SULFUR CHEMISTRY IN THE EARLY AND PRESENT ATMOSPHERE OF MARS

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Introduction: Atmospheric sulfur species resulting from volcanic emissions impact the composition and chemistry of the atmosphere, impact the climate, and hence, the habitability of Mars and impact the mineralogy and composition of the surface of Mars. The geochemical/photochemical cycling of sulfur species between the interior (via volcanism), the atmosphere (atmospheric photochemical and chemical processes) and the deposition of sulfuric acid on the surface of Mars is an important, but as yet poorly understood geochemical/photochemical cycle on Mars. There is no observational evidence to indicate that Mars is volcanically active at the present time, however, there is strong evidence that volcanism was an important and widespread process on early Mars. The chemistry and photochemistry of sulfur species in the early and present atmosphere of Mars will be assessed using a one-dimensional photochemical model. Since it is generally assumed that the atmosphere of early Mars was significantly denser than the present 6-millibar atmosphere, photochemical calculations were performed for the present atmosphere and for the atmosphere of early Mars with assumed surface pressures of 60 and 350-millibars, where higher surface pressure resulted from enhanced atmospheric concentrations of carbon dioxide (CO₂). The following sections include the results of earlier modeling studies, a summary of the one-dimensional photochemical model used in this study, a summary of the photochemistry and chemistry of sulfur species in the atmosphere of Mars and some of the results of the calculations.

Earlier Studies: Modeling of early Mars suggests a warm, wet climate to explain the fluvial geomorphology seen on the surface of Mars [1]. To increase the atmospheric surface temperature, models of early Mars suggest high levels of atmospheric CO₂ [1,2]. Subsequent analysis of CO₂ cloud formation causing surface cooling has caused inconsistencies in the CO₂ warming middle atmosphere ,, CO₂ clouds would be abated and in turn lead to sulfur species formation as found presently in Martian surface data [5, 7]. Bullock and Moore [4] suggest acidic water from this precipitation would limit carbonate formation and lead to sulfate species precipitation as seen for example at West Candor Chasma [8], Meridiani Planum, and various regions in Valles Marineris [9] on Mars. SO₂ would help sustain a thick CO₂ atmosphere as described by Yung et al. [6] as limited carbonate formation would not sequester the CO₂ out of the atmosphere. Bullock and Moore [4] suggests this change in the atmosphere but did not model the effects of SO₂ in such an atmosphere for viability of this constituent’s lifetimes in model atmospheres. Thus, here a one dimensional steady state model will be used to address the introduction of volcanic sulfur into the early Martian atmosphere.

The Photochemical Model of the Mars Atmosphere: The photochemical model that will be used in this research will be the model reported by Nair et al. [10] updated with additional methane and sulfur chemistry from Summers et al. [11] and Wong et al. [12]. This photochemical model, originated at Caltech/JPL, solves the one-dimensional continuity equation for steady-state conditions for the species listed in Nair et al. (10).

\[
\frac{\partial n}{\partial t} + \frac{\partial \Phi}{\partial z} = P_i - L_i
\]

is solved where \( n \) are the concentrations, \( \Phi_i \) are the vertical diffusive fluxes, and \( P_i \) and \( L_i \) are the chemical loss and production terms for each indexed species.

Since the steady state term leads to \( \frac{\partial n}{\partial t} = 0 \), the continuity equation can be solved giving the indexed species vertical flux by the equation:

\[
\Phi_i = -D_i \left( \frac{dn}{dz} + \frac{n_i}{H_i} \frac{(1 + \alpha) dT}{dz} \right) = -K \left( \frac{dn}{dz} + \frac{n_i}{H_i} \frac{dT}{dz} \right)
\]

where \( D_i \) is the molecular diffusion coefficient, \( K \) is the eddy diffusion coefficient, \( T \) is the temperature, \( \alpha \) is...
thermal diffusion factor (which is taken to be zero), and \( H \) is the scale height of the background atmosphere [10].

The 27 species used in Nair et al. (10) have been augmented by Summers et al. [11] with an additional 37 species. The addition of these species required additional reactions to be added to the model. Where possible JPL photochemical data was used. For a complete discussion of parameter value settings used in the model see Nair et al. [10] and references within.

The water profile shows both Nair et al. (10) high and low water mixing ratios and the saturation water level for the current temperature range. Water is initially held constant within the model and below saturation under 40 km as shown in Figure 1. Although reactions were updated, initial model runs show agreement with Nair et al. [10]. Thus, changes can be made to represent early Martian atmosphere from this working current Martian atmospheric model.

