface temperatures, the mole fraction of $N_2$ (and CO$_2$) dramatically decreases and absorption approaches that of a pure-H$_2$O atmosphere.
Figure 3.3: Temperature profiles for (a) 300 K (blue dashed curve), (b) 1000 K (green circles), and (c) 2000 K (red dashed curve) surface temperatures illustrating the moist adiabatic (M), dry adiabatic (D), and stratospheric regions (S).

Figure 3.4: Outgoing longwave radiances (OLR) for the three surface temperatures in Figure 3.3.
As with $F_{IR}$, $F_S$ also increases initially. However, above ~ 400 K, the H$_2$O mole fraction becomes high enough for significant H$_2$O Rayleigh scattering to occur, leading to a reduction in $F_S$ (Fig. 3.2). These trends can also be understood in terms of the planetary albedo$^4$ ($A_p$), as it exhibits opposite behavior to that of $F_S$ (Kasting et al 1993). At higher surface temperatures, increased solar absorption is related to a reduction of $A_p$ down to a minimum value of ~0.167 at 400 K (Fig. 3.5). Rayleigh scattering increases $A_p$ to a maximum value of ~0.187 before reaching the asymptotic result of ~0.172 at temperatures exceeding 2000 K.

![Figure 3.5](image.png)

**Figure 3.5:** Planetary albedo as a function of surface temperature for an Earth-like planet around the Sun.

The IE can then be computed by determining the equivalent stellar flux ($S_{\text{eff}}$) that corresponds to each of the computed limits. As explained elsewhere (Kasting et al 1993; Kopparapu et al 2013), the effective flux $S_{\text{eff}}$, is the ratio of $F_{IR}$ to $F_S$. When $S_{\text{eff}}$ is 1, a planet is in radiative-energy balance. A lower $S_{\text{eff}}$ means that the planet must move

$^4$ The planetary albedo is the ratio of the reflected portion of the incident radiation to the total incident radiation at the top of the atmosphere (TOA).
outward to satisfy radiative-energy balance. Likewise, a higher $S_{\text{eff}}$ requires that the planet moves inward to satisfy radiative-energy balance.

The tropopause, which is defined for our purposes as the top of the convective layer, moves up from 10 km to 100 km as $T_s$ increases from 280 to 380 K in 20 K step sizes (Fig. 3.6). (We assume an isothermal stratosphere when doing inverse calculations, so this definition of the tropopause is more useful than the usual definition, which is that it represents the temperature minimum.) During this transition, fH$_2$O in the stratosphere, which is the vertical region above the tropopause, increases from $\sim 10^{-5}$ to $\sim 1$ (Fig. 3.6). The moist greenhouse (or water-loss) limit is encountered at 340 K, corresponding to a rapid increase in stratospheric fH$_2$O content. As Ingersoll (1969) has shown, the cold trapping of water vapor at the tropopause becomes inefficient once tropospheric water vapor concentrations exceed $\sim 20\%$, leading to a quickly growing convective region as surface temperatures continue to rise. At these high altitudes, photolysis reactions break apart the H$_2$O molecules into H and OH radicals, with H being light enough to easily escape into space. At these moderately high H$_2$O concentrations, hydrogen escape is diffusion-limited$^5$, that is it depends on how quickly hydrogen in all its forms (H$_2$O, CH$_4$, H$_2$ etc.) can diffuse across the homopause, the critical level below which the atmosphere is well-mixed. The diffusion-limited escape rate ($\Phi_H$) for H atoms can be expressed as (Walker 1977, Kasting et al 1993):

$$\Phi_H = \frac{b_i}{H_a} \cdot \frac{f_{\text{tot}}(\text{H}_2)}{1 + f_{\text{tot}}(\text{H}_2)} \approx \frac{b_i f_{\text{tot}}(\text{H})}{H_a} \text{ cm}^{-2}\text{ sec}^{-1}$$

Here, $b_i$ is a weighted molecular diffusion coefficient for H and H$_2$ against the background gas (e.g., air), $H_a (= kT/mg)$ is the pressure scale height, and $f_{\text{tot}}(\text{H})$ is the total hydrogen mixing ratio in all its forms: $f_{\text{tot}}(\text{H}) = f(\text{H}) + 2 f(\text{H}_2) + 2 f(\text{H}_2\text{O}) + ...$ Hydrogen in these warm, moist atmospheres is predominantly in the form of H$_2$O, so $f_{\text{tot}}(\text{H}) \approx 2 f(\text{H}_2\text{O})$ in this case. The ratio $b_i/H_a$ is approximately $2 \times 10^{13}$ cm$^2$s$^{-1}$ for the Earth, and should vary by no more than a factor of 2 or 3 for most Earth-like planets (Kasting et al 1993). At 340 K, stratospheric fH$_2$O is $\sim 0.3\%$ and the corresponding $S_{\text{eff}}$ is 0.993. At these concentrations, the total volume of Earth’s oceans (2x10$^{28}$ H atoms cm$^{-2}$) is lost in $\sim 4 - 5$ Ga, corresponding to the age of the solar system (although loss is even faster at higher stratospheric fH$_2$O). The corresponding water-loss limit occurs at $d = 1/ S_{\text{eff}}^{0.5} = 1.01$ AU. Thus, under the assumption of a fully-saturated atmosphere and no negative cloud

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$^5$ At still much higher fH$_2$O concentrations than those exhibited at the moist greenhouse, escape becomes energy-limited. That is, it depends on how quickly chemical reactions proceed in converting hydrogen in all its forms (H$_2$, CH$_4$, H$_2$O, etc) into H$_2$. 21
feedback, present Earth would be in a moist greenhouse regime (but see below for further discussion of the moist greenhouse limit).

Figure 3.6: Water vapor profiles for an Earth-like planet around the Sun.

The second IE limit is the runaway greenhouse limit, which occurs once the surface temperature exceeds the critical point of water (647 K). At this point, a planet’s entire water inventory resides in the atmosphere and is lost to space on extremely short timescales.

The value of $S_{\text{eff}}$ at 647 K is $\sim 1.01$, corresponding to a distance of 0.99 AU (Fig. 3.7). Unlike the original study conducted by Kasting et al (1993), which found a large gap in $S_{\text{eff}}$ between the two IE limits, less than 2% $S_{\text{eff}}$ separates the runaway and moist greenhouse thresholds computed here, as the extra absorption from HIThEM has diminished the distinction between the two limits. At this point, the astute reader will realize that Earth should currently be undergoing a moist greenhouse if these limits were correct, which is obviously not the case. This discrepancy is related to the oversimplifying assumptions used in the 1-D model (explained in greater detail in Section 3.13).

A recent 3-D GCM analysis by Leconte et al (2013) computes a runaway greenhouse limit for our solar system at 0.95 AU. These authors also argue that a separate moist greenhouse should not be encountered because the tropopause temperature is likely to be well below 200 K, thereby limiting the abundance of H$_2$O at high altitudes. The Leconte et al limit is clearly a better estimate than our own 1-D inner edge calculations (Kasting et al 1993, Kopparapu et al 2013) because their 3-D model self-consistently computes the
effects of sub-saturation and clouds. Thus, the Leconte et al limit is taken to be the new conservative inner edge limit and is extrapolated accordingly to other stars in Section 3.11.

Two empirical limits on the habitable zone inner edge can be defined in addition to this Leconte et al limit. As mentioned in Section 3.4, the recent Venus limit is based on the inference that the Venusian atmosphere has not had water on its surface for at least 1 Ga (Kasting et al 1993). At 1 Ga, the solar luminosity was \( \sim 92\% \) that of present according to standard solar evolutionary models (Gough 1981). The flux at Venus' orbit today is 1.92 times the flux received at Earth’s orbit. Thus, the flux at Venus' orbit 1 Gya was 0.92 x 1.92 = 1.76 times that of present day. The corresponding orbital distance with today’s solar luminosity is then \( d = 1/1.76^{0.5} = 0.75 \) AU, slightly farther than the location of Venus (0.72 AU). However, a recent paper has cogently argued that Venus may have actually lost its water during the magma ocean stage (Hamano et al 2013), suggesting that planets that received this amount of stellar flux may become uninhabitable. This ‘early Venus limit’\(^6\) would be computed at \( \sim 4.56 \) Ga, when solar luminosity was \( \sim 70\% \) that of today. The effective solar flux at Venus' orbit at that time was 0.7x1.92 = 1.35, corresponding to an orbital distance today of \( d = 1/1.35^{0.5} = 0.86 \) AU. Should the Hamano et al (2013) analysis be correct, the empirical HZ would shrink in size by only \( \sim 0.1 \) AU, leaving it still relatively wide.

\(^6\) The early Venus limit is valid so long that the curve \( F_{IR} \) (Fig 3.2) does not have a large bump right before it asymptotes. If it does, the critical flux at the peak of the bump is greater than that at the runaway trigger point \( (F_s = F_{as}) \), making it impossible to accurately determine the runaway point.
3.8 Sensitivity of HITEMP and HITRAN to surface temperatures

Although HITEMP has ~ 2000 times as many lines as does HITRAN 2008, our tests revealed that the solar absorption from those additional lines is negligible for temperatures up to ~360 K (Fig. 3.8-3.9). However, atmospheric path lengths become large enough at even higher temperatures that absorption from weaker lines becomes substantial. At 373 K, the partial pressure of water ($p_{H_2O}$) is ~ 1 bar, whereas at 647 K, $p_{H_2O}$ is ~220 bar. The self-broadened water vapor optical depth (τ) is $\propto p_{H_2O}^3$, so optical depths at the critical point are ~ 5 orders of magnitude larger than those at 373 K, resulting in large opacities even for the weakest lines. Nevertheless, HITRAN’s relatively smaller line population density also allows the continuum to impact it to a greater extent than it does HITEMP (Fig. 3.8 – 3.9).
3.9 Sensitivity of computed habitable zone limits to the H$_2$O continuum

The Baranov-Paynter-Serio (BPS) continuum of Paynter and Ramaswamy (2011) is largely based on absorption measurements of the far wings within the shortwave (2000 – 3000 cm$^{-1}$) and longwave (800 – 1200 cm$^{-1}$) window regions. Whereas this far wing absorption in these window regions is negligible for standard terrestrial conditions, its contribution becomes significant at elevated surface temperatures. Nevertheless, absorption in the 8 – 12 micron window region is strongest, decreasing outgoing longwave radiation by over 30% for $T_s > 400$ K. As a result, ignoring continuum absorption increases $S_{eq}$ and decreases the moist and runaway greenhouse distances to 0.9 and 0.82 AU, respectively. By turning the continuum off, infrared emission to space increases and Earth becomes colder. Thus, the planet needs to be pushed closer to the Sun and receive the additional flux it requires to achieve radiative-energy balance again.

Fig. 3.8: Net absorbed solar flux as a function of surface temperature comparing the HITEMP 2010 (red with circles) and HITRAN 2008 line lists (blue) with (solid) and without (dashed) the BPS continuum of Paynter and Ramaswamy (2011) for a fully-saturated 1-bar N$_2$ atmosphere containing 330 ppm CO$_2$. The assumed surface albedo is 0.306.
Fig. 3.9: Planetary albedo as a function of surface temperature comparing the HITEMP (red with circles) and HITRAN (blue) databases with (solid) and without (dashed) the BPS continuum of Paynter and Ramaswamy (2011) for the same atmospheric conditions as in Fig. 3.8.
Figure 3.10: Comparison of outgoing IR radiation ($F_{IR}$) from the top of the atmosphere with (solid) and without (dashed) the BPS water continuum (Paynter & Ramaswamy 2011). Continuum absorption in the 8 – 12 micron region decreases the outgoing IR at ~600 K from ~404 W/m$^2$ to 280 W/m$^2$. Unlike the case for solar wavelengths (Fig. 3.8 – 3.9), both HITRAN and HITEMP yield similar results in the thermal infrared.

3.10 The outer edge of the habitable zone for our solar system

The outer edge (OE) computation is akin to pushing a planet farther and farther away from its star, while incrementing CO$_2$, to determine its maximum distance before condensation and Rayleigh scattering effects outstrip the greenhouse effect and reduce temperatures to below freezing (described in Section 3.5). The underlying hypothesis is that atmospheric CO$_2$ should readily accumulate as the surface temperature drops from 288 K to 273 K, because the silicate weathering rate depends on temperature (Walker et al. 1981). This feedback should therefore extend the OE to farther distances than would be predicted in the absence of an active carbonate-silicate cycle. In our model, the outgoing infrared flux ($F_{IR}$) starts at ~116 W/m$^2$ at 1 bar $p$CO$_2$ and decreases to a constant value of ~67 W/m$^2$ at 10 bar $p$CO$_2$ as the atmosphere becomes opaque at all infrared wavelengths (Fig. 3.11a). In contrast, the net absorbed solar flux ($F_S$) decreases monotonically from 227 W/m$^2$ to 153 W/m$^2$ as Rayleigh scattering effects become more pronounced at higher $p$CO$_2$ levels (Fig. 3.11a). Likewise, the planetary albedo also increases from 0.33 to 0.55 over the same $p$CO$_2$ range due to the aforementioned Rayleigh scattering (Fig. 3.11b).
Dividing \( F_s \) into \( F_a \) produces a “bowl-shaped” \( S_{\text{eff}} \) curve with a minimum of \(-0.37\) at 8 bar \( p\text{CO}_2 \). To the left of the \( S_{\text{eff}} \) minimum, \( F_{\text{IR}} \) decreases faster than does \( F_S \), so the greenhouse effect continues to intensify until its maximum at 8 bar. In other words, as \( S_{\text{eff}} \) decreases the planet is too warm and needs to be pushed farther and farther from its star to equilibrate to a temperature of 273 K. To the right of this minimum, \( F_{\text{IR}} \) plateaus while \( F_S \) continues to decrease as the combined effects of Rayleigh scattering and \( \text{CO}_2 \) condensation exceed the greenhouse effect (Figs. 3.11a and c).

The corresponding OE distance is \( d = 1/0.37^{0.5} = 1.64 \) AU. This defines the maximum greenhouse limit on the OE. In comparison, Kasting et al (1993) obtained 1.67 AU for this limit. Thus, even though the new model uses a weaker \( \text{CO}_2 \) CIA parameterization (Gruszka & Borysow 1997, Borysow & Gruszka 1998, Baranov et al 2004), the longer \( \text{CO}_2 \) lineshapes currently employed (Section 2) replace most of this missing absorption, resulting in an essentially unchanged OE.

The equivalent empirical distance at the OE, termed the “early Mars” limit (Kasting et al. 1993), is computed from the supposition that Mars had a warm and wet climate at \(-3.8\) Ga based on the geological evidence (Craddock & Howard 2002). The solar flux received at Mars’ orbit today is \(-43\%\) that received by Earth. At 3.8 Ga, the flux was 75\% as strong, so \( S_{\text{eff}} = 0.75 \times 0.43 = 0.32 \). Thus, the equivalent distance with today’s solar luminosity is \( d = 1/0.32^{0.5} = 1.77 \) AU. For comparison, Mars is located at 1.52 AU. Thus, present Mars is well within both the calculated and empirical limits for the OE of the habitable zone.
Figure 3.11: Outer edge calculations for our solar system, shown as a function of CO$_2$ partial pressure ($p$CO$_2$): (a) net outgoing IR flux and net absorbed solar flux, (b) planetary albedo, and (c) effective solar flux ($S_{\text{eff}}$). The maximum greenhouse limit, where the atmosphere becomes opaque to outgoing IR radiation, is at 1.64 AU ($S_{\text{eff}} = 0.37$). This is almost the same as the 1.67 AU obtained by Kasting et al (1993).
Table 3.1: Calculated habitable zone distances in our solar system

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<td></td>
<td>Greenhouse</td>
<td>Venus</td>
<td>Venus</td>
<td>Greenhouse</td>
<td>Mars</td>
</tr>
<tr>
<td>This thesis</td>
<td>0.95 AU¹</td>
<td>0.75 AU</td>
<td>0.86 AU</td>
<td>1.64 AU</td>
<td>1.77 AU</td>
</tr>
<tr>
<td>Kopparapu</td>
<td>0.97 AU</td>
<td>0.75 AU</td>
<td>-</td>
<td>1.67 AU</td>
<td>1.77 AU</td>
</tr>
<tr>
<td>et al. (2013)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kasting et</td>
<td>0.84 AU</td>
<td>0.75 AU</td>
<td>-</td>
<td>1.67 AU</td>
<td>1.77 AU</td>
</tr>
<tr>
<td>al. (1993)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹This is the inner edge value computed by Leconte et al (2013) for our solar system

3.11 Habitable zones boundaries around main-sequence stars

The same procedure used to compute the HZ edges of the previous sections can be used to determine the corresponding HZ boundaries for stars of different spectral classes. Kasting et al (1993) had performed a similar analysis for 3 stars (Teff = 3700, 5700, and 7200 K) corresponding to the M0, G0, and F0 spectral classes. The results of that study were then parameterized to determine HZ distances across the F0 – M9 Teff range (Selsis et al 2007). Here, we compare our results to those of these studies while extending the range of spectra classes to ~F0 – M9. Extending the range of Teff to encompass late M-dwarfs answers the demand for increased observations in this spectral range, including missions such as Penn State’s upcoming fiber-fed near-infrared (NIR) spectrograph Habitable Zone Planet Finder (HZPF) (Mahadevan et al 2012) and the upcoming Transiting Exoplanet Survey Satellite (TESS). Furthermore, several rocky planets have already been found in the HZs of M-dwarfs (Bonfils et al 2011, Vogt et al 2012).

Stellar effective temperatures between 2600 K and 7200 K (M9 - F0) were analyzed in this study. Earlier stars than F0 were not considered because their main sequence lifetimes are probably too short (< 2 Ga) for the minimum amount of time speculated that is needed for the emergence of life (Kasting et al 1993). The “BT_Settl” grid of models were the high resolution input spectra used for our climate model (Allard et al 2003, Allard et al 2007). These were then averaged and binned into our 38 solar wavelength intervals (0.23 – 4.54 µm). As with the Earth calculations, the stellar fluxes were normalized to 1360 W/m², ensuring that all distances are scaled the same way as for our Sun.
Both the IE and OE results are shown for 5 stars with representative \( T_{\text{eff}} \) values (2600, 3800, 4800, 5800, and 7200 K) within the spectral range of interest (Figures 3.12). The planetary albedo is higher for stars with higher \( T_{\text{eff}} \) (e.g. F stars) than for those with lower \( T_{\text{eff}} \) (e.g. M stars; Fig. 3.12a and c), for two reasons: 1) Rayleigh scattering, which is proportional to \( 1/\lambda^4 \), is higher at shorter wavelengths. According to Wien’s Law (\( \lambda_{\text{max}} = 2896/T \)) a 7200 K F star emits its peak energy at \( \sim 0.4 \) \( \mu \)m whereas a 3000 K M star emits its peak energy closer to 1\( \mu \)m. (For comparison, the Sun emits its peak energy at \( \sim 0.5 \) \( \mu \)m.) Thus, F stars emit their peak energy at shorter wavelengths which are more likely to get scattered back to space. 2) Both H\(_2\)O and CO\(_2\) absorb more strongly at NIR wavelengths than in the visible (VIS), increasing the amount of starlight absorbed by planetary atmospheres for redder (lower \( T_{\text{eff}} \)) host stars. These two effects combine to large effect, with \( A_p \) for the 2600 K M-star planet asymptotically approaching zero at high surface temperatures (Fig. 3.12a and c).

As with the solar system calculation, \( S_{\text{eff}} \) for both the IE and OE can be computed by dividing the resulting \( F_{\text{IR}} \) values as a function of surface temperature by the corresponding values of \( F_s \) for each star (Figs. 3.12b and d). F-stars have the highest \( S_{\text{eff}} \) values whereas M-stars have the highest ones. Based on the arguments made in the previous paragraph, planets around F-stars are comparatively cooler for a given level of insolation and need to be pushed closer in to their stars to exhibit the same net absorption as planets around redder stars. As discussed earlier, the OE \( S_{\text{eff}} \) values reach a minimum value above which Rayleigh scattering and CO\(_2\) condensation effects combine to outstrip the greenhouse effect. In the case of the 2600 K M dwarf, however, Rayleigh scattering effects are negligible (Fig. 3.12 a and c), resulting in an asymptotically constant \( S_{\text{eff}} \) value.

To facilitate computation for future studies using these HZ boundaries, expressions for \( S_{\text{eff}} \) (effective stellar fluxes at the top of the atmosphere) as a function of \( T_{\text{eff}} \) have been derived for all empirical and computed HZ limits in the \( T_{\text{eff}} \) range between 2600 K and 7200 K. As stated in Section 3.7, the previously computed 1-D moist and runaway greenhouse limits for the IE have been superseded by the 3D calculations of Leconte et al (2013):

\[
S_{\text{eff}} = S_{\text{eff}\odot} + A T_s + B T_s^2 + C T_s^3 + D T_s^4
\]  \hspace{0.5cm} (5)

where \( T_s = T_{\text{eff}} - 5780 \) K, \( A, B, C, \) and \( D \) are derived constants tabulated in Table 3.2, and \( S_{\text{eff}\odot} \) is the \( S_{\text{eff}} \) value for the Sun. Thus, eqn. (5) is normalized so that inputting 5780 K for \( T_{\text{eff}} \) yields \( S_{\text{eff}} = S_{\text{eff}\odot} \). The corresponding HZ distances are calculated from the following equation:
\[ d = \left( \frac{L}{L_\odot} \right)^{1/2} \left( \frac{S}{S_{\text{eff}}^\theta} \right) \]  

(6)

where \( \frac{L}{L_\odot} \) is the stellar luminosity in solar units. These expressions are derived in detail in Appendix E2.

Table 3.2: Coefficients to be used in HZ parameterization expressed by eq. (5)

<table>
<thead>
<tr>
<th>Constant</th>
<th>Early Venus</th>
<th>Recent Venus</th>
<th>Leconte et al. limit</th>
<th>Maximum Greenhouse</th>
<th>Early Mars</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_{\text{eff}} )</td>
<td>1.3395</td>
<td>1.764</td>
<td>1.107</td>
<td>0.37</td>
<td>0.3251</td>
</tr>
<tr>
<td>A</td>
<td>1.6561x10^{-4}</td>
<td>1.5014x10^{-4}</td>
<td>1.369x10^{-4}</td>
<td>6.7571x10^{-5}</td>
<td>5.929x10^{-5}</td>
</tr>
<tr>
<td>B</td>
<td>1.9526x10^{-8}</td>
<td>5.0399x10^{-9}</td>
<td>1.6142x10^{-8}</td>
<td>2.0636x10^{-9}</td>
<td>1.8107x10^{-9}</td>
</tr>
<tr>
<td>C</td>
<td>-1.019x10^{-11}</td>
<td>-8.1413x10^{-12}</td>
<td>-8.4239x10^{-12}</td>
<td>-3.3046x10^{-12}</td>
<td>-2.9x10^{-12}</td>
</tr>
<tr>
<td>D</td>
<td>-2.3618x10^{-15}</td>
<td>-1.3524x10^{-15}</td>
<td>-1.9524x10^{-15}</td>
<td>-5.5421x10^{-16}</td>
<td>-4.863x10^{-16}</td>
</tr>
</tbody>
</table>
Surface Temperature (K)

- $T_{\text{eff}} = 2600$ K
- $T_{\text{eff}} = 3800$ K
- $T_{\text{eff}} = 4800$ K
- $T_{\text{eff}} = 5800$ K
- $T_{\text{eff}} = 7200$ K

Planetary albedo

- $T_{\text{eff}} = 2600$ K
- $T_{\text{eff}} = 3800$ K
- $T_{\text{eff}} = 4800$ K
- $T_{\text{eff}} = 5800$ K
- $T_{\text{eff}} = 7200$ K
Figure 3.12: Habitable zone calculations for stellar effective temperatures corresponding to F \( (T_{\text{eff}} = 7200 \text{ K}) \), G \( (T_{\text{eff}} = 5800 \text{ K}) \), K \( (T_{\text{eff}} = 4800 \text{ K and 3800 K}) \), and M \( (2600 \text{ K}) \) spectral types. Inner edge results are given in (a) and (b), whereas the outer edge computations are shown in (c) and (d), respectively.

In Fig. 3.13, eq. (5) is used to calculate the moist greenhouse and maximum greenhouse limits as function of both distance and \( S_{\text{eff}} \). The moist greenhouse limit computed here is compared to the new Leconte et al limit, which has been extrapolated to other stars by scaling according to the 1-D runaway greenhouse limit. Stellar evolutionary data from Baraffe et al (1998) for \( T_{\text{eff}} \) between 3700 and 6000 K were used as inputs to equations (2) and (3) of the Selsis et al (2007) parameterization. To obtain stellar fluxes between 6000 K and 7200 K, a line was drawn from the \( S_{\text{eff}} \) point at 6000 K to the \( S_{\text{eff}} \) value of 4.3 for an F0 (7200 K) from Kasting et al (1993).

Although both our model and that of Leconte et al (2013) utilized the HITTEMP database, the \( S_{\text{eff}} \) values at the IE are ~10% larger for the Leconte et al limit (Fig 3.13a), which means that planets are cooler, consistent with initiation of moist and runaway greenhouse scenarios closer to the star than suggested by our 1-D calculations.
Using eq.(6), the corresponding HZ distances as a function of stellar mass at 5 Ga for both parameterizations are shown in Fig. 3.13b. Stellar masses above 1.2 solar masses are not included because their lifetimes are shorter than 5 Ga. The large differences seen in the last figure with $S_{\text{eff}}$ do not seem as pronounced with respect to distance ($d$) because of the log scale and also because $d \propto 1/S_{\text{eff}}^{0.5}$ whereas $S_{\text{eff}} \propto 1/d^2$, which varies more quickly.

