Photochemical instability of the ancient Martian atmosphere

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[1] We develop a 1-D steady state photochemical model of the modern Martian atmosphere and apply it to possible Martian atmospheres present and past. A unique feature of our model is that the major current sink of oxygen is dry deposition (surface reactions) of highly reactive, oxidized molecules (chiefly H2O2), rather than oxygen escape to space. Another difference is that we allow hydrogen to escape to space at the diffusion limit, which gives H escape fluxes ~70% higher than in other models. What results is a model with one free parameter: a dry deposition velocity to describe the surface sink of reactive molecules. An effective global average deposition velocity of 0.02 cm s−1 for H2O2 and O3 gives a good match to the observed abundances of O2, CO, and H2, the three abundant photochemical trace gases. We then apply our model to Martian atmospheres with different amounts of CO2, H2O, and solar forcing. We find that thick, cold, dry CO2 atmospheres are photochemically unstable with respect to conversion to CO. This may be pertinent to ancient Mars when the Sun was faint and O escape rates were likely high, for which the tipping point is computed to be ~10 mbar of CO2. The possible photochemical instability of cold thick CO2 atmospheres, and the high likelihood that CO was abundant even if CO2 were stable, has broad implications for early Mars.


1. Introduction

[2] To first approximation the Martian atmosphere is composed of CO2 and H2O and their photochemical byproducts [McElroy and Donahue, 1972; Yung and DeMore, 1998]. The major products are CO, O2, and H2; minor ones include H2O2 and O3. None of these are expected to have significant sources apart from photochemistry. Measured abundances of O2, CO, and H2 are reported to be 1200–2000 ppm, 800 ppm, and 17 ppm, respectively [Krasnopolsky, 2006]. From the dispersion seen in published estimates, the uncertainties in these abundances appear to be at least 30%. Figure 1 gives a schematic overview of Martian atmospheric photochemistry.

[3] The Martian atmosphere today is rather strongly oxidized. If there were no sinks on the photochemical products, the abundances of O2, CO, and H2 would sum to redox neutrality. It is convenient to define CO2, H2O2, and N2 as redox neutral [Kasting and Brown, 1998]. We can then approximate the net redox imbalance of the atmosphere by \( p_{\text{Ox}} \equiv 2p_{\text{O2}} - p_{\text{CO}} - p_{\text{H2}} \). In a redox neutral atmosphere \( p_{\text{Ox}} = 0 \). On Mars today \( p_{\text{Ox}} \approx 10 - 15 \) μbar. This superabundance of O2 represents a net buildup of oxygen generated by hydrogen escape to space. The source of the hydrogen is photolytic destruction of water vapor. On the basis of atomic hydrogen densities retrieved by fitting Mariner 6 and 7 Ly6 scattering data [Anderson and Hord, 1971], the current H escape flux has been widely taken to be \( \sim 2.4 \times 10^{8} \) molecules cm\(^{-2}\) s\(^{-1}\) [e.g., Nair et al., 1994; Krasnopolsky, 1995, 2006]. At this rate it takes 10\(^5\) years to build up the observed \( p_{\text{Ox}} \), which is comparable to the timescale for obliquity variations. The oxidation timescale is therefore long enough that we should not, in general, expect the oxidation state of the Martian atmosphere to be in steady state with its boundary conditions, although we do expect the composition of the atmosphere to be in steady state with the current oxidation state (i.e., the O2, CO, and H2 abundances should be in equilibrium with \( p_{\text{Ox}} \), but \( p_{\text{Ox}} \) itself need not be in steady state). With this caveat made, we will restrict our scope in this paper to steady state models.

[4] In steady state, oxygen sinks balance hydrogen loss to space (Figure 1). One widely discussed possibility is that oxygen also escapes to space at half the rate that H escapes, so that on net \( H_2O \) escapes [McElroy, 1972; Liu and Donahue, 1976; McElroy et al., 1977]. For example, McElroy [1972] showed that oxygen can escape to space from Mars after dissociative recombination of \( O_3^+ \) ions. The early studies pointed out that oxygen in the atmosphere is self-regulating, with \( H_2 \) formation and therefore hydrogen escape suppressed by the build up of \( O_2 \), a result that remains generally true. Most steady state photochemical models have imposed a fixed O escape flux at the upper boundary to balance H escape [e.g., Krasnopolsky, 1993,
However, a long list of spacecraft measurements and theoretical calculations presents a clear consensus that the O escape rate is of the order of $10^7$ atoms cm$^{-2}$ s$^{-1}$ or less, which is more than an order of magnitude short of what is needed to maintain redox balance [Fox and Hac, 1997; Lammer et al., 2003].

An alternative oxygen sink is reaction of oxidized gases with reduced minerals in the soil to make sulfates and ferric iron [Huguenin, 1973, 1976; McElroy and Kong, 1976; McElroy et al., 1977; Hunten, 1979; Bullock et al., 1994; Lammer et al., 2003]. Martian soils have long been known to be strongly oxidized, beginning from the simple observation that Mars is red, through the curious results obtained by the Viking biology experiments [Biemann et al., 1977; Klein, 1977; Oyama and Berdahl, 1979], to the famous adventures of the Mars Exploration Rovers [Squyres and Knoll, 2005]. Hydrogen escape is the only known process capable of oxidizing Mars, and therefore atmospheric gases are the only plausible oxidizing agents for the soils. This is a conclusion strongly and independently supported by the anomalous mass fractionations seen in the oxygen and sulfur isotopes in the SNC meteorites, distinctive fractionations that demand an atmospheric photochemical source [Farquhar et al., 2000, 2007; Nair et al., 1994].

Figure 1. Schematic overview of Martian atmospheric photochemistry. Solar UV splits CO$_2$ and H$_2$O into O$_2$, CO, H$_2$, and other species. Hydrogen escape can be described by an effusion velocity $v_{\text{eff}}$ that is less than or equal to the diffusion-limited velocity $v_{\text{lim}}$. The surface sink on highly oxidized species (e.g., H$_2$O$_2$ and O$_3$) is described by a deposition velocity $v_{\text{dep}}$. In steady state the net oxidation state of the atmosphere is determined by the ratio of $v_{\text{eff}}$ and $v_{\text{dep}}$. Oxygen escape to space is apparently negligible at present [Lammer et al., 2003] but is included in our models of ancient atmospheres, for which it is likely to be important.

[6] We agree with Lammer et al. [2003] that the redox budget today has to be balanced by a surface sink on oxygen. In most of our models we treat the oxygen sink as a dry deposition velocity, $v_{\text{dep}}$, on highly reactive oxidized species, the most important of which are hydrogen peroxide (H$_2$O$_2$) and ozone (O$_3$). (“Wet deposition” implies rainout, which is not currently a major process on Mars.) Hydrogen peroxide has been a popular candidate as a soil oxidant because it is produced by atmospheric photochemistry [Hunten, 1979] and it provides a good fit to the results of the Viking labeled release experiment [Oyama and Berdahl, 1979]. In section 5.4 we consider the effect of balancing the redox budget by applying a deposition velocity to O$_2$ itself (i.e., models in which O$_2$ gas is the chief oxidizing agent).

[7] A deposition velocity sweeps all the complexities of atmospheric mixing to the surface, sticking, and reacting with the surface (chemical composition, topography, etc) into a single parameter [Seinfeld and Pandis, 2006]. On Earth, $v_{\text{dep}}$ differs greatly between species; it is often highest when the surface is wet and the species soluble. Dry deposition is usually pictured as three resistances in series, one imposed by mixing through the lower atmosphere, one by molecular diffusion through the very thin laminar layer in contact with the surface, and the third by what happens when the molecule actually strikes the surface [Seinfeld and Pandis, 2006]. The two atmospheric transport terms are not independent, because the thickness of the thin laminar boundary layer is in part determined by atmospheric turbulence. The lower Martian atmosphere is both thinner and more turbulent than Earth’s. This means that both atmospheric transport terms are faster on Mars than on Earth. Hence the bottleneck on Mars is almost certainly uptake by the surface. The generally dry, oxidized surface suggests that dry deposition velocities of water soluble or highly oxidized species are not likely to be very high on Mars, but we will find that they do not have to be high; indeed, we
will find that they cannot be high. As a first approximation we assume that the same dry deposition velocity applies to all reactive species.

