

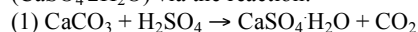
## SULFUR DIOXIDE AND THE PRODUCTION OF SULFURIC ACID ON PRESENT-DAY AND EARLY MARS: IMPLICATIONS FOR THE LACK OF DETECTED CARBONATES ON THE SURFACE.

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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 ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and anhydrate sulfate ( $\text{CaSO}_4$ ), 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 ( $\text{H}_2\text{SO}_4$ ) in solution, which leads to the formation of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) via the reaction:

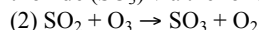


**Volcanic Sulfur:** Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is readily formed via atmospheric chemical reactions from sulfur dioxide ( $\text{SO}_2$ ), an important component of volcanic emissions. To-date, attempts to detect sulfur dioxide and other sulfur compounds in the present-day atmosphere 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 ( $\text{H}_2\text{O}$ ) and carbon dioxide ( $\text{CO}_2$ ), sulfur dioxide ( $\text{SO}_2$ ) is the most abundant gaseous component of Hawaiian volcanic emissions [7]. The chemical composition of volcanic emissions in percent of gaseous emissions are  $\text{H}_2\text{O}$ :  $\text{CO}_2$ :  $\text{SO}_2$  is 79.31%: 11.61%: 6.48% [7].

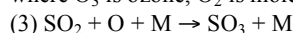
How much  $\text{SO}_2$  was produced on early Mars? Estimates for the amount of  $\text{SO}_2$  in the early atmosphere of Mars may be made by considering the release of magma and its accompanying gaseous emissions during the Tharsis formation [8]. Phillips et al. [8] have estimated that volcanism associated with the Tharsis formation produced about  $3 \times 10^8 \text{ km}^3$  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  $\text{CO}_2$  (assuming a  $\text{CO}_2$  content of 0.65 wt %) [8]. The weight percentage for  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are consistent with Hawaiian basaltic lavas. The release of  $\text{SO}_2$  to the atmosphere associated with the Tharsis formation may be estimated by using the ratio of volcanic emissions of  $\text{H}_2\text{O}$ :  $\text{CO}_2$ :  $\text{SO}_2$  for Hawaiian volcanoes [7] with the estimates of the magma and the accompanying gaseous  $\text{H}_2\text{O}$  and  $\text{CO}_2$  released to the atmosphere [8]. The release of  $\text{SO}_2$  to the atmosphere associated with the Tharsis formation produced on the order

duced on the order of a 1-bar  $\text{SO}_2$  atmosphere on Mars, which is comparable to the mass of the Earth's present-day atmosphere. This is an enormous quantity of atmospheric  $\text{SO}_2$ , which potentially could produce an enormous quantity of  $\text{H}_2\text{SO}_4$  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  $\text{SO}_2$  leads to the formation of  $\text{H}_2\text{SO}_4$  in the atmosphere of Mars via the intermediate production of sulfur trioxide ( $\text{SO}_3$ ) via the following chemical reactions:

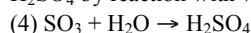


where  $\text{O}_3$  is ozone,  $\text{O}_2$  is molecular oxygen, and

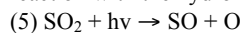


where  $\text{O}$  is atomic oxygen and  $\text{M}$  is any third body, usually  $\text{CO}_2$ .

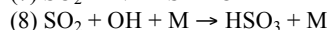
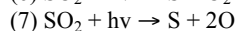
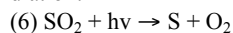
The  $\text{SO}_3$  formed in reactions (2) and (3) is converted to  $\text{H}_2\text{SO}_4$  by reaction with water vapor ( $\text{H}_2\text{O}$ ):



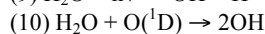
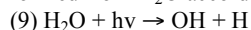
The environment associated with volcanic activity is very water-rich with abundant volcanic water in both gaseous and liquid phases. Sulfuric acid is very water-soluble and readily precipitates out of the atmosphere in the form of water droplets. However,  $\text{SO}_2$  is also destroyed via photolysis by solar ultraviolet radiation (Reactions 5-7) and by chemical reaction with the hydroxyl radical ( $\text{OH}$ ) (Reactions 8):



where  $h$  is Planck's constant and  $\nu$  is the frequency solar radiation.



The hydroxyl radical needed in reaction (8) is readily formed from  $\text{H}_2\text{O}$  according to the reactions:



where  $\text{O}(^1\text{D})$  is excited atomic oxygen.