It is second nature among astronomers to characterize stars by their $T_{\text{eff}}$ because additional information, such as radii, can be easily computed through brightness measurements. As a result, recent studies have begun using $T_{\text{eff}}$ to assess the potential habitability of exoplanets (Borucki et al 2011, Batalha et al 2013). Using the most optimistic HZ limits, Kasting (2011) used planetary emissivity ($\varepsilon$) and $A_p$ values of 0.9 and 0.3, respectively, to solve the energy balance equation and determined that in terms of $T_{\text{eff}}$, the habitable zone limits for our solar system range between 185 K and 303 K, representing the computed planetary emission temperatures. We must stress, however, that stellar fluxes ($S_{\text{eff}}$) are a much better metric than $T_{\text{eff}}$ for assessing potential habitability of exoplanets. This is because the definition of $T_{\text{eff}}$ requires an assumption about $A_p$, which is usually taken to be 0.3, a value that is only valid for present Earth at 1 AU from the Sun. However, as we have demonstrated, $A_p$ should be a strong function of both planetary and stellar effective temperatures. For an Earth-like planet around the Sun, $A_p$ decreases to below 0.16 near the IE (Fig. 3.5) and increases to ~0.45 at the OE. For an M9 star, the corresponding $A_p$ values are ~0.02 and 0.12. The $A_p$ values for a planet around an F0 star are ~0.25 and 0.53, respectively. Planetary albedo, in turn, impacts $T_{\text{eff}}$ and so a self-consistent criterion for determining HZ boundaries cannot be specified in terms of $T_{\text{eff}}$. 
Figure 3.13: (a) Habitable zone fluxes and (b) corresponding distances from our model for different stellar effective temperatures. The inner HZ fluxes from our model (red dash line) for the moist greenhouse case are compared to the Leconte et al limit (red solid line). Outer edge fluxes (blue solid line) are calculated for the maximum greenhouse limit.
3.12 The effects of methane and hydrogen on the habitable zone

The baseline HZ calculations in Kopparapu et al. (2013) and Kasting et al. (1993) assume CO$_2$-H$_2$O atmospheres and do not include any other greenhouse gases. However, another greenhouse gas that may have implications for the HZ is H$_2$. Indeed, H$_2$ concentrations of 10-20% have been invoked to warm early Earth (Wordsworth & Pierrehumbert 2013a) and early Mars (Ramirez et al. 2013). Although H$_2$ may extend the OE, an H$_2$-rich Earth-sized planet located at 10 AU would have a contrast ratio with the Sun 100 times worse than that between the Earth and the Sun. For a Mars-sized planet, this contrast ratio worsens by nearly another factor of 4 because its radius is only half that of the Earth. Thus, such distant planets would pose a severe technological challenge for proposed flagship missions (i.e., TPF) to detect (Kasting et al. 2013).

Furthermore, it is unlikely that such H$_2$-rich atmospheres could persist once life originated because evolving methanogens would have consumed the H$_2$, forming CH$_4$ instead (Pavlov et al. 2000, Wordsworth & Pierrehumbert 2013a). This, then, raises a second question: Can high atmospheric CH$_4$ concentrations extend the outer edge of the HZ? To answer this question, we performed forward calculations with our 1-D climate model. In such a calculation, the solar flux is specified and the surface temperature at that flux is computed. Inverse calculations are inadequate for this application because CH$_4$ absorbs well in the upper atmosphere, invalidating the assumption of a fixed stratospheric temperature. Our methodology was as follows: We picked 4 representative stars from F-M spectral classes (2600 K, 4400 K, 5800 K, and 7200 K) and calculated the corresponding $S_{\text{eff}}$ needed to converge to a temperature of 273 K due to a gradual increase in $p$CO$_2$. We analyzed a span of mixing ratios ($1 \times 10^{-5}, 1 \times 10^{-4}, 1 \times 10^{-3}, 1 \times 10^{-2}$). We assumed that 1% fCH$_4$ is a reasonable upper limit for habitable planets, for two reasons: 1) Outgassing of H$_2$ needs to be balanced by escape to space, and atmospheric CH$_4$ contributes to the escape rate; and 2) CH$_4$ fluxes computed by Kharecha et al. (2005) based on a simple Archean biosphere model only support CH$_4$ concentrations up to about this level (Pavlov et al. 2000). Even higher CH$_4$ concentrations are theoretically possible, although organic haze is produced at CH$_4$/CO$_2$ ratios greater than ~0.1, generating an anti-greenhouse effect (Haqq-Misra et al. 2008).

Somewhat surprisingly, adding CH$_4$ to our model did not move the OE of the habitable zone farther out. Instead, increased CH$_4$ tends to cool the planet’s surface for two reasons. First, CH$_4$ only has only one strong thermal-infrared absorption feature at ~7.7 µm, which is located far from an Earth-like planet’s Wien peak, dampening its greenhouse efficacy (Wordsworth & Pierrehumbert 2013a). Second, near-infrared absorption in the upper atmosphere tends to oppose the greenhouse effect (Figs. 3.14 - 3.15). As upper atmospheric near-infrared absorption increases, so does heating, producing large stratospheric inversions that cool the planet’s surface in the case of M-stars (Fig. 3.15).
This anti-greenhouse effect is enhanced for later stars because near-infrared absorption increases the redder the stellar energy distribution (SED). That said, at low enough concentrations (up to ~100 ppm), CH$_4$ does create a slight net warming effect for planets around late-type stars, because the greenhouse effect dominates over the near-IR absorption. CH$_4$ has a somewhat stronger warming effect for planets around F-stars, pushing the OE of the HZ out from ~3.12 AU to 3.2 AU for a star with $T_{\text{eff}} = 7200$ K (Fig. 3.16). That's because the SED for these stars is shifted towards the blue, where CH$_4$ absorption is weaker.

Finally, additional sensitivity studies for the IE (not shown) suggest that 20% H$_2$ only moves the IE outward by about 0.01 AU. The small influence of H$_2$ appears to be due to the high water vapor absorption, which masks the contribution coming from H$_2$ CIA. Therefore, neither CH$_4$ nor H$_2$ appear to alter the conclusion that the traditional CO$_2$-H$_2$O HZ remains the best navigation tool for future space missions attempting to locate potentially habitable exoplanets.
Figure 3.14: (a) Stellar spectra for the Sun; F0, and M3 spectral classes and (b) near-infrared/visible CH$_4$ absorption spectrum at a pressure of 0.1 bar and 300 K. Additional CH$_4$ lines (not shown) that exist between 0.3 µm and 1 µm were derived from Karkoschka et al (1994).
Figure 3.15: Temperature profiles for 1 bar CO₂ cold planet atmospheres ($S/S_0 = 0.303$) under solar-, F0-, and M3-class insolation as a function of altitude, with and without the addition of 1% CH₄. The surface albedo ($A_s$) is 0.2. Only a slight temperature inversion forms in the M3 CH₄-free case due to near-IR absorption by CO₂. The larger inversions with the solar (max: ~21 K) and M3-class (max: ~50 K) insolation cases are due to significant near-IR absorption by CH₄, resulting in a surface temperature decrease of ~13 K for the M3-class planet.
Fig. 3.16: Stellar effective temperature versus the effective stellar flux incident on a planet. The corresponding locations for Gliese 581d and Tau Ceti f are shown for comparison. The traditional habitable zone (HZ) outer edge (black) is exposed to (a) 10% and 20% $H_2$, respectively (purple), and (b) 1% $CH_4$ (green).
3.13 Discussion

The various computed and empirical HZ boundaries as a function of stellar $T_{\text{eff}}$ and $S_{\text{eff}}$ are shown in Fig. 3.17. The Early Mars, Recent Venus, and Early Venus limits were scaled with the maximum greenhouse, moist greenhouse, and runaway greenhouse limits, respectively. Data for the plotted exoplanetary systems were taken from exoplanets.org.

The blue shaded region represents the computed HZ limits that are bounded by the Leconte et al limit (at the inner edge) and the maximum greenhouse (at the outer edge). A key difference from the equivalent plot in Kopparapu et al (2013) is the addition of the early Venus limit (dashed line), which moves the empirical IE limit for our solar system from 0.75 to 0.86 AU. As discussed earlier, this limit is valid if Venus lost its water during accretion (Hamano et al 2013). However, until more definitive information is known about the evolutionary history of early Venus, the optimistic recent Venus limit should continue to be considered as well (Kasting 1988).

Figure 3.17: Various habitable zone (HZ) boundaries for stars with different $T_{\text{eff}}$. The boundaries of the blue shaded region are determined by the Leconte et al limit on the left boundary and by the maximum greenhouse effect on the right boundary. Some of the currently known exoplanets are also shown, although there is an ongoing discussion regarding the existence of Gliese 581g.
The Leconte et al limit improves upon the 1-D result of 1.01 AU because the latter implies Earth is in the moist greenhouse regime. However, if Earth was indeed undergoing a moist greenhouse, H escape rates would be over 5 orders of magnitude larger than the miniscule 3 kg/sec measured for the modern Earth (Catling & Zahnle 2009). Admittedly, the 1-D calculations are deceiving because they assume a fully-saturated atmosphere that maximizes the greenhouse effect. Realistically, Earth is far from being fully-saturated, as it has an average surface relative humidity of ~77%, decreasing to under 10% at the tropopause (Manabe & Wetherald 1967). Furthermore, the 1-D calculations assumed zero cloud feedback; that is, the same cloud radiative forcing for present Earth is assumed across all temperatures. Finally, Earth is further stabilized because dry air from the descending branch of the Hadley cells permits for a larger outgoing infrared flux (Pierrehumbert 1995). For these reasons, the Leconte et al limit should be used as the new conservative IE limit, replacing all previous 1-D estimates.

Regarding the proper usage of these limits, an important question to habitable planet hunters is which ones to utilize and under what circumstances. For current missions, such as Kepler and RV surveys, the most conservative limit (i.e., the Leconte et al limit) should be used because it provides a lower limit on $\eta$. In designing a new telescope (e.g. Terrestrial Planet Finder or Darwin), the conservative limit will ensure that the instrument is not undersized. However, the optimistic limits (recent Venus and early Mars) should be employed when analyzing mission data to avoid missing potentially habitable planets, including desert planets closer in to their stars (Abe et al 2011). Such closer in planets, should they exist, would be harder to detect because the resolution angle is smaller, requiring a bigger telescope.

For stellar $T_{\text{eff}} \leq 4000$K, the close proximity of these planets to these stars raises additional concerns for habitability. Close-in K- and M-star planets would be exposed to high levels of UV radiation, although elevated oxygen levels can potentially shield some of its harmful effects (Segura et al 2003). Another potential concern for close-in planets with low eccentricities is the possibility of synchronous rotation, in which one side of a planet always faces the star. However, the lack of water on the dark side results in an extremely weak ice-albedo feedback, leaving the warm starlit side unaffected (Joshi 2003). Moreover, recent GCM results show that increased convection near the substellar point produces thick water clouds, greatly increasing the planetary albedo. This moves the IE for synchronously rotating planets, which likely encompasses HZ planets orbiting late-K – M stars (Edson et al 2011), much farther in than the 1-D limits computed here (Yang et al 2013) (Fig. 3.17). Thus, there is no reason to suppose that habitable, synchronously rotating planets do not exist.

Moreover, using 3D GCMs, there have been attempts to compute OE limits significantly different from the 1-D ones, all with limited success. Previous work has suggested that CO$_2$ clouds may push the OE out if high fractional CO$_2$ cloud cover is assumed (Forget &
Pierrehumbert 1997, Mischna et al 2000). This is because the CO$_2$ ice crystals formed at sizes that can scatter the thermal infrared energy back to the surface (ibid). However, a recent 3-D GCM result that computed a realistic fractional cloud cover percentage for early Mars (50%) found that the greenhouse effect from this mechanism is small, even assuming the most favorable parameters (Forget et al 2012). Furthermore, the Toon et al (1989) two-stream method used in many climate models appears to overestimate the efficacy of this mechanism. Kitzmann et al (2010) replaced the Toon et al (1989) scheme with DISORT (Discrete Ordinance Radiance Transfer) and the increase in streams resulted in a greatly reduced greenhouse effect from CO$_2$ ice crystal backscatter for planets around M-stars. Moreover, even the well-known ice-albedo feedback cycle would not move in the OE because these dense CO$_2$ atmospheres are so optically thick that surface energy rising will not be able to influence the radiative budget (Shields et al 2013).

Recent work on the Archean Earth has suggested yet another way by which the outer edge may be pushed outward (Charnay et al 2013, Wolf & Toon 2013). In their analysis, Charnay et al (2013) found that the disappearance of clouds at low temperatures increased absorption and helped stave off ice-albedo feedback, producing equatorial liquid water belts for mean surface temperatures as low as 248 K. Thus, if a planet can keep from becoming completely snow-covered, then habitable regions can potentially exist in the warm equatorial regions even if mean temperatures are well below the freezing point. However, even if these studies are correct, at a mean surface temperature of 248 K, our model predicts that the outer edge moves out only from 1.64 AU to 1.67 AU. Thus, barring special conditions like small H$_2$-rich planets near the OE (Section 3.11), the 1-D results seem to be relatively robust.

### 3.14 Conclusions

New estimates for HZs around F, G, K, and M main-sequence stars have been computed that update the original 1-D results by Kasting et al (1993) using (1) revised H$_2$O and CO$_2$ absorption coefficients, (2) a more accurate formulation for H$_2$O Rayleigh scattering, (3) new CO$_2$ collision-induced absorption coefficients, (4) a more complete water continuum, and (5) parameterized stellar spectra for the $T_{\text{eff}}$ range of interest.

The new inner edge for the solar system is at 0.95 AU. This result does not come from our 1-D work, but from the 3-D model of Leconte et al. (2013). The OE, defined by the maximum greenhouse effect of CO$_2$, is located at 1.64 AU. 1-D and 3-D calculations agree fairly well for this habitable zone boundary. Methane is a modest greenhouse gas for planets around early stars and creates a strong anti-greenhouse effect for planets around stars later than mid-K. Although H$_2$ can extend the OE significantly, the existence of rocky planets with multi-bar H$_2$ atmospheres is speculative, and these planets would also be difficult to detect using currently envisioned observational techniques.
4. WARMING EARLY MARS WITH CO$_2$ AND H$_2$

4.1 About Chapter 4 and Ramirez et al (2013)

Most of this chapter is taken verbatim from Ramirez et al (2013), which was published in Nature Geoscience. The following are the most conspicuous changes made to the original version: (1) The main text and Supplementary Info have been combined into one chapter, (2) more subsections have been added, (3) the Methods Summary is embedded within the text, and (4) the reference style has been changed to match that used in the rest of the thesis. Finally, there is additional discussion herein about the possibility of a northern ocean on Mars and implications for ice-albedo feedback.

4.2 Introduction

The climate of early Mars has been a topic of debate for at least the last 30 years. Nearly all researchers agree that the martian valleys and valley networks were formed by running water (Carr 1995). Debate has persisted as to how warm the surface must have been to form these features and how long this warmth must have lasted (Jakosky et al 2005). The widely cited impact hypothesis (Segura et al 2002, Segura et al 2008, Segura et al 2012) suggests that large impacts occurring during the Heavy Bombardment Period could have heated the surface for brief intervals and that the valleys were formed by water that rained out following these events. Other authors (Pollack et al 1987) have argued that the martian climate was warmed by the greenhouse effect of a dense CO$_2$-H$_2$O atmosphere, perhaps supplemented with SO$_2$ (Johnson et al 2008). But the SO$_2$ warming mechanism has difficulties because of photochemical production of sulfate aerosols, which act to cool the climate (Tian et al 2010), and the calculation in Johnson et al (2008) is no longer believed because of errors in the CO$_2$ absorption coefficients (Mischna et al 2013). Furthermore, all recent one-dimensional CO$_2$-H$_2$O climate models (Kasting 1991, Tian et al 2010, Wordsworth et al 2010a) have been unable to produce above-freezing surface temperatures because of a combination of two factors: 1) CO$_2$ condensation, which reduces the tropospheric lapse rate, thereby lowering the greenhouse effect, and 2) Rayleigh scattering, which causes the planet’s albedo to become high as the surface pressure becomes large (Kasting 1991). Forget and Pierrehumbert (1997) were able to produce mean surface temperatures above the freezing point of water by including explicit CO$_2$ ice clouds with 100 percent cloud cover. However, 3-D climate models predict much smaller fractional CO$_2$ cloud cover and greatly reduced surface warming (Forget et al 2012, Wordsworth et al 2012).
An updated 1-D climate calculation illustrates the basic problem (see Fig. 4.1). When solar luminosity is greater than 80 percent of today’s value, increased CO$_2$ partial pressure is capable of bringing Mars’ mean surface temperature above 273 K. But for solar luminosities less than or equal to 80 percent of today, corresponding to time periods prior to ~2.8 Gyr ago (Gough 1981), no amount of CO$_2$ can produce a warm surface. Instead, a dense CO$_2$ atmosphere would simply condense out globally in a 1-D climate model or at the poles in a more realistic 3-D climate model (Forget et al 2012). The perceived difficulty in producing a stable, warm climate on early Mars has bolstered support for the impact hypothesis, along with other “cold early Mars” theories.

![Mean surface temperature as a function of surface pressure for a fully saturated (95% CO$_2$, 5% N$_2$) early Mars atmosphere at different solar insolation levels. The assumed surface albedo is 0.216. These results agree to within a few degrees with those of Tian et al (2010), largely because increased absorption in the far wings of CO$_2$ and H$_2$O lines (see Appendix A) compensated for the loss of absorption arising from the updated CO$_2$ CIA parameterization (Wordsworth et al 2010a).](image)

**Fig. 4.1:** Mean surface temperature as a function of surface pressure for a fully saturated (95% CO$_2$, 5% N$_2$) early Mars atmosphere at different solar insolation levels. The assumed surface albedo is 0.216. These results agree to within a few degrees with those of Tian et al (2010), largely because increased absorption in the far wings of CO$_2$ and H$_2$O lines (see Appendix A) compensated for the loss of absorption arising from the updated CO$_2$ CIA parameterization (Wordsworth et al 2010a).
Since the impact hypothesis was proposed, other workers have pointed out that the valleys are more extensive than originally realized (Hynek & Phillips 2003), and some have argued that the amount of time and surface runoff needed to form them was much larger than had been previously assumed (Barnhart et al 2009, Hoke et al 2011). Hoke et al (2011) performed detailed hydrologic modeling of several different valleys listed in their Table 3. The larger ones (e.g., the 2°N, 34°E Naktong east valley) require episodic runoff rates of 0.5 cm/day, along with intermittent runoff averaging ~10 cm/yr for (3-4)×10^7 yr. These high flow rates are needed to lift eroded material off the river bed and keep it in suspension. According to Hoke et al (2011), the estimated runoff total for this one valley is 3-4 million meters, or more than three orders of magnitude more than the amount of rainwater provided by the impact hypothesis. So, these authors envision an entirely different, and much wetter, scenario for martian valley formation. Here, we propose a mechanism for supplying these significantly larger rainfall amounts.

4.3 Methods

We included H_2 CIA, along with other updates, in our existing 1-D radiative-convective climate model (Kopparapu et al 2013, Ramirez et al 2013). For a detailed description of the climate model see Section 2. The troposphere was assumed to be fully saturated with H_2O in most of our simulations. This produces a slight overestimate for the surface temperature, but the error should be generally small. More importantly, the effect of clouds on the planetary albedo is not calculated accurately in our model; instead, the atmosphere is assumed to be cloud-free, and the surface albedo is adjusted to a value (0.216) that allows the model to reproduce Mars’ current mean surface temperature, 218 K, given current solar insolation. This surface albedo is held fixed for all calculations. More complex, 3-D climate models are needed to treat clouds and relative humidity more realistically.

The following additional updates were made to the climate model (described in Section 2):

1) We included collision-induced absorption (CIA) caused by the interaction of H_2 with CO_2. CO_2 is an anisotropic molecule that picks up a strong dipole moment when its bending mode is activated, necessitating extra quantum mechanical treatments that are at this stage considered experimental (L. Frommhold, personal communication). Therefore, we modeled CO_2-H_2 CIA using measured absorption coefficients for N_2-H_2 CIA (Borysow & Frommhold 1986). We believe that this approach is conservative, as Burch et al (1969) determined that self-broadening of permitted CO_2 transitions was ~30% more effective than foreign-broadening by N_2. The lower moment of inertia of H_2, coupled with its widely-spaced rotational levels, results in absorption over a large swath of the thermal infrared, including the 200-600 cm\(^{-1}\) and the 8-12 \(\mu\)m regions (Kasting 2013) (Figs A6-A7).
Indeed, collision-induced absorption by H₂ broadened by other molecules such as Ar, N₂, or even itself all produce absorption over the same spectral range (Richard et al. 2012). Subsequently, the same would be true for CO₂-H₂. Although CO₂ is more effective at Rayleigh scattering than is N₂, our CO₂-H₂ cases still produce more surface warming than does our N₂-H₂ case (Fig. 4.2). Thus, the increase in Rayleigh scattering as CO₂ increases is outstripped by increased absorption within the 15 micron band. This suggests that CO₂ would have to broaden H₂ considerably less effectively than N₂ does for our mechanism to fail, contrary to the available evidence (Burch et al 1969). Consequently, we use the N₂-H₂ CIA data of Borysow and Frommhold (1986) as a lower bound for the calculation of CO₂-H₂ opacity (τ₁). This lower bound parameterization is then:

\[ \tau_1 = H_i \frac{n}{n_0} W_{H_2} \cdot f_{CO_2} \]

Here, \( H_i \) is a constant (see below) with units of amagat\(^2\) cm\(^{-1}\), \( W_{H_2} \) is the H₂ path length in atmosphere-centimeters, \( n \) is number density, and \( n_0 \) is Loschmidt’s constant (2.687×10\(^{19}\) molecules/atm-cm\(^3\)). The quantity \( f_{CO_2} \) represents the foreign broadening by CO₂. This lower bound estimate resulted in mean surface temperatures above 273 K at ~ 2.5 bar for 10% H₂ and ~1.5 bar for 20% H₂.

The N₂-H₂ collision-induced absorption coefficients, \( H_i \), used in eq.(7) are tabulated in Appendix C. N₂-H₂ CIA coefficients, like other absorption coefficients in our model, are interpolated log-linearly (linear in \( T \), logarithmic in the absorption coefficient) between the values shown in Table CI.

2) We also incorporated self-broadening by H₂-H₂ pairs (Borysow 2002), using the following equation for the opacity, \( \tau_p \):

\[ \tau_p = H_i \frac{n}{n_0} W_{H_2} \cdot f_{H_2} \]

Here, \( f_{H_2} \) is the hydrogen mixing ratio. Inspection of the above two equations reveals that self-broadening by H₂ is less important than foreign-broadening when H₂ is the secondary greenhouse gas. This is because the pathlength (\( W_{H_2} \)) is a linear function of the mixing ratio, and \( \tau_1 \) is a quadratic function of \( f_{H_2} \). In contrast, \( \tau_1 \) is approximately linear in \( f_{H_2} \) at low mixing ratios. Furthermore, a comparison of the tabulated data for foreign- and self-broadening of H₂ (Tables CI and CII, respectively) shows that H₂ foreign broadening is
generally more effective at any given temperature and frequency. We conducted a sensitivity study to quantify the effect of removing the H\textsubscript{2} self-broadening component. Our results showed that the maximum surface temperatures decreased by no more than 2-3 K when this was done.

3) Our climate model now includes Rayleigh scattering by H\textsubscript{2} (Dalgarno & Williams 1962). This addition had a negligible effect on our results.

4) Our model can now perform calculations involving multiple solar zenith angles, increasing the accuracy of shortwave absorption.

4.4 Greenhouse warming by models that include H\textsubscript{2}

The utility of H\textsubscript{2} as a greenhouse gas for terrestrial planets was pointed out several years ago by Stevenson (1999) and has been studied more quantitatively by recent authors (Pierrehumbert & Gaidos 2011, Wordsworth & Pierrehumbert 2013a). Recent work has shown that early Earth could have been kept warm by greenhouse warming from collision-induced absorption (CIA) caused by the interaction of H\textsubscript{2} molecules with N\textsubscript{2} (Wordsworth & Pierrehumbert 2013a). These collisions excite the pure rotational levels of H\textsubscript{2} and, at the same time, allow it to absorb electromagnetic radiation to lift it from one rotational state to the next. At room temperature, the absorption spectrum of H\textsubscript{2} extends right through the 8-12 \( \mu \)m “window region”, allowing it to be an effective greenhouse gas on either early Earth or Mars (Wordsworth & Pierrehumbert 2013a, Kasting 2013, Ramirez et al 2013). One difference between the two planets is that Mars has long been deficient in N\textsubscript{2} (Fox 1993), and so the main broadening gas there may instead have been CO\textsubscript{2}. Collisional excitation of H\textsubscript{2} by CO\textsubscript{2} has not been studied, but there is no reason to suppose that it would be any less efficient than excitation by N\textsubscript{2}. Indeed, collisional broadening of permitted absorption lines is stronger for CO\textsubscript{2} (Section 4.7). Below, we conservatively assume that H\textsubscript{2}-CO\textsubscript{2} CIA is of the same strength as H\textsubscript{2}-N\textsubscript{2} CIA, for which the excitation cross sections have been calculated theoretically (Borysow & Frommhold 1986).

To determine the possible effect of H\textsubscript{2} on martian paleoclimate, we performed a series of calculations for hypothetical paleoatmospheres containing various amounts of CO\textsubscript{2} and H\textsubscript{2} (Fig. 4.2). The assumed solar luminosity was 0.75 times present, which is appropriate for 3.8 Gyr ago (Gough 1981). When H\textsubscript{2} was absent, the mean surface temperature never exceeded 230 K, regardless of how much CO\textsubscript{2} was present. This temperature is similar to
values found previously by our group: published maximum temperatures for this solar flux were ~225 K and 231 K (Kasting 1991, Tian et al 2010). Wordsworth et al (2010a) could reach only 217 K for a 1-bar CO\(_2\) atmosphere, but their model did not include H\(_2\)O.

**Fig. 4.2:** (a) Surface temperature and (b) planetary albedo as a function of surface pressure for different atmospheric compositions. The assumed solar luminosity is 0.75 times present, appropriate for 3.8 Gyr ago. Any remaining gas not accounted for in the legend is considered to be N\(_2\). Solid curves correspond to fully saturated atmospheres, while the model represented by the dashed curve assumes 50% tropospheric relative humidity. At 273 K and 10% H\(_2\), a difference of only ~3-4 K separates the fully saturated and 50% relative humidity cases, indicating that the vast majority of the greenhouse warming is caused by H\(_2\)-CO\(_2\) collision-induced absorption.
When 5 percent H$_2$ was included in our new climate model, the calculated maximum surface temperature nearly reached 273 K as CO$_2$ was increased, and it exceeded 273 K when the solar radiation calculation was done more accurately (Fig 4.3). The corresponding surface pressure for this simulation was ~4 bar (or ~3 bar in the more accurate calculation).