[8] In this paper, we first describe the photochemical model. This is followed by a discussion of the key boundary conditions, especially hydrogen escape. The model is applied and tuned to current Mars. We then consider how the model responds to changing amounts of CO₂ and H₂O, and how it responds to higher levels of solar UV and to significant rates of O escape driven by a much more vigorous ancient solar wind. This leads into a discussion of the photochemical stability of the CO₂ atmosphere.

2. General Code Features

[9] There are many published steady state 1-D photochemical models of the Martian atmosphere [McElroy and Donahue, 1972; Liu and Donahue, 1976; McElroy et al., 1977; Krasnopolsky, 1993, 1995, 2006; Nair et al., 1994; Atreya and Gu, 1994; Wong et al., 2003]. These codes resemble each other in their fundamental structure; our code, which is based on the photochemistry model for early Earth described by Kasting et al. [1989] and Kasting [1990], is similar. The version used here was developed from the 1989 version; many of its features are described by Kasting et al. [1989] and Kasting [1990]. We have successfully used the new code to study sulfur photochemistry of Earth’s atmosphere during the Archean [Zahnle et al., 2006; Claire et al., 2006].

[10] Our model uses a uniform 1 km resolution grid and time marches to a steady state using the reverse Euler method. Vertical transport occurs by eddy transport and, for H and H₂, molecular diffusion. For Mars we have described eddy transport by \( K = 10^6 \text{ cm}^2 \text{s}^{-1} \) for \( z < 20 \text{ km} \) and \( K = 10^6 \sqrt{N(z)/N(20 \text{ km})} \text{ cm}^2 \text{s}^{-1} \) for \( 20 < z < 110 \text{ km} \). The surface pressure is 6.3 mbar, and the composition is 95% CO₂. The temperature profile is \( T = T_0 - 1.4z \) for \( z < 50 \text{ km} \) and isothermal above. In our standard model, \( T_0 = 211 \text{ K} \). The model is insensitive to temperature save for the effect temperature has on absolute humidity. For water vapor we use a fixed 17% relative humidity near the surface to give 9.5 precipitable microns of water. Lower temperatures aloft cause the relative humidity to rise with altitude, and water can condense. In our nominal models the global average relative humidity in the stratosphere is typically \( \sim 60\% \), but there is some variation because of the way water condensation has been implemented.

[11] Chemical species, reactions, and photolysis channels important to C-H-O Martian photochemistry in the modern atmosphere are listed in Table 1. Where possible the reaction rates are those recommended by Sander et al. [2003], or updated reaction rates taken from the online NIST database (http://kinetics.nist.gov). The list was current as of November 2007. Table 1 lists the specific sources for the specific reaction rates taken from the NIST database. Of course, some reactions are very poorly known and some are not known at all. Usually the model is insensitive to poorly known reaction rates, because these are usually not very important reactions. But there are exceptions to this generalization. We give two examples of sensitive reactions that we found through error and trial. The reaction between H and HO₂ has three reported channels. The H₂ abundance predicted by the model is sensitive to the branching ratio for forming H₂ and O₂. According to Sander et al. [2003], different experiments have reported this branching ratio as \( 0.08 \pm 0.04, 0.09 \pm 0.045 \), and 0.29 (no error given). This wide range of possibilities generates a wide range of outcomes, as this is one of the chief reactions making H₂. Low values of this branching ratio produce generally better fits to Mars. We use 0.08 in our models.

[12] A second example of an uncertain reaction is the three-body formation of the formyl radical (HCO): \( H + CO + M \rightarrow HCO + M \), where M is CO₂. The uncertainty here is in the temperature dependence of the reaction. According to most reports this should be a slow reaction at Martian temperatures, but there is at least one study that gives this reaction a relatively small activation energy [Wagner and Bowman, 1987], so that it would dominate the H₂ formation rate under Martian conditions. We found that when using the Wagner and Bowman rate, we inevitably predicted H₂ mixing ratios greater than 100 ppm, far in excess of what is present on Mars. We conclude that a high rate of HCO formation at low temperatures is inappropriate. We have adopted the intermediate temperature dependence recommended by Baulch et al. [1994], which makes the reaction generally unimportant. Consequently formaldehyde is not an important photochemical product in the models reported here.

[13] For completeness we have included nitrogen photochemistry. Species and reactions used in the code are listed in Table 2. Upper boundary conditions are inflows of \( 2 \times 10^6 \text{ cm}^{-2} \text{s}^{-1} \) for N and \( 2 \times 10^7 \text{ cm}^{-2} \text{s}^{-1} \) for NO. These are created by ionospheric chemistry which is not included in this model. The magnitudes of the N and NO fluxes are consistent with those used by Krasnopolsky [1995]. Redox balance is maintained by imposing an upper inflow boundary flux of \( 2 \times 10^7 \text{ cm}^{-2} \text{s}^{-1} \) on CO. These influxes are implicitly balanced by upward flows of N₂ and CO₂. Overall, the influence of nitrogen photochemistry on the C-H-O system appears to be relatively small, and we will not discuss it further here.

3. Boundary Conditions

[14] A steady state model of the current Martian atmosphere's redox state can be described by two free parameters, one of which controls hydrogen escape and the other controls oxygen loss. In our models, the two parameters are the hydrogen effusion velocity \( v_{\text{eff}} \) and the deposition velocity \( v_{\text{dep}} \) of highly reactive species, respectively. Here we discuss how we pick these two parameters.

3.1. Hydrogen Escape

[15] A feature of our code is that we truncate the vertical extent of the atmosphere at 110 km. We do not attempt to construct an ionosphere, a thermosphere, or an exosphere, and we do not attempt to explicitly compute hydrogen escape. Instead we use a hydrogen effusion velocity \( v_{\text{eff}} \) to describe how quickly hydrogen escapes from the top of the model. We express \( v_{\text{eff}} \) as a fraction of the diffusion-limited effusion velocity \( v_{\text{lim}} \). Advantages of our approach are simplicity and clarity: our discussion of hydrogen escape is presented directly in terms of a firm physical upper limit. Moreover, as we shall argue below, the actual rate of H
Table 1. Basic H, C, O Reactions

