# SULFUR DIOXIDE AND THE PRODUCTION OF SULFURIC ACID ON PRESENT-DAY AND EARLY MARS: IMPLICATIONS FOR THE LACK OF DETECTED CARBONATES ON THE SURFACE.

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Introduction: Measurements from the Viking Landers and Mars Pathfinder have shown that sulfur is a significant component of the surface of Mars [1]. However, one of the major and most surprising findings of the Mars Exploration Rovers [2] and the ESA Mars Express OMEGA instrument [3, 4, 5] is how widespread sulfate minerals, in the form of gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrate sulfate ($CaSO_4$), actually are on the surface of Mars. Perhaps even more surprising is the lack of detection of carbonates on the surface of Mars. These two findings-the widespread distribution of sulfates and the lack of detection of carbonates-may be related. The widespread distribution of sulfates on Mars indicates a past watery and acidic environment on surface of Mars, an environment that could readily lead to the destruction of surface carbonates, should they have existed. Calcium carbonate is readily destroyed by reaction with sulfuric acid (H_2SO_4) in solution, which leads to the formation of gypsum ($CaSO_4 \cdot 2H_2O$) via the reaction:

(1) $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 \cdot H_2O + CO_2$
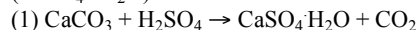
Volcanic Sulfur: Sulfuric acid (H_2SO_4) is readily formed via atmospheric chemical reactions from sulfur dioxide (SO_2), an important component of volcanic emissions. To-date, attempts to detect sulfur dioxide and other sulfur compounds in the present-day atmosphere of Mars have been unsuccessful [6]. However, there is a good possibility that sulfur dioxide was an abundant constituent of the early atmosphere of Mars. The source of sulfur dioxide in the early atmosphere of Mars was volcanic emissions. After water vapor (H_2O) and carbon dioxide (CO_2), sulfur dioxide (SO_2) is the most abundant gaseous component of Hawaiian volcanic emissions [7]. The chemical composition of volcanic emissions in percent of gaseous emissions are H_2O: CO_2: SO_2 is 79.31%: 11.61%: 6.48% [7].

How much SO_2 was produced on early Mars? Estimates for the amount of SO_2 in the early atmosphere of Mars may be made by considering the release of magma and its accompanying gaseous emissions during the Tharsis formation [8]. Phillips et al. [8] have estimated that volcanism associated with the Tharsis formation produced about 3 x 10^8 km^3 of igneous material, equivalent to a 2-km-thick global layer. In addition, the Tharsis formation released huge amounts of water vapor, carbon dioxide and sulfur dioxide to the atmosphere. The Tharsis formation released the equivalent of a 120-m-thick global layer of precipitable water (assuming a water content of 2 weight percent (wt %) in the magma and produced a 1.5-bar atmosphere of CO_2 (assuming a CO_2 content of 0.65 wt %) [8]. The weight percentage for H_2O and CO_2 are consistent with Hawaiian basaltic lavas. The release of SO_2 to the atmosphere associated with the Tharsis formation may be estimated by using the ratio of volcanic emissions of H_2O: CO_2: SO_2 for Hawaiian volcanoes [7] with the estimates of the magma and the accompanying gaseous H_2O and CO_2 released to the atmosphere [8]. The release of SO_2 to the atmosphere associated with the Tharsis formation produced on the order

duced on the order of a 1-bar SO_2 atmosphere on Mars, which is comparable to the mass of the Earth's present-day atmosphere. This is an enormous quantity of atmospheric SO_2, which potentially could produce an enormous quantity of H_2SO_4 that readily precipitated out of the atmosphere onto the surface of Mars destroying any existing surface carbonates and is the source of the widespread and abundant sulfates on the surface of Mars.

The Production of Sulfuric Acid on Mars: As indicated, volcanic SO_2 leads to the formation of H_2SO_4 in the atmosphere of Mars via the intermediate production of sulfur trioxide (SO_3) via the following chemical reactions:
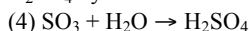
(2) $SO_2 + O_3 \rightarrow SO_3 + O_2$
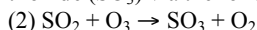
where O_3 is ozone, O_2 is molecular oxygen, and

(3) $SO_2 + O + M \rightarrow SO_3 + M$
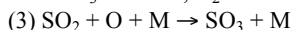
where O is atomic oxygen and M is any third body, usually CO_2.
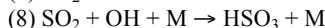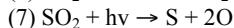
The SO_3 formed in reactions (2) and (3) is converted to H_2SO_4 by reaction with water vapor (H_2O):

(4) $SO_3 + H_2O \rightarrow H_2SO_4$

The environment associated with volcanic activity is very water-rich with abundant volcanic water in both gaseous and liquid phases. Sulfuric acid is very water-soluble and readily precipitates out of the atmosphere in the form of water droplets. However, SO_2 is also destroyed via photolysis by solar ultraviolet radiation (Reactions 5-7) and by chemical reaction with the hydroxyl radical (OH) (Reactions 8):

(5) $SO_2 + hv \rightarrow SO + O$
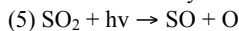
where h is Planck's constant and v is the frequency solar radiation.