![Graph](image)

**Figure 4.3:** (a) Surface temperature and (b) planetary albedo as a function of surface pressure for two 95% CO$_2$, fully-saturated early Mars ($S/S_o = 0.75$) atmospheres containing 5% N$_2$, 5% H$_3$, and 5% H$_2$ with a relative humidity of 50%. The assumed surface albedo is the same as that used in Fig. 4.2. A 6-point gaussian integration scheme was used over the sun-lit hemisphere (num = 6). The cosine-weighted average solar flux factor was ~0.503, which compares to the true value of 0.50. The mean temperature for the baseline 5% N$_2$ case rose from 230 K (Fig. 4.2) to 246 K here. With six gauss points, even the 50% relative humidity scenario reaches the freezing point with 5% H$_2$ and just under ~3 bars total surface pressure.
Warming by CO₂ ice clouds (Forget & Pierrehumbert 1997, Forget et al 2012), or H₂O cirrus clouds (Urata & Toon 2013), both of which were neglected in these calculations, would increase the mean surface temperature still further; thus, we take 5 percent as a reasonable minimum estimate for the H₂ concentration needed to produce a mean surface temperature above freezing. Higher H₂ concentrations allow the freezing point to be reached at lower surface pressures. For 10 percent H₂ this threshold was reached at ~2.5 bar, and for 20 percent H₂ it was reached at ~1.6 bar. This latter value is right at the upper limit of 1.6 bar calculated recently based on the size distribution of secondary craters from impacts (Kite et al 2013). Those calculations assume a weak soil target strength consistent with river alluvium; for a harder bedrock surface the pressures could rise many bars. H₂-N₂ collisions could also conceivably have warmed Mars to this temperature for N₂ partial pressures >2 bar, although N₂ is less likely to have been present in abundance, as already noted.

Finally, we acknowledge that the goal of reaching a mean surface temperature of 273 K may be somewhat artificial, as both temperatures and precipitation rates vary as a function of latitude and altitude. Wolf and Toon (2013) used a 3-D climate model to show that half of Earth’s early oceans could have remained unfrozen at a mean temperature of only 260 K. Similarly, Charnay et al (2013) found that equatorial liquid water belts could have persisted in the Archean at mean surface temperatures as low as 248 K. The reduced cloud cover at these lower temperatures would have decreased the planetary albedo, offsetting the cooling from ice-albedo feedback at lower latitudes. Thus, in contrast to previous energy balance studies (Budyko 1969, Sellers 1969), the Archean Earth could have been in an intermediate state between ice-free and completely ice-covered solutions, and the same could be true for early Mars. Certainly, if the inference of an early Martian ocean is eventually found to be correct (Clifford & Parker 2001), a warmer northern hemisphere and equatorial regions would be consistent with this above scenario. Indeed, this seems to be supported by our own preliminary analysis, which reveals that many of the oldest and largest ancient valley networks (e.g., Nanedi Valles, Naktong Valles, Nigral Valles) seem to be concentrated near the equator, where surface temperatures should have been, on average, the highest. Nonetheless, more realistic climate simulations may show that the valleys could have formed at somewhat lower concentrations of H₂ and/or CO₂.

4.5 Sources and sinks for H₂ and CO₂

Both H₂ and CO₂ would have to have been abundant on early Mars for this greenhouse warming mechanism to have succeeded. We assume that early Mars, like early Earth, was volcanically active and would have released H, C, and S-bearing gases. We begin our analysis by considering outgassing of hydrogen on modern Earth. On Earth, the dominant outgassed form of H for subaerial volcanism is H₂O (Holland 1984), which has an outgassing rate of 1.0×10^{14} mol yr⁻¹ (Jarrard 2003). The H₂:H₂O ratio in subaerial volcanic
gases can be estimated by considering thermodynamic equilibrium at typical outgassing conditions (1450 K, 5 bar pressure) (Holland 1984) for the following reaction:

\[
2 \text{H}_2\text{O} \rightleftharpoons^{K_9} 2 \text{H}_2 + \text{O}_2
\]  \(9\)

The \(\text{H}_2/\text{H}_2\text{O}\) ratio, \(R\), is given by the relation

\[
\frac{p\text{H}_2}{p\text{H}_2\text{O}} \equiv R = \left(\frac{K_9}{f\text{O}_2}\right)^{0.5}
\]  \(10\)

Here, \(p\text{H}_2\) and \(p\text{H}_2\text{O}\) are the partial pressures of \(\text{H}_2\) and \(\text{H}_2\text{O}\) in the released gas, and \(f\text{O}_2\) is the oxygen fugacity of the system, which is set by the magma. Solving for the equilibrium constant \(K_9\) yields:

\[
K_9 = \frac{p\text{H}_2^2 \cdot f\text{O}_2}{p\text{H}_2\text{O}^2} = e^\frac{-\Delta G_1^0}{RT}
\]  \(11\)

Here, \(\Delta G_1^0\) is the change in Gibbs free energy for the reaction at standard state. The free energies of formation of \(\text{H}_2\) and \(\text{O}_2\) are defined as zero at all temperatures. Using data from the NIST-JANAF thermochemical tables (Chase & Force 1998), the free energy of formation of \(\text{H}_2\text{O}\) at 1200 °C is \(\Delta G_1^0(\text{H}_2\text{O}) = -165.58\) kJ/mol, so the free energy change for the reaction is just

\[
\Delta G_1^0 = -2 \cdot \Delta G_1^0(\text{H}_2\text{O}) = 331.16\ \text{kJ/mol}
\]  \(12\)

Using eq. (12) above, the equilibrium constant at 1200 °C is \(K_9 \approx 1.80 \times 10^{-12}\) atm. For the relatively oxidized Earth, the oxygen fugacity is near the QFM (quartz-fayalite-magnetite)
54

synthetic buffer, for which \(fO_2 \cong 10^{-8.5}\) at these P-T conditions (Mastenbrook 1963), and so the predicted \(H_2:HO\) ratio is 0.024. Multiplying by the outgassing rate for \(H_2O\) gives a subaerial \(H_2\) outgassing flux of \(2.4 \times 10^{12}\) mol/yr, or \(1 \times 10^{10}\) \(H_2\) molec cm\(^{-2}\) s\(^{-1}\). (The actual \(H_2\) outgassing rate scales as \(R/(1+R)\), as can be demonstrated from mass balance, but this ratio reduces to \(R\) when \(R << 1\).) This value is essentially identical with the estimate of total \(H_2\) outgassing by Holland (2009). About half of Holland’s total \(H_2\) flux comes from submarine \(H_2S\), which is readily photolyzed (Tian et al 2008). This can be demonstrated by adopting a methodology in which \(H_2O\), \(CO_2\), \(N_2\), and \(SO_2\) are assigned “neutral” oxidation states to evaluate the contribution of other gases to the atmospheric redox budget (Kasting & Brown 1998, Kasting & Canfield 2012). Thus, \(H_2S\) can be converted to \(SO_2\) and \(H_2\) equivalents by (Pavlov et al 2001):

\[
\begin{align*}
H_2S + hv & \rightarrow HS + H \\
H_2O + hv & \rightarrow H + OH \\
CO_2 + hv & \rightarrow CO + O \\
HS + O & \rightarrow H + SO \\
SO + OH & \rightarrow SO_2 + H \\
H + CO + M & \rightarrow HCO + M \quad \text{ }(\times3) \\
H + HCO & \rightarrow H_2 + CO \quad \text{ }(\times3) \\
CO + OH & \rightarrow CO_2 + H
\end{align*}
\]

\[
\text{Net: } H_2S + 2 H_2O \rightarrow SO_2 + 3 H_2
\]

The particular reaction sequence shown here is by no means the only one that would have operated in the primitive atmosphere, but it is a particularly effective one because the two boldface reactions provide a catalytic cycle for producing \(H_2\) (Pinto et al 1980). \(H_2S\) can also react directly with \(OH\) to produce \(H_2O + HS\), and \(H\) can react with \(HS\) to produce \(H_2 + S\). Regardless of how the actual reaction path proceeds, each mole of \(H_2S\) outgassed is equivalent to 3 moles of outgassed \(H_2\), if the sulfur is removed as \(SO_2\). If the \(H_2S\) is oxidized to sulfate, then an additional mole of \(H_2\) is produced.

Thus, the above chemistry implicitly accounts for the contribution from \(H_2S\) in the \(H_2\) budget. However, scaling the outgassing rate in this manner might actually underestimate the \(H_2S\) flux, considering that Mars’ mantle appears to be exceptionally rich in sulfur (Gaillard & Scaillet 2009). The \(H_2\) outgassing rate for modern Earth is uncertain by at least a factor of 5 (Holland 2009), so trying to refine our estimate further would have limited benefit.

How might these outgassing fluxes scale for early Mars? It is difficult to be certain, partly because we do not know whether Mars ever experienced plate tectonics. We can make some crude analogies, however. The geothermal heat flux on Mars during the Noachian era is thought to have been similar to that of modern Earth (Montési & Zuber 2003), so it is plausible to assume that the total \((H_2O+H_2)\) outgassing rate per unit area was the same on
the two planets. The H$_2$ mole fraction should have been higher on Mars, though, because Mars' mantle is thought to be more reduced. Martian meteorites (SNCs) have fO$_2$'s ranging from QFM down to IW (iron-wüstite) or below (Stanley et al 2011, Grott et al 2011). (The IW O$_2$ buffer is about 4 log units below QFM.) The shergottites, which are the most primitive SNCs petrologically, and hence most like the mantle, have fO$_2$ values of ~IW+1 (Grott et al 2011). And ALH84001, the oldest martian meteorite, is at IW−1, suggesting that the early martian mantle may have been even more reduced (Grott et al 2011).

A leading hypothesis postulates that the small size of Mars precluded the planet from crystallizing silicate perovskites which would have raised its mantle oxidation state (Wade & Wood 2005). For a larger planet such as Earth, perovskite (FeAlO$_3$) is stable for pressures > 23 GPa:

$$3\text{FeO} + \text{Al}_2\text{O}_3 = 2\text{FeAlO}_3 + \text{Fe}^0$$

At the corresponding depths in the early terrestrial mantle (below 660 km), perovskite would have crystallized from the magma ocean, dissolving ferric (Fe$^{+3}$) iron as FeAlO$_3$ as Fe$^0$ metal was being produced. This Fe$^0$ would have partitioned into the core, while the Fe$^{+3}$-containing perovskite would have dissolved into the magma ocean and oxidizing it. Thus, on Earth, the magma ocean would become progressively oxidized as the dissolved Fe would reprecipitate into perovskite, promoting further oxidation (Wade & Wood 2005). However, Mars is much too small to achieve such high internal pressures so its mantle stayed relatively reduced, with the iron remaining as Fe$^{+2}$.

The prediction of a highly reduced early martian mantle is in conflict with a recent analysis based on S and Ni abundances and the Mn/Fe ratio of Gusev crater rocks, which suggest that the upper part of Mars’ mantle was more oxidized in the distant past (Tuff et al 2013). But these data might also be explained by later alteration (Ming et al 2006), so the bulk of the evidence still favors a highly reduced early mantle.

Assume for the moment that Mars’ mantle fO$_2$ was near IW+1, roughly 3 log units below the terrestrial value. Eq. (10) then predicts that the H$_2$:H$_2$O ratio, $R$, in the released gas should increase by a factor of 32. The rate of H$_2$ outgassing should increase by a smaller amount ($\propto R/(1+R)$), assuming that the total outgassing rate of (H$_2$+H$_2$O) remains constant. The three-log-unit decrease in mantle fO$_2$ compared to Earth should increase H$_2$ outgassing by a factor of ~20, so the expected H$_2$ outgassing rate on early Mars should be of the order of (1×10$^{16}$ cm$^{-2}$s$^{-1}$)×20 = 2×10$^{17}$ cm$^{-2}$s$^{-1}$. This direct flux of H$_2$ could
have been augmented by ~50% by an indirect flux of hydrogen from CH$_4$. For instance, we can write

$$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2 \quad (14)$$

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (15)$$

Thus, one mole of CH$_4$ yields 4 moles of H$_2$, and one mole of CO yields one mole of H$_2$. This input of hydrogen should have been balanced by escape of hydrogen to space. If hydrogen escaped at the diffusion limit (Hunten 1973, Walker 1977), the escape rate in these same units would be given by

$$\Phi_i(\text{H}_2) = \frac{b_i}{H_a} \cdot \frac{f(T)(\text{H}_2)}{1 + f(T)(\text{H}_2)} \cong \frac{b_i f(T)(\text{H}_2)}{H_a} \quad (16)$$

Here, $b_i$ is a weighted molecular diffusion coefficient for H and H$_2$ in air (or CO$_2$), $H_a$ ($= kT / mg$) is the pressure scale height, and $f(T)(\text{H}_2)$ is the total hydrogen volume mixing ratio: $f(T)(\text{H}_2) = 0.5 f(\text{H}) + f(\text{H}_2) + f(\text{H}_2\text{O}) + ...$. If H$_2$ is the dominant H-bearing species, then $f(T)(\text{H}_2) \cong f(\text{H}_2)$. All quantities are evaluated at the homopause, near 130 km altitude on present Mars, where molecular diffusion begins to exceed mixing by turbulent eddies. Counter-intuitively, Mars’ lower gravity decreases the hydrogen escape rate compared to Earth because the scale height, $H_a$, appears in the denominator of eq. (16). For a homopause temperature of ~160 K, $b_i / H_a \cong 1.6 \times 10^{13} \text{ cm}^2\text{s}^{-1}$. Inserting this value into eq. (16) and equating H$_2$ escape with H$_2$ outgassing yields $f(\text{H}_2) \cong 0.013$. This is a factor of 4 less than the minimum H$_2$ mixing ratio of 0.05 needed to produce Earth-like surface temperatures on early Mars, according to Fig. 4.2. At a mantle $f(\text{O}_2)$ of IW–1, the H$_2$ outgassing flux would be another factor of 2 higher, making it $4 \times 10^{11} \text{ cm}^2\text{s}^{-1}$ and yielding an atmospheric H$_2$ mixing ratio of ~0.025, about half the minimum H$_2$ concentration needed to produce a warm early Mars (Fig. 4.2).

These numbers are all very uncertain, though. Volcanic outgassing rates on early Mars could have been considerably higher than those on modern Earth, and/or hydrogen may have escaped at less than the diffusion-limited rate. Calculations with our own 1-D hydrodynamic escape model, which is based on that of Tian et al (2008), suggest that the
diffusion limit would have been achieved. However, such 1-D calculations may overestimate the actual escape rate. The escape geometry is at least 2-dimensional, as solar radiation impinges on only one side of the planet. A third dimension is required if magnetic fields are included and if the planet’s magnetic axis is inclined relative to its orbital plane. For neutral, nearly isothermal atmospheres escaping from hot Jupiter exoplanets, geometry alone reduces the mass loss rate by nearly a factor of 4 (Stone & Proga 2009). That would bring the predicted atmospheric H$_2$ mixing ratio in our model up to 10 percent if Mars’ mantle was at IW$-1$, or 5 percent at IW$+1$. Accounting for partial ionization of the escaping gases and their interaction with a planetary magnetic field, which might have existed up until $\sim$3.9-4.0 Ga (Werner 2008), might slow the escape even further, so H$_2$ mixing ratios of 20 percent are not impossible. More complicated magnetohydrodynamic escape models would be needed to study this possibility.

Availability of CO$_2$ must also be considered. On Earth, the atmospheric CO$_2$ abundance is controlled over long time scales by the balance between production by volcanism and loss by weathering of silicate minerals followed by precipitation of carbonates. CO$_2$ is predicted to accumulate in the atmosphere when the climate is cold because of slower weathering (Walker et al 1981), and this feedback process could have been important on early Mars, as well (Pollack et al 1987). On Mars, however, the total carbon inventory is uncertain, and additional terms in the CO$_2$ budget must be considered. Carbonate minerals are observed in martian dust and in the SNC meteorites (Bandfield et al 2003, Lammer et al 2013). If the carbonate content of the dust is representative of the uppermost 2 km of crust, then the crust could contain the equivalent of 5 bar of CO$_2$ (Lammer et al 2013). This inference is speculative, however, and the apparent lack of large carbonate outcrops in the martian subsurface (Bandfield et al 2003) suggests that much of Mars’ CO$_2$ was lost by escape to space. CO$_2$ can be lost by both thermal and nonthermal loss processes (Terada et al 2009, Tian et al 2009). Thermal escape, which might initially have been very fast, presents the greatest hurdle for maintaining a dense early martian atmosphere. Thermal (hydrodynamic) loss of both C and O is predicted when the solar extreme ultraviolet (EUV) flux is more than $\sim$5 times the modern solar mean, which would likely have been the case during the first several hundred million years of Mars’ history (Ribas et al 2005). Modeling suggests that the best time to accumulate CO$_2$ would be 3.8-4.0 Gyr ago, when solar activity had declined but when volcanoes were still active (Tian et al 2009).

A second concern is whether enough CO$_2$ would have been supplied from volcanoes to maintain a dense atmosphere. Phillips et al (2001) estimated that 1.5 bar of CO$_2$ would have been emitted by Tharsis alone. But, because of Mars’ much lower mantle oxygen fugacity, some authors have suggested that most of Mars’ carbon would have been retained in the mantle as graphite (Stanley et al 2011, Grott et al 2011). These studies estimate upper limits of $\sim$1 bar on outgassed CO$_2$ if Mars’ mantle $f'O_2$ was near IW$+1$. Just recently, however, Wetzel et al (2013) have studied this system experimentally and have
shown that carbon would be stored in reduced silicate melts as a mixture of iron carbonyl, Fe(CO)$_5$, and CH$_4$. Upon outgassing, iron carbonyl would dissociate to form CO. According to their estimates, initial solidification of a 50 km-thick crust would have released 1 bar of CO and 1.3 bar of CH$_4$. Both of these reduced gases would have helped to build up the inventory of atmospheric H$_2$. Earlier we estimated the rate of H$_2$ outgassing on early Mars by making an analogy to modern Earth, assuming that outgassing of H$_2$S scaled proportionately with H$_2$. For the carbon-bearing gases, we can make a similar analogy. On Earth, the main carbon-bearing volcanic gas is CO$_2$, for which the estimated global release rate is $(7.5 \pm 2) \times 10^{12}$ mol/yr (Jarrard 2003), or $\sim 2.8 \times 10^{10}$ cm$^{-2}$s$^{-1}$. (We will use areal outgassing rates here, so as not to have to account for the different surface areas of Earth and Mars.) By converting from partial pressure to volume units (thereby accounting for the mass of O and H), we calculate that 30% of the outgassed carbon would have been released as CO, and 70% would have been released as CH$_4$. If we assume that early Mars outgassed carbon at the same rate per unit area as modern Earth—the same assumption made in the main text for total hydrogen—the equivalent H$_2$ outgassing rate can be estimated by multiplying the CO$_2$ outgassing rate given above by 0.3 for CO and by 0.7×4 for CH$_4$, where the factor of 4 comes from the stoichiometry of reaction S7. The net equivalent outgassing of H$_2$ is then $8.7 \times 10^{10}$ cm$^{-2}$s$^{-1}$. By comparison, the estimates given for combined (H$_2$ + H$_2$S) outgassing in the main text were $1 \times 10^{10}$ cm$^{-2}$s$^{-1}$ for modern Earth, $2 \times 10^{11}$ cm$^{-2}$s$^{-1}$ for early Mars at a mantle $f$O$_2$ of IW+1, and $4 \times 10^{11}$ cm$^{-2}$s$^{-1}$ for early Mars at IW−1. So, outgassing of CH$_4$ and CO would have made an appreciable, but not dominant, contribution to the atmospheric redox budget of early Mars.

Once in the atmosphere, both of these gases would have been oxidized by the byproducts of water vapor photolysis (Haqq-Misra et al 2008), yielding $\sim 5.2$ bar of CO$_2$ as an initial atmospheric inventory. CO$_2$ would have been continuously removed by carbonate formation and by escape, so recycling and/or continued juvenile outgassing would have been needed to maintain its abundance. To complicate matters, CO might have been more abundant than CO$_2$ if the carbon was outgassed in reduced form (Zahnle et al 2008). Although CO is not an effective greenhouse gas, calculations with N$_2$-H$_2$ mixtures (Fig. 4.2a) show that the surface can still be warmed above the freezing point even if the accompanying gas is not radiatively active.

4.6 Greenhouse effect of CH$_4$ in a CO$_2$-H$_2$ early Mars atmosphere

As discussed earlier, if Mars’ early mantle was highly reduced, some C would have been outgassed in the form of CH$_4$. Thus, CH$_4$ would be expected to have contributed to the greenhouse effect. Here, we assess the climatic effect of adding 1% CH$_4$ and various combinations of CO$_2$ and H$_2$ to representative fully-saturated 3-bar atmospheres with a surface temperature of 230 K. The instantaneous radiative forcing, defined here as the reduction in outgoing infrared radiation at the top of the atmosphere, caused by such an addition is shown in Table 4.1. Any remaining gas in these calculations is assumed to be
N₂. In all cases, the additional radiative forcing from CH₄ is no more than 1 W/m². By comparison, H₂ absorption produced 6 - 22 W/m² forcing for H₂ concentrations of 5-20% (Fig. A5- A6).

Selected temperature-altitude profiles for the 95% CO₂, 5% H₂ case are given in Fig. 4.4. H₂O and CO₂ cloud-forming regions are shown for the 3-bar case. Clouds are not included explicitly in the radiative transfer model, but their formation does affect the tropospheric lapse rate. As noted above, the greenhouse contribution from CH₄ is expected to be small in a dense CO₂ early Mars atmosphere. However, CH₄ absorbs strongly in the near-IR and could have contributed significantly to heating of the mid and upper atmosphere, thereby inhibiting CO₂ cloud formation (Fig. 4.5). As previous studies have suggested that backscattering from CO₂ ice clouds would warm the surface under high fractional cloud cover (≥ 0.5) (Forget & Pierrehumbert 1997, Mischna et al 2000, Forget et al 2012), this could conceivably result in surface cooling as compared to the zero-CH₄ case, but perhaps not by that much, as Kitzmann et al (2013) suggest that the two-stream method may have overestimated the warming coming from the backscatter of CO₂ ice crystals. To determine how important this process might be, this effect should be investigated with a more elaborate 3-D climate model that includes clouds.

Figure 4.4: Selected vertical temperature profiles for the fully-saturated 95% CO₂ 5% H₂ case shown in Fig. 4.2. As the total atmospheric pressure increases from 6×10⁻³ bar to 3 bar, the magnitude of the greenhouse effect from the combined effects of the CO₂ greenhouse and H₂ collision-induced absorption is ~70 K.
Figure 4.5: Temperature-altitude profiles for fully-saturated 3-bar CO$_2$ early Mars ($S/S'_0 = 0.75$) atmospheres with 1% CH$_4$ and no CH$_4$. The surface albedo is the same as in Fig. 4.2. The calculated surface temperature is ~230 K in both cases. Addition of 1% CH$_4$ has little direct effect on surface temperature, but it decreases the size of the CO$_2$ cloud deck from ~50 km to ~20 km. This effect may prove important in 3D GCMs that include clouds and in assessing the intensity of CO$_2$ condensation at the poles and at higher elevations. Sensitivity studies that included both self-broadened and foreign-broadened CH$_4$ CIA (assuming CO$_2$-CH$_4$ broadens as well as N$_2$-CH$_4$) had a small effect, increasing surface temperatures to just over 231 K. The CH$_4$ self-broadening component is small because CH$_4$ composes only 1% of the atmosphere. N$_2$-CH$_4$ CIA absorbs most strongly in the far-IR, which is masked by the pure rotation band of water.
Table 4.1: CH₄ radiative forcing for select atmospheres

<table>
<thead>
<tr>
<th>fCO₂</th>
<th>fH₂</th>
<th>CH₄ radiative forcing (W/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.95</td>
<td>0</td>
<td>0.9</td>
</tr>
<tr>
<td>0.94</td>
<td>0.05</td>
<td>1</td>
</tr>
<tr>
<td>0.79</td>
<td>0.20</td>
<td>0.43</td>
</tr>
</tbody>
</table>

4.7 Conclusions

In summary, the formation of valleys and valley networks on early Mars is most easily explained if the climate was warm for long time periods. An H₂-CO₂-H₂O greenhouse is capable of sustaining mean surface temperatures > 0 °C at 3.8 Gyr ago, provided that H₂ and CO₂ were maintained at reasonably high concentrations (5 percent for H₂, >1.3 bar for CO₂) by volcanic outgassing. CO also works in combination with H₂ at slightly higher surface pressures. High concentrations of H₂ would have been promoted by outgassing from a strongly reduced martian mantle, perhaps augmented by geometric or magnetic limitations on the rate at which H₂ escaped to space. CO₂ could have been supplied either directly if the mantle was relatively oxidized or indirectly as CO and CH₄ if the mantle was highly reduced. More detailed exploration of Mars’ surface, including searches for buried carbonates, could provide additional evidence to test this hypothesis.
5. CAN INCREASED ATMOSPHERIC CO₂ LEVELS TRIGGER A RUNAWAY GREENHOUSE?

5.1 About Chapter 5

A lot of this chapter is taken verbatim from a manuscript originally written in the format of a *Nature Geoscience* article, which the following reflects. However, the manuscript was eventually rewritten and sent to *Astrobiology*. The reference style was changed from its original *Nature Geoscience* incarnation to match that of the rest of the thesis.

5.2 Introduction

In his book *“Storms of My Grandchildren”* (Hansen 2010), veteran climate scientist James Hansen speculated that mankind’s continued burning of fossil fuels could conceivably trigger a *runaway greenhouse*, an atmospheric catastrophe in which surface temperatures become high enough to completely vaporize the oceans. On a water-rich planet like Earth, this phenomenon would occur if the surface temperature were to exceed the critical temperature for water (647 K for pure H₂O). Alternatively, some authors (Rennó 1997, Goldblatt et al 2013) prefer to define the runaway greenhouse as a situation in which the absorbed solar flux exceeds the outgoing infrared flux. In practice, these two definitions are equivalent, because a sustained imbalance in the radiation budget inevitably leads to evaporation of the ocean. Definitions aside, Hansen’s conjecture has received some disturbing support from recent climate calculations (Goldblatt et al 2013), although the CO₂ concentration at which the runaway is predicted to occur, 30,000 ppmv, or ~100 times the Preindustrial Atmospheric Level (PAL), is a factor of 10 higher than that which might result from the burning of all fossil fuels. This result contradicts previous predictions (Kasting & Ackerman 1986) that surface liquid water would remain stable for CO₂ increases up to 100 bar. Which, if either, of these two predictions is correct? Here, we use our own 1-D climate model to try to answer this question.