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Reaction Rate$^a$</th>
<th>Reference$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O + O(1D)</td>
<td>→ OH + OH</td>
<td>2.2 × 10$^{-10}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>H$_2$ + O(1D)</td>
<td>→ OH + H</td>
<td>1.1 × 10$^{-10}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>H$_2$ + O</td>
<td>→ OH + H</td>
<td>1.34 × 10$^{-15}$ (T/298)$^{0.52}$ e$^{-1460/T}$</td>
<td>Robie et al. [1990]</td>
</tr>
<tr>
<td>H$_2$ + OH</td>
<td>→ H$_2$O + H</td>
<td>5.5 × 10$^{-12}$ e$^{-2880/T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>H + O$_2$</td>
<td>→ OH + O$_2$</td>
<td>1.4 × 10$^{-10}$ e$^{-4780/T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>H + O$_2$ + M</td>
<td>→ HO$_2$ + M</td>
<td>7.5 × 10$^{-11}$ e$^{-T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>H + HO$_2$</td>
<td>→ H$_2$ + O$_2$</td>
<td>1.4 × 10$^{-31}$ (300/T)$^{1.6}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>H + H$_2$O</td>
<td>→ H$_2$O + O</td>
<td>5.3 × 10$^{-11}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>H + CO$_2$</td>
<td>→ OH + O + OH + H</td>
<td>1.0 × 10$^{-10}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>OH + O</td>
<td>→ H + O$_2$</td>
<td>2.2 × 10$^{-11}$ e$^{-1220/T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>OH + HO$_2$</td>
<td>→ H$_2$O + O$_2$</td>
<td>4.8 × 10$^{-11}$ e$^{-250/T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>OH + O$_3$</td>
<td>→ HO$_2$ + O$_2$</td>
<td>1.7 × 10$^{-12}$ e$^{-940/T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>HO$_2$ + O</td>
<td>→ OH + O$_2$</td>
<td>3.0 × 10$^{-11}$ e$^{-200/T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>HO$_2$ + O$_3$</td>
<td>→ OH + 2O$_2$</td>
<td>1.0 × 10$^{-14}$ e$^{-490/T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>HO$_2$ + O$_3$</td>
<td>→ H$_2$O + O$_2$</td>
<td>2.3 × 10$^{-11}$ e$^{-1000/T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>H$_2$O$_2$ + O</td>
<td>→ H$_2$O + H$_2$O</td>
<td>4.3 × 10$^{-13}$ e$^{-1600/T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>O + O$_2$ + M</td>
<td>→ O$_2$ + M</td>
<td>1.2 × 10$^{-32}$ (300/T)$^{2.6}$</td>
<td>Nair et al. [1994]</td>
</tr>
<tr>
<td>O + O$_2$ + M</td>
<td>→ O$_3$ + M</td>
<td>1.5 × 10$^{-33}$ (300/T)$^{2.4}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>O + O$_3$</td>
<td>→ O$_2$ + O$_2$</td>
<td>1.0 × 10$^{-12}$ e$^{-2000/T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>OH + OH</td>
<td>→ H$_2$O + O</td>
<td>8.0 × 10$^{-12}$ e$^{-2000/T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>OH + O$_3$</td>
<td>→ H$_2$O + O$_2$</td>
<td>4.2 × 10$^{-12}$ e$^{-700/T}$</td>
<td>Baulch et al. [1992]</td>
</tr>
<tr>
<td>O$_2$(P) + N$_2$</td>
<td>→ O$_2$(P) + N$_2$</td>
<td>1.8 × 10$^{-11}$ e$^{-110/T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>O$_2$(D) + O$_2$</td>
<td>→ O$_2$(P) + O$_2$</td>
<td>3.2 × 10$^{-11}$ e$^{-70/T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>CO + OH</td>
<td>→ CO$_2$ + H</td>
<td>1.5 × 10$^{-13}$ (1+0.6)e$^{-T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>CO + O$_2$ + M</td>
<td>→ CO$_2$ + M</td>
<td>2.2 × 10$^{-33}$ e$^{-1780/T}$</td>
<td>Int [1974]</td>
</tr>
<tr>
<td>H + CO$_2$</td>
<td>→ H + O + CO</td>
<td>2.4 × 10$^{-33}$ e$^{-1570/T}$</td>
<td>Baulch et al. [1994]</td>
</tr>
<tr>
<td>H + HCO</td>
<td>→ H + CO$_2$</td>
<td>1.8 × 10$^{-10}$ e$^{-T}$</td>
<td>Friedrichs et al. [2002]</td>
</tr>
<tr>
<td>HCO + CO$_2$</td>
<td>→ HCO + CO</td>
<td>4.5 × 10$^{-11}$ e$^{-T}$</td>
<td>Friedrichs et al. [2002]</td>
</tr>
<tr>
<td>OH + HCO</td>
<td>→ OH + CO$_2$</td>
<td>1.7 × 10$^{-10}$ e$^{-T}$</td>
<td>Baulch et al. [1992]</td>
</tr>
<tr>
<td>O + HCO</td>
<td>→ O + CO$_2$</td>
<td>5.0 × 10$^{-11}$ e$^{-T}$</td>
<td>Baulch et al. [1992]</td>
</tr>
<tr>
<td>O + HCO</td>
<td>→ O + CO</td>
<td>5.0 × 10$^{-11}$ e$^{-T}$</td>
<td>Baulch et al. [1992]</td>
</tr>
<tr>
<td>H$_2$O + CO</td>
<td>→ H$_2$O + CO</td>
<td>2.14 × 10$^{-12}$ e$^{-1990/T}$</td>
<td>Baulch et al. [1994]</td>
</tr>
<tr>
<td>H + H + M</td>
<td>→ H + M + H</td>
<td>2.3 × 10$^{-33}$ (298/T)$^{0.6}$ e$^{-T}$</td>
<td>Baulch et al. [1992]</td>
</tr>
<tr>
<td>HCO + O$_2$</td>
<td>→ HCO + O$_2$</td>
<td>5.2 × 10$^{-12}$ e$^{-T}$</td>
<td>R. Atkinson et al. [1992]</td>
</tr>
<tr>
<td>H$_2$O + CO</td>
<td>→ H$_2$O + HCO</td>
<td>9.0 × 10$^{-12}$ e$^{-T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>H + OH + M</td>
<td>→ H$_2$O + M</td>
<td>1.7 × 10$^{-30}$ (298/T)$^{2}$ e$^{-T}$</td>
<td>Baulch et al. [1992]</td>
</tr>
<tr>
<td>OH + OH + M</td>
<td>→ H$_2$O$_2$ + M</td>
<td>2.6 × 10$^{-11}$ e$^{-T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>H$_2$O + O</td>
<td>→ HCO + OH</td>
<td>3.4 × 10$^{-31}$ (300/T)$^{d,e}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>H$_2$O$_2$ + O</td>
<td>→ OH + HO$_2$</td>
<td>1.4 × 10$^{-12}$ e$^{-2000/T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>O$_2$(D) + CO</td>
<td>→ CO + O</td>
<td>6 × 10$^{-11}$ e$^{-T}$</td>
<td>Davidson et al. [1978]</td>
</tr>
<tr>
<td>CO$_2$ + O(1D)</td>
<td>→ CO$_2$ + O</td>
<td>7.4 × 10$^{-11}$ e$^{-110/T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>O$_2$ + O(1D)</td>
<td>→ O$_2$ + O</td>
<td>1.2 × 10$^{-10}$ e$^{-T}$</td>
<td>Sander et al. [2003]</td>
</tr>
<tr>
<td>O$_2$ + O(1D)</td>
<td>→ O$_2$ + O + O</td>
<td>1.2 × 10$^{-10}$ e$^{-T}$</td>
<td>Sander et al. [2003]</td>
</tr>
</tbody>
</table>

Reactsants Products Photolysis Rate$^a$ Reference

$^a$Two-body rates are in cm$^{-3}$ s$^{-1}$; 3-body rates are in cm$^{-3}$ s$^{-1}$; photolysis rates [s$^{-1}$].

$^c$High density limit (k$_{3o}$) for three-body reaction [cm$^{-3}$ s$^{-1}$].
$^d$Low density limit for three-body reaction [cm$^{-3}$ s$^{-1}$].

$^e$The reported rate in air has been multiplied by a factor of 2.5 to account for CO$_2$ as third body [Nair et al., 1994].

$^f$The model is sensitive to this very uncertain reaction rate.

$^g$This is sometimes reported as an addition to form CO$_2$.

$^h$Photolysis rates are evaluated at the top of the atmosphere [s$^{-1}$] for a 57.3° slant path, and reduced by a factor of 2 to account for night.
escape from Mars seems to be quite close to the diffusion limit. Aeronomical details do not matter if escape is diffusion-limited.

3.1.1. Diffusion-Limited Flux

[16] The diffusion-limited flux \( \phi_{\text{lim}} \) is the highest possible in a hydrostatic atmosphere [Hunten, 1974]. The diffusion limit can be written

\[
\phi_{\text{lim}} = f_{\text{tot}}(H) b_{ij} \left( \frac{1}{H_a} \frac{1}{H_i} \right),
\]

where \( f_{\text{tot}}(H) \) is the total hydrogen mixing ratio in the stratosphere (adequately approximated by \( f(H_2) \) for Mars), \( b_{ij} \) is the binary diffusion coefficient between CO\(_2\) and the escaping species \( j \), and \( H_a \) and \( H_i \) are the scale heights of CO\(_2\) and \( i \). The binary diffusion coefficient between H\(_2\) and CO\(_2\) is approximated by [Marrero and Mason, 1972]

\[
b_{ij}(\text{CO}_2, \text{H}_2) = \frac{31.4}{k_B} T^{0.75} e^{-11.7/T} \text{[cm}^{-1} \text{s}^{-1}] \]

where \( k_B \) is the Boltzmann constant and the temperature \( T \) is in K. To our knowledge the binary diffusion coefficient between H and CO\(_2\) has not been measured; we take it to be 1.8\( \times \) bigger than for H\(_2\) in CO\(_2\), which is the ratio of binary diffusion coefficients of H and H\(_2\) in helium [Marrero and Mason, 1972].