The Photochemistry and Chemistry of Sulfur Species in the Atmosphere of Mars: Once comparable results were demonstrated sulfur boundary conditions could be added to the model for both \( \text{SO}_2 \) and \( \text{H}_2\text{SO}_4 \). \( \text{SO}_2 \) is proposed to enter the early atmosphere through volcanic emission while \( \text{H}_2\text{SO}_4 \) condenses out of the atmosphere once the sulfur dioxide has cycled through chemical reactions in a proposed sulfur cycle shown in Figure 2 [5]. Rates for influx and deposition of chemicals were estimated through two distinct methods. \( \text{SO}_2 \) influx, as a constituent of volcanic emission of similar Earth volcanoes, is dependent upon the amount of volcanic activity and the constituent make up of the expelled gases. Estimates have been made of the amount of \( \text{SO}_2 \) that entered the early atmosphere of Mars through analysis of surface geology and chemical make up of gases expelled from volcanoes on the Earth and compared to Martian volcanoes and chemical analysis of surface rock. Levine and Summers (5) estimate \( \text{SO}_2 \) emissions for Mars to be between \( 4-8 \times 10^{11} \) moles S/year. This implies that an averaged upward flux rates would be approximately \( 1 \times 10^{10} \text{cm}^{-2}\text{s}^{-1} \) during the early volcanic period on Mars. This boundary condition was added to the model.

With the introduction of \( \text{SO}_2 \) into the atmosphere it is crucial to set a condensation rate for \( \text{H}_2\text{SO}_4 \). The \( \text{H}_2\text{SO}_4 \) must have an exit path in the atmosphere as well as a deposition rate on the surface of Mars. A pseudo reaction rate is found for \( \text{H}_2\text{SO}_4 \) condensation and the surface boundary condition of \( \text{H}_2\text{SO}_4 \) is fixed to be \( 1 \times 10^{-1} \text{cm/s} \), in line with this downward transport and precipitation out of the atmosphere and onto the surface. Models were then rerun to see affects of the introduction of sulfur species on the model.

With the introduction of sulfur into the model the reaction to changes in atmospheric water should be examined. Three water scenarios will be used. Starting with the water profile used in the present day Martian model presented by Nair et al. [10] and augmented with water saturation curves, a new water profile is generated for each of the three temperatures curves from Kasting [3] for each partial pressure of \( \text{CO}_2 \) corresponding to 6, 60 and 350-millibar atmospheres.

All water vapor added to the model was limited by the water saturation curves for the given temperatures present at each elevation. This constraint is initially necessary so that no water clouds would be formed and therefore requiring additional changes within the atmospheric model. The water profile above approximately 20 km is kept constant as the minimum water saturation seen for each model for simplicity. Sulfur species are not highly sensitive to the changes made to the water profiles with saturations limits. Now that water has been seen not to influence sulfur species we need to examine how the differing \( \text{CO}_2 \) levels affect the levels of sulfur species in the models. For these scenar-
rios the water profiles will be reset to the 1x Nair et al. (11) model augmented with the water saturation curve. Initial results demonstrate that the surface lifetime of SO₂ increases with increasing CO₂. The calculated SO₂ lifetime increases by three orders of magnitude from approximately half a day to a bit over 1.5 years while CO₂ increases by less than 2 orders of magnitude (from 6 to 350-millibars of CO₂) showing sensitivity to the major atmospheric constituent of present day Mars.

The surface influx value estimated for sulfur dioxide is dependent upon volcanic activity that is not tightly bounded both because of the variability of volcanic activity and the basis of Earth’s volcanic output for the SO₂ estimates, therefore additional model runs need to examine the sensitivity of the results to changes in the sulfur species themselves. Since the surface influx is estimated from volcanic emissions of sulfur dioxide, SO₂ influx values will be changed to mimic the variability of volcanic activity during active periods. Holding the water profile as outlined above for each model, changes were made in the SO₂ upward flux boundary condition to examine how the sulfur cycle would be affected by changes to the upward flux of SO₂. The upward flux values were changed by an order of magnitude larger and smaller than the estimated flux value used at this point in the model. Changes by an order magnitude in the surface flux of SO₂ leads to similar flux. Therefore, the SO₂ flux profile appears unaffected by the change in the amount of SO₂ emission. Finally, inspection of the H₂SO₄ flux profiles also show similar flux profiles except for changes between 10-20 km.

With SO₂ lifetime in the atmosphere increasing from approximately one day to one year with enhanced concentrations of carbon dioxide, the sulfur dioxide reacts with oxygen species or breaks up due to photolysis creating new sulfur species such as SO and SO₃. These species are short-lived and relatively insensitive to the increase in CO₂. H₂SO₄ will be produced after SO₂ react with photons and oxygen species. It then accumulates in the atmosphere and precipitates out onto the planetary surface.

Since H₂SO₄ accumulates in the atmosphere, a pseudo-reaction rate is introduced into the model to remove the sulfuric acid out of the atmosphere and model the precipitation on to the surface. This reaction is entered into the model reactions as: H₂SO₄ + M → PROD where M is a non-specific molecule and PROD is an end product removed from further atmospheric analysis. Thus, H₂SO₄ molecules are effectively removed from the atmosphere as desired. In setting a value for the reaction rate one must mimic the rate of condensation of H₂SO₄ out of the atmosphere. To estimate this value we start by estimating the condensation time constant for H₂SO₄, τ. This condensation time constant is translated into a reaction rate for entry into the model by solving 

\[ \dot{n} = k_n H_{2SO_4} n_M \]

for the \( k \) where \( \tau = \frac{n}{\dot{n}} \). The initial value used as the initial reaction rate for H₂SO₄ is \( 5 \times 10^{-23} \) cm³ s⁻¹. Condensation rate sensitivities were also run for this pseudo-reaction rate, changing the rate by an order of 10, larger and smaller. The range of parameters used in the photochemical calculations in this paper is summarized in table 1.