A possible reason for the different behavior of the two high-CO₂ climate models is their different absorption coefficients. The Goldblatt et al (2013) climate model utilized the new HITEMP database (Rothman et al 2010) for H₂O absorption in place of the older HITRAN database (Rothman et al 1998). This change results in greater absorption of incoming solar radiation, thereby lowering the planet’s albedo and destabilizing the climate. In their model, the reported net absorbed solar flux, \( F_s \), for a pure H₂O atmosphere at surface temperatures >500 K was 294 W/m². The net outgoing infrared flux, \( F_{IR} \), for these warm atmospheres was 282 W/m², which is 12 W/m² lower than the
absorbed flux. Because $F_s > F_{IR}$, a transient perturbation such as a CO$_2$ increase could, in principle, trigger a runaway greenhouse.

A problem with this analysis is that the fluxes shown in Fig. 2 of Goldblatt et al (2013) do not match the values cited in their text: the asymptotic (high temperature) value of $F_s$ appears to be ~286 W/m$^2$, not 294 W/m$^2$, independent of the assumed surface albedo. This can be checked by recalculating $F_s$ using the data shown in the insert to their Fig. 2a. In a globally averaged climate model, $F_s \equiv \frac{S}{4}(1 - A)$. The solar flux, $S$, assumed by Goldblatt et al (2013) is 1372 W/m$^2$. The planetary albedo, $A$, shown in the insert is ~0.165; thus, the calculated value of $F_s$ is 286 W/m$^2$. When these more accurate values are used, $F_s$ exceeds $F_{IR}$ by only ~4 W/m$^2$, and so a small change in either flux could determine whether this particular model will go runaway.

5.3 Methods

For more details on the climate model, refer to thesis Section 2.

Our base modern Earth calculation assumes a 1-bar atmosphere consisting of 78% N$_2$, 21% O$_2$, 1% Ar, and ozone. The surface pressure and atmospheric composition change at higher temperatures as more H$_2$O vapor and/or CO$_2$ is added (or removed). As CO$_2$ concentrations rise, its average atmospheric abundance is dependent on mixing with the remaining atmospheric gases (more details in Appendix D).

The climate simulations are performed in two different ways depending both on the ozone concentration present in the upper atmosphere as well as whether or not foreign broadening by terrestrial air can be approximated by self-broadening by CO$_2$ and H$_2$O. At lower surface temperatures, ozone forms a prominent stratospheric inversion and it is critical to properly compute the evolution of stratospheric temperatures. In this case, forward calculations are performed. At temperatures exceeding ~ 305 K (and pCO$_2$ > 6x10$^{-3}$ bar), the forward calculation method becomes unstable because of the strong water vapor feedback. However, the ozone layer is depleted and the stratospheric inversion disappears, facilitating the use of inverse calculations. With this technique, the surface temperature is gradually incremented from 200 K to 1000 K, assuming a moist adiabatic troposphere and a stratosphere that is isothermal at 200 K. The solar flux required to maintain radiative equilibrium at each temperature is then computed. At those same lower surface temperatures, the base model, which assumes foreign broadening can be approximated by self broadening, overestimates absorption because self broadening is generally stronger than foreign broadening. In this regime, we derived mixed CO$_2$-H$_2$O coefficients that correctly compute foreign broadening using the following grid of 4 temperatures (200 K, 250 K, 300 K, 350 K), 5 pressures (1x10$^{-3}$ bar – 10 bar), 4 CO$_2$ mixing ratios (1x10$^{-4}$-1x10$^{-1}$), and 8 H$_2$O mixing ratios (1x10$^{-4}$-1x10$^{-1}$). Rayleigh scattering is performed as described in the erratum to Kopparapu et al (2013).
Upper tropospheric relative humidity was parameterized as in Kasting and Ackerman (1986):

\[
RH = R_{\text{surf}} \left[ \frac{P}{P_s} - 0.02 \right]^{\Omega} \right] \Omega
\]

Here, \( R_{\text{surf}} \) (~ 0.8) is the surface RH, \( RH \) is the RH at some height above the surface, \( P \) is the pressure at a given height, and \( P_s \) is the surface pressure. \( \Omega = 1 \) produces a standard Manabe-Wetherald RH distribution (Manabe & Wetherald 1967). For the calculations shown here, this assumption was replaced by

\[
\Omega = 1 - \frac{q_o - q_{o_{288}}}{0.1 - q_{o_{288}}}
\]

Here, \( q_o \) is the saturation H\(_2\)O mixing ratio at the surface, and \( q_{o_{288}} = 0.0166 \) is the surface saturation mixing ratio at 288 K.

Our surface relative humidity (RH) parameterization is similar to that used by Kasting et al (2013). It is based on the requirement that the net convective (latent + sensible) heat flux, \( F_{\text{net}} \), must balance the net absorbed radiative (solar + thermal-IR) flux (Ramanathan 1981, Boer 1993, Trenberth 1998, Allen & Ingram 2002, Held & Soden 2006, Soden & Held 2006). We start from the following commonly used expression (Garratt 1992) for the latent heat flux, \( F_L \), (in units of W/m\(^2\)):

\[
F_L = L C_D u \rho (q_o - q_i)
\]

Here, \( L \) is the latent heat of vaporization of water (2.5×10\(^6\) J/kg), \( C_D \) is the drag coefficient at layer 1 just above the surface, \( u \) is the mean horizontal wind speed near the surface in m/s, \( \rho \) is the atmospheric sea level mass density in kg/m\(^3\), \( q_o \) is the surface H\(_2\)O mixing ratio.
saturation mixing ratio, and \( q_1 \) is the H\(_2\)O mixing ratio at layer 1. Defining the Bowen ratio, \( B \), as the ratio of the sensible heat flux to the latent heat flux, we can write:

\[
F_{\text{net}} = L C_D u \rho q_o (1 - R_{\text{surf}}) (1 + B) \tag{20}
\]

The drag coefficient \( (C_D) \) and wind speed \( (u) \) are both unknown and cannot be self-consistently calculated in our 1-D model. Thus, we make the simplifying assumption that the product \( C_D \cdot u \) remains constant at all surface temperatures. This assumption is reasonable because \( C_D \) does not vary greatly over water surfaces (Arya 2001) and because most of Earth’s surface is ocean. Evaluating eq. (20) at the present mean surface temperature of 288 K allows us to solve for the product \( C_D \cdot u \):

\[
C_D \cdot u = \frac{F_{\text{net}}^{288}}{\rho_{288} L q_o^{288} (1 - R_{\text{surf}}^{288}) (1 + B_{288})} \tag{21}
\]

The relevant values for the quantities in the above equation at 288 K are: \( F_{\text{net}}^{288} = 97 \) W/m\(^2\), \( \rho_{288} = 1.225 \) kg/m\(^3\), \( q_o^{288} = 0.0166 \), \( R_{\text{surf}}^{288} = 0.8 \), and \( B_{288} = 0.59 \). The above expression can then be substituted into eq. (20) to give:

\[
R_{\text{surf}} = 1 - (1 - R_{\text{surf}}^{288}) \left( \frac{F_{\text{net}}}{F_{\text{net}}^{288}} \right) \left( \frac{\rho_{288}}{\rho} \right) \left( \frac{q_o^{288}}{q_o} \right) \left( \frac{1 + B_{288}}{1 + B} \right) \tag{22}
\]

\( R_{\text{surf}} \) is plotted as a function of surface temperature in Fig. 5.1.
Fig. 5.1: Surface relative humidity as a function of increasing surface temperature, as calculated from eq. (22).

A 3-D model would contain additional parameters (wind speed and surface roughness) and thus might not produce the same result. These complications are bypassed in eq. (22) by normalizing all parameters to present global average values.

The photochemical model of Segura et al (2003) was used to assess the evolution and subsequent depletion of the ozone layer as water vapor concentrations increase. We refer the reader to Segura et al (2003) for a full photochemical model description. However, the following updates were made:

1) The H$_2$O and CO$_2$ UV absorption cross sections were replaced, including high temperature (up to 400 K) cross sections for CO$_2$ (Yoshino et al 1996, Parkinson et al 2003, Karaiskou et al 2004, Ityaksov et al 2008, Venot et al 2013).


The two models were run sequentially, with the climate model calculations being done first, and with the results then used as input for the photochemical model. The resulting change in ozone concentrations was not fed back into the climate model, as sensitivity calculations revealed this had little effect on the results.
5.4 New high-CO$_2$ climate calculations

To clarify whether a CO$_2$-induced runaway greenhouse is possible, we used our own recently updated, 1-D climate model (Kopparapu et al 2013, Ramirez et al 2013) to reexamine this problem. Our model also uses the HITEMP database (Rothman et al 2010) for H$_2$O, along with the HITRAN 2008 database (Rothman et al 2009) for CO$_2$. However, unlike Goldblatt et al (2013), who performed line-by-line radiative transfer calculations, our model uses the correlated-\(k\) method (Fu & Liou 1992) to estimate average absorption coefficients over relatively broad spectral intervals (see Methods). This makes our model computationally much faster, allowing us to adjust the mean surface temperature, \(T_s\), by time-stepping until flux balance is achieved. By contrast, Goldblatt et al (2013) performed static radiative flux calculations at fixed values of \(T_s\). Despite making this approximation, the net absorbed solar flux in our model ranges from 284 W/m$^2$ at 500 K to 287 W/m$^2$ at 2000 K (Fig. 5.2a), in close agreement with the asymptotic value from Goldblatt et al (2013). The calculated planetary albedo at high surface temperatures is 0.166, which is essentially the same as the Goldblatt et al (2013) value. We used the same two values of surface albedo for this calculation as they did, 0.12 and 0.25. The net outgoing thermal radiation flux at high surface temperatures is 282 W/m$^2$ (Fig. 5.2b), which matches the Goldblatt et al (2013) value precisely. As explained in Chapter 3, our new value for \(F_{IR}\) is somewhat lower than the 291 W/m$^2$ reported in Kopparapu et al (2013) after correcting an error in our H$_2$O, thermal-IR, \(k\)-coefficients. This value is slightly higher than the 280 W/m$^2$ computed in Chapter 3 because the solar flux we assumed there was 1360 W/m$^2$, 12 W/m$^2$ lower than the flux assumed by Goldblatt et al (2013). Additional radiative flux comparisons with the Goldblatt et al (2013) model and with SMART (Meadows & Crisp 1996), upon which it is based, are given in Appendix A. The wavelength-integrated fluxes calculated by our radiative transfer model agree with those calculated by SMART to within 1 percent at high surface temperatures and 4 percent for the modern Earth. A second model, which agrees more closely with SMART for modern Earth, is used as a check on these calculations.

Note that for pure H$_2$O atmospheres both our model (Fig 5.2c) and that of Goldblatt et al. (Fig. 2c) appear to be unstable against warming at low surface temperatures, as the absorbed solar flux exceeds the outgoing infrared flux for \(T_s < 500\) K even when cloud feedback is implicitly included by adopting a high surface albedo. Earth’s climate is not unstable, though; if it was, we would not be here. Stability is ensured by several factors, most importantly Rayleigh scattering by N$_2$ and O$_3$, which increases the planetary albedo, and the “radiator fin” behavior of the descending branch of the Hadley cells (Pierrehumbert 1995) where the highly undersaturated air allows for a large outgoing infrared flux. This shows that it can be misleading to use radiative flux calculations of pure H$_2$O atmospheres to evaluate climate stability.
Figure 5.2: Top of atmosphere fluxes for a pure H$_2$O atmosphere with a surface albedo of 0.12 (green) and 0.25 (purple), respectively. Steady-state climates are found when the net outgoing flux is zero; stable steady states exist when the slope of the net outgoing flux is positive. The planetary albedo at high surface temperatures is 0.166. Six solar zenith angles were used in this calculation.

We next adjusted the surface albedo, $A_S$, in our (cloud-free) model so that it reproduced the observed surface temperature of modern Earth, $T_s = 288$ K, assuming a
solar constant, $S$, of 1360 W/m$^2$ and modern atmospheric composition. As has been shown in previous climate calculations by our group (Kasting & Ackerman 1986, Pavlov et al 2000, Haqq-Misra et al 2008), normalizing $A_S$ in this manner simulates the net effect of cloud forcing, without including clouds explicitly, and ensures that the computed surface temperature does not drift towards warmer or cooler values. The required value of $A_S$ is 0.315, considerably higher than the value of 0.25 computed by Goldblatt et al (2013). Our model requires a higher surface albedo to offset the increased greenhouse effect from assuming that broadening by air can be approximated by CO$_2$ and H$_2$O self-broadening. Our alternative model, described in Appendix A2, treats foreign broadening correctly and requires a lower surface albedo. The results shown here, however, use the high-surface albedo model, because that model remains valid at high surface temperatures.

With the climate model now properly normalized, we then increased atmospheric CO$_2$ pressures incrementally from its present value, $5 \times 10^{-4}$ bar in our units (see below), up to 100 bar, following a methodology similar to that of Kasting and Ackerman (1986) (See Fig. 5.3). Thus, there is a key difference in our methodology from that of Goldblatt et al (2013). Whereas our model directly assesses temperature responses caused by increased CO$_2$ pressure, Goldblatt et al (2013) incremented surface temperatures while keeping CO$_2$ concentrations constant. As in the earlier calculation, the quantity ‘CO$_2$ pressure’ shown on the horizontal axis is the pressure that CO$_2$ would exert if no other gases were present (Appendix E1). The actual CO$_2$ partial pressure is lower than this because lighter gases, primarily N$_2$ and O$_2$, dilute the CO$_2$ by causing it to diffuse to higher altitudes. Our choice of units ensures that CO$_2$ pressure varies linearly with added CO$_2$. Again following Kasting and Ackerman (1986), we assumed that upper tropospheric relative humidity, RH, increases with $T_S$ (Section 5.8). Such a change is probably required for pressure balance, as Goldblatt et al (2013) also point out. 3-D climate calculations would be needed to test this parameterization, although doing so would likely require improvements to 3-D models, as most of them treat water vapor as a minor atmospheric constituent (i.e., the change in pressure is neglected when it condenses). One recent study of warm, moist atmospheres (Leconte et al 2013) does treat water vapor as a major constituent; however, these authors do not report changes in upper tropospheric RH as the climate warms.
Figure 5.3: (a) Planetary albedo, (b) surface temperature, and (c) surface relative humidity versus CO$_2$ pressure for the simulations with RH feedback included (eqs. 20 - 22). The assumed surface albedo is 0.315.
Unlike either of the two previous 1-D calculations (Kasting & Ackerman 1986, Goldblatt et al 2013), we also assumed that surface RH increases with $T_S$, approaching values close to unity at very high surface temperatures (Fig 5.1), and thus at high CO$_2$ pressures (Fig. 5.3c). This latter assumption should be relatively robust, as surface energy balance requires such an increase to keep the latent heat flux from growing to unphysical values (Kasting et al 2013). 3-D climate models that include explicit boundary layer physics have additional degrees of freedom that might modify this behavior, but we predict that those models, too, will approach saturation near the surface as $T_S$ becomes high and the saturation vapor pressure of water becomes large. This prediction should be tested by running such models under high-CO$_2$ conditions.

The results shown in Fig. 5.3 are considerably warmer than those in Kasting and Ackerman (1986), reaching ~ 460 K at 1x10$^{-2}$ bar. Moreover, the calculated planetary albedos are somewhat lower as a consequence of the increased absorption of sunlight by H$_2$O. For the first CO$_2$ doubling, our model predicts 2.3 K of warming, which agrees exactly with one recent 3-D calculation (Schmittner et al 2011). (Removing all RH feedbacks reduces this value slightly to 2.2 K.) This is near the middle of the range of values, 1.5 - 4.5 K, predicted by the Intergovernmental Panel on Climate Change (Solomon & Head 1991) for doubled CO$_2$. The abrupt increase in $T_S$ near 6x10$^{-3}$ bar of CO$_2$ (12 PAL) marks the point at which the upper troposphere becomes highly saturated in our model. A similar increase in $T_S$ occurred at ~60 PAL in the model of Kasting and Ackerman (1986). A 3-D climate model with a more realistic hydrologic cycle would be unlikely to predict such a sharp transition in either $T_S$ or RH (see further discussion below). Although a runaway greenhouse state was not triggered in our model it could have been achieved with just a few more W/m$^2$. However, given that our surface RH parameterization and separate CO$_2$ and H$_2$O coefficients probably overestimate the absorption, Earth is probably much safer from a runaway than predicted here. At low CO$_2$ concentrations (<~ 0.05 bar), Earth’s atmosphere is stable against a runaway primarily because atmospheric dilution by N$_2$ and O$_2$ which increases the albedo by causing Rayleigh scattering, as mentioned earlier (“radiator fin” behavior does not exist in a 1-D model). At higher CO$_2$ pressures, Earth’s climate is stable for another reason. As pointed out in Kasting and Ackerman (1986) , CO$_2$ has a high Rayleigh scattering cross section; hence, adding CO$_2$ to the atmosphere increases the planetary albedo, thereby partially offsetting the increased greenhouse effect. Or, to think of this problem another way, if a pure H$_2$O atmosphere is just on the edge of stability, as indicated in Fig. 5.2, an atmosphere diluted with strongly scattering, more poorly absorbing CO$_2$ should be stable against runaway climates. Additional calculations (not shown) in which the surface albedo was held constant at 0.12 indicate that runaway does not occur in that case either; thus, this conclusion appears robust, at least for cloud-free atmospheres.
5.5 The effect of clouds in warm, moist atmospheres

In reality, the climate at higher CO$_2$ levels would likely be affected by cloud feedback. Clouds have a complex effect on climate: low, water clouds tend to cool the surface, whereas high cirrus clouds warm it (Choi & Ho 2006). Whether cloud feedback is positive or negative depends on which types of clouds change the most, and how. In doubled CO$_2$ experiments for the modern Earth, many current 3-D climate models predict that cloud feedback is positive for doubled CO$_2$, because cirrus clouds increase fastest as the climate warms slightly (Brient & Bony 2012). But researchers using 1-D models have predicted that cloud feedback should be negative for much warmer atmospheres, because clouds add little to their already-high infrared opacity, whereas their effect on planetary albedo remains significant (Kasting 1988).

We investigated cloud feedback using a methodology similar to that of Kasting (1988), except that we were careful to specify cirrus clouds at atmospheric temperatures below the freezing point and water clouds at temperatures above it; also, our cloud decks were thinner (~1 km in depth) in order to maximize cirrus warming. This vertical resolution was achieved by increasing the number of layers in our model from 100 to 200. For water clouds, we assumed a log-normal particle size distribution and a mean radius of 15 µm, and published parameterizations were used to determine optical parameters (Slingo 1989, Hu & Stamnes 1993). For cirrus clouds, we used a gamma distribution of particle sizes (Hansen & Travis 1974) with a mean radius of 30 µm. Optical properties were computed using appropriate cirrus cloud parameterizations (Hong et al 2009). The wavenumber-dependent optical depths ($\tau$) were found from the following equation ((Slingo 1990, Platt 1997):

$$\tau = \frac{3Q_{\text{eff}} \cdot \text{IWC} \cdot \Delta z}{4r\rho}$$  \hspace{1cm} (23)

Here, $Q_{\text{eff}}$ is the wavenumber-dependent extinction efficiency, $\rho$ is the mass density of ice, $r$ is the particle radius, IWC is the ice water content (g/m$^3$), and $\Delta z$ is the vertical path length of the layer (m). Values for $Q_{\text{eff}}$ and IWC were taken from Yang et al (1997) and Platt (1997), respectively. $Q_{\text{eff}}$ was set equal to 2 across the thermal-infrared because extinction efficiencies for ice crystals $> - 25$ µm radius approach this value (Yang et al 1997).
First, we compare our new results with those of Kasting (1988). The solid and dashed curves in Fig. 5.4 illustrate the effect of 100% and 50% cloud cover on both the net fluxes at the top of the atmosphere and planetary albedo for a 5-bar CO\(_2\) atmosphere. Optical properties and flux data are listed in Tables 5.1 and 5.2, respectively. The first 5 rows are the cirrus cloud decks. As found in previous work (Kasting 1988), water clouds have little impact on the outgoing radiative flux at the top of the atmosphere, \(F_{\text{IR}}\) (Fig. 5.4a). However, the addition of cirrus clouds shows that high clouds exhibit more warming than originally shown by Kasting (1988), reducing \(F_{\text{IR}}\) to a minimum value of 182 W/m\(^2\) at 8x10\(^{-4}\) bar and 100% cloud cover. The net absorbed solar flux, \(F_s\), decreases by a factor of \(\sim 2.5\), corresponding to an increase in planetary albedo from 0.25 to \(\sim 0.65\) (Fig 5.4b), exhibiting a similar trend to that of Kasting (1988). Our maximum planetary albedo value is lower than the corresponding maximum of \(\sim 0.8\) calculated by Kasting (1988) because that study used thicker clouds and smaller water droplets (5 \(\mu\)m radius), which are more strongly reflective.
Figure 5.4: Effect of a single cloud layer on the (a) net absorbed solar ($F_s$) and outgoing infrared ($F_i$) fluxes at the top of the atmosphere and (b) planetary albedo for a 405 K and 5-bar CO$_2$ atmosphere. The surface albedo is 0.125. Solid and dashed curves are for 100% and 50% cloud cover, respectively. The vertical dashed lines mark the pressures associated with the location of the tropopause (left) and the freezing point of water (right). All pressures are calculated at the midpoints of the cloud deck.
Table 5.1: Cloud decks and associated properties for 15 μm water droplets and 30 μm cirrus particles and the 5-bar CO₂ atmosphere of Fig. 5.4

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<td>8.162</td>
<td>0.78</td>
<td>402</td>
<td>2.698</td>
<td>439.7</td>
</tr>
</tbody>
</table>

ᵃValues are listed at the midpoint of the cloud deck. Read 1.0(5) as 1.0 x 10⁵.
Table 5.2: Computed fluxes for the different cloud decks for the same atmosphere as Table 5.1.

<table>
<thead>
<tr>
<th>Pressure (bar)(^a)</th>
<th>Altitude (km)(^a)</th>
<th>(F_{IR})</th>
<th>(F_s)</th>
<th>(S_{EFF})</th>
<th>(\Delta T (K)^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.57(-4)</td>
<td>68.4</td>
<td>257</td>
<td>257</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>7.84(-4)</td>
<td>63.2</td>
<td>182.1</td>
<td>226.1</td>
<td>0.805</td>
<td>+55</td>
</tr>
<tr>
<td>3.6(-3)</td>
<td>55.3</td>
<td>200.6</td>
<td>220.6</td>
<td>0.909</td>
<td>+9</td>
</tr>
<tr>
<td>1.68(-2)</td>
<td>46.7</td>
<td>215</td>
<td>137.7</td>
<td>1.56</td>
<td>-11</td>
</tr>
<tr>
<td>3.78(-2)</td>
<td>41.8</td>
<td>234.4</td>
<td>114.9</td>
<td>2.04</td>
<td>-20</td>
</tr>
<tr>
<td>2.07(-1)</td>
<td>30.6</td>
<td>256.1</td>
<td>170.2</td>
<td>1.50</td>
<td>-29</td>
</tr>
<tr>
<td>8.25(-1)</td>
<td>20.45</td>
<td>256.3</td>
<td>185.9</td>
<td>1.38</td>
<td>-51</td>
</tr>
<tr>
<td>2.75</td>
<td>10.62</td>
<td>256.3</td>
<td>210.6</td>
<td>1.22</td>
<td>-79</td>
</tr>
<tr>
<td>4.86</td>
<td>5.62</td>
<td>256.3</td>
<td>223.4</td>
<td>1.15</td>
<td>-79</td>
</tr>
<tr>
<td>8.162</td>
<td>0.78</td>
<td>256.3</td>
<td>232</td>
<td>1.10</td>
<td>-35</td>
</tr>
</tbody>
</table>

\(^a\)Values are listed at the midpoint of the cloud deck.

\(^b\)Predicted change in surface temperature when the cloud deck is included
Results are summarized in Fig. 5.5 in terms of the effective solar flux, $S_{\text{eff}} = F_{\text{IR}}/F$, needed to maintain the atmosphere in steady state. (The latter two quantities were defined at the end of the previous section.) $S_{\text{eff}} > 1$ indicates that the albedo effect of clouds dominates their greenhouse effect, so that clouds cool the climate; $S_{\text{eff}} < 1$ means that the cloud greenhouse effect dominates, so that clouds warm the climate. The two mid-level cloud decks exhibit net warming, with $S_{\text{eff}}$ values below 1 and optical depths in the single digits (Tables 5.1-5.2). This result agrees with satellite observations from Choi and Ho (2006), suggesting that cirrus clouds warm for visible/near-IR optical depths less than 10. However, the net effect of these cirrus clouds is to cool the surface, as the average $S_{\text{eff}}$ value for these 5 decks is nearly 30% above the clear sky value (Table 5.2). Therefore, the increase in high clouds and the disappearance of low clouds, as suggested by recent studies (Brient & Bony 2012, Leconte et al 2013), does not necessarily yield positive cloud radiative forcing, because relatively low and warm ($-240 \text{ K} - 270 \text{ K}$) cirrus clouds may cool the climate instead. Although cirrus cloud coverage increases most rapidly with increased surface temperature in many 3-D climate models (Brient & Bony 2012, Leconte et al 2013), our results suggest that overall cloud forcing may still be negative in moist and optically thick atmospheres even if water clouds are entirely absent.