[17] Krasnopolsky and Feldman [2001] report that the H\(_2\) abundance in the lower atmosphere is 17 ppm. The corresponding diffusion-limited flux would be \( 3.7 \times 10^3 \) H atoms cm\(^{-2}\) s\(^{-1}\). This is only about 50% bigger than the conventional estimate of \( 2.4 \times 10^3 \) H atoms cm\(^{-2}\) s\(^{-1}\) [Nair et al., 1994]. The near coincidence is a broad hint that H escape is diffusion-limited.

[18] Diffusion-limited escape is naturally expressed as a velocity. The diffusion-limited velocity is

\[
\nu_{\text{lim}} = \phi_f / \alpha_a
\]

This is applied at the top of the grid:

\[
\nu_{\text{lim}} = \frac{b_{ij} \left( \frac{1}{H_a} \frac{1}{H_i} \right)}{N_a}
\]

In equation (3), the density \( N_a \) refers to the atmospheric density [cm\(^{-3}\)] at the altitude where \( \nu_{\text{lim}} \) is being evaluated. In our model we evaluate \( \nu_{\text{lim}} \) and \( N_a \) at 110 km.
We can define a general hydrogen effusion velocity $v_{\text{eff}}$ at the top of the grid by analogy to $v_{\text{lim}}$. In the absence of chemical sources and sinks, the ratio $v_{\text{eff}}/v_{\text{lim}}$ is constant. We define effusion velocities for H and H$_2$ at 110 km.

3.1.2. Jeans Escape

[20] It is interesting to consider how diffusion interacts with Jeans escape. Jeans escape is evaluated at the exobase, the altitude above which atmospheric atoms and molecules no longer collide with each other [Jeans, 1925; Walker, 1977].

$$\phi_{\text{Je}} = f_e N_e \sqrt{\frac{kT}{2\pi m_j}} \left(1 + \frac{R_e}{H_e}\right) e^{-R_e/H_e},$$

where $N_e$ and $f_e$ refer to the exobase density and the hydrogen mixing ratio at the exobase, respectively, and $R_e$ refers to the location of the exobase. In the limit where escape is small and hydrogen a minor constituent, the exobase is defined by the major constituent. It is usual to define $N_e$ by setting the mean free path equal to the scale height $H_e$. [21] The hydrogen mixing ratio at the exobase $f_e$ is related to the total hydrogen mixing ratio at the homopause $f_{\text{hom}}(H)$ by integrating the diffusion equation [Zahnle et al., 1990]; a simple analytic solution is obtained if we assume an isothermal atmosphere and ignore eddy diffusion above the homopause.

$$\frac{f_e}{f_{\text{hom}}(H)} = \frac{\phi_{\text{Je}}}{\phi_{\text{lim}}} + \left(1 - \frac{\phi_{\text{Je}}}{\phi_{\text{lim}}}\right) \exp\left\{\left(R_e - R_h\right) \left(\frac{1}{H_e} - \frac{1}{H_f}\right)\right\}. \quad (5)$$

One usually thinks of a species as relaxing to its own scale height above the homopause, but this is not so for hydrogen in diffusion-limited escape. Rather, escape reduces the scale height, and in the diffusion limit $f_e \to f_{\text{hom}}$. Equations (1), (4), and (5) can be solved for the ratio $\phi_{\text{Je}}/\phi_{\text{lim}}$. The altitude of the exobase is $R_e = R_h + H_f \ln (N_j/N_e)$ in the isothermal atmosphere. For $m_j \ll m_e$, the binary diffusion coefficient is related to the mean free path $H_d$ and the thermal velocity $\bar{c} = \sqrt{8kT/\pi m_j}$ by $b_{uj} = \frac{1}{2}H_d\bar{c}N_e$ [Jeans, 1925, pp. 312–314]. The result is

$$\phi_{\text{lim}} = 1 - \frac{4}{3} \left(1 - \frac{H_f}{H_e}\right) \frac{R_e}{H_e} e^{-R_e/H_e}.$$

Two end-member cases are plotted on Figure 2, one in which all H$_2$ is photochemically dissociated into atomic H (labeled H), and the other where H$_2$ escapes as H$_2$. The true situation lies somewhere between, in which hydrogen escapes mostly or entirely as H but most of the hydrogen is in the form of H$_2$. An arbitrary intermediate example, in which 10% of the H$_2$ is converted to H at the exobase, is shown for illustration. Figure 2 makes the general point that for plausible conditions on Mars, the hydrogen escape rate should approach the diffusion limit.

3.1.3. Current Hydrogen Escape

[22] Hydrogen escape fluxes are not observed directly, a point emphasized by Hunten [1990]. Rather, they are (for Mars) inferred from the altitude profile of atomic hydrogen above the exobase, which has itself been obtained by inverting limb soundings of scattered solar Ly$\alpha$. For Mars the best data were obtained by Mariners 6 and 7. Anderson and Hord [1971] described their inferred atomic hydrogen profile in terms of a density and temperature at the exobase. They assumed that the hydrogen atoms obeyed a Maxwellian velocity distribution at the exobase to obtain the spatial distribution of hydrogen atoms, taking into account that some hydrogen atoms would be in satellite or escape orbits. Anderson and Hord’s exobase parameters are given in Table 3. The corresponding Jeans escape flux is $1.5 \times 10^8$ atoms cm$^{-2}$ s$^{-1}$, but given the uncertainty in the temperature, $350 \pm 100$ K, the Jeans flux is uncertain to a factor of 2. Nair et al. [1994] deduced a total hydrogen

Table 3. Inferred H Escape Fluxes

<table>
<thead>
<tr>
<th>Model</th>
<th>Spacecraft</th>
<th>$n_{\text{esc}}(H)$ [cm$^{-3}$]</th>
<th>$T_{\text{esc}}$ [K]</th>
<th>$\phi_{\text{Je}}$ [cm$^{-2}$ s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anderson and Hord [1971]</td>
<td>Mariner 6</td>
<td>$3 \pm 1 \times 10^4$</td>
<td>350 ± 100</td>
<td>$1.8^{+0.2}_{-0.1} \times 10^{10}$</td>
</tr>
<tr>
<td>Anderson and Hord [1971]</td>
<td>Mariner 7</td>
<td>$2.5 \pm 1 \times 10^4$</td>
<td>350 ± 100</td>
<td>$1.5^{+0.1}_{-0.1} \times 10^{10}$</td>
</tr>
<tr>
<td>Galli et al. [2006b]</td>
<td>Mariner 6</td>
<td>$7.1^{+0.7}_{-0.6} \times 10^4$</td>
<td>350 ± 100</td>
<td>$4.1^{+0.3}_{-0.2} \times 10^{10}$</td>
</tr>
<tr>
<td>Galli et al. [2006b]</td>
<td>Mariner 7</td>
<td>$3.4^{+0.3}_{-0.3} \times 10^5$</td>
<td>425 ± 100</td>
<td>$3.8^{+0.3}_{-0.3} \times 10^{10}$</td>
</tr>
<tr>
<td>Galli et al. [2006b]</td>
<td>Mars Express</td>
<td>$6.4^{+0.6}_{-0.6} \times 10^7$</td>
<td>1000 ± 100</td>
<td>$4.3^{+0.4}_{-0.3} \times 10^{9}$</td>
</tr>
</tbody>
</table>
escape flux of $2.4 \times 10^8$ by tuning their photochemical model to give Anderson and Hord’s H densities and then adding to this Jeans escape by $H_2$ at the same temperature as $H$.

