1 Characterization of a Thick Ozone Layer in Mars' Past

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Abstract

All three terrestrial planets with atmospheres support O\textsubscript{3} layers of some thickness. While currently only that of Earth is substantial enough to be climatically significant, we hypothesize that ancient Mars may also have supported a thick O\textsubscript{3} layer during volcanically quiescent periods when the atmosphere was oxidizing. To characterize such an O\textsubscript{3} layer and determine the significance of its feedback on the Martian climate, we apply a 1D line-by-line radiative-convective model under clear-sky conditions coupled to a simple photochemical model. The parameter space of atmospheric pressure, insolation, and O\textsubscript{2} mixing fraction are explored to find conditions favorable to O\textsubscript{3} formation. We find that a substantial O\textsubscript{3} layer is most likely for surface pressures of 0.3–1.0 bar, and could produce an O\textsubscript{3} column comparable to that of modern Earth for O\textsubscript{2} mixing fractions approaching 1%. However, even for thinner O\textsubscript{3} layers, significant UV shielding of the surface occurs along with feedback on both the energy budget and photochemistry of the atmosphere. In particular, CO\textsubscript{2} condensation in the middle atmosphere is inhibited and the characteristics of H\textsubscript{2}O dissociation are modified, shifting from a direct photolysis dominated state similar to modern Mars to a more Earth-like state controlled by O(1\text{D}) attack.

Keywords: Atmospheres, chemistry; Atmospheres, structure; Mars, atmosphere; Mars, climate; Photochemistry.
1. Introduction

It is now known that all three atmosphere-bearing terrestrial planets—Venus, Earth, and Mars—possess an O₃ layer (Montmessin et al. 2011). In the O₂ rich atmosphere of modern Earth, O₃ has a significant impact on the solar and thermal radiation budgets, being the second most important absorber of shortwave radiation and third most important gas affecting longwave radiative forcing (Kiehl & Trenberth 1997). This results in O₃ providing substantial photochemical feedback to the climate (Hauglustaine et al. 1994). Stratospheric O₃ also performs the vital role of shielding surface organisms from damaging solar UV radiation. In contrast, the O₃ layers observed on Venus and Mars are of scientific interest only as probes into atmospheric photochemistry, being too thin to have significant climate feedback and providing hardly any UV attenuation.

But this may not always have been the case. The terrestrial planets' atmospheres have undergone major evolution since their formation (Hunten 1993), and it is known that Earth's atmosphere was not always so favorable to the formation of an O₃ layer (Kasting & Donahue 1980). By the same token, it is possible that the other terrestrial planets may have been more favorable to the formation of a stable O₃ layer than they are at present. If this was the case, the resulting energy budget and photochemistry feedbacks could be important in understanding the planets' climate evolution and habitability. In this paper we explore this possibility for Mars.

In order to identify conditions in Mars' past which would have favored a thick O₃ layer it is important to understand the reactions governing the production and destruction of O₃. Summarizing the arguments of Hiscox & Lindner (1997), we begin by examining the production of O₃ via the reaction
\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]

where M is some third body, mostly likely O\(_2\) or N\(_2\) for Earth and CO\(_2\) for Venus and Mars. The kinetics of this reaction have a negative dependence on temperature, making O\(_3\) production faster at lower temperatures. And it is immediately obvious that increasing the concentrations [O], [O\(_2\)], or [M] will increase the production rate of O\(_3\). In the atmospheres we consider, much of the O and O\(_2\) are derived from the photolysis of CO\(_2\), so the presence of a denser Martian atmosphere will amplify the concentrations of all three species. On the other hand, destruction of the oxidizing species O, O\(_2\), and O\(_3\) in the Martian atmosphere is largely controlled by catalytic reactions involving HO\(_x\) (H, OH, HO\(_2\)) produced by H\(_2\)O photolysis. This means that a drier atmosphere will have less HO\(_x\), increasing [O] and [O\(_2\)] and reducing the destruction rate of O\(_3\). A thick and cold atmosphere will also contribute to reducing HO\(_x\) by shielding H\(_2\)O from UV and lowering its vapor pressure, respectively. From this analysis, Hiscox & Lindner (1997) concluded that a dense, cold, and dry atmosphere would be most favorable to the production of a thick O\(_3\) layer on Mars.

These conditions are somewhat at odds with those considered in many previous paleoclimate studies of Mars. One of the primary drivers in studying Mars' past is explaining the chemical and morphological evidence for surface modification by persistent liquid water (Carr & Head 2010). Climate modeling struggles to achieve surface temperatures above 273 K simply by assuming a thicker CO\(_2\) atmosphere (Kasting 1991), and efforts to explain this discrepancy often rely on additional greenhouse gases like CH\(_4\), H\(_2\)S, and SO\(_2\) (Halevy et al. 2009; S.S. Johnson et al. 2008; Kasting 1997; Squyres & Kasting 1994). These species require a reducing atmosphere and major geochemical source, conditions which are most easily met by large scale volcanic
activity, and result in a picture of early Mars not unlike Archean Earth (Halevy et al. 2007; S.S. Johnson et al. 2009; Tian et al. 2010). Under such a warm, wet, and reducing scenario, oxidizing species would be rapidly destroyed both in the atmosphere and in aqueous solution at the surface (Kasting et al. 1979; Kasting & Walker 1981; Kasting et al. 1985). What little \( \text{O}_3 \) could exist under such conditions would have negligible feedback on the climate.

However, Martian volcanism has been episodic throughout the planet's history, with the most recent large scale caldera activity ending ~100–200 Ma (Neukum et al. 2010; Robbins et al. 2011). During volcanically quiescent geologic periods (such as the current time), any climate-influencing volcanic gases would become depleted and the atmosphere would relax to a colder, drier state. This would allow for the accumulation of oxidizing species such as \( \text{O}_2 \) and \( \text{O}_3 \) (Kasting 1995). Our characterization of \( \text{O}_3 \) climate feedback processes is pertinent to these volcanically quiescent periods of Mars' history.

The photochemistry relevant to a thick \( \text{CO}_2 \) atmosphere lacking volcanism has been examined by several authors (Hiscox & Lindner 1997; Rosenqvist & Chassefière 1995; Segura et al. 2007; Selsis et al. 2002; Zahnle et al. 2008). The ability of trace amounts of a strong UV absorber (\( \text{SO}_2 \)) to modify the ancient Martian atmosphere's temperature structure has also been demonstrated (Yung et al. 1997). However, the feedback between a photochemical product such as \( \text{O}_3 \) and the planetary thermal structure has received less attention. Hiscox & Lindner (1997) made the case that a Martian \( \text{CO}_2 \) atmosphere thick enough to support liquid water at the surface would also produce an \( \text{O}_3 \) layer substantial enough to shield the surface from UV radiation and contribute to the greenhouse effect. However, their analysis was rough and somewhat qualitative, lacking detailed photochemical calculations. The studies of Rosenqvist & Chassefière (1995),
Segura et al. (2007), and Zahnle et al. (2008) used a fixed temperature profile for their photochemical calculations. Selsis et al. (2002) did examine feedback between O$_3$ photochemistry and the temperature profile, but this was not the focus of the study and a converged solution was not achieved due to excessively long run times.

Here we take a complementary approach, solving for the equilibrium temperature profile using a radiative-convective model coupled to a simplified photochemical model. This provides a first order estimate of stratospheric O$_3$ concentration while ensuring timely convergence. We explore the parameter space of atmospheric pressure, insolation, and O$_2$ mixing fraction to search for conditions likely to support a substantial O$_3$ layer and then examine the significance and robustness of its feedback on the climate.

2. Model Description

2.1 Radiative-Convective Model

Radiative-convective equilibrium is solved for using a 1D line-by-line (LBL) model. The decision to use LBL is motivated by recent concerns that standard 1D models of ancient Mars, such as used by Pollack et al. (1987) and Kasting (1991), suffer from serious parameterization issues (Halevy et al. 2009; L. Kaltenegger, pers. comm., 2009; Wordsworth 2010a). There has also been recent work demonstrating that correlated-k parameterizations commonly used for Earth result in radiative forcing by H$_2$O and O$_3$ which can deviate significantly from those given by LBL calculations (Forster et al. 2011; Tvorogov et al. 2005). While LBL calculation is more fundamentally correct than other methods and is important for benchmarking the accuracy of alternative techniques, it has been rejected for many applications in the past because it is
computationally slow (Liou 2002). However, given new optimization techniques and the steady advance in computing power, such models are becoming more common in planetary science (Corrêa et al. 2005; Letchworth & Benner 2007; Kuntz & Höpfner 1999; Quine & Drummond 2002; Wells 1999).

In our model the atmosphere is divided into layers at a vertical resolution of 2 km, with the domain extending from the planet's surface up to the altitude where atmospheric pressure approaches $10^{-6}$ bar (0.1 Pa). The low pressure limit is chosen to avoid the complex effects encountered in the upper atmosphere. These include the onset of the ionosphere, violation of local thermodynamic equilibrium, transition of the dominant mass transfer mechanism from eddy diffusion to molecular diffusion at the homopause, and transition of the dominant heat transfer mechanism from radiation to conduction at the mesopause (Bougher et al. 2008, López-Valverde et al. 1998).

