

SULFUR VOLATILES IN THE EARLY MARTIAN ATMOSPHERE. S. S. Johnson¹, M. T. Zuber¹, T. L. Grove¹, A. A. Pavlov², and M. A. Mischna³, ¹Department of Earth, Atmospheric and Planetary Science, Massachusetts Institute of Technology, 77 Massachusetts Avenue, 54-810, Cambridge, MA 02139, ssj@mit.edu, ²Lunar and Planetary Laboratory, Department of Planetary Sciences, Space Sciences 401, University of Arizona, Tucson, AZ 85721, ³Jet Propulsion Laboratory, M/S 183-401, 4800 Oak Grove Drive, Pasadena, CA 91109.

Introduction: Data recently returned from Mars spacecraft suggest that sulfur chemistry may have played a prominent role in the planet's early evolution. Although the Martian atmosphere contains virtually no sulfur species at present, both soils and outcrop observed by landed missions have high sulfate abundances [1,2]. The OMEGA hyperspectral imager has also identified sulfates from orbit on localized layered terrains that extend beyond these landing sites [3].

Degassed sulfur volatiles can act as powerful greenhouse gases and may have been important atmospheric components during periods of enhanced volcanic activity on Mars [4,5]. Isotopic analyses in Martian meteorites further support this view, reflecting deposition of sulfur species created by atmospheric chemical reactions [6].

Here we present results from a model for sulfur delivery to the Martian surface and its potential atmospheric effects.

Sulfur Volatile Release: Volatile degassing associated with the formation of the Tharsis igneous province, a volume of 3×10^8 km³ thought to be largely emplaced by the end of the Noachian [7], almost certainly affected the early climate. Yet it remains unclear to what extent the more deeply intruded magma in the Tharsis province communicated with the atmosphere. For this reason, we explore the consequences of sulfur volatiles on climate following large, discrete volcanic events.

Sulfur solubility: Using a batch melting model we obtain a high sulfur solubility in Martian silicate melts in equilibrium with metal sulfide [8]. Because of the unique negative pressure dependence for sulfur solubility that dominates the positive temperature dependence in systems that contain FeO, magma from mantle source regions in this model will arrive at the base of the lithospheric lid undersaturated in sulfur regardless of ascent velocity and melt fraction volume [9].

At that stage a final equilibration will take place before the liquid melt is advected to the planet's surface. While significant cooling in passage through the crust could affect the Sulfur Solubility Limit (SSL), here we assume that chemical and thermal halo effects insulate the magma. In calculating the SSL in liquid silicate conditions, we use the formula:

$$\ln(SSL) = \frac{A}{T} + B + C \left(\frac{P}{T} \right) + D \cdot nbo/t + \ln a_{FeS}^{sulfide}$$

SSL is in ppm, T in Kelvin, and P in bars [9]. Constants A , B , C and D are derived from a fit to experimental data [10]. nbo/t , the ratio of non-bridging oxygen anions to tetrahedrally coordinated cations, is found using APXS compositional results from Gusev Crater basalts [11]. The value $a_{FeS}^{sulfide}$ is taken to be ~ 1 as metallic sulfides are close to stoichiometric FeS in experimental results [1,10]. Petrology experiments on a Gusev basalt composition document a three-phase multiple saturation of ol + opx + spi near the liquidus at 10 kbars and 1583 K [12], giving rise to a high sulfur solubility of ~ 1400 ppm.

Tharsis-radial dikes: We investigate two models for the volume of lava thought to be rapidly emplaced by dike intrusions associated with Tharsis-radial graben: a lower bound "Hanna Model," 1500 km³ [13]; and an upper bound "Wilson Model," 60,000 km³ [14]. Volatiles associated with the emplacement of these wide dikes were released quickly, aided by convective overturn in forming collapse craters and generating explosive eruptions, as likely in the Memnonia Fossa region [15].

Radiative Effects: For both H₂S and SO₂ end-members for the exsolved sulfur volatiles associated with these volcanic events, we find the additional greenhouse warming from absorption in wavelength windows complimentary to CO₂. We use *Mars-WRF* [16], a three-dimensional GCM adapted for Martian conditions, to investigate sulfur volatile influxes into 50 mb and 500 mb background CO₂ atmospheres at 50% relative humidity. We follow a correlated-k approach to calculating atmospheric absorption for an atmosphere of variable CO₂ and H₂O abundance and fixed H₂S or SO₂ abundance (associated with "Wilson" or "Hanna" volumes in a 50 or 500 mb atmosphere). A conservative figure of 75% present-day solar luminosity was incorporated into our model although recent work suggests that past solar luminosity may have been higher [17].

The GCM operates at a resolution of $5^\circ \times 5.625^\circ$ with 25 vertical, terrain-following levels of increasing thickness with height. The vertical extent of the domain reaches to ~ 90 km. Surface albedo and thermal inertia are derived from TES observations.

Results suggest that large-scale sulfur volatile release in the early Martian atmosphere may have gen-

erated additional atmospheric heating of up to 15 K for H₂S pulses and 25 K for SO₂ pulses (Fig. 1), and localized conditions conducive to the presence of transient liquid water (Fig. 2).