**Results of Photochemical Calculations:**

1. Enhanced CO₂ concentrations significantly enhance the lifetime of atmospheric sulfur dioxide.
2. Water mixing ratio limited at saturation does not influence the introduction of sulfur species with water, likely volcanic emissions. More work needs to be done with water saturation and cloud formation for definitive result.
3. Surface flux boundary conditions do not show great sensitivity to order of magnitude changes to the upward flux of SO₂. This is important as upward flux could change by orders of magnitude since volcanic activity was not constant over geological time scales.
4. H₂SO₄ formed in the atmosphere (the predominant product of SO₂) condensed onto the surface with the introduction of SO₂ into a predominately CO₂ atmosphere — this could address the apparent lack of carbonates on the surface of Mars and explain the sulfur minerals found on the surface.

**Conclusions:** Atmospheric sulfur species resulting from volcanic emissions impact the composition and chemistry of the atmosphere, impact the climate, and hence, impact the habitability of Mars and impact the mineralogy and composition of the surface of Mars. The geochemical and photochemical cycling of sulfur species between the interior (via volcanism), the atmosphere (atmospheric photochemical and chemical processes) and the deposition of sulfuric acid on the surface of Mars is an important, but as yet poorly understood cycle on Mars. Many questions about sulfur species and their relationship to the geology, geophysics, atmospheric composition, chemistry and climate and habitability of Mars may have to await the future exploration of Mars by human explorers [12, 13, 14, 15, 16].

**References:**


Table 1: Range of Atmospheric Parameters for Photochemical Calculations in This Paper.

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>Description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CO₂</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. SP = 6mbar</td>
<td>Similar to current surface pressure Pₛ = 0.006 bar</td>
<td>Kasting [3]</td>
</tr>
<tr>
<td>b. SP = 60mbar</td>
<td>10x 1.a.</td>
<td>Kasting [3]</td>
</tr>
<tr>
<td>c. SP = 350mbar</td>
<td>Maximum pressure before CO₂ cloud formation in stratosphere Pₛ = 0.35 bar</td>
<td>Kasting [3]</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Nair high temp. curve</td>
<td>Model present day temp.</td>
<td>Nair et al [10]</td>
</tr>
<tr>
<td>b. Kasting 1.a. temp. curve</td>
<td>Model curve augmented with appropriately fitted Nair curve above 60km</td>
<td>Kasting [3]</td>
</tr>
<tr>
<td>c. Kasting 1.b. temp. curve</td>
<td>Model curve augmented with appropriately fitted Nair curve above 60km</td>
<td>Kasting [3]</td>
</tr>
<tr>
<td>d. Kasting 1.c. temp. curve</td>
<td>Model curve showing warmest temperature with only CO₂ in atmosphere and without cloud formation augmented with appropriately fitted Nair curve above 40 km</td>
<td>Kasting [3]</td>
</tr>
<tr>
<td><strong>H₂O</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Nair/saturation curve</td>
<td>Nair water curve limited in values by H₂O saturation curve for temperature curves above and remaining constant above 20 km</td>
<td>Nair et al [10]</td>
</tr>
<tr>
<td><strong>Boundary Conditions SO₂</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. surface flux BC = 1.06x10¹⁰ cm²s⁻¹</td>
<td>Estimated flux value from comparison to Earth shield volcano output</td>
<td>Levine &amp; Summers [5]</td>
</tr>
<tr>
<td>b. surface flux BC =1.06x10¹¹ cm²s⁻¹</td>
<td>10x estimated amount</td>
<td>Levine &amp; Summers [5]</td>
</tr>
<tr>
<td>c. surface flux BC = 1.06x10⁹ cm²s⁻¹</td>
<td>1/10th estimated flux</td>
<td>Levine &amp; Summers [5]</td>
</tr>
<tr>
<td><strong>H₂SO₄ Condensation Rate</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. pseudo reaction rate to model condensation of H₂SO₄ = 5x10⁻¹⁰ cm⁻³ s⁻¹</td>
<td>Estimated using theory from Summers and Strobel</td>
<td>Summers &amp; Strobel [17]</td>
</tr>
<tr>
<td>b. pseudo reaction rate = 5x10⁻²² cm⁻³ s⁻¹</td>
<td>10x estimated value</td>
<td>Summers &amp; Strobel [17]</td>
</tr>
<tr>
<td>c. pseudo reaction rate = 5x10⁻¹⁹ cm⁻³ s⁻¹</td>
<td>1/10x estimated value</td>
<td>Summers &amp; Strobel [17]</td>
</tr>
</tbody>
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