[23] Aerobraking experienced by more recent spacecraft suggests that the Martian exosphere as a whole is considerably colder, closer to $\sim 200$ K than to $\sim 350$ K [Lichtenegger et al., 2006]. The colder background atmosphere suggests that the atomic hydrogen is better described by two populations, one at the atmospheric temperature of $\sim 200$ K, and the other warmer or hot. A similar effect has been inferred on Venus, where there also appear to be two different populations of exospheric hydrogen, one of which is hot and dominates escape [Donahue et al., 1997]. In neither case is the origin of the hot $H$ fully understood. Possibilities include charge exchange with solar wind protons and dissociative reactions between $H_2$ and $CO_2$ and $O^+$ that make hot $H$ atoms [Galli et al., 2006a, 2006b; Lichtenegger et al., 2006]. It is also probable that the “double-humped” non-Maxwellian velocity distribution function for $H$ atoms above the exobase [Barakat et al., 1995] is better approximated by two Maxwellsians than by one Maxwellian.

[24] Galli et al. [2006b] fit two-component models both to new data from Mar's Express and to the old Mariner 6 and 7 data. Galli et al. base their H profiles on 1D Monte Carlo modeling of atoms at and above the exobase. The Monte Carlo models do not presume that the velocity distribution function is Maxwellian. Their results are reported in Table 3. Applied to the Mariner data, Galli et al.’s model gives somewhat denser or warmer conditions than Anderson and Hord’s [1971]. Mars Express encountered distinctly different conditions than did the two Mariners. Galli et al.’s best fit to the Mars Express data is both hotter ($\sim 1000$ K) and thinner. A key point is that all three of Galli et al.’s fits give the same Jeans escape flux of $\sim 4 \times 10^8$ atoms cm$^{-2}$ s$^{-1}$, despite markedly different temperatures. Such a coincidence is expected of diffusion-limited escape, where escape is limited deep in the atmosphere, but not of temperature-limited escape, for which escape would be higher when the temperature is higher. Moreover, and quite independently, the deduced escape flux is close to the expected diffusion-limited escape flux of $3.5 \times 10^8$ atoms cm$^{-2}$ s$^{-1}$ for 17 ppm $H_2$.

[25] Other workers have also found that a Maxwellian velocity distribution can underestimate densities above the exobase, and hence underestimate escape. Barakat and Schunk [2007] compared Monte Carlo simulations of the distribution of a trace low mass constituent above an exobase to results obtained using various fluid dynamic approximations, including the usual 5-moment approximation and Grad’s 13-moment approximation. The Monte Carlo simulations are presumably most nearly correct. Barakat and Schunk found that the familiar 5-moment approximation, which is derived from the Boltzmann equation by assuming a Maxwellian velocity distribution to close the system of moment equations [Schunk, 1975], underestimates the number density of the low mass trace species by about a factor of 2. Grad’s 13-moment approximation, which uses a complicated, non-Maxwellian velocity distribution to close the system of moment equations [Schunk, 1975], does quite well. Cui et al. [2008] applied Grad’s 13-moment approximation to diffusion-limited escape of $H_2$ from Titan. Temperatures and densities in Titan’s exosphere are obtained directly by in situ sampling with the Cassini spacecraft. Cui et al. [2008] deduce a hydrogen escape flux 2.5$\times$ higher than what simple Jeans escape predicts.

[26] The higher densities seen in Galli et al.’s [2006b] models are consistent with these other results. The more accurate velocity distribution functions, such as Grad’s, have more fast moving, outbound atoms than does the Maxwellian. The net result is that Anderson and Hord’s [1971] Maxwellian H profile is likely to underestimate the hydrogen abundance above the exobase, and hence underestimate how fast hydrogen escapes from Mars, compared to Galli et al.’s more nuanced model.

[27] We conclude that at present, the totality of the evidence suggests that hydrogen escape from Mars is diffusion-limited, and therefore rather higher than it has usually been taken to be. We suspect that relatively low $H$ escape rates have been favored historically because they have been tethered to the theoretical construct that $H$ escape must be balanced by O escape, and many studies have consistently shown that the O escape rate is small [Lammer et al., 2003]. We therefore repeat our agreement with Lammer et al. [2003]: the main sink on O is at the surface. The $H$ escape rate is then freed to reach the diffusion limit. Diffusion-limited escape is an important simplification that reduces our models to a one-parameter family.

### 3.2. Oxygen Deposition

[28] As a first approximation, we implement dry deposition by assuming a single deposition velocity $v_{dep}$ that we apply to all reactive gases. In the current Martian atmosphere, hydrogen peroxide ($H_2O_2$) and ozone ($O_3$) are the most important reactive gases. Both are strong oxidants that by entering the soil make the soil strongly oxidizing as well. We show below that our models work best with $0.1 < v_{dep} < 0.03$ cm s$^{-1}$. This is much smaller than the corresponding deposition velocities on Earth. For comparison, $v_{dep}$ for $H_2O_2$ and $O_3$ over continents are about 1.0 and 0.07 cm s$^{-1}$, respectively [Seinfeld and Pandis, 2006]. It is expected that $v_{dep}$ would be higher for these gases on Earth where liquid water is a common surface.

[29] Bullock et al. [1994] addressed the diffusion and reaction rates of $H_2O_2$ in Martian soils. They considered two end-member cases, one with the least $H_2O_2$ in the soil that can account for the Viking observations, the other imposing the characteristic $10^5$–$10^7$ year loss timescale deduced by Chyba et al. [1989] from the thermal sensitivity seen in the Viking labeled release experiments. If we use the same parameters that Bullock et al. used in their model, we find that their results can be described by $H_2O_2$ deposition velocities between $0.03$ cm s$^{-1}$ ($10^5$ year timescale) to 0.6 cm s$^{-1}$ (minimum $H_2O_2$). Our photochemical models predict about $6 \times$ more $H_2O_2$ in the atmosphere near the surface than Bullock et al. assumed, which suggests that $v_{dep}$ should be $6 \times$ smaller. The corresponding range of dry deposition velocities is $0.005 < v_{dep} < 0.1$ cm s$^{-1}$. Our results are consistent with this range.

[30] A consequence of applying a deposition velocity to $H_2O_2$ is that the surface must be a net sink of $H_2O_2$. In other words, our construction implicitly assumes that peroxides eventually react with ferrous iron or reduced sulfur to make ferric iron and sulfate. Accumulated over 4 Ga, the average thickness of the oxidized rind would be tens of meters
At present O escape does not appear to be important for Mars [Lammer et al., 2003]. However, the consensus is that O escape was vastly greater in the past, as a consequence of higher solar EUV radiation and much bigger solar winds [Luhmann, 1997; Lammer et al., 2003]. An oxygen escape flux of $10^7$ cm$^{-2}$ s$^{-1}$ today might scale to escape fluxes as high as $10^9$ cm$^{-2}$ s$^{-1}$ 2.5 Ga and $10^8$ cm$^{-2}$ s$^{-1}$ at 3.5 Ga [Lammer et al., 2003]. At $10^5$ cm$^{-2}$ s$^{-1}$, oxygen escape provides a reducing force on the atmosphere that would be of the same order of magnitude as volcanic activity at levels seen on Earth today. At these rates of escape, O escape becomes a major driver on the atmosphere.

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boundary conditions are on hydrogen escape and the H$_2$ mixing ratio. The reported H$_2$ mixing ratio of 17 ppmv [Krasnopolsky and Feldman, 2001] is approached in the limit that $v_{\text{eff}} \rightarrow v_{\text{lim}}$. This demands a hydrogen escape rate of \( \frac{N}{C_2} \times 10^{-8} \) H atoms cm$^{-2}$ s$^{-1}$. Lower hydrogen escape fluxes correspond to greater amounts of H$_2$ in the atmosphere. The corresponding deposition velocity $v_{\text{dep}} = 0.02$ cm s$^{-1}$. This is model A in Table 4.