As one last test, we maximized the possibility of triggering a runaway greenhouse by inserting the cirrus cloud deck with the strongest positive forcing (line 2 of Table 5.2) and evaluating its effect on surface temperature in the absence of any other clouds. This was done by computing how much the surface temperature must rise for radiative-energy equilibrium ($S_{\text{eff}} = 1$) to be again achieved. The calculated surface temperature for this case rose from 405 K to 460 K, as shown by the last column of Table 5.2. This surface temperature, while hot, is still 187 K lower than the critical temperature of water, suggesting that even cirrus clouds are incapable of triggering a runaway greenhouse. A similar analysis performed for each of the remaining cloud decks produced surface temperature decreases as high as 79 K for some of the lowest water clouds (Table 5.2, last column), reaffirming the idea that most clouds should cool the climate. Consequently, cloud feedback appears unlikely to alter our conclusion that CO$_2$-induced runaway greenhouses are not possible. If anything, cloud feedback should make the climate more stable in the very high surface temperature regime.
Figure 5.5: Effect of a single cloud layer on the planetary radiation balance for the 5-bar CO$_2$, 1-bar N$_2$ 405 K atmosphere in Figure 5.4. The horizontal scale shows the pressure at the center of the assumed, 1-km thick cloud deck; the vertical scale represents the effective solar flux, $S_{\text{eff}}$, required to maintain steady state. Solid and dashed curves are for 100% and 50% cloud cover, respectively. The vertical dashed lines mark the pressures associated with the location of the tropopause (left) and the freezing point of water (right). For cloud-free conditions, $S_{\text{eff}} = 1$. Values of $S_{\text{eff}} > 1$ mean that the cloud cools the surface: $S_{\text{eff}} < 1$ means that the cloud warms the surface.

5.6 Human health issues at modest CO$_2$ increases

Just because Earth’s climate is stable does not imply that future CO$_2$ increases are not dangerous. In addition to long-term threats such as sea level rise, heat stress on humans is a significant issue, especially in the tropics (Sherwood & Huber 2010). Sherwood and Huber (2010) argue that hyperthermia will be induced within hours when the local wet bulb temperature exceeds ~35 °C, two degrees below the human body temperature. According to their 3-D climate calculations, this wet bulb temperature would be reached seasonally and diurnally over some parts of the globe once the mean surface temperature exceeds 295 K. For $T_s = 300$ K, hyperthermia would spread even further and render most regions of the planet uninhabitable. Our base model predicts that these thresholds would be reached at CO$_2$ levels of ~1300 ppmv (4 PAL) and ~2600 ppmv (8 PAL), respectively (Fig. 5.6). For the alternative (low albedo surface) model, the corresponding CO$_2$ levels are
1800 ppmv (5.5 PAL) and 3500 ppmv (10.6 PAL). Also shown in Fig. 5.6 are results from a recent 3-D climate model study by Caballero and Huber (2013). They compute significantly higher heat stress thresholds of ~ 2160 ppmv and ~5000 ppmv CO$_2$, respectively, for modern surface boundary conditions. When they use Paleogene boundary conditions, though, with no ice and vegetated deserts, their predicted surface temperatures are fairly close to our own. The Paleogene simulation may be a good analog for what might happen as atmospheric CO$_2$ increases in the future. However, even the Paleogene 3-D calculation might underpredict surface temperatures at high CO$_2$ concentrations because the climate model used, CCSM3, does not treat water vapor as a major constituent. Recall that our model assumes increased upper tropospheric RH at high surface temperatures, based on the idea that condensation of a major constituent should lead to pressure changes that, in turn, may make it more difficult for that constituent to condense.

**Figure 5.6:** Surface temperature as a function of CO$_2$ concentration (ppmv) for our model for both the high and low albedo simulations (black curves) and for the modern (blue dashed curve) and Paleogene (green dashed curve) models of Caballero and Huber (2013). The dashed horizontal lines at 300 K and 295 K represent published heat stress thresholds from Sherwood and Huber (2010). Localized thermal stress on humans begins to become significant at 295 K and becomes widespread above 300 K.
Which, if either, of these two heat stress thresholds might be reached from burning fossil fuels? Estimates of economically recoverable fossil fuel reserves are in the range of 2000-5000 Gt C (Rogner 1997, Mohr 2010, Patzek & Croft 2010, Rutledge 2011). Values near the lower end of this range assume that recoverable coal is less abundant than previously believed (Rutledge 2011). 1 PAL of CO\(_2\) (330 ppmv) corresponds to ~ 700 Gt C; thus, if one were to burn all 5000 Gt of carbon instantaneously, atmospheric CO\(_2\) would increase by a factor of ~8, to over 2600 ppmv, reaching at least the lower of the two postulated heat stress thresholds and making parts of the world uninhabitable by humans. The higher threshold could be reached if our 1-D climate calculations are correct. If the recoverable fossil fuel reserves are closer to 2000 GtC, then CO\(_2\) could still increase to 4 PAL in our simulation, reaching the lower heat stress threshold. Neither of these CO\(_2\) estimates includes the vast quantities of methane gas hydrates thought to reside on the seafloor (Kvenvolden 1988), and thus may be regarded as conservative.

5.7 Effect of increased temperatures on stratospheric ozone levels

An additional health threat is triggered in our model if atmospheric CO\(_2\) exceeds ~3600 ppmv (12 PAL), producing a wet stratosphere. A wet stratosphere, were it to occur, would likely destroy stratospheric ozone in addition to leading to water loss. Indeed, this phenomenon, along with the surface temperature increase itself, would pose a more immediate threat to surface life. The ozone would be destroyed by various catalytic cycles involving HO\(_x\) species (H + OH + HO\(_2\)) produced from H\(_2\)O photolysis. A representative set of reactions describing the process is the following:

\[
\begin{align*}
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2 \\
\text{HO}_2 + \text{O} & \rightarrow \text{OH} + \text{O}_2 \\
\text{Net:} \quad \text{O} + \text{O}_3 & \rightarrow 2\text{O}_2
\end{align*}
\]

To determine when this process would start to become important, we performed a series of calculations with the 1-D photochemical model (described in Section 5.8). Temperature and atmospheric water vapor profiles calculated by the climate model were used as inputs for the photochemical model, then the latter model was iterated to steady state to determine the effect on ozone. The average path length of ozone in today’s atmosphere is ~0.3 atm-cm. For small increases in CO\(_2\), the effects on ozone are minimal: O\(_3\) concentrations actually increase slightly in the stratosphere because the cooler temperatures there lead to a decrease in the rate of reactions that destroy ozone. This increase in stratospheric ozone is accompanied by a slight loss of ozone in the troposphere. The net result is that the overall ozone path length remains approximately constant up to CO\(_2\) concentrations of ~12 PAL, after which the ozone is quickly depleted (Fig. 5.7). At 12 PAL and above, ozone is destroyed at an alarming rate as the stratosphere becomes
wet. By the time 12 PAL of CO$_2$ is reached, the ozone path length has dropped to ~3% of its original value.

Figure 5.7: Ozone profiles for different atmospheric CO$_2$ levels: a) 1 PAL (blue line), b) 2 PAL (dashed purple), and c) 12 PAL (green line with circles).

High stratospheric H$_2$O would also result in increased rates of water loss by way of photodissociation followed by hydrogen escape—a phenomenon sometimes termed a moist greenhouse (Kasting 1988). However, atmospheric CO$_2$ concentrations would presumably be restored to more normal values by silicate weathering within a few million years (Walker et al 1981), before substantial water loss could occur. Furthermore, high CO$_2$ cooling rates in the upper atmosphere might keep the stratosphere cold and prevent water loss from occurring, in any case (Leconte et al 2013, Wordsworth & Pierrehumbert 2013b).
5.8 Conclusions

In summary, Earth’s atmosphere appears to be stable against a CO$_2$-induced runaway greenhouse, contradicting Goldblatt et al (2013), but in agreement with older calculations (Kasting & Ackerman 1986). However, the threat to human health from unrestrained fossil fuel burning remains acute, with direct heat stress to humans posing the most immediate danger. If our calculations and those of other climate modelers (Sherwood & Huber 2010, Caballero & Huber 2013) are even approximately correct, holding atmospheric CO$_2$ increases to less than a factor of 6 above preindustrial values is essential to human health and survival.
6. THESIS SUMMARY AND SIGNIFICANCE

The work herein is composed of three distinct, but connected, topics: (a) a re-evaluation of the boundaries of the habitable zone, (b) a greenhouse solution for early Mars using CO$_2$-H$_2$, and (c) an assessment of the likelihood that increases in $p$CO$_2$ can trigger a runaway greenhouse on present Earth.

The new conservative estimates for the inner and outer edges of the habitable zone are at 0.95 AU and 1.64 AU, respectively. The former limit, computed by Leconte et al (2013), replaces previously computed 1-D runaway and moist greenhouse limits. These new HZ boundaries compare to the 0.95 AU and 1.67 AU values first derived by Kasting et al (1993) and the 0.99 AU and 1.67 AU values recently derived (Kopparapu et al 2013). Although permitted absorption by CO$_2$ is stronger with the newer HITRAN 2008 linelist, this is almost completely offset by its weaker collision-induced absorption, resulting in a virtually unchanged outer edge limit. A wide habitable zone has positive implications for next generation telescopes attempting to find Earth-sized planets in the habitable zone.

This thesis is the first study to illustrate a viable warm and wet greenhouse climate for early Mars. Although a CO$_2$-H$_2$O greenhouse alone is insufficient to produce a warm climate, it is shown that ~5-20% H$_2$, along with ~1.3 - 4 bar CO$_2$ could have generated surface temperatures above freezing and led to a wet climate capable of producing the ancient valleys. Because of the highly-reduced early Martian mantle, H$_2$ outgassing rates would have been high enough to keep H$_2$ abundant and outpace escape. CO and CH$_4$ could have been stored as Fe-carbonyl, forming abundant CO$_2$ from the interaction with the products of water vapor photolysis. Oxidation of CH$_4$ could have further supplemented atmospheric H$_2$ although its potency as a greenhouse agent on early Mars is very limited.

In contrast, the additional H$_2$O absorption lines afforded by HITTEMP 2010, as first demonstrated by Goldblatt et al. (2013), render Earth more susceptible to a runaway greenhouse than previously imagined (Kasting and Ackerman, 1986). However, implementation of HITTEMP in our model finds that Earth is stable against a runaway greenhouse for any amount of CO$_2$, directly contradicting the conclusions of Goldblatt et al (2013). Furthermore, our cloud study is the first to demonstrate that not even cirrus clouds can trigger a runaway greenhouse, even if warming is maximized. In fact, relatively low-lying and warm (~240 – 270 K) cirrus clouds may actually cool the climate even if high cloud cover is predicted to increase at higher surface temperatures (Bony and Brient, 2007). Thus, in spite of increased water vapor absorption, the implication is that the habitable zone remains relatively wide, affirming recent 3-D calculations (Leconte et al 2013).
7. FUTURE WORK

Future work would require improving how relative humidity is computed both at the surface and at the cold trap. Accurately computing upper atmospheric humidity is particularly important for determining the moist greenhouse limit and, ultimately, the inner edge. Moreover, while LTE (local thermodynamic equilibrium) processes accurately characterize the lower atmosphere, non-LTE processes dominate the upper atmosphere where the radiative transfer can get extremely complicated (Dickinson 1976). The radiative transfer scheme of Feautrier seems to be particularly well-suited for handling such non-LTE conditions (Mihalas 1978) and should be tested in future 1-D and 3-D models. Future GCM studies should also assess the possibility that low-lying cirrus clouds can also cool climate. To assess this possibility, and resolve cirrus clouds properly in general, vertical resolution needs to be greatly increased over what was used in current models such as that in Leconte et al (2013). Moreover, ozone was neglected in 1-D studies of the inner edge for convenience, but 3-D models should include this important gas because its heating contribution to the upper atmosphere may influence cold trap temperatures. Furthermore, these same GCMS and 1-D models still employ overly-simplified convective schemes, such as that in Manabe and Wetherald (1967), which have been shown to overestimate precipitation in the tropics (Frierson 2007). State-of-the-art schemes, such as the one used by the Goddard Institute of Space Studies (GISS) Model E2, employ a mass flux approach which tracks how a parcel’s ascent entrains air from the environment so that convection penetrates more deeply in moist atmospheres than dry ones (personal communication, Anthony Del Genio, NASA Goddard Institute of Space Studies). Moreover, Hamano et al (2013) had used their 1-D climate model to calculate a critical distance beyond which planets retain their oceans during planetary accretion. However, their analysis assumed that cloud albedo during this magma ocean stage can be approximated by the present Earth’s. Thus, this analysis should be revisited with a 3-D GCM that self-consistently calculates cloud cover. The potential challenge with this problem is in ensuring the GCM functions in the runaway greenhouse regime.

At the outer edge, the H₂-CO₂ greenhouse problem for early Mars should be revisited in 3-D, making full use of dynamical, microphysical, and cloud processes. One potential issue with the H₂-CO₂ greenhouse for early Mars is that it requires an exceptionally reduced mantle. Although the SNCs generally point to a reduced martian mantle, nearly all of them were formed after the period of interest, raising questions about their applicability to this earlier epoch in geologic history. To date, only the ALH84001 meteorite exhibits unequivocal evidence for a highly reduced early mantle. Plus, at least one study argues that Mars’ upper mantle was oxidized very early in its history, assuming alteration processes do not explain their trends (Tuff et al 2013). Another problem is that methanogens would have consumed the H₂ in a H₂-rich atmosphere, which implies that early Mars could not have had life (Section 3.12). This may be a concern for optimistic
astrobiologists hoping to one day find life on the Red Planet. Thus, it may also be fruitful to continue examining other greenhouse solutions for early Mars, perhaps in addition to H2, such as SO2 and H2S, given the high sulfur abundances measured on the martian surface (Dreibus & Wanke 1985). Although these gases tend to rain out in the form of sulfate aerosols, diminishing the greenhouse effect (Tian et al 2010, Forget et al 2012), the highly-reducing conditions of a H2-rich atmosphere may decrease the rate of such a process. Alternatively, sulfate aerosols may serve as ice nuclei for CO2 ice crystals (Tabazadeh et al 1997), which augments the greenhouse effect by increasing fractional cloud cover and the efficacy of the backscattering mechanism of Forget and Pierrehumbert (1997). Photochemical studies should also be performed to analyze the effectiveness of H2O vapor photolysis in thick early Mars CO2 atmospheres containing minor CH4. The questions to answer here are whether H2O vapor photolysis will be inhibited by: 1) the dense CO2 atmosphere blocking enough sunlight to prevent further production of CO2, and 2) if enough H2 equivalents will be outgassed by photolyzing H2S. All of these greenhouse warming scenarios are fruitful avenues for future research, however, it is equally important to demonstrate why leading cold early Mars hypotheses (Segura et al 2008, Segura et al 2012) are untenable. For instance, the 80 W/m² net absorbed flux computed by Segura et al (2012) is a factor of 3 smaller than what is considered to be necessary to sustain a runaway greenhouse (Kasting et al., 1993, Goldblatt et al 1993, Kopparapu et al 2013, Ramirez et al 2014). Furthermore, Segura et al (2008) claim that impact-generated steam atmospheres could have produced enough rainfall (50 – 500 m) to form the ancient valleys. However, their analysis assumes an exceptionally soft martian regolith with the hardness of loamy silt (Schwab & Frevert 1985). Much larger water amounts would be required had a more appropriate consolidated sediment or bedrock hardness been assumed. Thus, the errors in these previous calculations should be brought to light.

Lastly, the following radiative transfer experiments should be attempted in 3-D models:

1) For problems that do not stray too far from present Earth conditions, mixed CO2-H2O coefficients should be derived in place of separate coefficients. First, what would normally be 8 x 8 calculations for 8-term separate CO2 and H2O coefficients, would reduce by a factor of 8 if mixed coefficients were used. Mixed line cutoffs also allows water continua, requiring specific line cutoffs for H2O (e.g., 25 cm⁻¹ for BPS), to be overlain without double-counting far wing absorption. Furthermore, foreign broadening is that for terrestrial air which is more accurate than assuming it can be approximated by self-broadening by H2O and CO2. However, in CO2- and H2O-dominated atmospheres, foreign broadening can no longer be approximated by terrestrial air, partially invalidating this approach.
Although Voigt line profiles are the most standard lineshape used in paleoclimate modeling studies, this line parameterization neglects collisional narrowing effects, which influences the Doppler broadening of spectral lines (Van Vleck & Weisskopf 1945, Rautian & Sobel’man 1967, Varghese & Hanson 1984). Thus, studies should assess the radiative behavior of the standard Voigt line profile to other ones, such as the Rautian, van-Vleck Weisskopk, and Galtry (ibid) parameterizations, for a suite of atmospheric scenarios from low to high pressures.

Kitzmann et al (2013) have shown that using different radiative transfer schemes can yield different answers for greenhouse warming arising from the backscatter of CO$_2$-ice crystals. This may be related to the number of streams used. More studies should compare the commonly-used Toon et al (1989) scheme with others (e.g. DISORT, Feautrier’s Method) for a wide range of atmospheric scenarios (Feautrier 1964, Rybicki 1971, Stamnes et al 2000).

The two-stream method of Toon et al (1989) should be compared against schemes that use multiple streams in order to assess how the fluxes change in general.
APPENDIX A: RADIATIVE TRANSFER FLUX COMPARISONS

A1 Early Mars irradiance and vertical flux profile comparisons versus SMART

We have checked the accuracy of our new climate model by comparing our output fluxes for given atmospheric composition against both published results and the well-validated LBL radiative transfer model, SMART (Meadows & Crisp 1996). Although SMART also accesses the HITRAN and HITEMP linelists as does KSPECTRUM, its development was entirely independent, making it an ideal comparison tool. For these comparisons against SMART we used 70 layers (instead of the baseline 100) because numerical accuracy issues with SMART did not allow comparison at even higher vertical resolution. However, we’ve verified that the errors in the calculated fluxes from using fewer layers was very small, typically 0.1 – 0.2 W/m². These represent an entire suite of radiative transfer flux comparisons for early Mars and they produce excellent agreement when compared against both SMART and Fig. 2c of Wordsworth et al (2010a) for the same dense CO₂ atmosphere used by the latter authors (see Fig. A1-A6). The last 2 figures demonstrate the radiative effect of different H₂ concentrations on a warmer (273 K) early Mars atmosphere.
Figure A1: Temperature-pressure profiles for a 2 bar 95% CO₂ 5% N₂ dry early Mars atmosphere ($S/S_0 = 0.75$) used for flux comparisons in Fig. A2-A6. The surface temperature is 250 K and stratospheric temperature is fixed at 167K. This test profile is not an output of the nominal runs in main text.
Figure A2: Emission spectra for the atmosphere in Fig. A1, comparing (a) the old model CO₂ coefficients against those of both (b) the new model (this paper), and (c) the line-by-line model SMART (Meadows & Crisp 1996). All three models use the GBB CO₂ CIA parameterization (Gruszka & Borysow 1997, Borysow & Gruszka 1998, Baranov et al 2004). Our computed outgoing longwave radiative (OLR) flux (88.2 W/m²) is in excellent agreement with Wordsworth et al (2010a) Fig 2c and comes to within ~0.2% of SMART. Our old model underestimates CO₂ absorption by ~20 W/m² because of relatively short line truncation (~25 cm⁻¹), which neglects much of the far wing contribution at higher pressures (Halevy et al 2009). Note that previous simulations by our group using the old model (Pavlov et al 2000, Haqq-Misra et al 2008, Tian et al 2010) had implemented the Kasting et al (1984) CO₂ CIA parameterization, which overestimated continuum absorption. Here, we decided to use the GBB CO₂ CIA parameterization for ease of comparison with all three cases.
Figure A3: Surface downwelling longwave radiative (DLR) spectral flux comparisons for the atmosphere in Fig. A1. The longer CO$_2$ line shapes used by both our new model and by SMART explain the ~14% and 11% higher surface downwelling fluxes, respectively, as compared to our old model. Our slightly larger (~3.6%) surface flux as compared to SMART is likely due to the line profile differences discussed in the caption to Fig. A2.
Figure A4: Downwelling longwave radiative (DLR) broadband flux comparisons for the atmosphere in Fig. A1. Fluxes calculated by SMART and by our new model agree well at most heights, although our model has a slightly stronger (~3.6%) greenhouse effect at the surface.
Figure A5: Upwelling longwave radiative broadband flux comparisons for the atmosphere in Fig. A1. Our new model is in excellent agreement with SMART at all heights, whereas the flux calculated by our old model is higher by as much as 19.4 W/m$^2$ in the stratosphere.
Figure A6: Emission spectrum for a 2-bar early Mars ($S/S_0 = 0.75$) atmosphere containing 95% CO$_2$ and 5% N$_2$ (blue), 95% CO$_2$ and 5% H$_2$ (red), or 80% CO$_2$ and 20% H$_2$ (green). The surface temperature is 273K, and the stratospheric temperature is fixed at 167 K. Adding 5% and 20% H$_2$ reduces the outgoing infrared flux by ~6 W/m$^2$ and 22 W/m$^2$, respectively. Vertical infrared flux profiles for these cases are shown in Fig. A7.
Figure A7: Infrared (IR) flux profiles for the 2-bar, 273 K surface temperature atmosphere shown in Figure A6. Although all scenarios yielded a similar downwelling IR flux, the 5% and 20% H$_2$ cases resulted in ~6 and 22 W/m$^2$ reductions in upwelling IR, respectively, greatly, enhancing the greenhouse effect. Coupled with a strong CO$_2$ greenhouse effect, these radiative forcings from H$_2$ increase atmospheric temperatures above freezing.
A2 Modern Earth vertical flux profile comparisons versus SMART using both separate and mixed CO$_2$-H$_2$O coefficients

We also compared our model against Goldblatt et al (2013) for a representative modern Earth atmosphere (Figs. A8-A9). Because we convolve absorption coefficients derived for pure H$_2$O and CO$_2$, our model makes the implicit assumption that foreign broadening by terrestrial air (N$_2$ and O$_2$) can be approximated by H$_2$O and CO$_2$ self-broadening. This assumption is accurate for the CO$_2$- and H$_2$O-dominated atmospheres beyond the transition point at $\sim$ 305 K (or 310 K for the alternative low albedo model explained below), but results in an overestimate of thermal-IR absorption for atmospheres dominated by N$_2$, as self-broadening is generally stronger than foreign broadening. We compensate for our $\sim$10 W/m$^2$ lower top of atmosphere outgoing thermal radiation flux (Fig. A8) by assuming a high surface albedo, 0.315, which results in $\sim$ 10 W/m$^2$ less solar absorption being absorbed (Fig. A9).

To assess the effect of these broadening assumptions, we repeated a subset of our calculations using a set of mixed CO$_2$-H$_2$O coefficients that correctly include foreign broadening. These coefficients are time consuming to calculate because one must calculate coefficients for four different parameters: pressure, temperature, CO$_2$ mixing ratio, and H$_2$O mixing ratio. Hence, we do not have coefficients over the entire temperature range of interest, but we do have parameters in the critical transition region between the modern atmosphere and a moist, H$_2$O-rich atmosphere. As expected, when we use these mixed coefficients, we obtain considerably better agreement with for the modern Earth atmosphere (Fig.s A10-A11).
**Fig. A8:** Upwelling and downwelling vertical infrared flux comparisons between (a) our model (solid red curves) and (b) SMART (black dashed curves) for a modern Earth atmosphere. H$_2$O and CO$_2$ are self-broadened, as for the calculations shown in Section 5. Upwelling thermal fluxes agree to within 4%, and downwelling thermal fluxes agree to within 1% at most heights.
Fig. A9: Upwelling and downwelling vertical shortwave flux comparisons between: (a) our model (solid red curves) and (b) SMART (black dashed curves) for the modern Earth atmosphere in Fig. A8. H$_2$O and CO$_2$ are self-broadened, as in Fig. A8. The assumed surface albedo is 0.274.
Fig. A10: Upwelling and downwelling vertical infrared flux comparisons between (a) our model (solid blue curves) and (b) SMART (red dashed curves) for a modern Earth atmosphere. Terrestrial air is assumed for foreign broadening. The calculated outgoing longwave radiation (OLR) in our model is 266 W/m$^2$, only 3 W/m$^2$ higher than that computed by SMART.
Fig. A11: Upwelling and downwelling vertical shortwave flux comparisons between: (a) our model (solid blue curves) and (b) SMART (red dashed curves) for the modern Earth atmosphere in Fig. A10. Terrestrial air is assumed for foreign broadening as in Fig. A4. The assumed surface albedo is 0.274. The top of atmosphere net absorbed flux is 260 W/m$^2$ for our model whereas SMART obtains 258 W/m$^2$.

Using 6 solar zenith angles to improve the accuracy in our solar calculation, we recomputed the surface albedo needed to produce a surface temperature of 288 K for modern Earth. The required albedo in this case was 0.25, the same value obtained by Goldblatt et al (2013). We then repeated the high-CO$_2$ calculations discussed in Section 5, again using 6 solar zenith angles, and found that the temperature sensitivity for a CO$_2$ doubling was still 2.3 K, the same as in the original calculation. At a CO$_2$ pressure of 2×10$^{-3}$ bar, surface temperatures with the new model were ~1 K cooler than before. As CO$_2$ pressure increases above this value, the transition point to a moist atmosphere (see Fig. 5.2b) is delayed by 5 K (310 K at ~ 9×10$^{-3}$ bar or 18 PAL), so it now occurs at the same temperature as that predicted by Goldblatt et al (2013). At still higher CO$_2$ pressures, the absorption coefficients used in the main text become increasingly valid, and so we expect that those solutions are accurate. Thus, the calculations shown in the main text may err on the side of overestimating the greenhouse effect, but that means that triggering a runaway greenhouse with CO$_2$ is even more unlikely than shown there. This sensitivity
study also confirms a recent suggestion that errors in foreign broadening assumptions should be relatively small compared to other potential issues (Wordsworth & Pierrehumbert 2013b).

A3 Steamy atmosphere OLR comparisons

Fig. A12: Outgoing longwave radiation vs. wavenumber for the 0 – 2000cm\(^{-1}\) region comparing our OLR (blue solid curve) to that of SMART (red solid curve) for a 6.5 bar steam atmosphere with a 400 K surface temperature (black blackbody curve). The stratospheric temperature is 200 K. Although both models appear to be in good agreement, our model has higher opacities in both the 8 – 12 micron region as well as at around 400 cm\(^{-1}\). These differences are likely attributable to spectral resolution differences and different assumptions about line profiles. Our model uses Voigt line profiles, whereas SMART utilizes van Vleck-Weisskopf and Rautian line profiles. The assumed surface albedo is 0.3.
A4 Radiative comparisons with the NASA GCMS for early Mars

Additional vertical flux profile comparisons are shown below that compare our climate model versus both the NASA Ames and KDM (k-distribution method) GCMs, updating the similar ones shown in Mischna et al (2012). Again, the comparisons shown are for a 0.5 bar early Mars (~75% present day insolation) atmosphere assuming both dry (Figs A13-A14) and fully-saturated (Fig A15-A16) conditions. The temperature profile is the same one used in Fig. A1. Unlike Mischna et al (2012), however, the assumed surface albedo for these atmospheres is 0.265 instead of 0.2. To accommodate this higher surface albedo, the solar constant used here (33.17% of present day) is slightly higher than that used in other early Mars calculations.