The balance between  $\text{SO}_2$  forming  $\text{H}_2\text{SO}_4$  (reactions 2-4) and  $\text{SO}_2$  being destroyed via photolysis (reactions 5-7) and via chemical reaction with  $\text{OH}$  (reactions 8) and not forming  $\text{H}_2\text{SO}_4$  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:  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HO}_2$ ,  $\text{OH}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{O}$ ,  $\text{O}(^1\text{D})$  and  $\text{O}_3$  from the surface to 100 km for the present-day Mars atmosphere. For these calculations, the lower boundary values of  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}$  and  $\text{H}_2$  are fixed to current observed values and the water vapor profile is specified [9].

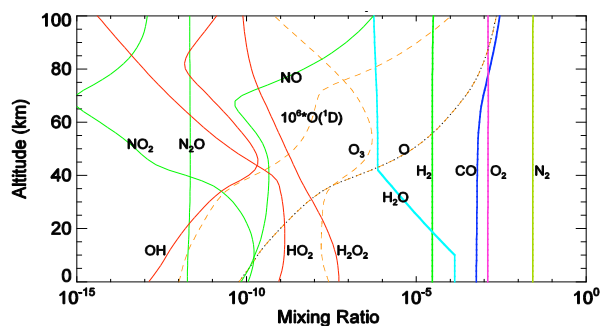


Figure 1. Calculated vertical distribution of trace gases in the atmosphere of Mars from the surface to 100 km [9].

**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  $\text{CO}_2$  atmosphere on the atmospheric lifetime of  $\text{SO}_2$ , we have added  $\text{SO}_2$  chemistry to the photochemical model [9] and have performed calculations on the atmospheric lifetime of  $\text{SO}_2$  for enhanced atmospheric concentrations of  $\text{CO}_2$  (1, 2, 10 and 100 times the present atmospheric level of  $\text{CO}_2$ ). The present-day Mars atmospheric density profile of  $\text{CO}_2$  and the enhanced  $\text{CO}_2$  profiles are shown in Figure 2. The calculated,

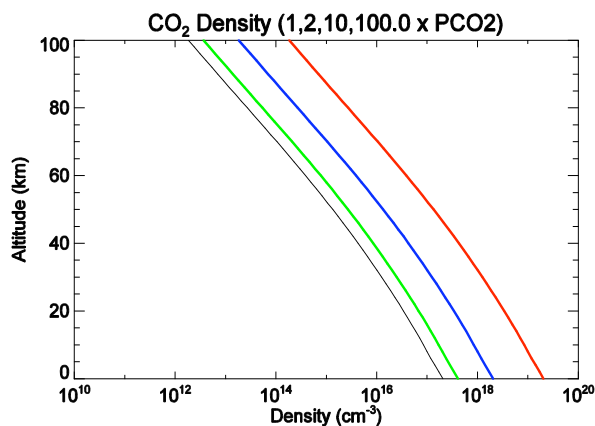


Figure 2. The vertical distribution of  $\text{CO}_2$  density in the atmosphere of Mars from the surface to 100 km for  $\text{CO}_2 = 1, 2, 10$  and  $100x$  present atmospheric level.

atmospheric lifetime for  $\text{SO}_2$  for the present-day  $\text{CO}_2$  level and for enhanced atmospheric levels of  $\text{CO}_2$  is shown in Figure 3. The calculations shown in Figure 3 indicate that the lifetime of  $\text{SO}_2$  in the lower atmosphere of Mars increases significantly as the  $\text{CO}_2$  content of the atmosphere increases. The lifetime of  $\text{SO}_2$  increased from about  $6 \times 10^4$  sec. (less than a day) to more than  $10^8$  sec. (more than 6 years) as the atmospheric  $\text{CO}_2$  level increases from the present-day level to 100 times the present-day level. These calculations indicate that  $\text{SO}_2$  remains in the atmosphere for a very long time,

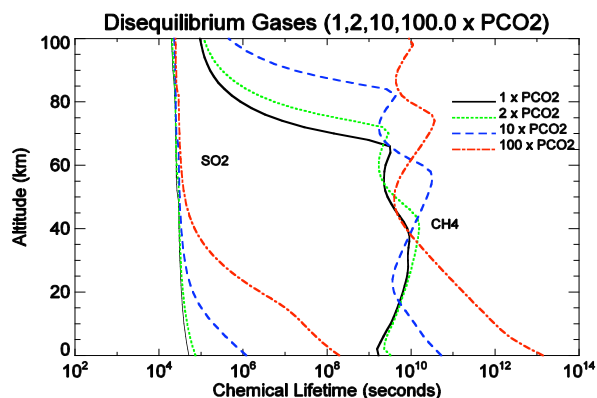


Figure 3. The atmospheric lifetime of  $\text{SO}_2$  and  $\text{CH}_4$  in the atmosphere of Mars from the surface to 100 km for  $\text{CO}_2 = 1, 2, 10$  and  $100x$  present atmospheric level.

thereby, allowing  $\text{SO}_2$  to be converted to  $\text{H}_2\text{SO}_4$ . The  $\text{H}_2\text{SO}_4$  eventually precipitates out of the atmosphere in droplets.