Radiation is divided into two spectral regions: a UV region from 119 nm to 400 nm at 1 nm resolution and a visible/infrared (VIR) region ranging from 25000 cm$^{-1}$ (400 nm) to 0 cm$^{-1}$ with a non-uniform grid. The resolution of the pre-computed VIR grid varies from $2^{-15}$–1 cm$^{-1}$ in order to resolve individual radiative lines at one half-width or better, and is optimized for the input parameters of a given run (i.e. surface pressure, species' concentrations). The solar radiation source in the UV is taken from the ASTM E-490 reference spectrum and VIR radiation uses the synthetic spectrum provided by the AER group (Clough et al. 2005), which is generated from the Kurucz (1992) solar source function. Solar fluxes are scaled by 1/4th to account for global and diurnal averaging. Absorption by CO$_2$, H$_2$O, and O$_3$ is considered in both spectral regions and O$_2$ is included in the UV.
UV cross-sections are obtained from various authors via the MPI-Mainz-UV-VIS Spectral Atlas of Gaseous Molecules and Sander et al. (2011). Temperature dependent CO$_2$ UV cross-sections are used via linear interpolation of data at 295 K and 195 K, being held constant below 195 K. The temperature sensitive Schumann-Runge bands of O$_2$ in the UV are computed via the method of Minschwaner et al. (1992) and binned at 1 nm.

VIR cross-sections are calculated line-by-line using the 2008 HITRAN database (Rothmann et al. 2009). Pressure broadening and line shifting of H$_2$O lines by CO$_2$ instead of air is implemented using the results of Brown et al. (2007). This increases pressure-broadened half-widths by a factor of 1.7 on average relative to terrestrial air. Based on this, pressure-broadened half-widths of O$_3$ lines in air are multiplied by 1.7, as data on CO$_2$ pressure-broadening of O$_3$ is lacking. A Voigt line shape profile is used out to 40 Doppler half-widths from the line center and beyond that a van Vleck–Weisskopf profile is used. For H$_2$O and O$_3$ a Lorentzian wing cut-off of 25 cm$^{-1}$ from the line center is used, while sub-Lorentzian CO$_2$ wings are treated by using empirical $\chi$-factors with a cut-off of 500 cm$^{-1}$ (Halevy et al. 2009; Wordsworth et al. 2010a). The $\chi$-factor of Perrin & Hartmann (1989) is used in the range 0–3000 cm$^{-1}$, that of Tonkov et al. (1996) is used for 3000–6000 cm$^{-1}$, and that of Meadows & Crisp (1996) is used > 6000 cm$^{-1}$.

For H$_2$O and O$_3$ only the most common isotopologues are used (H$^{16}$OH, $^{16}$O$^{16}$O$^{16}$O), while for CO$_2$ the three most common isotopologues are considered ($^{16}$O$^{12}$C$^{16}$O, $^{16}$O$^{13}$C$^{16}$O, $^{16}$O$^{12}$C$^{18}$O).

Also, for each layer weak radiative lines are excluded from calculations based on the criterion of optical depth $\tau < 0.01$ at the line peak when integrated across the overhead atmospheric column. These measures are taken for computational economy, and including rarer species and weaker lines has a negligible (< 1 K) effect on the temperature profile.
Collision induced absorption (CIA) by CO\textsubscript{2} is accounted for using the “GBB” parameterization of Wordsworth et al. (2010a), which is based on the experimental work of Baranov et al. (2004) and Gruszka & Borysow (1998). The Chappuis and Wulf continua of O\textsubscript{3} in the VIR are sampled at 1 cm\textsuperscript{-1} from the MT\_CKD continuum model (Clough et al. 2005). Rayleigh scattering cross-sections for CO\textsubscript{2} are calculated from its refractive index. In the UV the refractive index is taken from Bideau-Mehu et al. (1973), while in the VIR the results of Old et al. (1971) are used. In both regions the King correction factor is taken from Alms et al. (1975).

For radiative transfer the plane-parallel approximation is used and treatment follows a two-stream method, applying the technique of Toon et al. (1989) for scattering of solar radiation. The planet's surface is taken to be a Lambertian reflector with an albedo of 0.20 for solar radiation and an emissivity of 1.0 for thermal radiation. A moist pseudoadiabatic lapse rate is used in the troposphere, with the surface as an H\textsubscript{2}O source at a specified relative humidity (RH). Above the surface the mixing fraction of H\textsubscript{2}O is given a simple “step” profile, being held constant until the condensation altitude, at which point its vapor pressure curve is followed up to the cold trap based on the temperature profile. Above this the mixing fraction is again assumed to be constant. Unless otherwise specified, a relatively dry surface value of RH=20% is used for all the results given here, comparable to modern Mars (Zahnle et al. 2008). In regions where the CO\textsubscript{2} atmosphere is super-saturated the lapse rate is set so that the temperature profile matches its vapor pressure. Clear sky conditions are assumed.

For calculation of the tropospheric lapse rate, it is necessary to know the heat capacity \(c_p\) of the atmosphere, dominated in this case by CO\textsubscript{2}. From statistical mechanics, the zero-pressure heat capacities of a rigidly rotating linear molecule with internal vibrational modes are
\[
\frac{c_p}{R} = 1 + \frac{c_v}{R} = 1 + \frac{3}{2} + \frac{2}{2} \sum_j \left( \frac{\theta_j}{T} \right)^2 \frac{e^{-\theta_j}}{e^T - 1} \]

where \(R\) is the universal gas constant, \(T\) is the gas temperature, and \(\theta_i\) is the characteristic temperature of the \(j\)th vibrational mode. For \(\text{CO}_2\) at low planetary temperatures \((T < 373 \text{ K})\) only the low energy vibrational modes \(v_1 = 1330 \text{ cm}^{-1} (\theta_1 = 1910 \text{ K})\) and doubly degenerate \(v_2 = 667 \text{ cm}^{-1} (\theta_2 = 960 \text{ K})\) need to be considered. Within this temperature range, Eq. (1) produces zero-pressure \(c_p\) values in excellent agreement (< 0.1% difference) with the values generated by the NIST REFPROP program v9.0 (Lemmon 2010), which uses an elaborate \(\text{CO}_2\) equation of state (EOS) from Span & Wagner (1996) (see Fig. 1). For \(T > 140 \text{ K}\) it also compares well with the \(c_p\) parameterization derived from the Venusian atmosphere by Lebonnois et al. (2010). There is a greater discrepancy with the expression used by Kasting (1991), however a review of the literature reveals that this formulation originated in a paper by Eastman (1929) and is intended for application from 300–2500 K.

![Figure 1: Comparison of CO\(_2\) specific heat capacity formulations.](image-url)
For non-zero pressures the heat capacity must be corrected for the non-ideal nature of the
gas. In this we follow the appendix of Wordsworth et al. (2010b). To summarize, the Redlich-
Kwong EOS of Li et al. (2006) is used, having the form

\[
p = \frac{RT}{v-b} - \frac{a}{v(v-b)^{\frac{1}{2}}}\sqrt{T}
\]

where \( p \) is pressure, \( v \) is volume, and \( a \) and \( b \) are parameters specific to the gas under
consideration. For the relatively low pressures considered here, this may be expressed as a Virial
expansion

\[
\frac{pv}{RT} \approx 1 + \frac{B}{v} = 1 + \frac{1}{v} \left( b - \frac{a}{RT^{3/2}} \right)
\]

which can be used to calculate the pressure correction to the heat capacity via the definition

\[
c_p(p, T) = c_p(0, T) - T \int_0^P \left( \frac{\partial^2 v}{\partial T^2} \right) dp' = c_p(0, T) - T p \left( \frac{\partial^2 B}{\partial T^2} \right)
\]

In the formulation of Li et al. (2006), the parameter \( a \) is dependent on both \( p \) and \( T \),
having the form \( a = a_1(T) + a_2(T)p \). Because of the relatively low pressures relevant to Mars' past
(\( \leq 5 \) bar) we neglect the small pressure correction to \( a \) and differentiate \( B \) analytically.
Calculating \( c_p \) by this method agrees well with the NIST REFPROP program over the range of
pressures and temperatures considered in this study.

Sensitivity testing with respect to the value of \( c_p \) found that the surface temperature is not
strongly affected by the use of our formulation as compared to that of Kasting (1991). Although
the lapse rate increases significantly, a concurrent lowering in the height of the tropopause limits
the surface temperature increase to at most a few K.