Figure 5 addresses how easily H escapes by changing $v_{\text{eff}}$ while $v_{\text{dep}}$ is held fixed at 0.02 cm s$^{-1}$; this is effectively the partial derivative of the model with respect to $v_{\text{eff}}$. Lowering $v_{\text{eff}}$ makes the atmosphere more reducing. The loss of oxidant to the surface is chiefly through H$_2$O, and because the H$_2$O ground level mixing ratio is insensitive to how easily H escapes, the oxygen sink is proportional to $v_{\text{dep}}$. Bigger losses of H$_2$O to the surface require bigger losses of H to space, which for fixed $v_{\text{eff}}$ is accomplished by raising $f(H_2)$. The shading indicates the range of models generally consistent with modern Mars. Model A in Table 4 is for $v_{\text{dep}} = 0.02$ cm s$^{-1}$, in the middle of the shaded region.

Table 4 compares our nominal model results to other published models and to Mars. Our nominal photochemical model (model A) does a good job with O$_2$, H$_2$, and H$_2$O$_2$, while falling a little short with CO. The simplest way to improve the agreement with CO is to consider a drier stratosphere. Model B shows that a globally averaged relative humidity of 17% (the average relative humidity at the ground), if imposed at all altitudes, raises the CO abundance to match what is observed without affecting the other major photochemical products. The success of model B suggests that the Martian stratosphere might be rather dry. To create a dry stratosphere would seem to require efficient atmospheric circulation through effective cold traps; this is not a good problem for a 1D model. It would be better addressed with a GCM.

There are enough differences between our models and other published models that direct comparisons are difficult to make. These differences include temperature structure, eddy diffusion, chemical reaction rates, boundary conditions, and numerical convergence. In our models the H$_2$ mixing ratio is a chemical product that we predict. Our model predicts that the H$_2$ mixing ratio should be \( \sim 20 \) ppmv.

Figure 6. How certain key observables vary with deposition velocity ($v_{\text{dep}}$) when the escape velocity is held fixed at the limiting flux ($v_{\text{eff}} = v_{\text{lim}}$). All reactive atmospheric species are subject to the same value of $v_{\text{dep}}$, while $v_{\text{dep}} = 0$ for CO, O$_2$, and H$_2$. The shading indicates the range of $v_{\text{dep}}$ that provides a good match to the Martian atmosphere. The model breaks down for $v_{\text{dep}} > 0.2$ cm s$^{-1}$: the surface oxygen sink becomes so big that reducing sinks become saturated and the CO mixing ratio increases dramatically; \( p_{\text{CO}_2} \) is set to 6.28 mbar. The CO runaway may be artificial because we have not included a surface sink on CO.
if and only if escape is diffusion-limited. This is shown in Figures 4 and 5.

5. Historic and Ancient Mars

[41] The Martian atmosphere is not compositionally constant. The amounts of H₂O and CO₂ in the atmosphere change seasonally. It is likely that H₂O and CO₂ evolve in response to obliquity variations and other changing orbital parameters, volcanism, the evolving Sun, and sundry other factors. Here we consider how the steady state photochemistry responds to changing levels of H₂O, CO₂, and the linked affects of the evolving solar UV radiation and solar wind. As a first step we will in effect take the partial derivatives of our standard model with respect to H₂O, CO₂, and UV. For this exercise we treat CO₂, H₂O, and the Sun as independent variables. We hold the other boundary conditions constant; in particular H escapes in the diffusion limit and H₂O₂ and O₃ are delivered to the surface with νdep = 0.02 cm s⁻¹.

5.1. Changing CO₂

[42] Figure 7 shows how our nominal model responds to changes in pCO₂. Temperature structure, relative humidity, eddy diffusivity, and boundary conditions are the same as for model A. The general trend is that the atmosphere becomes more oxidized as it gets thinner, and more reduced as it gets thicker. The chief reason for this is that water vapor photolysis is relatively more important in the thinner atmosphere. This is because there is less CO₂ but the same amount of water vapor (which depends on surface temperature). Therefore there is more OH in the thinner atmosphere. With more OH there is less CO (CO + OH → H + CO₂ is the chief reaction destroying CO) and more O₂ (O + OH → H + O₂ is the chief reaction making O₂). Conversely, a thicker CO₂ atmosphere reduces the relative importance of H₂O photolysis, which favors CO over O₂.

[43] Thinner CO₂ atmospheres than today are not discussed as often as thicker atmospheres. At times of low obliquity it is expected that the polar caps expand and pCO₂ drop to as low as a millibar [Toon et al., 1980; Manning et al., 2006]. We find that in steady state, such an atmosphere would be 2% O₂. It is unlikely that such episodes would leave an observable chemical imprint, given that the current atmosphere is quite oxidizing as is.

[44] Thick CO₂ atmospheres have been widely posited to explain fluvial features of ancient Mars [Pollack et al., 1987; Haberle, 1998; Forget and Pierrehumbert, 1997]. Even today, at times of higher obliquity, it is possible that pCO₂ will increase significantly if there exist hidden stores of CO₂ that can be easily mobilized [Nakamura and Tajika, 2003; Manning et al., 2006]. We find that for pCO₂ ≈ 10 mbar, CO is as abundant as O₂. Atmospheres with pCO₂ > 50 mbar begin to look rather poisonous. As pCO₂ approaches 100 mbar the atmosphere becomes unstable with respect to CO. Many discussions of early Mars have
confidently assumed that at least this much CO$_2$ was once present (see review by Haberle [1998]). Yet the photochemistry suggests that such an atmosphere might not be stable.

[45] What is going wrong for CO$_2$ in Figure 7 is that (1) the atmosphere is very dry and (2) the oxygen sink depends on H$_2$O$_2$ and O$_3$, which are made by three-body reactions and therefore easier to make in a denser atmosphere. Thus increasing CO$_2$ tends to make the atmosphere more reducing. The safety valve should be H escape, but H escape is insensitive to CO; meanwhile, the lack of water vapor lets CO build up.

[46] A weakness of these models is that they have only atmospheric gas phase sinks for CO. The models neglect surface sinks that might remove CO. Given that gas-phase photochemistry models tend to predict too little CO, additional major surface sinks are unlikely to be very important today. But surface sinks would almost certainly become important if CO were a major gas. CO has a well-known affinity for Fe, and Fe is abundant in surface minerals on Mars. At some level, minerals might catalyze the reaction of CO with photochemically generated H$_2$O$_2$ and O$_3$ to make CO$_2$.

5.2. Changing H$_2$O

[47] Atmospheric composition is sensitive to absolute humidity. Like $p$CO$_2$, humidity is expected to vary as the obliquity, eccentricity, and longitude of perihelion precess. For simplicity we vary atmospheric water vapor by raising and lowering the temperature, holding relative humidity constant. The atmosphere is held to $p$CO$_2$ = 6.28 mbar, and other boundary conditions are the same as in model A. This is a relatively crude approach but it is adequate to illustrate the sensitivities.

[48] Figure 8 gives both the surface temperature and the corresponding water column as the independent variable. To first approximation, the CO/CO$_2$ ratio is inversely proportional to the amount of water vapor in the atmosphere, as expected. The apparent sensitivity of CO to surface temperature is almost entirely attributable to the water vapor abundance. Photochemical products of water vapor act as catalysts that help O$_2$ and CO recombine to CO$_2$. The model predicts that CO replaces CO$_2$ as the major C-bearing gas for $T < 192$ K. This prediction is interesting but should not be taken very seriously because it depends on the presumption that the boundary conditions that describe the current atmosphere remain applicable to the colder atmosphere. In particular, surface sinks on CO are neglected, which may be unrealistic when CO has become a major gas.