(6) $SO_2 + hv \rightarrow S + O_2$

(7) $SO_2 + hv \rightarrow S + 2O$

(8) $SO_2 + OH + M \rightarrow HSO_3 + M$
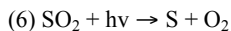
The hydroxyl radical needed in reaction (8) is readily formed from H_2O according to the reactions:

(9) $H_2O + hv \rightarrow OH + H$

(10) $H_2O + O(^1D) \rightarrow 2OH$
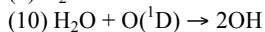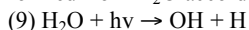
where $O(^1D)$ is excited atomic oxygen.

The balance between SO_2 forming H_2SO_4 (reactions 2-4) and SO_2 being destroyed via photolysis (reactions 5-7) and via chemical reaction with OH (reactions 8) and not forming H_2SO_4 can be assessed with the use of a photochemical model. We have performed these calculations with a one-dimensional photochemical model with the chemistry of oxygen, hydrogen and nitrogen species and vertical eddy diffusion [9]. Figure 1 shows the calculated mixing ratio for the following oxygen/hydrogen/nitrogen atmospheric species: N_2, O_2, CO, H_2, H_2O, H_2O_2, HO_2, OH, N_2O, NO, NO_2, O, $O(^1D)$ and O_3 from the surface to 100 km for the present-day Mars atmosphere. For these calculations, the lower boundary values of N_2, O_2, CO and H_2 are fixed to current observed values and the water vapor profile is specified [9].
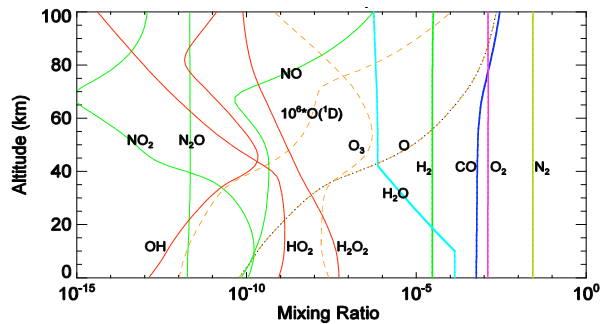
Figure 1. Calculated vertical distribution of trace gases in the atmosphere of Mars from the surface to 100 km [9].

The Early Atmosphere of Mars: There is considerable speculation that in its early history, the mass of the atmosphere of Mars was considerably greater than the present-day atmosphere. Subsequently, Mars lost a significant amount of its original atmosphere via the "sand blasting" effect of the solar wind, once Mars lost its planetary dipole magnetic field, which originally protected the atmosphere from the solar wind [10]. To assess the impact of a thicker CO_2 atmosphere on the atmospheric lifetime of SO_2, we have added SO_2 chemistry to the photochemical model [9] and have performed calculations on the atmospheric lifetime of SO_2 for enhanced atmospheric concentrations of CO_2 (1, 2, 10 and 100 times the present atmospheric level of CO_2). The present-day Mars atmospheric density profile of CO_2 and the enhanced CO_2 profiles are shown in Figure 2. The calculated,
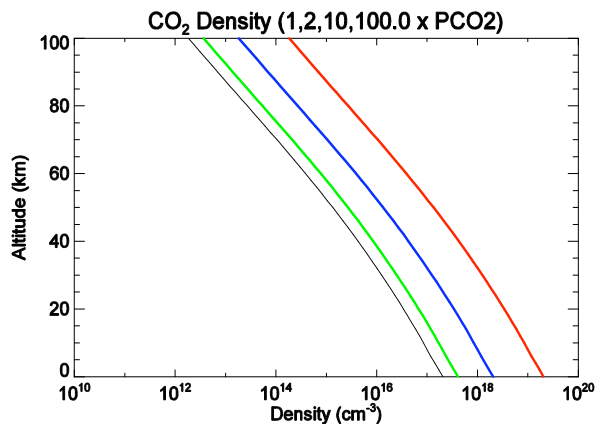

Figure 2. The vertical distribution of CO_2 density in the atmosphere of Mars from the surface to 100 km for CO_2 = 1, 2, 10 and 100x present atmospheric level.

