SULFUR CHEMISTRY IN THE EARLY AND PRESENT ATMOSPHERE OF MARS

J.S. Levine[1] and M.E. Summers.[2] [1]Science Directorate, NASA Langley Research Center, Hampton, VA 23681 (joel.s.levine@nasa.gov), [2]Department of Physics and Astronomy, George Mason University, Fairfax, VA 22030.

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 (CO_2). 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 CO_2 [1,2]. Subsequent analysis of CO_2 cloud formation causing surface cooling has caused inconsistencies in the CO_2 warming wet model's approach, as well as the observed lack of carbonates found on the Martian surface [3,4,5].

Although differing in the chemistry, several scientists, beginning in 1997 with Yung et al. [6] proposed atmospheric sulfur dioxide (SO_2) as a potential solution for the early warm and wet climate of Mars. Yung et al. (6) proposed that with sufficient SO_2 present in the middle atmosphere„ CO_2 clouds would be abated and more surface warming could take place with higher CO_2 concentrations.

Subsequent theories on the introduction of SO_2 address the additional question of sequestered carbonates. Acidic water from precipitation of H_2SO_4 due to volcanic release of SO_2 and H_2S could halt carbonate formation 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. SO_2 would help sustain a thick CO_2 atmosphere as described by Yung et al. [6] as limited carbonate formation would not sequester the CO_2 out of the atmosphere. Bullock and Moore [4] suggests this change in the atmosphere but did not model the effects of SO_2 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). The equation,

$$\frac{\partial n_i}{\partial t} + \frac{\partial \Phi_i}{\partial z} = P_i - L_i$$

is solved where n_i are the concentrations, Φ_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 $\frac{\partial n_i}{\partial t} = 0$, the continuity equation can be solved giving the indexed species vertical flux by the equation:

$$\Phi_i = -D_i\left(\frac{dn_i}{dz} + \frac{n_i}{H_i} + \frac{n_i(1+\alpha)}{T}\frac{dT}{dz}\right) - K\left(\frac{dn_i}{dz} + \frac{n_i}{H_i} + \frac{n_i}{T}\frac{dT}{dz}\right)$$

where D_i is the molecular diffusion coefficient, K is the eddy diffusion coefficient, T is the temperature, α 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.

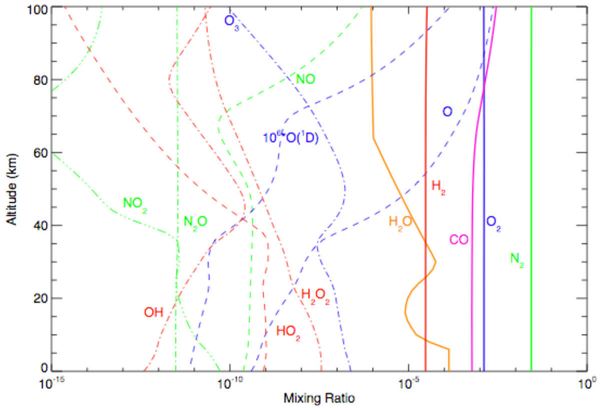

Figure 1. Calculated trace species in the atmosphere of Mars (CO_2 = 6 mbar).

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 SO_2 and H_2SO_4. SO_2 is proposed to enter the early atmosphere through volcanic emission while H_2SO_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. 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 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 SO_2 emissions for Mars to be between 4-8 x 10^{11} moles S/year. This implies that an averaged upward flux rates would be approximately 1 x 10^{10} $cm^{-2}s^{-1}$ during the early volcanic period on Mars. This boundary condition was added to the model.

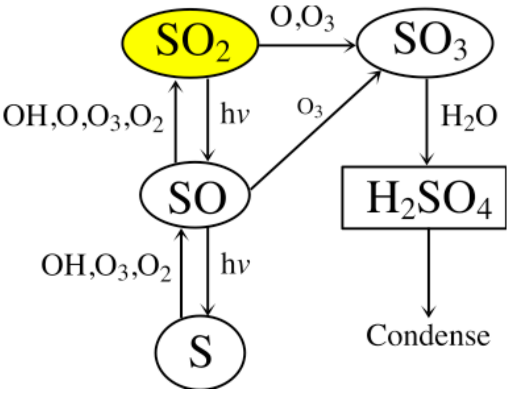

Figure 2. The photochemistry and chemistry of sulfur species in the atmosphere of Mars. A surface boundary condition provides influx of SO_2 into the atmosphere is estimated from early volcanic emissions on Mars.

With the introduction of SO_2 into the atmosphere it is crucial to set a condensation rate for H_2SO_4. The H_2SO_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 H_2SO_4 condensation and the surface boundary condition of H_2SO_4 is fixed to be $1x10^{-1}$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 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 CO_2 levels affect the levels of sulfur species in the models. For these scenarios 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 SO_2 increases with increasing CO_2. The calculated SO_2 lifetime increases by three orders of magnitude from approximately half a day to a bit over 1.5 years while CO_2 increases by less than 2 orders of magnitude (from 6 to 350-millibars of CO_2) 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 SO_2 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, SO_2 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 SO_2 upward flux boundary condition to examine how the sulfur cycle would be affected by changes to the upward flux of SO_2. The upward flux values were changed by an order of magnitude larger and smaller than the estimated flux value used to this point in the model. Changes by an order magnitude in the surface flux of SO_2 leads to similar flux. Therefore, the SO_2 flux profile appears unaffected by the change in the amount of SO_2 emission. Finally, inspection of the H_2SO_4 flux profiles also show similar flux profiles except for changes between 10-20 km.