As discussed in Mischna et al (2012), our model exhibits both a stronger greenhouse effect and absorbs more solar radiation than either of the NASA GCM models for this atmosphere. These discrepancies are almost certainly due to differences in CO$_2$ absorption as the same overall magnitudes and trends are displayed in both the dry and fully-saturated flux profiles (Figs. A13 – A16). A possible reason for this discrepancy arises from different truncation schemes employed in the models. Whereas the climate model herein used a 500 cm$^{-1}$ truncation, KDM utilized variable cutoffs ranging from 25cm$^{-1}$ to 500cm$^{-1}$ at different pressure levels and wavenumber bands (Mischna et al 2012). Although this was done to reduce computational time, truncating far wings at short distances can weaken the greenhouse effect of a dense CO$_2$ atmosphere by 10s of W/m$^2$ (Wordsworth et al 2010a). Moreover, KDM used truncation distances as short as 100cm$^{-1}$ in the 8 – 12 micron window region at P = 0.1 bar, a critical pressure level above which a significant amount of atmospheric emission occurs in planetary atmospheres (Robinson & Catling 2014). Our excellent agreement with both SMART and Wordsworth et al (2010a) for dense early Mars atmospheres (Fig. A2-A5), models that had used similarly long CO$_2$ line shapes as those used in our model, lend further support that the line cutoffs used in these two GCM are too short. Indeed, the Ames GCM utilizes even shorter line cutoffs than KDM (personal communication, Richard Freedman, SETI and Robert Haberle, NASA Ames). The following temperature- and pressure-dependent truncation scheme was used to compute line cutoffs with the Ames GCM (personal communication, Richard Freedman):

$$W = W_o \left(\frac{P}{P_o}\right) \sqrt[\frac{T_o}{T}]$$

(A1)

Here, $W_o$ is 25 cm$^{-1}$, and the reference pressure ($P_o$) and temperature ($T_o$) are 1 bar and 296 K, respectively. The minimum cutoff used was 25cm$^{-1}$, so although eqn. (A1) computes an even shorter line truncation (~14cm$^{-1}$), 25cm$^{-1}$ was used, which is still
extremely short compared to both our model and KDM. Moreover, the Ames GCM, normally used to study tenuous atmospheres like early Mars, ignored the effects of CO$_2$ CIA, which become significant in denser atmospheres (Section 4). These two effects likely explain why the Ames model predicts less absorption than the other two models. However, given the variable truncation scheme used by KDM, the fluxes computed in our model are perhaps the most accurate for this atmosphere.

This analysis underscores the inherent conflict regarding increased accuracy at the cost of additional computational time, and vice versa. Until computer power is greatly enhanced, GCM performance may be improved if mixed CO$_2$-H$_2$O coefficients were used in place of convolving separate CO$_2$ and H$_2$O coefficients.

Figure A13: Vertical solar flux profiles comparing (a) our climate model (blue) versus that of (b) KDM (green) and (c) Ames (red) for a dry early Mars (75% present solar insolation) atmosphere. The KDM and Ames models reflect ~4 W/m$^2$ more solar radiation out to space than in our climate model.
Figure A14: Vertical infrared flux profiles comparing (a) our climate model (blue) versus that of (b) KDM (green) and (c) Ames (red) for a dry early Mars (75% present solar insolation) atmosphere. The KDM and Ames models emit ~10 and 15 W/m$^2$ more infrared radiation out to space, respectively, than does our climate model. Surface dowelling fluxes are ~15 W/m$^2$ smaller for the Ames GCM.
Figure A15: Vertical solar flux profiles comparing (a) our climate model (blue) versus that of (b) KDM (green) and (c) Ames (red) for a fully-saturated early Mars (75% present solar insolation) atmosphere. The KDM and Ames models reflect ~ 4 W/m$^2$ more solar radiation out to space than in our climate model.
Figure A16: Vertical infrared flux profiles comparing (a) our climate model (blue) versus that of (b) KDM (green) and (c) Ames (red) for a fully-saturated early Mars (75% present solar insolation) atmosphere. The KDM and Ames models emit ~10 and 15 W/m² more infrared radiation out to space, respectively, than does our climate model. Surface downwelling fluxes are ~15 W/m² smaller for the Ames GCM.

A5 Additional radiative comparisons with Goldblatt et al. (2013)

As discussed in the main text, the wavelength-integrated radiative fluxes calculated by our climate model agree well with Goldblatt et al (2013) for the case of warm, pure H₂O atmospheres. Here, we show additional comparisons between the two models.

We have compared our broadband surface downwelling and net outgoing thermal flux spectra against the line-by-line spectra of Goldblatt et al (2013) for the 400 K pure water atmosphere shown in their Fig.1 (Figs. A17-A18). As in other recent papers from our group (Kopparapu et al 2013, Ramirez et al 2013), we used KSPECTRUM (Wordsworth et al 2010a), a line-by-line radiative transfer program, to generate absorption
spectra. We then wrote another program that converts these spectra into correlated-\(k\) coefficients for use in our climate model (Kopparapu et al. 2013, Ramirez et al. 2013). Internal comparisons of these spectra have revealed that the van Vleck-Weisskopf and Rautian profiles between \(\sim 5\)–\(15\) microns used by Goldblatt et al. (2013) produce more far-wing absorption than do our Voigt line profiles. This may explain our higher outgoing thermal flux between 10-15 microns when we compare our model against SMART (Meadows & Crisp 1996), the radiative transfer model used by Goldblatt et al. (2013) (Fig. A17). However, this difference is offset by the smaller amount of absorption by the model at shorter wavelengths (Fig. A17).

Figure A17: Net outgoing thermal flux spectrum in a pure water atmosphere for a 400 K surface temperature, comparing SMART (Meadows & Crisp 1996) (blue) versus our model (green). The black curve is the blackbody emission flux at the specified surface temperature. The integrated area under both curves (including emission beyond the x-axis limits shown) is \(-282 \, \text{W/m}^2\).
APPENDIX B. WATER CONTINUUM DESCRIPTION AND COMPARISON

As discussed in Section 1 a previous version of the climate model had used the Roberts et al (1976) H$_2$O continuum. Like BPS, Roberts et al (1976) (hereafter, R76) is an empirical continuum with coverage limited to the 8 -12 micron band. This is inadequate for studies of extremely warm and wet atmospheres because the shortwave window regions become influential in very moist atmospheres (Pierrehumbert 2010). Thus, R76 was replaced with the BPS (Baranov-Paynter-Serio) continuum (Paynter & Ramaswamy 2011). BPS is overlain beyond the assumed line cutoff of 25cm$^{-1}$ for H$_2$O. The BPS model is based on a slightly different approach to other continuum models such as MT-CKD or CKD (Clough et al 1989, Clough et al 2005, Mlawer et al 2012), in that the continuum coefficients are derived directly from empirical measurements, not from analytical fits (Paynter & Ramaswamy 2011). The continuum is formulated from various laboratory data combined for many spectral regions and temperatures up to 363 K (Serio et al 2008, Baranov et al 2008, Paynter et al 2009, Baranov & Lafferty 2011). In regions with insufficient data (e.g. above ~ 7500 cm$^{-1}$), BPS uses MT_CKD 2.5. BPS consistently predicts stronger absorption in the shortwave windows presumably because it utilizes empirical data that includes dimer effects, which are not explicitly assumed in other continuum formulations (Paynter et al 2009). In contrast, MT-CKD assumes that the dominant continuum absorption mechanism arises from collisions of monomers whereas CKD is based on sublerntzian “chi-factor” functions that transform the far wings up to great distances from the line center (> 1000 cm$^{-1}$) (Shine et al 2012) (Clough et al 1989).

B1 Baranov-Paynter-Serio (BPS) Mathematical description

As described in Paynter and Ramaswamy (2011), the optical depth of the BPS self continuum ($\tau_s$) is

$$\tau_s(\nu, T) = \frac{P_w L}{kT} \left( \frac{P_w}{P_o} \right) \left( \frac{T_o}{T} \right) C_s(\nu, T)$$

Thus, the self continuum is proportional to the partial pressure of water ($P_w$) squared. The equivalent for the foreign continuum ($\tau_f$) is expressed as
Here, $C_s$ and $C_f$ are the self and foreign continuum coefficients, respectively, $P_i$ is the total pressure of all other gases besides water, $T$ is temperature, $\nu$ is wavenumber, $k$ is Boltzmann’s constant, and $L$ is the atmospheric layer path length (in distance units). $T_o$ and $P_o$ are the reference temperature and pressure, equal to 296 K and 1 bar, respectively (ibid).

Combining both eqns. above yields the total optical depth ($\tau$)

$$\tau = \frac{PL}{kT} \left( \sum_{i=1}^{X} SF_i \right) + \left( \frac{P_w}{P_o} \right) \left( \frac{T_o}{T} \right) C_s(\nu, T) + \left( \frac{P_f}{P_o} \right) \left( \frac{T_o}{T} \right) C_f(\nu, T)$$

(B3)

Where there is a total of $X$ water vapor lines, $S$ is the line strength, and $F$ is the line shape function cut off at 25 cm$^{-1}$ and excluding the line base term (ibid).

Owing to large uncertainties in the self continuum temperature dependence, BPS uses the exact form used by CKD and MT CKD

$$C_s(T) = C_s(T_o) \frac{\tanh \left( \frac{C_2 \nu}{2T_o} \right)}{\tanh \left( \frac{C_2 \nu}{2T} \right)} \exp(\sigma_v(T - T_o))$$

(B4)

Where $C_2$ is 1.4388 cm-K. Radiation field effects are described by the hyperbolic tangent terms although this only has a significant effect at wavenumbers $\sim 500$ cm$^{-1}$. $\sigma$ is the
temperature dependence coefficient that varies as a function of wavenumber (ibid). Equivalently, the temperature dependence for the foreign continuum is

\[ C_f(T) = C_f(T_0) \frac{\tanh \left( \frac{C_2 \nu}{2T_0} \right)}{\tanh \left( \frac{C_2 \nu}{2T} \right)} \]  

(B5)

Thus, aside from the tanh terms that impact low wavenumber values, the foreign continuum is assumed to be temperature independent.

**B2 Comparison of BPS against other continuum formalisms of the 8 -12 micron window region.**

MT-CKD had also been considered for the climate model but it severely underestimates absorption in the window regions at temperatures higher than ~ 300 K. The following figures are the resultant comparisons in the 8 – 12 micron window region between BPS, MT-CKD, and R76 at 3 different temperatures (296, 340, and 400 K). The squiggly behavior exhibited by BPS is the result of its empirical nature.
Figure B1: Absorption cross-sections in the 8 -12 micron window region comparing the (a) MT-CKD (black), (b) R76 (red), and (c) BPS (blue) continua for a 1-bar 296 K atmosphere with surface $f_{H_2O} = 0.1\%$. The three formulations show good agreement although R76 exhibits cross-sections ~30% stronger at ~1100 cm$^{-1}$.
Figure B2: Absorption cross-sections in the 8 -12 micron window region comparing the (a) MT-CKD (black), (b) R76 (red), and (c) BPS (blue) continua for a ~1.3-bar 340 K atmosphere with surface $f_{H_2O} = 0.2$. R76 and BPS demonstrate good agreement whereas MT_CKD absorption is markedly weaker.
Figure B3: Absorption cross-sections in the 8 -12 micron window region comparing the (a) MT-CKD (black), (b) R76 (red), and (c) BPS (blue) continua for a 4-bar 400 K atmosphere with surface $f_{\text{H}_2\text{O}} = 0.75$. BPS cross-sections lie intermediate between those of the other two parameterizations.
APPENDIX C: TABLES OF COLLISION-INDUCED ABSORPTION (CIA) DATA

Table CIA: N$_2$-H$_2$ Collision-induced absorption coefficients in the 0 - 1000 cm$^{-1}$ spectral range.

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<th>Wavenumber interval (cm$^{-1}$)</th>
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Table CIB: \( \text{N}_2\text{H}_2 \) Collision-induced absorption coefficients in the 1000 - 2050 cm\(^{-1}\) spectral range.

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Table CIIA: \( \text{H}_2\text{H}_2 \) Collision-induced absorption values in the \( 0-1000 \text{ cm}^{-1} \) spectral range.

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Table CIIB: $\text{H}_2-\text{H}_2$ Collision-induced absorption values in the 1000 - 2050 cm$^{-1}$ spectral range.

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</tr>
<tr>
<td>1950 - 2050</td>
<td>3.93x10$^{-09}$</td>
<td>1.37x10$^{-08}$</td>
<td>2.42x10$^{-08}$</td>
</tr>
</tbody>
</table>
Table CIII: CO$_2$CO$_2$ Collision-induced absorption values in the 0-495 cm$^{-1}$ and 1108-1850 cm$^{-1}$ spectral ranges.

<table>
<thead>
<tr>
<th>Wavenumber interval(cm$^{-1}$)</th>
<th>T = 150K</th>
<th>T = 200K</th>
<th>T = 300K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 40</td>
<td>4.16x10$^{-5}$</td>
<td>4.16x10$^{-5}$</td>
<td>1.46x10$^{-5}$</td>
</tr>
<tr>
<td>40 - 100</td>
<td>9.93x10$^{-5}$</td>
<td>9.93x10$^{-5}$</td>
<td>5.09x10$^{-5}$</td>
</tr>
<tr>
<td>100 - 160</td>
<td>2.18x10$^{-5}$</td>
<td>2.18x10$^{-5}$</td>
<td>1.94x10$^{-5}$</td>
</tr>
<tr>
<td>160 - 220</td>
<td>3.23x10$^{-6}$</td>
<td>3.23x10$^{-6}$</td>
<td>5.09x10$^{-6}$</td>
</tr>
<tr>
<td>220 - 280</td>
<td>4.26x10$^{-7}$</td>
<td>4.26x10$^{-7}$</td>
<td>1.20x10$^{-6}$</td>
</tr>
<tr>
<td>280 - 330</td>
<td>6.36x10$^{-8}$</td>
<td>6.36x10$^{-8}$</td>
<td>3.06x10$^{-7}$</td>
</tr>
<tr>
<td>330 - 380</td>
<td>1.1x10$^{-8}$</td>
<td>1.1x10$^{-8}$</td>
<td>8.63x10$^{-8}$</td>
</tr>
<tr>
<td>380 - 440</td>
<td>1.57x10$^{-9}$</td>
<td>1.57x10$^{-9}$</td>
<td>2.11x10$^{-8}$</td>
</tr>
<tr>
<td>440 - 495</td>
<td>2.04x10$^{-10}$</td>
<td>2.04x10$^{-10}$</td>
<td>4.80x10$^{-9}$</td>
</tr>
<tr>
<td>1108 - 1200</td>
<td>3.14x10$^{-7}$</td>
<td>2.94x10$^{-7}$</td>
<td>2.93x10$^{-7}$</td>
</tr>
<tr>
<td>1200 - 1275</td>
<td>7.91x10$^{-6}$</td>
<td>6.48x10$^{-6}$</td>
<td>5.8x10$^{-6}$</td>
</tr>
<tr>
<td>1275 - 1350</td>
<td>4.73x10$^{-5}$</td>
<td>3.55x10$^{-5}$</td>
<td>2.08x10$^{-5}$</td>
</tr>
<tr>
<td>1350 - 1450</td>
<td>4.68x10$^{-5}$</td>
<td>3.52x10$^{-5}$</td>
<td>2.08x10$^{-5}$</td>
</tr>
<tr>
<td>1450 - 1550</td>
<td>1.87x10$^{-6}$</td>
<td>1.62x10$^{-6}$</td>
<td>1.58x10$^{-6}$</td>
</tr>
<tr>
<td>1550 - 1650</td>
<td>6.04x10$^{-8}$</td>
<td>6.04x10$^{-8}$</td>
<td>6.04x10$^{-8}$</td>
</tr>
<tr>
<td>1650 - 1750</td>
<td>2.30x10$^{-9}$</td>
<td>2.30x10$^{-9}$</td>
<td>2.30x10$^{-9}$</td>
</tr>
<tr>
<td>1750 - 1850</td>
<td>8.66x10$^{-11}$</td>
<td>8.66x10$^{-11}$</td>
<td>8.66x10$^{-11}$</td>
</tr>
</tbody>
</table>
APPENDIX D: K-DISTRIBUTION METHOD
DESCRIPTION

Line by line (LBL) radiative transfer methods such as SMART (Meadows & Crisp 1996) and LBLRTM (Clough et al 2005) are the most exact ways of computing radiation but are also the most time intensive. Using SMART, a simple one-step radiative flux calculation can take about an hour because radiance calculations are required for all frequencies and grid points. Thus, these radiative transfer methods are impractical for performing forward calculations, which may take dozens, or even hundreds of steps to achieve convergence. In contrast, the correlated-k method is a much faster approach while retaining most of the accuracy of LBL calculations (Fu & Liou 1992, Kato et al 1999).

D1 Summary of theory for correlated-k method

For a homogeneous atmosphere, the total transmissivity (T) within a spectral interval ($\Delta \nu$) for a given path ($\mu$) can be defined as the integral (or sum) of all transmissivities for each subinterval ($\Delta\nu / \Delta \nu$) :

$$T(\mu) = \int_{\Delta \nu} \frac{e^{-k_{uv}} d\nu}{\Delta \nu}$$

The irregularly varying absorption cross-sections ($k_{uv}$) can be arranged in order of increasing intensity such that the normalized probability distribution $f(k)$ of the cross-section $k_{uv}$ becomes a proxy for subinterval width, yielding:

$$T(\mu) = \int_0^{\infty} e^{-k_{uv}} f(k) dk$$

where the minimum and maximum values of $f(k)$ are 0 and $\infty$ for convenience. It follows that integrating $f(k)$ over the subinterval is 1 (or a probability of 100%).
Moreover, \( f(k) \) can be cumulatively added for all subintervals, generating a cumulative probability distribution function \( g(k) \) of the form:

\[
g(k) = \int_0^k f(k) \, dk \tag{D3}
\]

Here \( g(0) = 0 \), \( g(k \to \infty) = 1 \), and \( dg(k) = f(k) \, dk \). Thus, \( g(k) \) is a smooth and monotonically increasing function that is readily amenable to Gaussian quadrature integration (Fig. D1):

\[
T(\mu) = \int_0^1 e^{-k(g)u} \, dg \approx \sum_{j=1}^{m_p} \sum_{i=1}^{n_q} w_j e^{-k_j u_i} \tag{D4}
\]

Here \( m_p \) represents a summation over a number of path lengths, \( n_q \) is the number of quadrature points, \( w_j \) are the Gaussian weights, and \( k_j \) are the resultant k-coefficients.
Figure D1: Absorption cross-sections versus cumulative distribution function (a) and (b) probability distribution $f(k)$ of absorption cross-sections for a 1 bar 300 K atmosphere for the interval 617 – 667 cm$^{-1}$. 
Numerical procedures for computing k-coefficients

A typical spectral interval may have hundreds or even thousands of spectral lines. If the subinterval resolution is sufficiently high, the probability distribution $f(k)$, by inspection of eqns. D1-D2, can be described as:

$$f(k) = \frac{1}{\Delta \nu} \frac{dv}{dk} = \frac{1}{\Delta \nu} \sum_j \left| \frac{\Delta \nu_j}{\Delta k} \right|$$  \hspace{1cm} (D5)

For a specific value of $k$ within subinterval, $f(k)$ is 0 if the maximum of a line ($k_{\text{max}}$) is smaller than $k$. The cumulative probability function is then:

$$g(k) = \frac{1}{\Delta \nu} \sum_j \int_0^k \frac{\Delta \nu_j}{\Delta k'} dk' = \frac{1}{\Delta \nu} \sum_j \int_0^k \Delta \nu_j (k) = \frac{n(0,k)}{N}$$  \hspace{1cm} (D6)

Here $n(0,k)$ denotes the number of lines that contribute to $k$ cumulatively. Finally, the total number of computational points is $N = \Delta \nu / \delta$, with the mean line spacing $\delta$, defined by:

$$\delta = \frac{\sum_{j=1}^N \nu_j}{N}$$  \hspace{1cm} (D7)

The assumption of spectral correlation

Note that the transmissivity expression in eq. D4 assumes that the atmosphere consists of just one absorber. Real atmospheres, however, are nonhomogeneous, consisting of multiple constituents that can absorb within a given spectral interval. Furthermore, the degree of spectral correlation between absorbing species varies depending on the gases involved as well as the exact temperature-pressure conditions of interest. Subsequently, in c-k methods, gases are assumed usually to be either spectrally or non-spectrally correlated. If two
absorbers are spectral correlated, the weights of each species are equal to one another and the resulting transmittance is simply given by:

\[
T(\mu) = \sum_{j=1}^{m_p} \sum_{i=1}^{n_q} w_i e^{-k_{\lambda_i} u_j} e^{-h_{\lambda_i} v_j}
\]

\[
= \sum_{j=1}^{m_p} \sum_{i=1}^{n_q} w_i e^{-(k_{\lambda_i} u_j + h_{\lambda_i} v_j)}
\]

\[
= T_x \cdot T_y
\]  \hspace{1cm} (D8)

Here, x and y are two different radiatively active species, respectively. Note that spectral correlation is unlikely, however, unless the second absorber is simply more of the first. Assuming gases are spectrally uncorrelated is the more usual approximation, and this is what is used in our climate model. However, it also is a rarely perfect assumption – especially if the absorbers have broad, overlapping far wings. Moreover, even this approach assumes that the gases are spectrally correlated in terms of path length (or vertical height in a climate model). For spectrally uncorrelated gases, the overlap between each of the spectral segments of each constituent gas needs to be considered. This is expressed mathematically as the term-by-term product of the individual exponential sums. For two species this is:

\[
T(\mu) = \sum_{j=1}^{m_p} \sum_{k=1}^{n_q} \sum_{i=1}^{n_z} w_i e^{-k_{\lambda_i} u_j} w_k e^{-k_{\lambda_k} v_j}
\]

\[
= T_x \cdot T_y
\]  \hspace{1cm} (D9)

with associated weights and gauss points for each of the individual species. Thus, for two gases the resulting sum will have \( n_{q,y} \times n_{q,z} \) coefficients for a given path. If there are three constituents, the number of terms goes as \( n_{q,z} \times n_{q,y} \times n_{q,z} \) coefficients for each path length, dramatically reducing the efficiency of the c-k method.

**Double gauss method**

To maximize radiative accuracy with the least number of terms we have employed the “double gauss” method described in Thomas and Stamnes (2002) in which the angular integral of intensity (I) over all angles (g) is broken into two hemispheres as follows:
In standard gaussian integration, roots and weights are usually based on the full range (-1 ≤ g ≤ 1). With two hemispheres, however, it is useful to relate the half-range quadratures to those for the full range. Using a linear transformation of the form $t = (2x - x_1 - x_2) / (x_2 - x_1)$ will map any interval $[x_1, x_2]$ on to [-1, 1] provided $x_2 > x_1$.

\[ \int_{x_1}^{x_2} dxI(x) = \int_{-1}^{1} dtI \frac{(x_2 - x_1) t + x_2 + x_1}{2} \frac{(x_2 - x_1)}{2} \]  

(D11)

Choosing $x_1 = 0$, $x_2 = 1$, $x = \mu$, and $t = g$, it can be found that

\[ \int_{0}^{1} d\mu I(\mu) = \frac{1}{2} \int_{-1}^{1} dgI \left( \frac{g + 1}{2} \right) \]  

(D12)

By applying Gaussian quadrature to each integral and setting $N_q$ for the half range:

\[ \int_{0}^{1} d\mu I(\mu) = \sum_{j=1}^{2N} w_j I(\mu_j) = \frac{1}{2} \int_{-1}^{1} d\mu I \left( \frac{g + 1}{2} \right) \]

\[ = \frac{1}{2} \sum_{j=-N}^{N} w_j I \left( \frac{g_j + 1}{2} \right) \]

(D13)
Therefore, in even orders, the half-range points and weights are related to the full-range ones by

$$\mu_j = \frac{g_j + 1}{2}, \quad w_j = \frac{1}{2} w_j'$$

The standard double gauss scheme described up to now computes \(N_0\) points that are equally distributed and spaced symmetrically in each hemisphere (half between \(0 \leq g \leq 0.5\) and the other between \(0.5 \leq g \leq 1\)). However, for improved resolution in the steeply rising function of \(g(k)\), which is particularly important at the lowest pressures (Fig. D2), a double gaussian split at 0.95 is often assumed, locating \(N_0\) points between \(0.95 \leq g \leq 1\). Given the linear transformation, both the weights and gauss points in eqn. (D14) are multiplied by 0.95, scaling these values to the shortened range between \(0 \leq g \leq 0.95\). As with standard double gauss, weights are symmetric about each hemisphere. Owing to this property, adding 0.95 to these gauss points yields the remaining ones in the steeply rising leg.

**Figure D2:** Absorption cross-section \((k)\) as a function of the cumulative distribution function \((g)\) across \(617 - 667 \text{ cm}^{-1}\) for a tenuous \(1 \times 10^{-3}\) bar \(350 \text{ K N}_2\text{CO}_2\text{H}_2\text{O}\) atmosphere. 16 term mixed \(\text{CO}_2\text{H}_2\text{O}\) coefficients were used, with 8 in the rising leg between 0.95 and 1.00, ensuring high accuracy.
APPENDIX E: DERIVATIONS OF KEY PHYSICAL FORMULAE

E1 Relationship between pressure and volume mixing ratio for CO₂

The CO₂ pressures referred to in the main text are not actual partial pressures, but the surface pressures that would exist if CO₂ did not mix with the remaining atmospheric gases. Although Dalton’s law states that the total atmospheric pressure is equal to the sum of the pressures of the individual gases, in an unbounded planetary atmosphere, vertical mixing reduces the mole fractions of heavier species near the surface.