5.3. The Young Sun

[49] The young Sun was a stronger source of photolytically active UV radiation and a much stronger source of solar wind than it is today [Lammer et al., 2003]. Oxygen escape cannot be neglected under these conditions. For simplicity we have combined these effects in a single parameter. We scale UV photolysis rates at short wavelengths ($\lambda < 175$ nm) as the square root of the O escape rate, and at longer wavelengths as the 0.3 power of O escape. These are arbitrary scalings that reflect the relative sensitivities of the different phenomena to the young Sun. Lammer et al. [2003] suggest that the O escape flux was $\sim 10^7$ cm$^{-2}$ s$^{-1}$ at circa 3.5 Ga. We vary O escape from $10^7$ cm$^{-2}$ s$^{-1}$ today to $10^{10}$ cm$^{-2}$ s$^{-1}$. Other model parameters are held fixed.

[50] Figure 9 shows the result of doing these things. The response of the atmosphere is dominated by O escape, which is the forcing that changes the most. Oxygen escape generates a more reduced atmosphere, which favors CO. Increased UV photolysis acting alone simply raises the abundances of the photochemical products (O$_2$, CO, and H$_2$) more or less uniformly. All the fluxes are raised proportionately. But in concert with higher O escape, the higher UV flux actually stabilizes CO$_2$ against conversion to CO, when compared to models run without the higher UV flux (not shown). The relative stability of CO$_2$ against high stellar UV emission has been remarked upon before [Kasting et al., 1984; Kasting, 1995; Segura et al., 2007] in studies that address how difficult it is to create O$_2$ atmospheres without oxygenic photosynthesis.

5.4. Changing CO$_2$: Alternative Oxygen Sinks

[51] Our nominal models assume that the chief vectors of soil oxidation are H$_2$O$_2$ and O$_3$. Hydrogen peroxide is...
especially attractive because its high solubility in water makes its uptake by surface microfilms of water relatively probable; it is certainly stickier and vastly more soluble than O\textsubscript{2}. On the other hand, O\textsubscript{2} is much more abundant. Huguenin [1973, 1976] suggested that photostimulated oxidation rates using O\textsubscript{2} exceed $10^8$ cm$^{-2}$ s$^{-1}$, comparable in order of magnitude to H escape.

[52] We implement the O\textsubscript{2} sink as a deposition velocity. This is not obviously a good proxy for what Huguenin suggested is happening, but it is our best choice at present. Huguenin [1973, 1976] showed that UV photostimulated oxidation of magnetite by O\textsubscript{2} gas in the presence of trace amounts of O\textsubscript{2} in the atmosphere. In these models, CO\textsubscript{2} remains stable for pCO\textsubscript{2} < 500 mbar. There is little difference between models generated by the three different types of boundary conditions where pCO\textsubscript{2} < 50 mbar.

Figure 10. How different boundary conditions on oxygen change the way the atmosphere responds to changing pCO\textsubscript{2}. The surface temperature and atmospheric water vapor are appropriate for Mars today. The bold curves refer to the nominal model in which soil is oxidized by H\textsubscript{2}O\textsubscript{2} and O\textsubscript{3}. These models become unstable at pCO\textsubscript{2} ≈ 100 mbar. The open symbols denote models in which the atmospheric redox budget is balanced by O escape to space. These become unstable at pCO\textsubscript{2} ≈ 50 mbar. The filled symbols denote models in which soil is oxidized by O\textsubscript{2}, in proportion to the amount of O\textsubscript{2} in the atmosphere. In these models, CO\textsubscript{2} remains stable for pCO\textsubscript{2} < 500 mbar. There is little difference between models generated by the three different types of boundary conditions where pCO\textsubscript{2} < 50 mbar.

6. Photochemical Stability of CO\textsubscript{2} Atmospheres

[54] The possible photochemical instability of CO\textsubscript{2} atmospheres is not a new topic. It was widely discussed early in the space age, both for Mars and Venus [McElroy and Hunten, 1970; McElroy, 1972; McElroy and Donahue, 1972]. The matter was seen to be puzzling because CO\textsubscript{2} is readily photodissociated, and the direct three-body recombination, CO + O + M → CO\textsubscript{2} + M, is spin-forbidden and therefore extremely slow at atmospheric temperatures. The solution for Mars is that photolysis of water vapor produces OH radicals that react readily with CO to make CO\textsubscript{2}; in effect water vapor photolysis catalyses the recombination of CO\textsubscript{2} [McElroy and Donahue, 1972]. Figures 7, 8, and 10 raise the question of the stability of CO\textsubscript{2} once again.

[55] Figure 11 maps out the range of photochemically stable CO\textsubscript{2} atmospheres in our nominal models, in which soil oxidation is by H\textsubscript{2}O\textsubscript{2} and O\textsubscript{3} at a fixed deposition velocity of 0.02 cm s$^{-1}$. These models scale the eddy diffusion coefficient inversely with the square root of atmospheric density, and impose temperature structures featuring a 1.4 K km$^{-1}$ temperature gradient extending...
from the surface upward to a 140 K isothermal upper atmosphere. We do not attempt to self-consistently compute the radiative-convective temperature structure of the atmosphere. The relative humidity is unchanged from our base model. Model C in Table 4 provides an exemplary computation of what today’s 6.3 mbar CO2 atmosphere might have looked like 3.5 Ga.

[56] Figure 11 shows two cases, one with modern UV irradiation and negligible oxygen escape, and the other with high rates of O escape (10⁷ cm⁻² s⁻¹) and enhanced UV (factor of 10 at Lyα and a factor of 4 at ~200 nm) that might be expected for Mars at circa 4 Ga. The boundary lines are for atmospheres in which the CO and CO2 mixing ratios are equal. It turns out, somewhat surprisingly, that the more aggressive high UV, high O escape models do not impact CO2 stability very much. Oxygen escape makes thin CO2 atmospheres somewhat less stable against conversion to CO, but CO2 photochemical stability on early Mars is debatable even without high rates of O escape.

[57] Figure 11 suggests that CO2 becomes photochemically unstable in thick, dry, cold atmospheres. At low surface temperatures, appropriate to a thin atmosphere and the faint young sun, CO2 can be unstable at surface pressures no higher than today. To put the photochemical instability boundary in context we show for comparison the relation between surface temperature and pCO2 according to Kasting’s [1991] greenhouse warming models for early (faint Sun, 0.75L⊙) and current Mars.

[58] The apparent photochemical instability of cold CO2 atmospheres is an interesting result, although what it means in practice is not exactly clear. First, it takes 10⁷ years for an oxygen escape flux of 10⁹ cm⁻² s⁻¹ to convert a 10 mbar CO2 atmosphere to CO. It takes ten times longer to do the same to 100 mbar of CO2. Thus, CO2 can be unstable yet persistent.

[59] Second, we have neglected CO surface deposition specifically and CO heterogenous chemistry more generally. It is reasonable to suspect that CO2, if abundant, would interact with Fe, for which it has a strong affinity, at the surface or in airborne dust, and it is reasonable to suspect that Fe at the surface or in dust might catalyze oxidation of CO by O2 [Huguenin, 1976], or by H2O2 and O3 that are being generated photochemically in the atmosphere. Such reactions would recombine CO2. However, such reactions do not appear to be important today. The chief failing of purely gas-phase photochemical models is that they do not produce enough CO. Major heterogenous sinks on CO would just exacerbate the problem. Indeed most speculation of this topic [Atreya and Gu, 1994; Krasnopolsky, 1995, 2006] has gone in the other direction, suggesting that dust acts preferentially as a sink on the reactive products of H2O photolysis, thus reducing the catalytic recombination of CO2, and thereby increasing CO. Still, heterogenous reactions of CO might become important if CO were hundreds or thousands of times more abundant than it is now.

[60] But if we accept our results at face value, we note that the intersection of the faint sun greenhouse curve and the high O-escape CO2 stability curve at ~10 mbar and ~200 K gives a valid equilibrium balance between photochemistry and the greenhouse effect. This is a stable solution because CO is a weaker greenhouse gas than CO2. Of course, other factors, such as CO2 condensation, are likely to be important.