With SO_2 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 SO_3. These species are short-lived and relatively insensitive to the increase in CO_2. H_2SO_4 will be produced after SO_2 react with photons and oxygen species. It then accumulates in the atmosphere and precipitates out onto the planetary surface.

Since H_2SO_4 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: $H_2SO_4 + M \rightarrow$ PROD where M is a non-specific molecule and PROD is an end product removed from further atmospheric analysis. Thus, H_2SO_4 molecules are effectively removing from the atmosphere as desired. In setting a value for the reaction rate one must mimic the rate of condensation of H_2SO_4 out of the atmosphere. To estimate this value we start by estimating the condensation time constant for H_2SO_4, 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 H_2SO_4 is 5 x 10^{-23} $cm^3 s^{-1}$. 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 CO_2 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 SO_2. This is important as upward flux could change by orders of magnitude since volcanic activity was not constant over geological time scales.
4. H_2SO_4 formed in the atmosphere (the predominant product of SO_2) condensed onto the surface with the introduction of SO_2 into a predominately CO_2 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:

[1] Pollack, J.B. et al., Icarus, **71**(2), 203-224 (1987).

[2] Plumlee, G., et al., Lunar and Planetary Institute MSATT Workshop on Chemical Weathering on Mars, p. 31-32 (1992).

[3] Kasting, J. F., Icarus, **94**,1-13 (1991).

[4] Bullock, M. and Moore, Geophysical Research Letters, **34**, (2007).

[5] Levine, J.S. and Summers, M. E., 3rd Intern. Workshop on the Mars Atmosphere: Modeling and Observations Paper #9016{2008}.
[6] Yung, Y.L. et al. Icarus, 130,pp. 222 (1997).
[7] Bibring, Jean-Pierre, et al., Science, **307**, pp. 1576 (2005).
[8] Mangold, N. et al., Icarus, **194(**2), 519-543 (2009).
[9] Dobrea, E.Z., et al., Icarus, **193**(2), 516-534 (2008).
[10] Nair, H, et al., Icarus, **111**, 124-150 (1994).
[11] Wong, A-S et al., J. Geophys. Research, 108, 5026-5037 (2003) with corrections in Volume **109 (**2004).
[12] Levine, J.S., Garvin, J.B. and Beaty, D.W., Journal of Cosmology, 12, 3627-3635 (2010).
[13] Levine, J.S., Garvin, J.B. and Head, J.W., Journal of Cosmology, 12, 3636-3646 (2010).
[14] Levine, J.S., Garvin, J.B. and Elphic, R.C., Journal of Cosmology, 12, 3647-3657 (2010).
[15] Levine, J.S., Garvin, J.B. and Hipkin, V., Journal of Cosmology, 12, 3658-3670 (2010).
[16] Levine, J.S., Garvin, J.B. and Doran, P.T., Journal of Cosmology, 12, 3671-3684 (2010).
[17] Summers, M.E. and Strobel, D.F., Astrophysical Journal, 346, 495-508 (1989).

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

Model Parameters	Description	Reference
CO_2		
a. SP = 6mbar	Similar to current surface pressure $P_s = 0.006$ bar	Kasting [3]
b. SP = 60mbar	10x 1.a.	Kasting [3]
c. SP = 350mbar	Maximum pressure before CO_2 cloud formation in stratosphere $P_s = 0.35$ bar	Kasting [3]
Temperature		
a. Nair high temp. curve	Model present day temp.	Nair et al [10]
b. Kasting 1.a. temp. curve	Model curve augmented with appropriately fitted Nair curve above 60km	Kasting [3]
c. Kasting 1.b. temp. curve	Model curve augmented with appropriately fitted Nair curve above 60km	Kasting [3]
d. Kasting 1.c. temp. curve	Model curve showing warmest temperature with only CO_2 in atmosphere and without cloud formation augmented with appropriately fitted Nair curve above 40 km	Kasting [3]
H_2O		
a. Nair/saturation curve	Nair water curve limited in values by H_2O saturation curve for temperature curves above and remaining constant above 20 km	Nair et al [10]
Boundary Conditions SO_2		
a. surface flux BC = $1.06\text{x}10^{10}$ $cm^{-2}s^{-1}$	Estimated flux value from comparison to Earth shield volcano output	Levine & Summers [5]
b. surface flux BC =$1.06\text{x}10^{11}$ $cm^{-2}s^{-1}$	10x estimated amount	Levine & Summers [5]
c. surface flux BC = $1.06\text{x}10^{09}$ $cm^{-2}s^{-1}$	1/10th estimated flux	Levine & Summers [5]
H_2SO_4 Condensation Rate		
a. pseudo reaction rate to model condensation of $H_2SO_4 = 5\text{x}10^{-20}$ cm^{-3} s^{-1}	Estimated using theory from Summers and Strobel	Summers & Strobel [17]
b. pseudo reaction rate = $5\text{x}10^{-22}$ cm^{-3} s^{-1}	10x estimated value	Summers & Strobel [17]
c. pseudo reaction rate = $5\text{x}10^{-19}$ cm^{-3} s^{-1}	1/10x estimated value	Summers & Strobel [17]