In our model the temperature profile is solved for by iteratively calculating the net flux $F_{net}$ for each layer in the atmosphere and then setting the net flux to zero. This is done by assuming that the absorbed flux is constant, and adjusting the emitted flux $F_{emt}$ by changing the layer temperature $T$. To find the necessary step size $\Delta T$, an estimate of the derivative $dF_{emt}/dT$ is required. We begin by taking the emitted flux to be

$$F_{emt} = \pi \int_0^{\infty} B(\nu, T)(1 - e^{-\tau(\nu, T)}) d\nu$$

(5)

By assuming that $e^{-\tau}$ has a weak dependence on temperature over the interval $\Delta T$, we may approximate the derivative as

$$\frac{dF_{emt}}{dT} \approx \pi \int_0^{\infty} \left[ \frac{dB}{dT} \right] (1 - e^{-\tau(\nu, T)}) d\nu$$

(6)

For the conditions considered here, the radiatively active $\nu_2 = 667 \text{ cm}^{-1}$ vibrational mode of CO$_2$ dominates thermal transfer where the atmosphere is in radiative equilibrium. This allows for two more useful approximations. First, thermal emission occurs in the high energy tail of the Planck function at the temperatures of interest ($T << \theta_2 = 960$ K), allowing the simplification

$$\frac{dF_{emt}}{dT} \approx \pi \int_0^{\infty} \frac{h\nu}{kT^2} B(\nu, T)(1 - e^{-\tau(\nu, T)}) d\nu$$

(7)

Second, by approximating the $\nu_2$ emission band as a $\delta$-function we may write

$$\frac{dF_{emt}}{dT} \approx \frac{h\nu_2}{kT^2} \pi \int_0^{\infty} B(\nu, T)(1 - e^{-\tau(\nu, T)}) d\nu$$

(8)
which is readily recognized as

\[
\frac{dF_{\text{emt}}}{dT} \approx \frac{h v^2}{k T^2} F_{\text{emt}}
\]

\[\text{(9)}\]

This simple formulation is surprisingly accurate under the conditions for which it is derived, with typical errors < 1% compared to a numerical integration without approximations. After application of the derived \(\Delta T\), a convective adjustment is applied in any layers where the lapse rate exceeds the pseudoadiabatic lapse rate.

An issue with convergence by this method arises when lower layers in the atmosphere become optically thick across the entire thermal IR. If there is a surplus of outgoing radiation at the top of the model, adjusting the surface temperature to achieve flux balance is no longer effective because changes must diffuse through the atmosphere up to space over several iterations. In the meantime, the surface receives little feedback and makes further changes, resulting in stability issues. This situation is typical of thick, warm, wet Martian atmospheres. Since modeling these climatic conditions is of general interest, the issue must be resolved. Our solution is to reduce temperatures throughout the optically thick region of the atmosphere along with the surface temperature. First we find the region between the surface and the altitude where the temperature drops below the planet's effective temperature \(T_{\text{eff}}\). After the normal iteration technique to balance radiative flux and convection is applied, the layer in this region with the smallest \(\Delta T\) value, \(\Delta T_{\text{min}}\), is identified. The temperatures of all layers in the region are then adjusted

\[
T_{\text{adj}} = T_{\text{norm}} - \Delta T_{\text{min}} + \Delta T_{\text{surf}}
\]

\[\text{(10)}\]
where \( T_{\text{adj}} \) is the adjusted temperature, \( T_{\text{norm}} \) is the normal unadjusted temperature, and \( \Delta T_{\text{surf}} \) is the negative temperature change normally made at the surface. This technique ensures that the planet cools when there is a surplus of outgoing flux, but retains the relative temperature changes between atmospheric layers in each iteration.

2.2 Photochemical Model

The photochemical model is constructed as a series of atmospheric layers co-located with those of the radiative-convective model. The concentration profiles of \( \text{CO}_2 \), \( \text{CO} \), \( \text{O}_2 \), and \( \text{H}_2\text{O} \) are fixed, while \( \text{O}_3 \), \( \text{O} \), and \( \text{O}(^{1}\text{D}) \) are solved for by assuming local equilibrium. The reactions considered and their rate coefficients are listed in Table 1. Photolysis rates are derived from the UV/VIS flux profiles generated by the radiative-convective model, with quantum efficiencies taken from the review of Sander et al. (2011). The Kinetic-PreProcessor (KPP) code is used to solve for photochemical equilibrium (Daescu et al. 2003; Damien et al. 2002; Sandu et al. 2003).

For simplicity and clarity, eddy diffusion transport and \( \text{H}_2\text{O} \) photochemistry after dissociation are neglected in the current model. While such a decision is not strictly accurate, it allows feedback mechanisms not associated with these processes to be examined independently and without obfuscation. The effects of neglecting these processes are most important in the troposphere and have qualitatively predictable consequences. These will be addressed later in the discussion.

For a real \( \text{CO}_2 \) atmosphere with no or little \( \text{H}_2\text{O} \) photochemistry, i.e. a “dry” atmosphere, \( \text{CO} \) and \( \text{O}_2 \) produced by photodissociation would exist at a stoichiometric ratio of 2:1 and could
accumulate to mixing fractions of $\sim 10^{-2}$ due to the inefficiency of CO$_2$ recombination via $k_{10}$ in the absence of HO$_x$ species (McElroy & Donahue 1972; Nair et al. 1994; Parkinson & Hunten 1972). Under a “humid” atmosphere (modern Mars falls into this category) the CO:O$_2$ ratio declines and the mixing fractions can be reduced by orders of magnitude (on modern Mars the ratio is roughly 1:2 with mixing fractions on the order of $10^{-3}$). In addition, the planetary surface may act as a reductant source via volcanism (Kasting et al. 1979) and oxidant sink via weathering (Kasting & Walker 1981; Kasting et al. 1985; Zahnle et al. 2008). These act to increase CO concentration and decrease O$_2$ concentration. However, quantitatively evaluating the impact requires detailed analysis and is fraught with uncertainties about the climate, geochemistry, and volcanism of ancient Mars (Tian et al. 2010).

| Reactants | Products | Rate Coefficient | Reference |
|-----------|----------|------------------|-----------|
| CO$_2$ + hv $\rightarrow$ CO + O | J$_1$ | (Sander et al. 2011) |
| CO$_2$ + hv $\rightarrow$ CO + O($^1$D) | J$_2$ | (Sander et al. 2011) |
| O$_2$ + hv $\rightarrow$ O + O | J$_3$ | (Sander et al. 2011) |
| O$_2$ + hv $\rightarrow$ O + O($^1$D) | J$_4$ | (Sander et al. 2011) |
| O$_3$ + hv $\rightarrow$ O$_2$ + O | J$_5$ | (Sander et al. 2011) |
| O$_3$ + hv $\rightarrow$ O$_2$ + O($^1$D) | J$_6$ | (Sander et al. 2011) |
| H$_2$O + hv $\rightarrow$ H + OH | J$_7$ | (Sander et al. 2011) |
| O($^1$D) + CO$_2$ $\rightarrow$ CO$_2$ + O | $k_8 = 1.63 \times 10^{-10} e^{60/T}$ | (Sander et al. 2011) |
| O($^1$D) + H$_2$O $\rightarrow$ HO + HO | $k_9 = 7.5 \times 10^{-11} e^{115/T}$ | (Sander et al. 2011) |
| CO + O + M $\rightarrow$ CO$_2$ + M | $k_{10} = 2.2 \times 10^{-33} e^{-1780/T}$ | (Inn 1974) |
| O + O + M $\rightarrow$ O$_2$ + M | $k_{11} = 2.5 \times 4.8 \times 10^{-33} (300/T)^2$ | (Campbell & Gray 1973) |
| O + O$_2$ + M $\rightarrow$ O$_3$ + M | $k_{12} = 2.5 \times 6.0 \times 10^{-34} (300/T)^{2.4}$ | (Sander et al. 2011) |
| O + O$_3$ $\rightarrow$ O$_2$ + O$_2$ | $k_{13} = 8.0 \times 10^{-12} e^{-2060/T}$ | (Sander et al. 2011) |

Table 1: Photochemical Reactions

* Rate constant multiplied by 2.5 for increased efficiency of CO$_2$ as third body.
For the purposes of this paper we simply assume that the CO:O$_2$ ratio is of order unity and a range of prescribed mixing fractions from $10^{-5}$ to $10^{-2}$ is examined for these species. Based on the work of Kasting & Donahue (1980), which quantified the impact of an O$_3$ layer on ancient Earth, within this range O$_2$ should be stable enough against catalytic destruction by HO$_x$ to maintain a roughly constant mixing fraction at all altitudes. This range of mixing fractions is also consistent with the CO$_2$-H$_2$O photochemical modeling results of Rosenqvist & Chassefière (1995), and thus is appropriate for a low volcanic outgassing rate and slow surface weathering under a cold, dry climate (Kasting 1995).