Calculations for the atmospheric lifetime of  $\text{CH}_4$  for the present-day  $\text{CO}_2$  level and for enhanced levels of  $\text{CO}_2$  are also included on Figure 3. There is great interest in the possibility that  $\text{CH}_4$ , 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  $\text{CH}_4$  increases from about  $2 \times 10^9$  sec. (several hundred Earth years) to about  $10^{13}$  sec. (more than  $3 \times 10^5$  Earth years) as the atmospheric  $\text{CO}_2$  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  $\text{SO}_2$ , photolysis (reactions 5-7) and reaction with OH (reaction 8) for the present atmospheric level of  $\text{CO}_2$  (1  $\times$   $\text{PCO}_2$ ) and 100

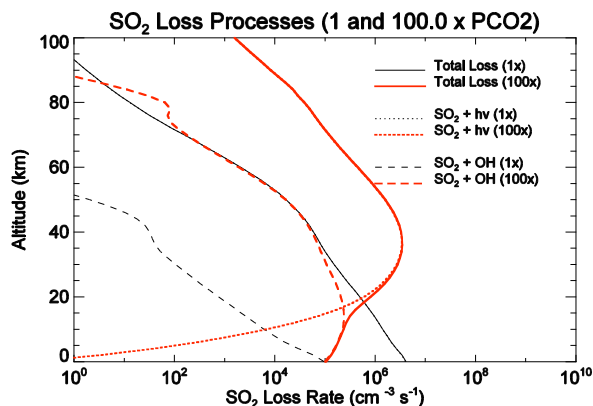


Figure 4. Loss processes for  $\text{SO}_2$  in the atmosphere of Mars from the surface to 100 km for  $\text{CO}_2 = 1$  and  $100x$  present atmospheric level of  $\text{CO}_2$ .

times the present atmospheric level (100  $\times$   $\text{PCO}_2$ ) is shown in Figure 4. These calculations show that in the present Mars atmosphere, the loss of  $\text{SO}_2$  at all altitudes is controlled by photolysis by solar ultraviolet radiation. However, for enhanced levels of atmospheric  $\text{CO}_2$ , photolysis is the dominant  $\text{SO}_2$  loss process only at high altitudes and at lower altitudes, the loss of  $\text{SO}_2$  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  $\text{SO}_2$ —on the order of a bar of atmospheric  $\text{SO}_2$ . In the present-day atmosphere of Mars, the lifetime of  $\text{SO}_2$  is relatively short with a lifetime of less than a day. The short lifetime of  $\text{SO}_2$  in the present Mars atmosphere makes the production of significant levels of  $\text{H}_2\text{SO}_4$  very difficult since the  $\text{SO}_2$  may be destroyed by various chemical and photochemical processes before the  $\text{SO}_2$  can be converted to  $\text{H}_2\text{SO}_4$ . However, photochemical calculations performed and described here, indicate that enhanced atmospheric levels of  $\text{CO}_2$  in the early atmosphere of Mars resulted in a significantly enhanced atmospheric lifetime for  $\text{SO}_2$ —up to several years. With a significantly enhanced atmospheric lifetime,  $\text{SO}_2$  could readily form large amounts of  $\text{H}_2\text{SO}_4$ , which precipitated out of the atmosphere in the form of droplets. The precipitated  $\text{H}_2\text{SO}_4$  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.

**References:** [1] Banin, A. (2005) *Science* 309, 888-890. [2] Squyres et al. (2004) *Science* 306, 1709-1714. [3] Bibring, J.-P., et al. (2005) *Science* 307, 1576-1581. [4] Gendrin, A. et al. (2005) *Science* 307, 1587-1591. [5] Langevin, Y. et al. (2005) *Science* 307, 1584-1586. [6] Krasnopolsky, V. A. (2005) *Icarus* 178, 487-492. [7] Holland, H. D. (1978) *The Chemistry of the Atmosphere and Oceans*, John Wiley and Sons, New York, p. 289. [8] Phillips, R. J. et al. (2001) *Science* 291, 2587-2591. [9] Summers, M. et al. (2003) *Geophys. Res. Lett.*, 29, 2171-2174. [10] Jakosky, B. M. and Phillips, R. J. (2002) *Nature*, 42, 237. [11] Formisano, V. et al. (2004) *Science* 306, 1758-1761. [12] Mumma, M. J. et al. (2004) American Astronomical Society Division of Planetary Science Meeting, 36, 26.02. [13] Krasnopolsky et al. (2004) *Icarus* 172, 537-547.