Mathematically, the CO₂ pressure, \( p\text{CO}_2' \), is related to the column masses of CO₂, \( M_{\text{CO}_2} \), and (non-CO₂-containing) air, \( M_{\text{AIR}} \), by the following expressions:

\[
p\text{CO}_2' = M_{\text{CO}_2} \cdot g = N_{\text{CO}_2} m_{\text{CO}_2} \cdot g \quad (E1)
\]

\[
p\text{AIR}' = M_{\text{AIR}} \cdot g = N_{\text{AIR}} m_{\text{AIR}} \cdot g \quad (E2)
\]

The prime on \( p\text{CO}_2 \) and \( p\text{AIR} \) is to indicate that these are not partial pressures, but their isolated surface pressures. Here, \( g \) is gravity, \( N_i \) is the column density of species \( i \) (where \( i \) is either CO₂ or air), and \( m_i \) is its molecular mass.

The total column number density is conserved when these gases are mixed, so that the total column number density, \( N_{\text{tot}} \), is given by:

\[
N_{\text{tot}} = N_{\text{CO}_2} + N_{\text{AIR}} \quad (E3)
\]
The volume mixing ratio for CO$_2$, $f_{CO_2}$, is equal to $N_{CO_2}/N_{tot}$. Substituting in values from eqs. E1 and E2 yields:

$$f_{CO_2} = \frac{p_{CO_2}'}{p_{CO_2}' + \frac{44}{m_{AIR}} p_{AIR}'}$$

(E4)

where, we have used the fact that the molecular mass of CO$_2$ is 44 g/mol. We use a value of 29 g/mol for $m_{AIR}$ and 1 bar for $p_{AIR}'$, which represents the combined total pressure of N$_2$, O$_2$, and Ar. Then $f_{CO_2}$ is used to compute a new mixing ratio $f_{CO_2}^{new}$ with respect to moist air. Mixing ratios with respect to moist air are recalculated for all noncondensible species.

**E2 Effective flux ($S_{eff}$) parameterization derivation**

The $S_{eff}$ equation (5 in Section 3.11) was written as a fourth order polynomial in the form

$$y = a + b T_* + c T_*^2 + d T_*^3 + e T_*^4$$

(E5)

Here $y$ is $S_{eff}$, $a$ is the $S_{eff}$ value for the sun, and $T_*$ is $T_{eff} - 5780$K, as also explained in Section 3.11.
First the above parameterization can be recast so that $T_e = 5780 \text{ K}$ gives the $y$ ($S_{\text{eff}}$ value) for our solar system.

$$y = a + b(T_e - 5780 + 5780) + c(T_e - 5780 + 5780)^2 + d(T_e - 5780 + 5780)^3 + \ldots$$  \hspace{1em} (E6)

$$e(T_e - 5780 + 5780)^4$$

Equation (E6) is still the same expression as eqn. (E5) but the equation can be rearranged into a more manageable form The $T_e - 5780\text{K}$ terms are factored out of eqn (E6) and treated as separate terms. The following polynomial expansions are then used to expand the various parenthetical components of eqn. (E6). A second order polynomial expansion is applied to expand the term multiplied by $c$

$$(a + b)^2 = a^2 + 2ab + b^2$$ \hspace{1em} (E7)

A third order polynomial expansion expands the term multiplied by $d$,

$$(a + b)^3 = a^3 + a^2b + 2a^2b + 2ab^2 + ab^2 + b^3$$ \hspace{1em} (E8)
And the final term in eqn. (E6) can be expressed in the form of a 4\textsuperscript{th} order polynomial expansion:

\[ (a + b)^4 = (a^3 + 3a^2b + 3ab^2 + b^3)(a + b) = a^4 + 4a^3b + 6a^2b^2 + 4ab^3 + b^4 \]  

(E9)

Summing all of the components (a – e) yields the following

\[ y = a + \ldots \]
\[ b(T_e - 5780) + \ldots \]
\[ 5780b + c\left[(T_e - 5780)^2 + 2(T_e - 5780)(5780) + (5780)^2\right] + \ldots \]
\[ d\left[(T_e - 5780)^3 + 3(T_e - 5780)^2(5780) + 3(T_e - 5780)(5780)^2 + (5780)^3\right] + \ldots \]  

(E10)
\[ e\left[(T_e - 5780)^4 + 4(T_e - 5780)^3(5780) + 6(T_e - 5780)^2(5780)^2 + \ldots \right] \]
\[ 4(T_e - 5780)(5780)^3 + (5780)^4 \]

Grouping the constants and factoring out the \( T_e - 5800 \) terms:

\[ y = a + 5780b + c(5780)^2 + d(5780)^3 + e(5780)^4 + \ldots \]
\[ (T_e - 5780)\left[b + 2c(5780) + 3d(5780)^2 + 4e(5780)^3\right] + \ldots \]
\[ (T_e - 5780)^2\left[c + 3d(5780) + 6e(5780)^2\right] + \ldots \]  

(E11)
\[ (T_e - 5780)^3\left[d + 4e(5780)\right] + \ldots \]
\[ (T_e - 5780)^4 e \]

So that
\[ S_{\text{eff}} = S_{\text{eff}}^0 + A(T_e - 5780) + B(T_e - 5780)^2 + \ldots \] 
\[ + C(T_e - 5780)^3 + D(T_e - 5780)^4 \]  
(E12)

Where:

\[ S_{\text{eff}}^0 = a + 5780b + c(5780)^2 + d(5780)^3 + e(5780)^4 \]

\[ A = b + 2c(5780) + 3d(5780)^2 + 4e(5780)^3 \]

\[ B = c + 3d(5780) + 6e(5780)^2 \]

\[ C = d + 4e(5780) \]

\[ D = e \]

It is clear now that \( T_e = 5780 \) K in equation (E12) gives \( S_{\text{eff}} \) for our solar system.

A fourth degree polynomial curve fit then computes \( a, b, c, d, \) and \( e \) from equation (E5) using input \( S_{\text{eff}} \) and \( T_{\text{eff}} \) values. These are finally used to compute \( S_{\text{eff}}^0, A, B, C, \) and \( D, \) which are the same constants used in Table 3.2 of the main text.

**E3 Schwarzschild’s equation**

This section first derives the differential and integral forms of Schwarzschild’s equation, which is the basic equation for radiative transfer in a non-scattering atmosphere. Although scattering in the infrared is negligible for cloud-free atmospheres, this assumption is obviously incorrect at solar frequencies. However, Schwarzschild’s equation is sufficient to illustrate the relationship between lapse rate and absorbed fluxes.
Differential form of Schwarzschild’s equation

Figure E1: Radiation of intensity $I_{\nu}$ at a frequency $\nu$ passing through a homogeneous layer of air of thickness $ds$.

If one considers the passage of radiation of frequency $\nu$ through a layer of air with infinitesimal thickness $ds$ (Fig. E1), measured along the propagation direction, then the resultant absorption reduces the intensity (or radiance) $I$ at a given height by an amount

$$dI_{\nu} = -k_a I_{\nu} ds$$  \hspace{1cm} (E13)

Here, $k_a$ is the absorption coefficient and the quantity $k_a ds$ represents the “absorptivity” of the medium. According to Kirchoff’s law, the absorptivity of a quantity of matter in local thermodynamic equilibrium (LTE)\(^7\) is equal to its emissivity. Thus,

$$dI_{\nu} = dI_{abs} + dI_{emit} = k_a (B_{\nu} - I_{\nu}) ds$$  \hspace{1cm} (E14)

where $B_{\nu}$ is the Planck function at a particular temperature and frequency, with temperature determined by height. The differential form of Schwarzschild’s Equation is then

\(^7\) A system is in local thermodynamic equilibrium when its Planckian temperature is equal to its Maxwellian temperature. This assumption is untrue in the thin upper atmosphere, where infrequent collisions cause excited molecules to de-excite before they can transfer their energy to neighboring molecules in the form of kinetic energy.
\[ \frac{dI_{\nu}}{ds} = k_a \left( B_{\nu} - I_{\nu} \right). \] (E15)

This fundamental non-scattering expression states that the radiance either increases or decreases with distance depending on the relation between \( B \) and \( I \).

**Integral form of Schwarzschild’s equation**

Equation (E15) can be written in terms of \( \tau \) by substituting \( d\tau = -k_a \, ds \), yielding

\[ \frac{dI_{\nu}}{d\tau} = I_{\nu} - B_{\nu}. \] (E16)

Equation (E16) can be integrated by first multiplying both sides by the integrating factor \( e^{-\tau} \)

\[ e^{-\tau} \frac{dI_{\nu}}{d\tau} = I_{\nu} e^{-\tau} - B_{\nu} e^{-\tau} \] (E17)

\[ e^{-\tau} \frac{dI_{\nu}}{d\tau} - I_{\nu} e^{-\tau} = -B_{\nu} e^{-\tau}, \] (E18)

\[ \frac{d}{d\tau} \left[ I_{\nu} e^{-\tau} \right] = -B_{\nu} e^{-\tau}. \] (E19)
This last expression can then be integrated on both sides from an arbitrary height ($\tau = \tau'$) to the surface ($\tau = \tau^*$):

$$\int_{\tau'}^{\tau^*} \frac{d}{d\tau} \left[I_\nu e^{-\gamma}\right] d\tau = -\int_{\tau'}^{\tau^*} B_\nu e^{-\gamma} d\tau,$$

(E20)

$$I_\nu e^{-\gamma} \bigg|_{\tau'}^{\tau^*} = -\int_{\tau'}^{\tau^*} B_\nu e^{-\gamma} d\tau,$$

(E21)

$$I_\nu(\tau^*)e^{-\gamma^*} - I_\nu(\tau')e^{-\gamma'} = -\int_{\tau'}^{\tau^*} B_\nu e^{-\gamma} d\tau,$$

(E22)

$$I_\nu(\tau') = I_\nu(\tau^*)e^{-(\gamma^* - \gamma')} + \int_{\tau'}^{\tau^*} B_\nu e^{-(\gamma^* - \gamma')} d\tau$$

(E23)

Thus, the total radiance observed at the top of the atmosphere ($\tau = 0$) is simply the attenuated radiative contribution from the far side of the path ($\tau = \tau'$) plus the integrated thermal emission component between $\tau = \tau^*$ and $\tau = 0$. If we make the additional simplification that the surface emits as a blackbody, intensity, $I_\nu(\tau)$, is equal to the Planck function $B_\nu$ evaluated at the surface temperature and the integral form of Schwarzschild’s equation becomes
\[ I_\nu(\tau') = B_\nu(\tau') e^{-(\tau' - \tau')} + \int_{\tau'}^{\tau} B_\nu(\tau) e^{-(\tau' - \tau)} d\tau \] (E24)

where \( B_\nu \) is a function of \( \tau \). Equation (24) represents the upward component of the specific intensity.

Relationship between lapse rate and fluxes through Schwarzschild’s Equation

The upward and downward components of the specific intensity at optical depth \( \tau' \) are

\[ I_{\text{up},\nu}(\tau') = B_\nu(\tau') e^{-(\tau' - \tau')} + \int_{\tau'}^{\tau} B_\nu(\tau) e^{-(\tau' - \tau)} d\tau \] (E25)

\[ I_{\text{down},\nu}(\tau') = \int_{\tau}^{\tau'} B_\nu(\tau) e^{-(\tau - \tau')} d\tau \] (E26)

where \( \tau^i = 0 \) and \( \tau^s \) are the respective optical depths at TOA and the surface. The tau terms in eq. (26) are reversed because radiance has to increase from TOA to the location at \( \tau' \).
Then integration by parts is performed with $u(\tau) = B_\nu(\tau)$, and $v(\tau) = -e^{-(\tau'-\tau)}$ for the upwelling and $v(\tau) = e^{-(\tau'-\tau)}$ for the downwelling components, respectively. The resultant integrals to evaluate are

$$\int_{\tau'}^{\tau'} uv = uv|_{\tau'}^{\tau'} - \int_{\tau'}^{\tau'} vdu \quad \text{and} \quad \int_{\tau'}^{\tau'} uv = uv|_{\tau'}^{\tau'} - \int_{\tau'}^{\tau'} vdu ,$$

yielding:

$$I_{\text{up},\nu}(\tau') = B_\nu(\tau') + \int_{\tau'}^{\tau'} \frac{dB_\nu}{d\tau} e^{-(\tau' - \tau)} d\tau \quad (E27)$$

$$I_{\text{down},\nu}(\tau') = B_\nu(\tau') - B_\nu(\tau') e^{-(\tau' - \tau)} - \int_{\tau'}^{\tau'} \frac{dB_\nu}{d\tau} e^{-(\tau - \tau')} d\tau \quad (E28)$$

Equations (E27) and (E28) may be combined to produce the net radiance (or intensity)

$$I_{\text{up},\nu}(\tau) - I_{\text{down},\nu}(\tau) = B_\nu(\tau') e^{-(\tau' - \tau')} + \int_{\tau'}^{\tau'} \left\{ \frac{dB_\nu}{d\tau} \right\} e^{-(\tau' - \tau')} d\tau \quad (E29)$$

This may be re-written in terms of temperature as

$$I_{\text{up},\nu}(\tau') - I_{\text{down},\nu}(\tau') = B_\nu(\tau') e^{-(\tau' - \tau')} + \int_{\tau'}^{\tau'} \frac{\partial T}{\partial \tau} \left( \frac{\partial B_\nu}{\partial T} \right) e^{-(\tau' - \tau')} d\tau \quad (E30)$$

$$= B_\nu(\tau) e^{-(\tau' - \tau')} + \int_{\tau'}^{\tau'} \left\{ \frac{\partial B_\nu}{\partial T} \right\} e^{-(\tau' - \tau')} d\tau$$
Here $T$ is temperature and $\Gamma$ is the lapse rate at a given layer (in terms of the change in optical depth). And the net thermal flux at a given layer can be expressed in terms of the intensity as

$$F(\tau) = 2\pi \int_0^1 \int_0^1 [I_{up,\nu}(\tau', \mu) - I_{down,\nu}(\tau', -\mu)] \mu d\mu d\nu$$

where the upwelling and downwelling rays are also averaged by the zenith angle $\mu$.

Thus, eqns (E28) and (E29) state that the net thermal flux at some level decreases as the lapse rate decreases, as was also shown in (Kasting et al. (1984)). This form of Schwarzschild’s equation illustrates why Wordsworth et al. (2010b) somewhat overestimated surface temperatures at the highest pressures in Fig. 3.1, as they themselves predicted it would. By neglecting the effects of condensation on the lapse rate, $\Gamma$ is too large, overestimating the absorption. Although Wordsworth et al. (2010b) are correct in stating that this omission does not compromise their results, this effect is crucial to incorporate in other applications such as: (a) a colder dense CO$_2$ atmosphere (e.g. early Mars) or (b) in very warm, moist climates (e.g. Section 5).
E4 Multilinear interpolation up to four dimensions

As explained in Section 5.3, a second model using mixed CO₂-H₂O coefficients was needed to properly analyze the low-pCO₂ regime in Section 5. A fourth dimensional interpolation scheme was used to compute $k$-coefficients as a function of pressure, temperature, fCO₂, and fH₂O. The concept is illustrated by starting with the simple case of linear interpolation before extrapolation to higher dimensions (Fig. E2).

**Figure E2:** Schematic to compute $y_2$ from linear interpolation of points A,B, and $x_2$.

In order to interpolate $y_2$, one starts from the equation of a line

$$y_2 = y_0 + m(x_2 - x_o)$$  \hspace{1cm} (E32)
Where the slope \( m \) is

\[
m = \frac{y_1 - y_0}{x_1 - x_0} \tag{E33}
\]

This slope expression can be substituted into eqn. (E32), yielding

\[
y_2 = y_0(x_1 - x_0) + (y_1 - y_0)(x_2 - x_0) \frac{x_2 - x_0}{x_1 - x_0} \tag{E34}
\]

After expanding the above expression and cancelling terms

\[
y_2 = y_0(x_1 - x_2) + y_1(x_2 - x_0) \frac{x_2 - x_0}{x_1 - x_0} \tag{E35}
\]

Thus, the interpolated value \( y_2 \) is merely \( y_0 \) times the projection of segment CB plus \( y_1 \) times the projection of segment AC. Dividing by the projection of the entire segment AB \( (x_1 - x_0) \), normalizes the sum of these projections. Moreover, these projected segments \( (x_1 - x_2) \) and \( (x_2 - x_0) \) are located opposite from their corresponding vertices (A or B). This convenient property permits extension to higher dimensionality.

**Bilinear interpolation**

Assuming a linear function in the form \( z = f(x,y) \) and given four points, A, B, C, and D, a rectangle can be defined (Fig. E3).
This rectangle is partitioned into four areas by the lines $x = x_2$ and $y = y_2$. To interpolate the value $z_4$ at $E$ (located at $x_2$ and $y_2$), we compute the areas of the rectangle partitions, normalizing them by dividing by the area ABCD.

Analogously, the four normalized areas, $N_a$, $N_b$, $N_c$, and $N_d$, each diagonally opposite from its vertex is

$$N_a = \frac{(x_1 - x_2)(y_2 - y_0)}{(x_1 - x_0)(y_1 - y_0)}$$ (E36)
\[ N_b = \frac{(x_2 - x_0)(y_2 - y_0)}{(x_1 - x_0)(y_1 - y_0)} \]  
(E37)

\[ N_c = \frac{(x_1 - x_2)(y_1 - y_2)}{(x_1 - x_0)(y_1 - y_0)} \]  
(E38)

\[ N_d = \frac{(x_2 - x_0)(y_1 - y_2)}{(x_1 - x_0)(y_1 - y_0)} \]  
(E39)

Note that the sign on all segments is positive.

The quantity \( z_4 \) is then computed through a weighted sum of the above normalized segments \((N_a - N_d)\):

\[ z_4 = z_a(x_0, y_1)N_a + z_b(x_1, y_1)N_b + z_c(x_0, y_0)N_c + z_d(x_1, y_0)N_d \]  
(E40)

Where \( z_a - z_d \) are a function of the respective \( x \) and \( y \) values shown in Figure E3. Note also that \( z_a - z_d \) are a function of the \( x \) and \( y \) variables not present in their respective normalized segments.

**Trilinear interpolation**

Assume a linear function of the form \( v = f(x,y,z) \). A right rectangular prism can be defined through eight vertices, \( A,B,C,D,E,F,G, \) and \( H \) (Figure E4).

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Figure E4: Schematic to interpolate $z_8$ given right rectangular prism $ABCDEFGH$. 
The prism is partitioned into eight volumes by the planes \( x = x_2, y = y_2, z = z_2 \).
Variables with the subscript 0 refer to one end of the prism, whereas those with subscript 1, the other. To interpolate the values \((\nu'_g)\) of the function at point \(I(x_2, y_2, z_2)\), the individual volumes of the prism \(ABCDEFGH\) are normalized by dividing each by the total volume of the prism.

These eight normalized volumes \(N_a, N_b, N_c, N_d, N_e, N_f, N_g,\) and \(N_h\), each diagonally opposite from its vertex, are given by

\[
N_a = \frac{(x_1 - x_2)(y_1 - y_2)(z_1 - z_0)}{(x_1 - x_0)(y_1 - y_0)(z_1 - z_0)}
\]  \hfill (E41)

\[
N_b = \frac{(x_1 - x_2)(y_2 - y_0)(z_1 - z_0)}{(x_1 - x_0)(y_1 - y_0)(z_1 - z_0)}
\]  \hfill (E42)

\[
N_c = \frac{(x_2 - x_0)(y_1 - y_2)(z_2 - z_0)}{(x_1 - x_0)(y_1 - y_0)(z_1 - z_0)}
\]  \hfill (E43)

\[
N_d = \frac{(x_2 - x_0)(y_2 - y_0)(z_1 - z_0)}{(x_1 - x_0)(y_1 - y_0)(z_1 - z_0)}
\]  \hfill (E44)

\[
N_e = \frac{(x_1 - x_2)(y_1 - y_2)(z_2 - z_0)}{(x_1 - x_0)(y_1 - y_0)(z_1 - z_0)}
\]  \hfill (E45)

\[
N_f = \frac{(x_1 - x_0)(y_2 - y_0)(z_1 - z_2)}{(x_1 - x_0)(y_1 - y_0)(z_1 - z_0)}
\]  \hfill (E46)

\[
N_g = \frac{(x_2 - x_0)(y_1 - y_2)(z_1 - z_2)}{(x_1 - x_0)(y_1 - y_0)(z_1 - z_0)}
\]  \hfill (E47)
There are 3 dependent variables \((x,y,z)\) for \(2^3 = 8\) normalization factors. Finally, \(\nu_8\) is computed through

\[

\nu_8 = z_0(x_0, y_0, z_0)N_a + z_1(x_0, y_1, z_1)N_b + z_2(x_1, y_0, z_1) + z_3(x_1, y_1, z_1)N_d \ldots + z_4(x_0, y_0, z_0)N_e + z_5(x_0, y_1, z_0)N_f + z_6(x_1, y_0, z_0)N_g + z_7(x_1, y_1, z_0)N_h
\]

\[(E49)\]

**Fourth dimensional linear interpolation for mixed CO\(_2\)-H\(_2\)O coefficient model**

The above interpolation scheme was employed for the mixed CO\(_2\)-H\(_2\)O k-coefficient model, which was used in Section 5. These mixed \(k\)-coefficients are a function of four parameters (for \(2^4 = 16\) normalization factors): pressure \((p)\), temperature \((t)\), H\(_2\)O vapor volume mixing ratio \((h)\), and CO\(_2\) volume mixing ratio \((c)\). For convenience, the symbols \(x,y,z\), and \(v\) are replaced with \(p,t,h\), and \(c\), respectively. These four variables are then interpolated to compute the absorption coefficient \(\kappa\) for a given set of conditions \((p_2,t_2,h_2,c_2)\).

The resultant normalization factors are

\[

N_1 = \frac{(p_1 - p_2)(t_1 - t_2)(h_1 - h_2)(c_2 - c_0)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)}
\]

\[(E50)\]

\[

N_2 = \frac{(p_2 - p_0)(t_1 - t_0)(h_1 - h_2)(c_2 - c_0)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)}
\]

\[(E51)\]
\[ N_3 = \frac{(p_2 - p_0)(t_2 - t_0)(h_1 - h_2)(c_2 - c_0)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)} \] (E52)

\[ N_4 = \frac{(p_2 - p_0)(t_2 - t_0)(h_2 - h_0)(c_2 - c_0)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)} \] (E53)

\[ N_5 = \frac{(p_1 - p_0)(t_1 - t_0)(h_2 - h_0)(c_2 - c_0)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)} \] (E54)

\[ N_6 = \frac{(p_1 - p_0)(t_1 - t_2)(h_2 - h_0)(c_2 - c_0)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)} \] (E55)

\[ N_7 = \frac{(p_1 - p_0)(t_1 - t_2)(h_2 - h_0)(c_1 - c_2)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)} \] (E56)

\[ N_8 = \frac{(p_2 - p_0)(t_1 - t_2)(h_2 - h_0)(c_1 - c_2)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)} \] (E57)

\[ N_9 = \frac{(p_2 - p_0)(t_1 - t_0)(h_2 - h_0)(c_1 - c_2)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)} \] (E58)
\[ N_{10} = \frac{(p_2 - p_0)(t_2 - t_0)(h_1 - h_2)(c_1 - c_2)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)} \]  
(E59)

\[ N_{11} = \frac{(p_2 - p_0)(t_1 - t_0)(h_1 - h_2)(c_1 - c_2)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)} \]  
(E60)

\[ N_{12} = \frac{(p_1 - p_2)(t_1 - t_0)(h_1 - h_2)(c_1 - c_2)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)} \]  
(E61)

\[ N_{13} = \frac{(p_1 - p_2)(t_2 - t_0)(h_1 - h_2)(c_1 - c_2)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)} \]  
(E62)

\[ N_{14} = \frac{(p_1 - p_2)(t_2 - t_0)(h_2 - h_0)(c_1 - c_2)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)} \]  
(E63)

\[ N_{15} = \frac{(p_1 - p_2)(t_1 - t_0)(h_1 - h_2)(c_2 - c_0)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)} \]  
(E64)

\[ N_{16} = \frac{(p_2 - p_0)(t_1 - t_0)(h_2 - h_0)(c_2 - c_0)}{(p_1 - p_0)(t_1 - t_0)(h_1 - h_0)(c_1 - c_0)} \]  
(E65)

Therefore, \( \kappa \) for a given set of conditions is
\[ \kappa(p_2,t_2,h_2,c_2) = N_1 \cdot \kappa(p_o,t_o,h_o,c_1) + N_2 \cdot \kappa(p_1,t_1,h_1,c_1) \\
+ N_3 \cdot \kappa(p_1,t_1,h_1,c_1) + N_4 \cdot \kappa(p_1,t_1,h_1,c_1) \\
+ N_5 \cdot \kappa(p_0,t_0,h_1,c_1) + N_6 \cdot \kappa(p_0,t_0,h_1,c_1) \\
+ N_7 \cdot \kappa(p_0,t_0,h_1,c_0) + N_8 \cdot \kappa(p_0,t_0,h_1,c_0) \\
+ N_9 \cdot \kappa(p_1,t_1,h_0,c_0) + N_{10} \cdot \kappa(p_1,t_1,h_0,c_0) \\
+ N_{11} \cdot \kappa(p_1,t_1,h_0,c_0) + N_{12} \cdot \kappa(p_1,t_1,h_0,c_0) \\
+ N_{13} \cdot \kappa(p_1,t_1,h_0,c_0) + N_{14} \cdot \kappa(p_1,t_1,h_0,c_0) \\
+ N_{15} \cdot \kappa(p_0,t_1,h_0,c_1) + N_{16} \cdot \kappa(p_0,t_1,h_1,c_1) \]  

(E66)

As explained in Section 2, temperatures are interpolated linearly whereas log-linear interpolation is used for pressures and mixing ratios.
APPENDIX F: ASSESSING THE REDLICH-KWONG EQUATION OF STATE FOR CO\textsubscript{2}

The climate model uses the Redlich and Kwong (1949) equation of state (EOS) for CO\textsubscript{2}, which is an empirical, analytical equation that relates the pressure, temperature, and volume of gases. As with other EOS, it accounts for non-ideality from perfect gas behavior. In its most basic form, the Redlich-Kwong equation can be expressed as (Murdock 1993):

\[
P = \frac{RT}{V_m - b} - \frac{a(T)}{\sqrt{TV_m (V_m + b)}},
\]

\[
a(T) = \frac{0.4275RT^{5/2}}{P_c},
\]

\[
b = \frac{0.08664RT_c}{P_c},
\]

Where \( P \) is the gas pressure, \( R \) is the gas constant, \( T \) is temperature, \( a(T) \) corrects for attractive potential of molecules, \( b \) is a constant that corrects for volume, \( T_c \) is the critical temperature, \( P_c \) is the critical pressure, and \( V_m \) is the molar volume, which is the molar mass of a substance divided by its mass density. For CO\textsubscript{2}, \( b \) is \( = 29.7 \text{ cm}^3 \). As explained in Kasting (1991), the values of \( a(T) \) were calculated from tabulated pressure and density data along the saturation vapor pressure curve (Newitt et al 1956, Vukalovich & Altunin 1968). Thus, this EOS should be exact for saturated conditions.