3. Results & Discussion

3.1 Comparison with Previous Radiative-Convective Models

As a validation of the radiative-convective model some test runs were performed without photochemistry to compare with the results of selected models in the literature. Under modern insolation a surface temperature of 273 K is achieved for a surface pressure of 2.5 bar, somewhat higher than the 2.2 bar reported by Pollack et al. (1987). This may be explained by our inclusion of CO$_2$ condensation (Kasting 1991) and differing treatment of CIA parameterization (Wordsworth et al. 2010a). The differences in H$_2$O profile structure and surface albedo between the two models also have minor influences. To compare with the model of Wordsworth et al. (2010a), the insolation is scaled by a factor of 0.75 at all wavelengths to approximate early solar conditions and H$_2$O is removed from the atmosphere. Under these conditions a peak surface temperature of 215 K is found at a surface pressure of ~ 1 bar, and condensation of the
atmosphere at the surface occurs near a temperature of 208 K and pressure of just over 2.7 bar. These results are comparable to those of Wordsworth et al. (2010a) for their “GBB” CIA parameterization (Baranov et al. 2004; Gruszka & Borysow 1998) with sub-Lorentzian wings for CO₂ lines. This is encouraging, as this model is the most similar to ours in the calculation of radiative cross-sections.

3.2 Parameter Space Study Without Photochemistry

Figure 2: Parameter space showing (a) surface temperature and (b) surface H₂O mixing fraction as a function of surface pressure P and insolation S (for modern Sun intensity S = 1.00). For each S track the pressure above which CO₂ condensation begins in the middle atmosphere is indicated by ◆.

To guide our search for atmospheres that would have been most conducive to the formation of O₃, we first use the radiative-convective model with no photochemistry to explore the parameter space of surface pressure P and insolation S, where S is the insolation as a fraction...
of modern intensity. A plot of the resulting surface temperature is shown in Fig. 2a, with the diamond symbols identifying for each value of \( S \) at what surface pressure \( \text{CO}_2 \) condensation begins in the middle atmosphere. Unlike the model of Kasting (1991), which produced \( \text{CO}_2 \) condensation at modern insolation levels for \( P \geq 0.35 \) bar, our model (without photochemistry) does not condense until \( P \geq 0.92 \) bar. This discrepancy is likely due to the differing treatment of NIR solar absorption between the models, with ours having greater stratospheric heating (J. F. Kasting & R. Ramirez, pers. comm., 2011). It is worth noting that both models calculate a globally averaged temperature profile and assume radiative-convective equilibrium. \( \text{CO}_2 \) condensation could still occur for \( P < 0.92 \) bar, as it does on Mars today, in cold regions at high latitude (Kelly et al. 2006) and in the mesosphere due to temperature fluctuations driven by atmospheric waves (Montmessin et al. 2006).

Surface \( \text{H}_2\text{O} \) mixing fraction \( f_{\text{H}_2\text{O}} \) is shown in Fig. 2b as a function of \( P \) and \( S \). It may be seen that for \( S > 0.85 \) there exists a local minimum for \( f_{\text{H}_2\text{O}} \). The reason for this minimum is as follows: For \( P < 0.3 \) bar the surface temperature increases only weakly with pressure, causing the vapor pressure of \( \text{H}_2\text{O} \) to rise less quickly than the \( \text{CO}_2 \) pressure and resulting in the decline of \( f_{\text{H}_2\text{O}} \). At \( P > 0.3 \) bar \( \text{H}_2\text{O} \) becomes an important greenhouse gas for these atmospheres and its positive feedback on temperature is strong enough to increase \( f_{\text{H}_2\text{O}} \) with increasing surface pressure. For \( S < 0.85 \) the surface temperature never rises enough for \( \text{H}_2\text{O} \) to become a significant greenhouse gas, and so its mixing fraction decreases monotonically with \( P \).

For the purpose of identifying conditions likely to support a thick \( \text{O}_3 \) layer, it is of interest to summarize here some of the results of Rosenqvist & Chassefière (1995). Modeling a \( \text{CO}_2-\text{H}_2\text{O} \) atmosphere with a fixed temperature profile and varying pressure, they identified three distinct
photochemical regimes for the O\textsubscript{2} mixing fraction \(f_{\text{O}_2}\), which may be compared with those for \(f_{\text{H}_2\text{O}}\) outlined above. For \(P < 0.1\) bar \(f_{\text{O}_2}\) declined with \(P\), while for \(0.1 < P < 1\) bar it rose with \(P\), and finally declined again at \(P > 1\) bar. The cause of rising \(f_{\text{O}_2}\) for \(0.1 < P < 1\) bar was determined to be increased shielding of \(\text{H}_2\text{O}\) against photolysis, resulting in decreased destruction of \(\text{O}_2\) by \(\text{HO}_x\). By \(P \approx 1\) bar this caused the atmospheric photochemistry to be insensitive to \(\text{H}_2\text{O}\) content. For \(P < 1\) bar they found that artificially reducing \(f_{\text{H}_2\text{O}}\) (making the atmosphere drier) also reduced \(\text{HO}_x\) and produced a higher \(f_{\text{O}_2}\).

Taking the results presented above concerning pressure and temperature with no photochemistry along with those of Rosenqvist & Chassefière (1995) concerning pressure at fixed temperature, it would seem that conditions favorable to \(\text{O}_3\) formation are most likely to be found at moderate pressures of 0.3–1.0 bar. The lower end of this range corresponds with our finding of a minimum mixing fraction of tropospheric \(\text{H}_2\text{O}\) for pressures ≥ 0.3 bar, while the upper end is determined by the finding of Rosenqvist & Chassefière (1995) that tropospheric \(\text{H}_2\text{O}\) is increasingly shielded as pressures approach 1 bar. Thus, within this range we expect a minimum of \(\text{H}_2\text{O}\) photolysis, with a corresponding maximum in accumulation of oxidizing species like \(\text{O}_2\) and \(\text{O}_3\).

In a broader context, focusing on atmospheric pressures of 0.3–1.0 bar is consistent with recent work suggesting that Mars had an atmosphere ≥ 0.2 bar at some time in its past (Manga et al. 2012) but has volcanically outgassed ≤ 1 bar \(\text{CO}_2\) over its history (Grott et al. 2011). It is also notable that this range falls within the 0.1–1 bar “dead zone” in Mars' history identified by Richardson & Mischna (2005). That study pointed out that within this range of pressures diurnal temperature highs would rarely reach the freezing point of water. Subsequently, loss of \(\text{CO}_2\) by
surface weathering would be limited, reducing its utility for explaining the modern observed pressure of 6 mbar. For climates in this “dead zone” we expect that feedback from O$_3$ would be relatively strong. If a significant positive effect on surface temperature exists, warming by O$_3$ might have helped stabilize ephemeral liquid water, facilitating continued weathering out of CO$_2$. We consider this possibility when investigating the effect of O$_3$ on the energy budget.

3.3 Parameter Space Study With Photochemistry

Based on the results of the previous section, and in order to more directly compare with previous work by Selsis et al. (2002), we select our nominal atmospheric model to have an O$_2$ mixing fraction $f_{O_2} = 10^{-3}$ with surface pressure $P = 1$ bar and a modern insolation intensity $S = 1.00$. We then vary $f_{O_2}$, $P$, and $S$ in turn to characterize their effect on the O$_3$ layer and its feedbacks.

3.3.1 O$_3$ Profile and Column

We begin our characterization of potential Martian O$_3$ layers by examining their concentration profiles and integrated column densities. Varying $f_{O_2}$, we find that with more O$_2$ the O$_3$ layer becomes thicker and its peak value larger and located at higher altitude (Fig. 3). This same behavior has been found by models examining the photochemistry of early Earth (Kasting & Donahue 1980), and is due to the increased availability of O$_2$ for O$_3$ production and decreased penetration of UV. In contrast, we find that varying $P$ and $S$ have little effect on the profile when altitude is plotted as pressure (not shown).
While increasing $f_{O_2}$ generally increases the O$_3$ column (Fig. 4), it eventually levels off at a value comparable to that of modern Earth (300 Dobson units ≈ $8.1 \times 10^{18}$ cm$^{-2}$). Again, this is in line with models of the early Earth (Kasting & Donahue 1980). We obtain an O$_3$ column of $7.5 \times 10^{18}$ cm$^{-2}$ for our most oxidizing atmosphere with $f_{O_2} = 1 \times 10^{-2}$. This is less than half of the $1.8 \times 10^{19}$ cm$^{-2}$ column of the “super ozone layer” reported by Selsis et al. (2002) for a 1 bar Martian atmosphere with $f_{O_2} = 2 \times 10^{-2}$. While our results are not directly comparable with those of Selsis et al. (2002) due to the different $f_{O_2}$, as previously mentioned we expect our O$_3$ column to be little different for higher $f_{O_2}$. Curiously, since the model of Selsis et al. (2002) contains catalytic HO$_x$ destruction of O$_3$ and ours does not, we would expect their model to produce a column smaller than ours, not larger. Furthermore, both models contain the majority of their O$_3$
in the stratosphere, so the detailed tropospheric photochemistry implemented in Selsis et al. (2002) cannot be the cause of disagreement. We considered the possibility that the difference was due to our diurnal averaging of solar flux for photochemistry (Krasnopolsky 2006), but a test run using average daytime insolation increases our $O_3$ column by only 10%. The model's insensitivity to solar flux also rules out the disagreement being caused simply by a differing choice in solar zenith angle (Kasting & Donahue 1980). We conclude that the discrepancy most likely comes about because the result of Selsis et al. (2002) is not a converged solution, and should only be considered as an upper limit. Our simple converged model thus provides a tighter constraint on the maximum stratospheric $O_3$ column in a thick Martian atmosphere, limiting it to very nearly the same value as on Earth.