7. Discussion

[61] In the early 1970s the discussion of CO2 stability on Mars centered on the kinetic inhibition against CO2 recombination. This is part of the matter here, but not all of it. What drives the instability seen in Figures 7 and 8 is the redox budget of the atmosphere. In these models CO builds up because the atmosphere loses O (through the surface sink and through escape to space) faster than it loses H to space. When CO becomes abundant, gas-phase chemical reactions involving CO have little further effect on O loss or H escape: all gas-phase channels are saturated, so that CO has to rise enormously to have any additional effect on the redox budget. Surface-catalyzed reactions between CO and peroxides to make CO2, which we have not included, are likely to provide an important stabilizing feedback when CO is abundant.

[62] Active volcanoes and meteorite impacts, which we have not included in these simulations, accentuate the imbalance and speed the growth of CO. Indeed, both mechanisms have been addressed in exactly this context in earlier work. Kasting et al. [1982] and Kasting [1990] addressed the question of CO2 instability on the context of ancient Earth. In the work by Kasting et al. [1982], CO runaways were triggered by too much volcanic H2 and CH4. These simulations implicitly invoked a strongly reduced early mantle, because the volcanic input needed to trigger a CO runaway was rather large. In the work by Kasting [1990], CO runaways were triggered by infall of reduced meteoritic materials during the late bombardment before 3.8 Ga when impact rates were high. The reduced material in the meteorites, in particular metallic Fe (which is abundant in many classes of meteorites), reacted with atmospheric CO2 at high temperatures to make CO and FeO. Thus the atmosphere became more reduced, and CO built up. Although Kasting [1990] used higher impact rates before 4.2 Ga than we would use today, the arguments made and conclusions reached in that study are qualitatively correct and, if anything, more powerfully applied to the cold dry climate of ancient Mars than to the warm wet climate of early Earth.

[63] An interesting point is that the stability question is asymmetric. Under plausible conditions a significant CO atmosphere can be converted to a CO2 atmosphere quickly, because the driver for oxidation is hydrogen escape, which can be fast, and the driver for recombination is water vapor, which can become very abundant very quickly if the right sort of event takes place (e.g., a major impact or a volcanic flood). As a specific example, if the atmosphere were hydrogen-rich or water-rich, diffusion-limited hydrogen escape rates can approach 10¹³ cm⁻² s⁻¹, which is fast enough to transform a 100 mbar CO atmosphere into a CO2 atmosphere in as little as 10⁴ years. These points taken together suggest that hysteresis is likely: transient warm wet epochs can quickly establish CO2 atmospheres that only slowly decay to CO in the long years after the warmth and the wet have gone away.

[64] Abundant CO might produce strong subsurface redox gradients, if oxidants are concentrated at the surface and...
CO permeates the deeper soils. A speculative possibility is that abundant CO might favor the formation of metal carbonyls. These are volatile substances that can provide a nontraditional means of mobilizing certain metals, particularly in locally reduced settings. Nickel and iron are the best known carbonyls; Ni(CO)4 is the most stable, the most volatile, and the most interesting. Metal carbonyls give us some hope that an ancient CO-rich atmosphere of Mars might have left behind some distinctive observable consequences. It is interesting that high Ni abundances have been reported by MER in Gusev soils [Yen et al., 2005, 2006]. The excess Ni has been interpreted as meteoritic contamination, and its evident mobility (it is enriched in hematite spherules) has been interpreted as transport by a chloride-rich brine [Yen et al., 2006]. These are plausible hypotheses; indeed a meteoritic source seems almost unsailable in the absence of alchemy. But the geochemical mobility of nickel at the Martian surface might also be explained by mobilization of nickel as a carbonyl, especially if the observed anomalies lie mostly with nickel, as Yen et al. [2005, 2006] suggest. Indeed iron-nickel meteorites would seem a perfect substrate for making carbonyls.

8. Conclusions

[66] One difference between our model and other 1D photochemical models is that we have assumed that the atmosphere’s redox budget is balanced by a surface sink on reactive oxidized gases, chiefly H2O2 and O3, that we have implemented as a deposition velocity. Our choice of a surface sink for oxygen, as opposed to O escape to space, is driven by the observational and theoretical consensus that O escape to space is currently negligible [Lammer et al., 2003]. The surface oxygen sink requires that hydrogen peroxide and ozone react with ferrous iron and sulfides; we do not address how this happens, although it is known that if water is temporarily present, alkaline earth and alkali hydroxides can form [Oyama and Berdahl, 1979], so it has been suggested that even in cold environments, thin films of water may have been important on Mars [Yen et al., 2005]. Mass balance suggests that the wave of oxidation penetrates the Martian crust at a rate of order of 10 m Ga⁻¹, less if sulfides are abundant.

[67] The other major difference between our model and other models is that we have accepted diffusion-limited hydrogen escape. The observed hydrogen escape flux is the least compelling of the constraints traditionally applied to photochemical models. One reason is that the escape flux is not directly measured: it is inferred from the observed number densities as fit to a model. Another reason is that the arguments in favor of diffusion-limited H escape from Mars are strong: (1) The assumption of a Maxwellian velocity distribution function used by Anderson and Hord [1971] predicts exospheric H densities and escape fluxes that are about half what more accurate velocity distribution functions predict [Galli et al., 2006b; Cui et al., 2008; Barakat and Schunk, 2007]. (2) The estimated escape fluxes using Galli et al.’s [2006a, 2006b] models are essentially identical to the diffusion-limited flux one obtains using Krasnopolsky and Feldman’s [2001] measurement of 17 ppmv H2 in the lower atmosphere. (3) Escape fluxes inferred from Galli et al.’s [2006a, 2006b] models are the same when the exobase temperature is 350 K, 425 K, and 1000 K; this implies that the bottleneck to escape is established at a lower altitude. (4) Our photochemical model predicts that the H2 mixing ratio should be ~20 ppmv if and only if escape is at the diffusion limit; by contrast the same model tuned to give the lower Anderson and Hord escape flux predicts H2 volume mixing ratios of 40–50 ppmv. These four arguments in favor of diffusion-limited flux are logically independent; that they converge on the same point is noteworthy.

[68] We then apply our model to Martian atmospheres that differ somewhat from today’s atmosphere. We include O escape for ancient Mars. We find that cold CO2 atmospheres can be photochemically unstable, especially on early Mars when the faint Sun encourages colder climates. For ancient Mars, CO2 stability would be further compromised by other sources of reducing power (active volcanism, a more reduced crust, and substantial exogenous input of reduced meteoritic iron during the late bombardment) that are not important today.

[69] Our results challenge the common assumption that early Mars was wrapped in a thick CO2 atmosphere. On the other hand it takes a long time to reduce a CO2 atmosphere to CO. We estimate that it could take as long as 10⁷ years to reduce a photochemically unstable 100 mbar CO2 atmosphere to CO, if an oxygen escape flux of 10⁹ cm⁻² s⁻¹ is indicative of the order of magnitude of the forcing. This is the same order of magnitude of forcing as modern terrestrial volcanism. Of course, the timescales would be shorter if volcanoes were more active, or reduced iron in impacts important, or if ferrous or sulfidic minerals were stronger sinks of oxidized gases or acids than today, or the O escape were faster; nonetheless the timescales for evolving the atmosphere were probably long enough that steady state solutions should be regarded as goals rather than as achievements. CO2 atmospheres can be unstable but persistent simply because there isn’t time enough to destroy them.

[70] Finally, it is worth pointing out that a lot of CO in an atmosphere is not just an inconvenience. For life it is an opportunity. The possible role of CO in the origin of life has been mooted many times, usually but not exclusively in the context of metabolism-first scenarios. CO is packed with energy. Methanogenesis takes CO and hydrogenates it with a catalyst based on iron-nickel sulfides; carboxydotrophy takes CO and oxidizes it with a catalyst based on iron-nickel sulfides [Ragsdale, 2004]. These are ancient metabolisms. The possibility that metabolism began with CO and an Fe- or Ni-based catalyst is quite reasonable, as Ragsdale [2004] notes in his review. A CO-rich early atmosphere may well make a cold young Mars seem a more attractive place to look for the first steps toward life.

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References


Sander, S. P., et al. (2003), Chemical kinetics and photochemical data for use in atmospheric studies, evaluation number 14, JPL Publ. 02-25.


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