The Redlich-Kwong formulation can also be cast with respect to the gas compressibility \((Z)\), as a function of temperature and pressure (Redlich & Kwong 1949).
\[ Z = \frac{PV_m}{RT} = \frac{1}{1 - \frac{h}{B(1 + h)}}, \]

where
\[ A^2 = \frac{a^2}{RT^2T_c^{2.5}} = \frac{0.4278T_c^{2.5}}{P_cT^{2.5}}, \]
\[ B = \frac{b}{RT} = \frac{0.0867T_c}{P_cT}, \]
\[ h = \frac{BP}{Z} = \frac{b}{V_m}. \]

\[ Z \] is the ratio of the molar volume of a gas to the molar volume of an ideal gas at the same temperature and pressure. At the critical point, \( Z \) is 1/3 for all gases. Thus, \( Z \) or \( \beta \) (=1/\( Z \)) measures the deviation of real gas behavior from that of an ideal (or perfect) gas. In general, gases become less ideal closer to a phase change, at lower temperatures, and higher pressures.

One concern with the Redlich-Kwong equation was that its applicability away from saturated conditions was unknown. Moreover, other more sophisticated EOS have since improved upon the Redlich-Kwong formulation (Peng & Robinson 1976, Duan et al 1992, Span & Wagner 1996, Wagner & Prüß 2002, Duan & Zhang 2006), validating the need to compare it versus more rigorous parameterizations.

It was decided to compare the Redlich-Kwong EOS versus that from Duan et al (1992) for CO\(_2\). The Duan et al (1992) EOS is a relatively simple parameterization that agrees very well (to within 1%) with more sophisticated formulations (Span & Wagner 1996, Wagner & Prüß 2002), sufficing as a check on the accuracy of the EOS currently employed. The Duan et al (1992) EOS can be described as:

\[ Z = \frac{PV}{RT} = 1 + \frac{BV_c}{V} + \frac{CV_c}{V^2} + \frac{DV_c^2}{V^4} + \frac{EV_c^3}{V^5} + \frac{FV_c^2}{V^2} \]
\[ \times \left( \beta + \frac{\gamma V_c^2}{V^2} \right) \exp \left( -\frac{\gamma V_c^2}{V^2} \right), \]
\[ V_t = \frac{V}{V_c}. \]
Here \( R = 83.14467 \text{cm}^3\text{bar}/(\text{K mol}) \) is the universal gas constant. For the end-members, the parameters \((B, C, D, \ldots \text{etc.})\) are defined as follows

\[
B = a_1 + \frac{a_2}{T_r^3} + \frac{a_3}{T_r^4},
\]

\[
C = a_4 + \frac{a_5}{T_r^2} + \frac{a_6}{T_r^3},
\]

\[
D = a_7 + \frac{a_8}{T_r^2} + \frac{a_9}{T_r^3},
\]

\[
E = a_{10} + \frac{a_{11}}{T_r^2} + \frac{a_{12}}{T_r^3},
\]

\[
F = \frac{\alpha}{T^3},
\]

\[
T_r = \frac{T}{T_c},
\]

\[
V_c = \frac{RT_c}{P_c},
\]

The parameters \(a_1 - a_{12}, \alpha, \beta, \text{and } \gamma\) for both CO\(_2\) and H\(_2\)O are given in both Duan et al (1992) and Duan and Zhang (2006). Input pressures and temperatures are used to compute \(V_c, T_r, \text{and } P_r\), respectively. However, in this virial form of the EOS, \(Z\) cannot be computed without solving for \(V_r\) (which needs \(V\)). The bisection method, programmed below, can then be employed to solve for the roots \(V\):

```
SUBROUTINE BISECTEOS(B,C,D,E,F,beta,gam,Pr,Tr,xmid)
! outputs xmid as Vr
implicit none
real :: FMID, FL, rtbis,dx, xmid, FUNC, x,x1,x2,B,C,D,E,F,beta,gam,Pr ,Tr
integer, parameter:: jmax = 100, xmax=180001  ! maximum number of allowed bisection iterations
dimension :: FUNC(xmax), x(xmax)
integer :: n,j
real, parameter :: tol=1.e-6

x(1)=-80000
do j =1,xmax-1
x(j+1) = x(j)+1
endo

x1= x(1) ! first x point
x2 =x(xmax) ! Last x point
```
do j = 1, xmax
   FUNC(j) = 1 + (B/x(j)) + C/(x(j)**2) + D/(x(j)**4) + E/(x(j)**5) + &
   F/(x(j)**2)*(beta + gam/(x(j)**2))*exp(-gam/(x(j)**2)) - (Pr/Tr)*x(j) ! the function
endo

FMID = 1 + (B/x2) + C/(x2**2) + D/(x2**4) + E/(x2**5) + &
   F/(x2**2)*(beta + gam/(x2**2))*exp(-gam/(x2**2)) - (Pr/Tr)*x2
FL = 1 + (B/x1) + C/(x1**2) + D/(x1**4) + E/(x1**5) + &
   F/(x1**2)*(beta + gam/(x1**2))*exp(-gam/(x1**2)) - (Pr/Tr)*x1

if (FL*FMID.ge.0) pause  ! Root must be bracketed in rtbis

if (FL.lt.0) then
   rtbis = x1;
   dx = x2-x1;
else
   rtbis = x2
   dx = x1-x2
endif

do n = 1, jmax
   dx = 0.5*dx
   xmid = rtbis + dx
   FMID = 1 + (B/xmid) + C/(xmid**2) + D/(xmid**4) + E/(xmid**5) + &
   F/(xmid**2)*(beta + gam/(xmid**2))*exp(-gam/(xmid**2)) - (Pr/Tr)*xmid
   if (FMID.le.0) rtbis = xmid
   if ((abs(dx).lt.tol).or.(fmid.eq.0)) exit
endo
end  ! ends subroutine

The calculation of $\beta$ then follows directly from $Z$. As expected, the agreement between both parameterizations is quite satisfactory for saturated conditions (Fig. F1).
Figure F1: Inverse of the compressibility factor ($\beta$) versus surface temperature along the CO$_2$ saturation vapor pressure curve. The two parameterizations agree very well until ~300 K. At 305 K, $\beta$ is somewhat larger with Redlich-Kwong.

For CO$_2$ at unsaturated conditions, Fig. F2 shows the computed $\beta$ values for temperatures of 216.5 K and 273 K. Overall, even away from saturation, both EOS yield very similar results.
Figure F2: \( \text{CO}_2 \) pressure versus \( \beta \) for unsaturated conditions for \( T = (a) \ 216.5 \text{ K} \) and 0.1 to 5 bar 30 bar and \( (b) \ 275 \text{ K} \) and 0.1 to 30 bar.
As a final check, several thermodynamic variables were computed with the Duan et al. (1992) EOS to validate those calculated by Redlich-Kwong. A central finite-differencing scheme was used to calculate the partial derivatives $\frac{\partial V}{\partial T}$ and $\frac{\partial^2 V}{\partial T^2}$ over the range of pressures ($i$) and temperatures ($j$) for non-ideal conditions ($\beta \neq 0$)

$$\frac{\partial V_{i,j}}{\partial T} = \frac{V_{i,j+1} - V_{i,j-1}}{2T_j - T_{j-1}}$$

$$\frac{\partial^2 V_{i,j}}{\partial T^2} = \frac{V_{i+1,j} - 2V_{i,j} + V_{i-1,j}}{(T_j - T_{j-1})^2}$$

These thermodynamic quantities were also confirmed to agree rather well with those computed with Redlich-Kwong, deeming it unnecessary to update the EOS.
APPENDIX G: USEFUL LINUX COMMANDS

Although the climate model simulations in this thesis were conducted in a LINUX command line environment, this author has no qualms in professing his great love for WINDOWS and preference for click-and-drag interfaces. Indeed, the author unabashedly admits that this entire thesis (and associated papers) was written with Microsoft Word supplemented with none other than MathType and Endnote. If these are blasphemous thoughts, note that the author grew up on DOS before the advent of the wonderful innovation that was Windows 95. So, perhaps the author is just strange. Nevertheless, learning LINUX was akin to being thrown into a swimming pool and having to learn how to sink or swim. In the physical sciences, this means adapting to the tools and traditions of the trade in order to properly excel in one’s own chosen discipline. If lucky, one day scientists will forego tradition in favor of practicality and upgrade to an appropriate click-and-drag user interface like the rest of us have enjoyed for so long. However, that would be dreaming! Alas, these are the state of affairs for now, so adapt we must indeed...

In the section that follows, it is assumed that the user knows basic commands (cd, ls, cp, mkdir, less, rm..etc) but isn’t aware of somewhat more advanced options that can make life a little easier. I thank my fellow colleague Ravi Kopparapu, a LINUX guru, for helping me become proficient enough to be able to perform my scientific tasks. As a result the author has learned some tricks over the years that will hopefully make the learning curve for future students (and faculty) less steep than it needs to be. However, if there is nothing else that readers take away from this appendix, the author strongly implores the usage of the TAB key to complete filenames. This is an extremely useful trick that saves a lot of time typing and prevents arthritis.

Starting at the command prompt (:/mars$), the common “ls” command lists all the files within a directory. However, the –l flag gives more information, including permissions, file sizes (in bytes), and dates created.

`: /mars$ ls –l`

drwxr-xr-x 2 moo moo 4096 Apr 12  2011 Climagliese.f
drwxr-xr-x 2 moo moo 4096 Jan 01  2014 Climastandard.f
drwxr-xr-x 2 moo moo 4096 Jan 23  2013 copies
drwxr-xr-x 2 moo moo 4096 Dec 23  2012 COUPLE
Here “moo” is the username. On the subject of permissions, the rwx symbols refer to read, write and execute permissions, respectively. The first set of permissions before the first hyphen break are “user” permissions, followed by “group” and finally, “other” permissions.

By further using the –t flag, these files and directories can be rearranged in order from most recent to latest:

```
$ ls –lt
```

```
drwxr-xr-x  2 moo moo 4096 Jan 01  2014 Climastandard.f
drwxr-xr-x  2 moo moo 4096 Jan 23  2013 copies
drwxr-xr-x  2 moo moo 4096 Dec 23  2012 COUPLE
drwxr-xr-x  2 moo moo 4096 Apr 12  2011 Climagliese.f
```

The asterisk (*) command is useful in executing a command on specific files only. For instance,

```
$ ls –lt *.f
```

```
drwxr-xr-x  2 moo moo 4096 Jan 01  2014 Climastandard.f
drwxr-xr-x  2 moo moo 4096 Apr 12  2011 Climagliese.f
```

Only lists the files with a .f extension. Finally, typing

```
$ ls –lt Climagliese.f
```

```
drwxr-xr-x  2 moo moo 4096 Apr 12  2011 Climagliese.f
```

Only gives information on the Climagliese.f file.

A few commands may be used to view the contents of files without opening them. The “less” command peeks at the top of the file and the up/down directional keys are used to scroll through the document. The “more” command is similar, except that the user scrolls through a page at a time with the spacebar. With the “head” and “tail” commands, the user specifies to view only certain sections of the document. The former allows prompts for the number of lines to be viewed starting from the top, whereas the latter gives the number of lines from the bottom. Thus,


`:mars$ head -30 Climagliese.f`

gives the first 30 lines of that file whereas

`:mars$ tail -30 Climagliese.f`

allows the last 30 lines to be viewed. Pressing “q” returns to the prompt. The “cat” command is similar in function to “more” except that the contents of several files are viewed sequentially

`:mars$ cat Climagliese.f Clima.f`

Some investigators may find useful to maintain version control over successive documents using the “diff” command.

`:mars$ diff Climagliese.f Clima.f`

The above only outputs the lines that differ between the two files.

All of these commands are tremendously useful for viewing large files that have long load times if otherwise opened.

The cp (copy) command is often used to transfer files from one directory to the next. For instance, to copy files from another directory into the current one, it may be tempting to give the entire path of the destination directory as:

`:mars$ cp ../../foo.f ~/abc/Desktop/mars/`

However, it is simpler to just type

`:mars$ cp ../../foo.f .`

Where the “.” alerts LINUX to apply the operation to the current directory, which in this case copies foo.f into the current location.

It is also common to change file permissions through the “chmod” command. For example, to give read and write permissions in Climagliese.f to the others(o) group then type

`:mars$ chmod o+rw Climagliese.f`

`drwxr-xr-x  2 moo moo 4096 Apr 12  2011 Climagliese.f`

The “o+rw” literally means add read and write permissions to the other group. To modify permissions for users and groups, replace “o” with “u” or “g”, respectively. Execute permission is granted through the “+x” option.
A somewhat dangerous (but exciting) chmod command is the following, which gives universal (read, write, and execute) permissions to users, groups, and others.

```bash
:/mars$ chmod 666 Climagliese.f
```

```
drwxr-xr-x  2 moo moo 4096 Apr 12  2011 Climagliese.f
```

To unzip .tar files the syntax is

```bash
:/mars$ tar –xvf venus.tar
```

The –x flag extracts the file while the –v option provides a running list of the files being unpacked. The –f flag instructs LINUX that the next argument will be the name of the new archive file. The equivalent command for unzipping a .bz2 file is

```bash
:/mars$ bunzip2 venus.tar
```

To create zip files, the –c flag is used. The next command is followed by the desired name of the zipped archive and the name of the file to be zipped

```bash
:/mars$ tar czf Climagliese.tar Climagliese.f
```

The secure copy (scp) command is necessary for transferring files from one account (or server) to another. The login password is requested at the second sever. The following syntax

```bash
:/mars$ scp  boo@mercury.geosc.psu.edu:~/abc/Desktop/Climagliese.f .
```

accesses the boo account Desktop directory in the Mercury server, copies Climagliese.f, and sends it to the current directory (note the .) on Mars.

The scp command can also be used to send files from the current directory to a location on a different server

```bash
:/mars$ scp  Climagliese.f boo@mercury.geosc.psu.edu:~/abc/Desktop/
```

The above instructs LINUX to send a copy of Climagliese.f to the Desktop of boo’s account on Mercury.

Either of these scp (or cp for that matter) can be used to transfer entire directories with the –r designation
The secure shell command (ssh) allows the user to switch to a new server:

:mars$ ssh -Y -l rmr5265 mercury.geosc.psu.edu

:mars$ scp -r venus.tar boo@mercury.geosc.psu.edu:~/abc/Desktop/

The –r moniker sends a copy of each file within venus.tar recursively to the Desktop on boo’s account on Mercury.

The above command allows to the user to switch from Mars to Mercury. The –Y designation exports graphics, so that graphical editors, like “gedit” (highly recommended), can be used. The –l flag specifies the user to login on the destination server, which prompts for the password.

Similar to the WINDOWS concept of “shortcuts”, a directory can be created that allows direct access to files in another location. In LINUX, this is performed through a “soft link” (ln -s)

:mars$ ln -s ~/abc/Desktop/Clima NEW_DIRECTORY

This soft link does not create a new instance of the files or directories within Clima, merely a direct pathway to them through the newly generated NEW_DIRECTORY (in this case). Thus, if one were to change directory (cd) into NEW_DIRECTORY and execute “ls”, the files within the Clima directory would be accessible. Note the space between the destination directory (Clima) and the new directory through which it is linked.

Another way to verify that the link has been properly created is to type “ls -lt” where NEW_DIRECTORY was formed

lrwxrwxrwx 1 moo moo   24 Jan  2 13:53 NEW_DIRECTORY ->
~/abc/Desktop/Clima

which shows the link between the NEW_DIRECTORY and Clima directories.

Soft links can also be created for files as well.
Finally, removing a link is quite simple:

```
/mars$ ln -s ~/abc/Desktop/Clima/Climagliese.f Climagliese.f

/mars$ unlink NEW_DIRECTORY

/mars$ unlink Climagliese.f
```

Sometimes the user may need to search for a specific text string that he/she has otherwise forgotten within the morass of files and directories. The “grep” command is expressly for this purpose:

```
/mars$ grep –R ‘THING’ *
```

This command recursively searches for every instance of the text string (THING) in all files within all subdirectories. Should the text string have a very high occurrence, however, the output stream will quickly flash through the screen. It would then be prudent to divide this output into manageable chunks through the “more” command, using the spacebar to scroll through, as explained earlier:

```
/mars$ grep –R ‘THING’ *|more
```

The pipe(|) symbol informs the shell to use the first command (left of the pipe) as the input into the second command (right of the pipe). By further adding the –i flag, the LINUX shell conducts a case-insensitive search (i.e., it can locate THING, ThInG, thing or any case variation thereof):

```
/mars$ grep –Ri ‘THING’ *|more
```

The more (or less) and grep commands can also be reversed such that a case-insensitive search can be performed on a single file:

```
/mars$ more Clima.f |grep –Ri ‘PARAMETER’
```

This command searches for every instance of the string ‘PARAMETER’ within Clima.f

To search for every instance of a string within 2 or more files, replace the more command with cat:
If we wish to run an executable (e.g., run.exe), we can issue the command

```
./run.exe
```

at the command prompt. This is sufficient for most circumstances. However, the screen output can be redirected to an output file with

```
./run.exe > output.out
```

With the “>” redirect sign. As a program runs, though, the prompt is no longer available. This problem can be solved by running the process in the background with an & at the end

```
./run.exe > output.out &
```

A run in process (ps) can be found with

```
ps –A|grep run
```

```
5468 ? 00:00:22 run.exe
```

Where the –A searches for all running processes on the server and the grep command finds instances called “run.” In this example, run.exe has been running for 22 seconds. To kill this process type

```
kil -9 5468
```

Where “5468” is the process number for this particular run.

Lastly, LINUX can execute multiple commands through the usage of the double ambersand (&&) like so

```
./runtot.exe > output.out && grep –i ‘PARAMETER’
```
Which executes a file and sends the output to a new file (output.out) that is searched for the text string ‘PARAMETER.’

One useful thing that is difficult to do even in WINDOWS (unless it is Excel), is the ability to cut and paste individual columns of data, even concatenating them within a new file. The cut command

```
:mars$ cut –c23-49 Climagliese.f > b1.dat
```

Extract the 23rd through 49th characters of each line and exports them to file called b1.dat.

The 55th through 70th characters of each line are extracted and exported to b2.dat

```
:mars$ cut –c55-70 Climagliese.f > b2.dat
```

The data from b1.dat and b2.dat can then be combined in the following statement

```
:mars$ paste b1.dat b2.dat> b3.dat
```

Where the paste command has combined both sets of data in b3.dat

To access the amount of disk space used within a directory, type

```
:mars$ du –hs
```

337 M

Here, the –h and –s flags print the sizes in readable format (e.g., 1K, 234M, 2G..etc) and gives the total, respectively. Without the –s flag, sizes are outputted for each file and subdirectory. In addition, the wordcount (wc) command

```
:mars$ wc Clima.f
```

1303 5060 44658

gives line numbers, words, and bytes of information, respectively.

To obtain system memory information type

```
:mars$ less /proc/meminfo
```

Finally, account disk space information can be accessed through the quota command
The vi editor

The equivalent of the Wordpad, Notepad, and Notepad++ text editors on WINDOWS also exist on the LINUX system. Among these include VI, VIM, NANO, PICO, GEDIT, and SciTE. Due to its user-friendly menu-driven format and color-coded text, the author’s favorite LINUX editor is certainly GEDIT. However, LINUX aficionados prefer to use editors that cater to the command line. The universal favorite seems to be VI, which is probably the standard LINUX editor. While working from a high performance supercluster outside of campus, GEDIT was unavailable and the author had no choice but to work in VI. Thus, the following commands represent those the author learned in the last few months of his Ph.D. program:

**Table GI: List of basic vi commands**

<table>
<thead>
<tr>
<th>Function</th>
<th>Command</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open file</td>
<td>vi [FILENAME]</td>
</tr>
<tr>
<td>To insert text</td>
<td>I</td>
</tr>
<tr>
<td>To replace text</td>
<td>SHIFT r</td>
</tr>
<tr>
<td>To change between writing and scrolling modes</td>
<td>ESC key</td>
</tr>
<tr>
<td>To delete lines below a point</td>
<td>Go to desired starting point, type number of lines to delete and press D twice</td>
</tr>
<tr>
<td>To save changes</td>
<td>:w</td>
</tr>
<tr>
<td>To quit</td>
<td>:q</td>
</tr>
<tr>
<td>To save changes and quit</td>
<td>:wq</td>
</tr>
<tr>
<td>To quit without saving changes</td>
<td>:q!</td>
</tr>
</tbody>
</table>
REFERENCES


Allen CCW, Cox AN. 2000. Allen’s astrophysical quantities: Springer


Borysow A. 2002. Collision-induced absorption coefficients of \( \text{H}_2 \) pairs at temperatures from 60 K to 1000 K. *ASTRONOMY AND ASTROPHYSICS - BERLIN* 390: 779-82


Brient F, Bony S. 2012. Interpretation of the positive low-cloud feedback predicted by a climate model under global warming. *Climate Dynamics*: 1-17


Catling DC, Zahnle KJ. 2009. The planetary air leak. *Scientific American* 300: 36-43


Choi YS, Ho CH. 2006. Radiative effect of cirrus with different optical properties over the tropics in MODIS and CERES observations. *Geophysical Research Letters* 33


Duan Z, Möller N, Weare JH. 1992. An equation of state for the CH$_4$-CO$_2$-H$_2$O system: I. Pure systems from 0 to 1000° C and 0 to 8000 bar. *Geochimica et Cosmochimica Acta* 56: 2605-17

Duan Z, Zhang Z. 2006. Equation of state of the H$_2$O, CO$_2$, and H$_2$O-CO$_2$ systems up to 10 GPa and 2573. 15 K: Molecular dynamics simulations with ab initio potential surface. *Geochimica et cosmochimica acta* 70: 2311-24


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Forget F, Wordsworth R, Millour E, Madeleine J-B, Kerber L, et al. 2012. 3D modelling of the early Martian Climate under a denser CO\textsubscript{2} atmosphere: Temperatures and CO\textsubscript{2} ice clouds. *Icarus*


Gruszka M, Borysow A. 1997. Roto-Translational Collision-Induced Absorption of CO\textsubscript{2} for the Atmosphere of Venus at Frequencies from 0 to 250 cm\textsuperscript{-1}, at Temperatures from 200 to 800 K. *Icarus* 129: 172-7


Hansen J. 2010. *Storms of My Grandchildren: The Truth About the Coming Climate Catastrophe and Our Last Chance to Save Humanity*. Bloomsbury USA


Jarrard RD. 2003. Subduction fluxes of water, carbon dioxide, chlorine, and potassium. *Geochemistry, Geophysics, Geosystems* 4


Karaiskou A, Vallance C, Papadakis V, Vardavas I, Rakitzis T. 2004. Absolute absorption cross-section measurements of CO₂ in the ultraviolet from 200 to 206 nm at 295 and 373 K. *Chemical physics letters* 400: 30-4


Mastenbrook H. 1963. *Frost-point hygrometer measurements in the stratosphere and the problem of moisture contamination (*Extraneous moisture contamination problems in balloon-borne frost-point hygrometer soundings of stratosphere*). Presented at INTERNATIONAL SYMPOSIUM ON HUMIDITY AND MOISTURE, 1ST, WASHINGTON, D. C


Mohr S. 2010. *Projection of world fossil fuel production with supply and demand interactions*: University of Newcastle


Span R, Wagner W. 1996. A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. *Journal of physical and chemical reference data* 25: 1509


Urata RA, Toon OB. 2013. Simulations of the Martian hydrologic cycle with a general circulation model: Implications for the ancient Martian climate. Icarus


Wall M. 2013. Ailing NASA telescope spots 503 new alien planet candidates. *Space.com*


Vita

Ramses Mario Ramirez was born in New York City and lived in Queens for nearly 12 years before residing in the Orlando metropolitan area until the age of 17. He attended Lake Howell High School and graduated in the top 1% of his class, finishing with *summa cum laude* honors. Afterwards, he matriculated to the Georgia Institute of Technology where he graduated with *High Honors* in aerospace engineering. During this time, he worked at Lockheed Martin for a number of summers, designing missiles and radar systems. After witnessing the rise of the field of exoplanets, however, and reconnecting with his childhood passions, Ramses decided to leave engineering and pursue a career in planetary science. He began this new trek by completing all of the geology major courses at the University of South Florida, finishing with a perfect 4.0. Under the tutelage of *Regent's Professor* Ronald Greeley at Arizona State University, Ramses went on to complete a Master’s of Science degree in planetary geology. In the remaining months of his Master’s, he met his soon-to-be Ph.D advisor at a school colloquium talk, becoming fascinated with habitable zones and early Mars. This led to the immediate decision to pursue a Ph.D. with *Evan Pugh Professor* Dr. Jim Kasting at Pennsylvania State University. Ramses has published a paper as primary author (*Warming early Mars with CO$_2$ and H$_2$*), is co-primary author on *Habitable zones around main-sequence stars: new estimates*, has another paper in review (*Can increased atmospheric CO$_2$ levels trigger a runaway greenhouse?*), and is a co-author on several papers. A *Bunton-Waller* and *Alfred P. Sloan* Scholar, Ramses finally obtained his Ph.D. in Geosciences with minor in Astrobiology in May 2014. Ramses is of Dominican descent so merengue and baseball are in his blood. He also enjoys swing dancing, Star Wars, and Dungeons and Dragons.