In the interest of assessing the potential habitability of these Martian atmospheres for primitive life, an estimate for the minimum $O_3$ column necessary to ensure bacterial survival from UV damage is included in Fig. 4. We follow Hiscox & Lindner (1997) in taking the minimum tolerable $O_3$ column range determined for Earth by François & Gérard (1988) and scaling it to account for the lower UV flux at Martian orbit. We find that, under this globally averaged, clear sky, 1 bar CO$_2$ atmosphere with modern insolation, surface UV conditions capable of allowing bacterial survival require $f_{O_2} > 10^{-5}$. Including clouds and dust in the atmosphere would further reduce the UV flux at the surface. It should also be noted that in the early solar system, the UV flux from the young Sun was generally less than that of the modern Sun at $\lambda > 200$ nm and greater at $\lambda < 200$ nm (Ribas et al. 2010). Since CO$_2$ absorbs virtually all radiation at $\lambda < 200$ nm regardless of O$_2$ and O$_3$ column, the use of a modern solar spectrum by François & Gérard (1988) somewhat overestimates the minimum $O_3$ column required to support
primitive surface life on Mars under the young Sun.

3.3.2 Energy Budget

While temperatures in the middle atmosphere strongly increase with more O\textsubscript{2} due to increased solar absorption by the O\textsubscript{3} layer, the surface temperature is not greatly affected (Fig. 5). Testing with the removal of the O\textsubscript{3} IR bands resulted in a surface temperature drop of at most ~ 1 K, indicating that the contribution of O\textsubscript{3} to the greenhouse effect in these models is weak. Solar absorption by thin O\textsubscript{3} layers primarily cause heating just above the tropopause, and the altitude and magnitude of peak solar heating by O\textsubscript{3} rises with increasing O\textsubscript{2} (Fig. 6). The majority of this heating is due to absorption in the UV/VIS wavelengths, as on Earth, and occurs above the 0.1 bar pressure level in the atmosphere where Rayleigh scattering becomes important. As a result, the planetary bond albedo is significantly reduced, with a decrease of 8.1% at f\textsubscript{O2} = 10^{-2} relative to an atmosphere without an O\textsubscript{3} layer. This corresponds to a 3.8% increase in solar energy.
absorbed by the planet. The portion of this energy injected into the upper troposphere suppresses
the thermal convective flux, resulting in a small warming effect at the surface. However, for
thick O₃ layers this is counteracted by an overall reduction in the amount of solar radiation
reaching the surface, as the majority of the O₃ absorption occurs high in the atmosphere and is
simply re-radiated to space thermally. A listing of convective, longwave, and shortwave fluxes at
the surface and top of the atmosphere for various values of $f_{O₂}$ are given in Table 2.

| $f_{O₂}$ | $\Delta F_{↑,surf}^{C}$ | $\Delta F_{↓,surf}^{L}$ | $\Delta F_{↓,surf}^{S}$ | $\Delta F_{↑,top}^{S}$ |
|---------|-------------------|-----------------|-----------------|-------------------|
| $10^{-3}$ | -0.3 (-0.6%) | +2.2 (+1.1%) | -0.6 (-0.6%) | -1.4 (-2.9%) |
| $10^{-4}$ | -0.6 (-1.2%) | +2.7 (+1.4%) | -1.3 (-1.3%) | -2.4 (-5.1%) |
| $10^{-3}$ | -1.6 (-3.2%) | -0.4 (-0.2%) | -1.9 (-2.0%) | -3.2 (-6.8%) |
| $10^{-2}$ | -2.3 (-4.8%) | -3.7 (-1.9%) | -2.4 (-2.5%) | -3.8 (-8.1%) |

Table 2: Effect of varying $f_{O₂}$ on O₃ energy budget forcing for $P = 1$ bar, $S = 1.00$. Each $\Delta F$ is
taken with respect to the atmosphere with $f_{O₂} = 0$ and as has units of W/m². Superscripts C
= convective, L = longwave, and S = shortwave.

Holding $f_{O₂} = 10^{-3}$ and lowering $S$ below 1.00 enhances the suppression of convection and
alters the change in downward surface IR flux from a slight decrease to an increase (Table 3). In
contrast, approximately constant relative reductions in the amount of solar radiation reaching the
surface and reflecting to space are maintained, so the net effect of reducing $S$ is to enhance the
relative surface warming effect of O₃. This suggests O₃ could act to buffer surface temperature
against reductions in solar flux, although the effect is very weak for the model considered here.
Table 3: Effect of varying $S$ on O$_3$ energy budget forcing for $P = 1$ bar, $f_{o_2} = 10^{-3}$. Each $\Delta F$ is taken with respect to the atmosphere with $f_{o_2} = 0$ and as has units of W/m$^2$. Superscripts are the same as in Table 2.

| $S$  | $\Delta F_{\uparrow,\text{surf}}^C$ | $\Delta F_{\downarrow,\text{surf}}^L$ | $\Delta F_{\downarrow,\text{surf}}^S$ | $\Delta F_{\uparrow,\text{top}}^S$ |
|------|-----------------------------------|-------------------------------------|----------------------------------|----------------------------------|
| 1.00 | -1.6 (-3.2%)                      | -0.4 (-0.2%)                       | -1.9 (-2.0%)                     | -3.2 (-6.8%)                     |
| 0.95 | -1.4 (-3.3%)                      | +0.8 (+0.5%)                       | -1.9 (-2.0%)                     | -3.1 (-6.9%)                     |
| 0.90 | -1.3 (-3.5%)                      | +2.1 (+1.5%)                       | -1.9 (-2.1%)                     | -3.0 (-7.0%)                     |
| 0.85 | -1.2 (-3.8%)                      | +2.6 (+2.1%)                       | -1.9 (-2.1%)                     | -2.8 (-7.1%)                     |
| 0.80 | -1.2 (-4.8%)                      | +2.3 (+2.2%)                       | -1.7 (-2.1%)                     | -2.7 (-7.1%)                     |
| 0.75 | -1.3 (-6.2%)                      | +2.0 (+2.4%)                       | -1.6 (-2.1%)                     | -2.6 (-7.2%)                     |

We also examine the effect of O$_3$ heating on CO$_2$ condensation in the middle atmosphere. Fig. 7 shows that while a 1 bar atmosphere with $f_{o_2} = 0$ at $S = 1.00$ condenses near the 0.1 bar level, an atmosphere with $f_{o_2} = 10^{-3}$ does not due to heating by O$_3$. And though CO$_2$ condensation is not completely suppressed at very low insolation ($S = 0.75$), it does continue to be inhibited at altitudes above the 0.1 bar level. This finding likely has ramifications for the ability of CO$_2$ clouds to warm the surface through scattering of IR (Forget & Pierrehumbert 1997; Mischna et al. 2000), though accurately quantifying the effect would require detailed microphysical modeling (Colaprete & Toon 2003).
3.3.3 H$_2$O Dissociation

The effect of O$_3$ on the column integrated H$_2$O dissociation rate is important because it plays a role in both the atmosphere's photochemistry and its loss over time. In general, the greater the amount of dissociation, the more the atmosphere will be dominated by the chemistry of HO$_x$ products and the more H$_2$ will be produced. Increasing the concentration of H$_2$ in the atmosphere directly increases its loss rate to space and thus the loss rate of H$_2$O from Mars, regardless of whether loss of H$_2$ is limited by the escape rate of H or diffusion of H$_2$ at the homopause (R.E. Johnson et al. 2008; Zahnle et al. 2008). The concentration of H$_2$ in the upper atmosphere can also indirectly affect the loss of other species by shielding them from the EUV which powers their non-thermal escape mechanisms (Fox 2003).
(a) Total H$_2$O Dissociation Column Rate [cm$^2$ s$^{-1}$]

(b) Fraction of Total H$_2$O Dissociation Column Rate from O$_2^{(3)}$D
Figure 8: Characterization of H$_2$O dissociation as a function of $f_{O_2}$ and $P$: (a) total column integrated dissociation rate (photolysis + O($^1$D) attack) and (b) fraction of dissociation attributable to O($^1$D) attack.