atmospheric lifetime for SO_2 for the present-day CO_2 level and for enhanced atmospheric levels of CO_2 is shown in Figure 3. The calculations shown in Figure 3 indicate that the lifetime of SO_2 in the lower atmosphere of Mars increases significantly as the CO_2 content of the atmosphere increases. The lifetime of SO_2 increased from about 6 x 10^4 sec. (less than a day) to more than 10^8 sec. (more than 6 years) as the atmospheric CO_2 level increases from the present-day level to 100 times the present-day level. These calculations indicate that SO_2 remains in the atmosphere for a very long time,
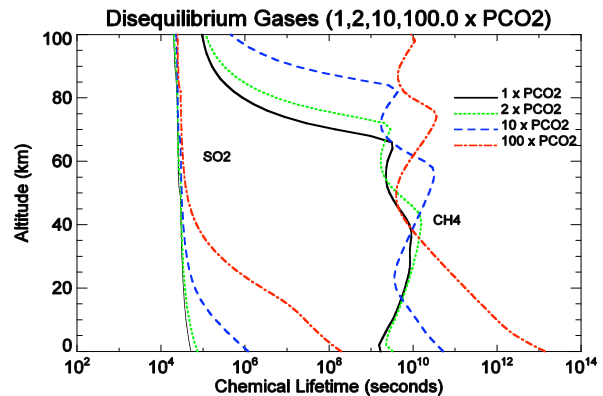

Figure 3. The atmospheric lifetime of SO_2 and CH_4 in the atmosphere of Mars from the surface to 100 km for CO_2 = 1, 2, 10 and 100x present atmospheric level.

thereby, allowing SO_2 to be converted to H_2SO_4. The H_2SO_4 eventually precipitates out of the atmosphere in droplets.

Calculations for the atmospheric lifetime of CH_4 for the present-day CO_2 level and for enhanced levels of CO_2 are also included on Figure 3. There is great interest in the possibility that CH_4, a gas of potential biogenic origin may exist in the atmosphere of Mars [11, 12, 13]. The photochemical calculations indicate that the atmospheric lifetime of CH_4 increases from about 2 x 10^9 sec. (several hundred Earth years) to about 10^{13} sec. (more than $3x10^5$ Earth years) as the atmospheric CO_2 level increases from the present-day level to 100 times the present-day level. The variation with altitude of the two major loss processes for atmospheric SO_2, photolysis (reactions 5-7) and reaction with OH (reaction 8) for the present atmospheric level of CO_2 (1 x PCO_2) and 100
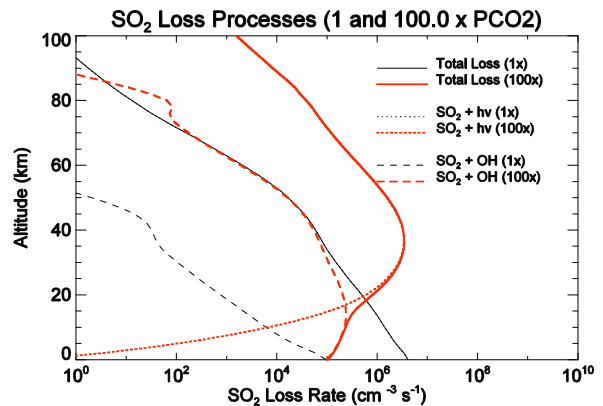

Figure 4. Loss processes for SO_2 in the atmosphere of Mars from the surface to 100 km for CO_2 = 1 and 100x present atmospheric level of CO_2.

times the present atmospheric level (100 x PCO_2) is shown in Figure 4. These calculations show that in the present Mars atmosphere, the loss of SO_2 at all altitudes is controlled by photolysis by solar ultraviolet radiation. However, for enhanced levels of atmospheric CO_2, photolysis is the dominant SO_2 loss process only at high altitudes and at lower altitudes, the loss of SO_2 is controlled by the reaction with OH.

Conclusion: In the early history of Mars, volcanic activity associated with the formation of the Tharsis ridge produced a very large amount of atmospheric SO_2--on the order of a bar of atmospheric SO_2. In the present-day atmosphere of Mars, the lifetime of SO_2 is relatively short with a lifetime of less than a day. The short lifetime of SO_2 in the present Mars atmosphere makes the production of significant levels of H_2SO_4 very difficult since the SO_2 may be destroyed by various chemical and photochemical processes before the SO_2 can be converted to H_2SO_4. However, photochemical calculations performed and described here, indicate that enhanced atmospheric levels of CO_2 in the early atmosphere of Mars resulted in a significantly enhanced atmospheric lifetime for SO_2 — up to several years. With a significantly enhanced atmospheric lifetime, SO_2 could readily form large amounts of H_2SO_4, which precipitated out of the atmosphere in the form of droplets. The precipitated H_2SO_4 then reacted with potential surface carbonates, destroying the carbonates and resulting in the abundant and widespread distribution of sulfates on the surface of Mars as detected by recent Mars missions.

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