As seen in Table 1, the two pathways by which H$_2$O may be dissociated are direct photolysis by UV and attack by O($^1$D). The vast majority of O($^1$D) in our models was produced by photolysis of O$_3$ ($J_6$). In Fig. 8 we map the total column integrated H$_2$O dissociation rate and the fraction dissociated by O($^1$D) in the parameter space of $P$ and $f_{O_2}$. In low pressure atmospheres the column integrated O($^1$D) attack rate is large because the low altitude O$_3$ layer produces abundant O($^1$D) near the H$_2$O rich upper troposphere. However, for high pressure atmospheres the O$_3$ layer is raised up into the H$_2$O poor stratosphere, reducing the contribution of O($^1$D) attack to H$_2$O dissociation. For $f_{O_2} \sim 10^{-5}–10^{-4}$ the O$_3$ layer provides little UV shielding, so the direct photolysis rate of H$_2$O is large at all surface pressures and tends to dominate dissociation. In the range $f_{O_2} \sim 10^{-4}–10^{-3}$ a substantial O$_3$ layer accumulates and strongly suppresses H$_2$O photolysis. This lowers the total dissociation rate and causes O($^1$D) attack to dominate at all surface pressures. When $f_{O_2} \sim 10^{-3}–10^{-2}$ a thick O$_3$ layer forms. At low surface pressure this strongly heats the cold trap, allowing more H$_2$O into the stratosphere where it can be directly photolysed or attacked by O($^1$D). This enhancement in dissociation is not seen in high pressure atmospheres because the O$_3$ layer is high above the cold trap and warms it only weakly.

The details of these effects are illustrated for a 1 bar atmosphere in Fig. 9. We see that for low $f_{O_2}$ most H$_2$O dissociation occurs by photolysis in the lower troposphere, similar to modern Mars (Nair et al. 1994). On the other hand, for high $f_{O_2}$ dissociation by O($^1$D) attack becomes
dominant, as on modern Earth (Levy 1971). This is due to the shielding of direct H$_2$O photolysis by O$_3$ UV absorption and the enhanced production of O($^1$D) by photolysis of O$_3$. The shielding of H$_2$O is partially counteracted by humidification of the stratosphere, increasing the rate of H$_2$O photolysis above the O$_3$ layer.

Figure 9: Comparison of H$_2$O dissociation profiles by photolysis and O($^1$D) attack for $f_{O_2} =$ $10^{-5}$ and $10^{-2}$. Line titles are in the format (dissociation type, $f_{O_2}$).

3.3.4 Effects of HO$_x$ and Transport

In the results presented here we have consciously omitted the effects of HO$_x$ chemistry and atmospheric transport on the O$_3$ profile. These effects are especially important in the upper troposphere, where the radiative forcing of O$_3$ is most sensitive to its concentration (Forster & Shine 1997) and heating of the cold trap can influence stratospheric photochemistry. We expect our model to overestimate the stratospheric O$_3$ concentration due to neglecting catalytic destruction by HO$_x$ and downward transport to the troposphere. Conversely, we underestimate
the tropospheric O₃ concentration because of the neglect of downward transport from the stratosphere, though this would be partially counteracted by HOₓ reactions. In terms of climate forcing, this means that cooling by stratospheric O₃ is too large and warming by tropospheric O₃ too low. This suggests that the current results *underestimate* the climate warming effect of O₃ under the conditions examined.

In the results presented here, the peak O₃ concentration is always above the tropopause. The location of this peak is determined by where the overhead column of O₃ absorbs most of the UV capable of splitting CO₂ and O₂ to O, thus cutting off the means of O₃ production (Chapman 1930). Including catalytic HOₓ destruction would reduce the O₃ column at a given altitude in the stratosphere, in turn lowering the altitude of peak O₃ concentration. This descent of the O₃ layer into the upper troposphere would strengthen some of the feedback effects identified in this study, such as inhibiting CO₂ condensation and enhancing H₂O dissociation. Including convective transport of O₃ from the stratosphere to the troposphere would have similar effects.

Taking into account the impact that O₃ can have on the H₂O dissociation rate, and vice versa, it is clear that a detailed model including HOₓ photochemistry and O₃ transport is needed to more accurately characterize the feedback of an O₃ layer on Martian climate. Such improvements will also allow us to calculate concentrations for O₂ and CO instead of using a prescribed range of values, narrowing the parameter space to explore. This work is currently underway.
4. Conclusions

We have explored here the possibility of a substantial O$_3$ layer accumulating in the Martian atmosphere for O$_2$ mixing fractions of $10^{-5}$ to $10^{-2}$, a range reasonable during the volcanically quiescent periods of Mars' history. Our study focused on atmospheres with surface pressures of 0.3–1.0 bar, as they are likely to have less HO$_x$ and thus more O$_2$ and O$_3$. We find that for modest O$_2$ mixing fractions of $f_{O_2} > 10^{-5}$ an O$_3$ layer capable of effectively protecting primitive life from UV radiation would form. As $f_{O_2}$ approaches $10^{-2}$ the O$_3$ column becomes comparable to that of modern Earth ($\sim 10^{19}$ cm$^{-2}$).

The presence of a thick O$_3$ layer decreases planetary albedo, up to 8.1% for a 1 bar atmosphere with O$_3$ column $\sim 10^{19}$ cm$^{-2}$. A portion of this extra heating goes toward inhibiting CO$_2$ condensation and weakening convection, both of which act to warm the surface for the clear sky conditions examined. However, for thick O$_3$ layers this surface warming is largely counteracted by stratospheric absorption of solar energy, which efficiently radiates back into space energy which otherwise would have reached the surface. Contribution of O$_3$ to the greenhouse effect is small under the conditions examined, with a surface temperature increase of only $\sim 1$ K. However, the net surface warming effect is likely underestimated due to our O$_3$ layers being biased toward higher altitudes. This results from the simplifications of neglecting HO$_x$ and eddy mixing in our photochemical model.

We also show that O$_3$ has a major influence on the column integrated dissociation rate of H$_2$O by decreasing UV radiation in the lower atmosphere, increasing the production of O($^1$D), and increasing stratospheric humidity. Increasing the thickness of the O$_3$ layer causes H$_2$O dissociation to shift from a “modern-Mars-like” state dominated by direct photolysis near the
surface to a “modern-Earth-like” state where photolysis is strongly suppressed and O(^1D) attack becomes dominant. For atmospheres > 0.5 bar, an increase in the thickness of the O_3 layer generally lowered the H_2O dissociation rate, with rates at f_{O_2} = 1 \times 10^{-2} being \sim 1/10^{th} their value at f_{O_2} = 1 \times 10^{-5}. This suggests the presence of a thick O_3 layer in Mars' past could have suppressed the photochemical production of H_3, and, consequently, the loss of H_2O to space. However, a more complete photochemical model is required to make a definitive assessment of how a thick O_3 layer would affect H_2 production on ancient Mars.

Acknowledgments

Thanks are given to D. Crisp, J. F. Kasting, and R. Ramirez for their helpful input on the radiative-convective model. This work was supported by a grant from the NASA Planetary Atmosphere program.
References

Alms, G.R., Burnham, A.K., Flygare, W.H., 1975. Measurement of the dispersion in polarizability anisotropies. J. Chem. Phys. 63, 3321–3326. doi:10.1063/1.431821

Baranov, Y.I., Lafferty, W.J., Fraser, G.T., 2004. Infrared spectrum of the continuum and dimer absorption in the vicinity of the $O_2$ vibrational fundamental in $O_2/CO_2$ mixtures. J. Mol. Spectr. 228, 432–440. doi:10.1016/j.jms.2004.04.010

Bideau-Mehu, A., Guern, Y., Abjean, R., Johannin-Gilles, A., 1973. Interferometric determination of the refractive index of carbon dioxide in the ultraviolet region. Opt. Commun. 9, 432–434. doi:10.1016/0030-4018(73)90289-7

Bougher, S.W., Blelly, P.L., Combi, M., Fox, J.L., Mueller-Wodarg, I., Ridley, A., Roble, R.G., 2008. Neutral Upper Atmosphere and Ionosphere Modeling. Space Science Reviews 139, 107–141. doi:10.1007/s11214-008-9401-9.

Brown, L.R., Humphrey, C.M., Gamache, R.R., 2007. $CO_2$-broadened water in the pure rotation and $ν_2$ fundamental regions. J. Mol. Spectr. 246, 1–21. doi:10.1016/j.jms.2007.07.010

Campbell, I.M., Gray, C.N., 1973. Rate constants for $O(^3P)$ recombination and association with $N(^4S)$. Chem. Phys. Let. 18, 607–609. doi:10.1016/0009-2614(73)80479-8
Carr, M., Head, J. W., 2010. Geologic history of Mars. Earth Planet. Sci. Lett. 294, 185-203. doi:10.1016/j.epsl.2009.06.042

Chapman, S., 1930. A Theory of Upper-Atmospheric Ozone. Memoirs of the Royal Meteorological Society 3, 103–125.

Clough, S.A., et al., 2005. Atmospheric radiative transfer modeling: a summary of the AER codes. JQSRT 91, 233–244. doi:10.1016/j.jqsrt.2004.05.058

Colaprete, A., Toon, O.B., 2003. Carbon dioxide clouds in an early dense Martian atmosphere. JGR 108, 5025. doi:10.1029/2002JE001967

Corrêa, M.P., Souza, R.A.F., Ceballos, J.C., Fomin, B., 2005. Preliminary results of simulations of a user-friendly fast line-by-line computer code for simulations of satellite signal. Anais XII Simpósio Brasileiro de Sensoriamento Remoto, Goiânia, Brasil, INPE, 363–370.

Daescu, D., Sandu, A., Carmichael, G.R., 2003. Direct and Adjoint Sensitivity Analysis of Chemical Kinetic Systems with KPP: II – Validation and Numerical Experiments, Atmospheric Environment 37, 5097–5114. doi:10.1016/j.atmosenv.2003.08.020

Damian, V., Sandu, A., Damian, M., Potra, F., Carmichael, G.R., 2002. The Kinetic PreProcessor
KPP – A Software Environment for Solving Chemical Kinetics. Computers and Chemical Engineering 26, 1567–1579. doi:10.1016/S0098-1354(02)00128-X.

Eastman, E. D., 1929. Specific heats of gases at high temperatures. Tech. Paper 445, Bureau of Mines.

Forget, F., Pierrehumbert, R.T., 1997. Warming early Mars with carbon dioxide clouds that scatter infrared radiation. Science 278, 1273–1276. doi:10.1126/science.278.5341.1273

Forster, P. M. de F., K. P. Shine, 1997. Radiative forcing and temperature trends from stratospheric ozone changes. JGR 102(D9), 10841–10855. doi:10.1029/96JD03510

Forster, P. M., et al., 2011. Evaluation of radiation scheme performance within chemistry climate models. JGR 116, D10302. doi:10.1029/2010JD015361

Fox, J.L., 2003. Effect of H₂ on the Martian ionosphere: Implications for atmospheric evolution. JGR 108(A6), 1223. doi:10.1029/2001JA000203

François, L.M., Gérard, J.C., 1988. Ozone, climate and biospheric environment in the ancient oxygen-poor atmosphere. Planet. Space Sci. 36, 1391–1414. doi:0.1016/0032-0633(88)90007-4
Grott, M., Morschhauser, A., Breuer, D., Hauber, E., 2011. Volcanic outgassing of CO₂ and H₂O on Mars. Earth Planet. Sci. Lett. 308, 391–400. doi:10.1016/j.epsl.2011.06.014

Gruszka, M., Borysow, A., 1998. Computer simulation of the far infrared collision induced absorption spectra of gaseous CO₂. Mol. Phys. 93, 1007–1016. doi:10.1080/002689798168709

Halvey, I., Zuber, M.T., Schrag, D.P., 2007. A Sulfur Dioxide Climate Feedback on Early Mars. Science 318, 1903–1907. doi:10.1126/science.1147039

Halevy, I., Pierrehumbert, R. T., and Schrag, D. P., 2009. Radiative transfer in CO₂-rich paleoatmospheres. JGR 114, D18112. doi:10.1029/2009JD011915

Hauglustaine, D.A., Granier, C., Brasseur, G.P., Mégie, G., 1994. The importance of atmospheric chemistry in the calculation of radiative forcing on the climate system. JGR 99(D1), 1173–1186. doi:10.1029/93JD02987

Hiscox, J.A., B.L. Lindner, 1997. Ozone and planetary habitability. Journal of the British Interplanetary Society 50, 109–114.

Hunten, D., 1993. Atmospheric Evolution of the Terrestrial Planets. Science 259, 915–920. doi:10.1126/science.259.5097.915
Inn, E.C.Y., 1974. Rate of recombination of oxygen atoms and CO at temperatures below ambient. J. Chem. Phys. 61, 1589–1590. doi:10.1063/1.1682139

Johnson, R.E., Combi, M.R., Fox, J.L., Ip, W.H., Leblanc, F., McGrath, M.A., Shematovich, V.I., Strobel, D.F., Waite, J.H., 2008. Exospheres and Atmospheric Escape. Space Science Reviews 139, 355–397. doi:10.1007/s11214-008-9415-3

Johnson, S.S., Mischna, M.A., Grove, T.L., Zuber, M.T., 2008. Sulfur-induced greenhouse warming on Early Mars. JGR 113, E08005. doi:10.1029/2007JE002962

Johnson, S.S., Pavlov, A.A., Mischna, M.A., 2009. Fate of SO₂ in the ancient Martian atmosphere: Implications for transient greenhouse warming. JGR 114, E11011. doi:10.1029/2008JE003313

Kasting, J.F., Liu, S.C., Donahue, T.M., 1979. Oxygen Levels in the Prebiological Atmosphere. JGR 84(C6), 3097–3107. doi:10.1029/JC084iC06p03097

Kasting, J.F., Donahue, T.M., 1980. The Evolution of Atmospheric Ozone. JGR 85(C6), 3255–3263. doi:10.1029/JC085iC06p03255

Kasting, J. F., Walker, J.C.G., 1981. Limits on Oxygen Concentration in the Prebiological
Atmosphere and the Rate of Abiotic Fixation of Nitrogen. JGR 86(C2), 1147–1158.

doi:10.1029/JC086iC02p01147

Kasting, J. F., Holland, H.D., Pinto, J.P., 1985. Oxidant Abundances in Rainwater and the Evolution of Atmospheric Oxygen. JGR 90(D6), 10497–10510.

doi:10.1029/JD090iD06p10497

Kasting, J. F., 1991. CO₂ Condensation and the Climate of Early Mars. Icarus 94, 1–13.

doi:10.1016/0019-1035(91)90137-I

Kasting, J.F., 1995. O₂ concentrations in dense primitive atmospheres: commentary. Planet. Space Sci. 43, 11–13. doi:10.1016/0032-0633(94)00203-4

Kasting, J.F., 1997. Warming Early Earth and Mars. Science 276, 1213–1215.

doi:10.1126/science.276.5316.1213

Kelly, N. J., et al., 2006. Seasonal polar carbon dioxide frost on Mars: CO₂ mass and columnar thickness distribution. JGR 111, E03S07. doi:10.1029/2006JE002678

Kiehl, J.T., Trenberth, K.E., 1997. Earth's Annual Global Mean Energy Budget. Bull. Amer. Meteor. Soc., 78, 197-208. doi:10.1175/1520-0477(1997)078%3C0197:EAGMEB%3E2.0.CO;2
Krasnopolsky, V.A., 2006. Photochemistry of the martian atmosphere: Seasonal, latitudinal, and diurnal variations. Icarus 185, 153–170. doi:10.1016/j.icarus.2006.06.003

Kuntz, M., Höpfner, M., 1999. Efficient line-by-line calculation of absorption coefficients. JQSRT 63, 97–114. doi:10.1016/S0022-4073(98)00140-X

Kurucz R.L., 1992. Synthetic infrared spectra in infrared solar physics. In: Rabin D.M., Jefferies J.T., (Eds.), IAU Symposium, 154. Kluwer Academic Press, Norwell, MA.

Lebonnois, S., Hourdin, F., Eymet, V., Crespin, A., Fournier, R., Forget, F., 2010. Superrotation of Venus' atmosphere analyzed with a full general circulation model. JGR 115, E06006. doi:10.1029/2009JE003458.

Lemmon, E.W., Huber, M.L., McLinden, M.O., 2010. NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 9.0, National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg.

Letchworth, K., Benner, D., 2007. Rapid and accurate calculation of the Voigt function. JQSRT 107, 173–192. doi:10.1016/j.jqsrt.2007.01.052
Levy, H., 1971. Normal Atmosphere: Large Radical and Formaldehyde Concentrations Predicted. Science 173, 141–143. doi:10.1126/science.173.3992.141

Li, H., Ji, X., Yan, J., 2006. A new modification on RK EOS for gaseous CO2 and gaseous mixtures of CO2 and H2O. Int. J. Energy Res. 30, 135–148. doi:10.1002/er.1129

Liou, KN., 2002. An introduction to atmospheric radiation. 2nd ed., Academic Press. p. 126

López-Valverde, M., Edwards, D., López-Puertas, M., Roldán, C., 1998. Non-local thermodynamic equilibrium in general circulation models of the Martian atmosphere 1. Effects of the local thermodynamic equilibrium approximation on thermal cooling and solar heating. JGR 103, 16799–16811. doi:10.1029/98JE01601

Manga, M., Patel, A., Dufek, J., Kite, E.S., 2012. Wet surface and dense atmosphere on early Mars suggested by the bomb sag at Home Plate Mars. Geophys. Res. Lett. 39, L01202. doi:10.1029/2011GL050192

McElroy, M.B., Donahue, T.M., 1972. Stability of the Martian atmosphere. Science 177, 986–988. doi:10.1126/science.177.4053.986
Meadows, V. S., Crisp, D., 1996. Ground-based near-infrared observations of the Venus nightside: The thermal structure and water abundance near the surface. JGR 101(E2), 4595–4622. doi:10.1029/95JE03567

Minschwaner, K., Anderson, G.P., Hall, L.A., Yoshino, K. 1992. Polynomial coefficients for calculating O$_2$ Schumann-Runge cross sections at 0.5 cm$^{-1}$ resolution. JGR 97(D9), 10103–10108. doi: 10.1029/92JD00661

Mischna, M.A., Kasting, J.F., Pavlov, A., Freedman, R., 2000. Influence of carbon dioxide clouds on early martian climate. Icarus 145, 546–554. doi:10.1006/icar.2000.6380

Montmessin, F., et al., 2006. Subvisible CO$_2$ ice clouds detected in the mesosphere of Mars. Icarus 183, 403–410. doi:10.1016/j.icarus.2006.03.015

Montmessin, F., et al., 2011. A layer of ozone detected in the nightside upper atmosphere of Venus. Icarus 216, 82–85. doi:10.1016/j.icarus.2011.08.010

Nair, H., Allen, M., Anbar, A.D., Yung, Y.L., Clancy, R.T., 1994. A Photochemical Model of the Martian Atmosphere. Icarus 111, 124–150. doi:10.1006/icar.1994.1137

Neukum, G., et al., 2010. The geologic evolution of Mars: Episodicity of resurfacing events and ages from cratering analysis of image data and correlation with radiometric ages of Martian
Old, J.G., Gentili, K.L., Peck, E.R., 1971. Dispersion of Carbon Dioxide. J. Opt. Soc. Am. 61, 89–90. doi:10.1364/JOSA.61.000089

Parkinson, T.D., Hunten, D.M., 1972. Spectroscopy and Aeronomy of O₂ on Mars. J. Atm. Sci. 29, 1380–1390. doi:10.1175/1520-0469(1972)029%3C1380:SAAOOO%3E2.0.CO;2

Perrin, M.Y., Hartmann, J.M., 1989. Temperature-dependent measurements and modeling of absorption by CO₂–N₂ mixtures in the far line-wings of the 4.3-μm CO₂ band. JQSRT 42, 311–317. doi:10.1016/0022-4073(89)90077-0

Pollack, J.B., Kasting, J.F., Rochardson, S.M., Poliakoff, K., 1987. The case for a wet, warm climate on early Mars. Icarus 71, 203–224. doi:10.1016/0019-1035(87)90147-3

Quine, B.M., and Drummond, J.R., 2002. GENSPECT: a line-by-line code with selectable interpolation error tolerance. JQSRT 74, 147–165. doi:10.1016/S0022-4073(01)00193-5

Ribas, I., et al., 2010. Evolution of the Solar Activity Over Time and Effects on Planetary Atmospheres. II. κ¹ Ceti, an Analog of the Sun when Life Arose on Earth. Astrophys. J. 714, 384–395. doi:10.1088/0004-637X/714/1/384
Richardson, M.I., Mischna, M.A., 2005. Long-term evolution of transient liquid water on Mars. JGR 110, E03003. doi:10.1029/2004JE002367

Robbins, S.J., Achille, G.D., Hynek, B.M., 2011. The volcanic history of Mars: High-resolution crater-based studies of the calderas of 20 volcanoes. Icarus 211, 1179–1203. doi:10.1016/j.icarus.2010.11.012

Rothman, L.S., et al., 2009. The HITRAN 2008 molecular spectroscopic database. JQSRT 110, 533–572. doi:10.1016/j.jqsrt.2009.02.013

Rosenqvist, J., Chassefière, E., 1995. Inorganic chemistry of O_2 in a dense primitive atmosphere. Planet. Space Sci. 43, 3–10. doi:10.1016/0032-0633(94)00202-3

Sander S.P., et al., 2011. Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 17, JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, CA.

Sandu, A., Daescu, D., Carmichael, G.R., 2003. Direct and Adjoint Sensitivity Analysis of Chemical Kinetic Systems with KPP: I – Theory and Software Tools, Atmospheric Environment 37, 5083–5096. doi:10.1016/j.atmosenv.2003.08.019

Segura, A., Meadows, V. S., Kasting, J. F., Crisp, D., Cohen, M., 2007. Abiotic formation of O_2
and O$_3$ in high-CO$_2$ terrestrial atmospheres. A&A 472, 665–679. doi:10.1051/0004-6361:20066663

Selsis, F., Despois, D., Parisot, J.-P., 2002. Signature of life on exoplanets: Can Darwin produce false positive detections? A&A 388, 985–1003. doi:10.1051/0004-6361:20020527

Span, R., Wagner, W., J., 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. Phys. Chem. Ref. Data 25, 1509–1596. doi:10.1063/1.555991

Squyres, S.W., Kasting, J.F., 1994. Early Mars: How Warm and How Wet? Science 265, 744–749. doi:10.1126/science.265.5173.744

Tian, F., Claire, M.W., Haqq-Misra, J.D., Smith, M., Crisp, D.C., Catling, D., Zahnle, K., Kasting, J.F., 2010. Photochemical and climate consequences of sulfur outgassing on early Mars. Earth Planet. Sci. Lett. 295, 412–418. doi:10.1016/j.epsl.2010.04.016

Tonkov, M.V., et al., 1996. Measurements and empirical modeling of pure CO$_2$ absorption in the 2.3-μm region at room temperature: Far wings, allowed and collision-induced bands. Appl. Opt. 35, 4863–4870. doi:10.1364/AO.35.004863

Toon, O.B., McKay, C.P., Ackerman, T.P., Santhanam, K., 1989. Rapid calculation of radiative
heating rates and photodissociation rates in inhomogeneous multiple scattering atmospheres. JGR 94(D13), 16287–16301. doi:10.1029/JD094iD13p16287

Tvorogov, S.D, Rodimova, O.B., Nesmelova, L.I., 2005. On the correlated $k$-distribution approximation in atmospheric calculations. Opt. Eng. 44, 071202. doi:10.1117/1.1955318

Wells, R.J., 1999. Rapid approximation to the Voigt/Faddeeva function and its derivatives. JQSRT 64, 29–48. doi:10.1016/S0022-4073(97)00231-8

Wordsworth, R., Forget, F., Eymet, V., 2010a. Infra-red collision-induced and far-line absorption in dense CO2 atmospheres. Icarus 210, 992–997. doi:10.1016/j.icarus.2010.06.010

Wordsworth, R., Forget, F., Selsis, F., Madeleine, J.-B., Millour, E., Eymet, V., 2010b. Is Gliese 581d habitable? Some constraints from radiative-convective climate modeling. A&A 522, A22. doi:10.1051/0004-6361/201015053

Yung Y. L., Nair H., Gerstell M. F., 1997. CO$_2$ Greenhouse in the Early Martian Atmosphere: SO$_2$ Inhibits Condensation. Icarus 130, 222–224. doi:10.1006/icar.1997.5808

Zahnle, K. J., Haberle, R. M., Catling, D. C., Kasting, J. F., 2008. Photochemical instability of the ancient Martian atmosphere. JGR 113, E11004. doi:10.1029/2008JE003160
Figure 1

The graph shows the variation of specific heat capacity ($c_p$) with temperature in units of [J/mol/K]. The plot includes data from various sources:

- **(Kasting 1991)**
- **(Lebonnois et al. 2010)**
- **This Study**
- **REFPROP v9.0**

The graph displays the trend and comparison of these datasets across different temperature ranges.
Figure 2a

- **Surface Temperature [K]**
- **Surface Pressure [bar]**

Freezing Point of Water

CO₂ Condensation Begins

CO₂ Saturation

S = 1.00

0.95

0.90

0.85

0.80

0.75
Figure 2b

Surface H$_2$O Mixing Fraction vs. Surface Pressure [bar] for different values of $S$. 

- $S = 1.00$
- $S = 0.95$
- $S = 0.90$
- $S = 0.85$
- $S = 0.80$
- $S = 0.75$
$f_{O_2} = 10^{-5}$

$10^{-4}$

$10^{-3}$

$10^{-2}$
Figure 5
$f_{O_2} = 0.0$

Solar Heating Rate [K day$^{-1}$] vs. Pressure [bar]
Figure 7

CO₂ Vapor Pressure

Pressure [bar]

Temperature [K]
Figure 8a Color

(a) Total H₂O Dissociation Column Rate [cm⁻² s⁻¹]
(a) Total H$_2$O Dissociation Column Rate [cm$^{-2}$ s$^{-1}$]
Figure 8b Color

(b) Fraction of Total H$_2$O Dissociation Column Rate from O($^1$D)
(b) Fraction of Total H$_2$O Dissociation Column Rate from O($^1$D)
Pressure [bar] vs. H$_2$O Dissociation Rate [$\text{cm}^{-3} \text{s}^{-1}$]

- $h\nu$, $10^{-5}$
- $O(^1\text{D})$, $10^{-5}$
- $h\nu$, $10^{-2}$
- $O(^1\text{D})$, $10^{-2}$