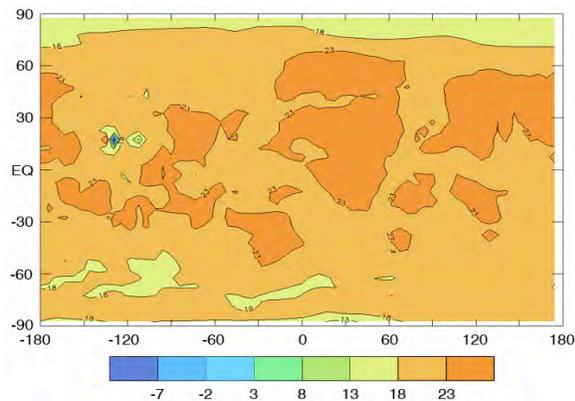


Figure 1. Additional greenhouse warming created by a “Wilson” level SO₂ pulse into a 500 mb CO₂ atmosphere (concentrated in the Northern lowlands as there is more atmosphere above those regions).

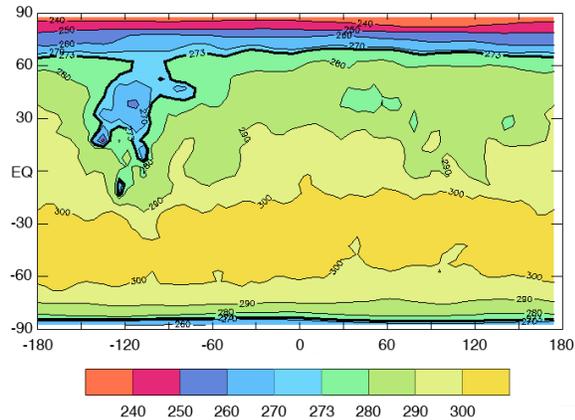


Figure 2. Annual maximum temperatures following a “Wilson” level SO₂ pulse into a 500 mb CO₂ atmosphere (highest levels in the southern highlands as Mars is closer to the sun in southern summer). The bold contour line is at 273K.

Timescales for Greenhouse Warming: To ascertain timescales for these warming events, we used a one-dimensional photochemical model developed for sulfur chemistry simulations in the Archean Earth atmosphere [18-20]. The model is divided into 100 vertical layers, each 2km in height, and includes 72 chemical species involved in 359 chemical reactions. At each layer, the continuity equation is solved for long-lived species, including transport by eddy and molecular diffusion.

For Mars, we set gravity to 373 cm/s², albedo to 0.215, and the tropopause to 15km. We employed a terrestrial eddy diffusion profile adjusted by the

square root of density for the Martian atmosphere. Rainout rates were determined by the parameterization of Giorgi and Chaimeides and scaled (down to a factor of 1/1000) to account for a less vigorous Martian hydrologic cycle [21]. The solar flux was modified to match UV rates at Mars in the distant past [22]. The vertical temperature profile was taken from our radiative transfer steady state simulation results.

Under weakly reducing conditions, we found that a “Wilson” level SO₂ volatile pulse into a thick CO₂ atmosphere would have persisted in the form of SO₂ for at least 500-5000 Martian years before conversion to sulfate aerosols, gravitational settling, and surface deposition. Additional photochemical modeling is underway.

Conclusions and Implications: It appears that large, episodic releases of sulfur volatiles early in Martian history may have generated short-lived but potent greenhouse warming events. We hypothesize that degassed sulfur volatiles, and the subsequent formation of sulfuric acid aerosols in the atmosphere, may have been responsible for: 1) producing dispersed sulfate platforms and ubiquitous sulfur-rich dust, 2) creating low enough pH levels to prevent surface carbonate formation on a global scale, and 3) generating the transient warm climate conditions prerequisite for presence of fluvial features on the Martian surface.

References: [1] Owen, T. *et al.*, in Mars (1992) 822. [2] Feldman, W.C. *et al.*, (2004) *GRL*, 31, L16702. [3] Gendrin, A.N. *et al.* (2005) *Science* 307 (5715), 1587-1591. [4] Postawko, S.E. and Kuhn, W.R. (1986) *JGR*, 91, D431-438. [5] Settle, M. (1979) *JGR*, 84, 8343-8354. [6] Farquhar, J. *et al.* (2000) *Nature*, 404, 50. [7] Phillips, R.J. *et al.* (2001) *Science*, 291, 2587-2591. [8] Johnson, S.S. *et al.* (2006) LPS XXXVII Abstract #2094. [9] Holzheid, A. & Grove, T.L. (2002) *American Mineralogist*, 87, 227-237. [10] Mavrogenes, J.A. & O’Neill, H.St.C. (1999) *Geochimica et Cosmochimica Acta*, 63, 1173-1180. [11] McSween, H.Y. *et al.*, (2006) *JGR*, 111, E02S19. [12] Monders, A.G. *pers. comm.* [13] Hanna, J. *pers. comm.* [14] Wilson, L. & Head, J. W. (2002) *JGR*, 107, 5057. [15] Scott, E.D. and Wilson, L. (2002) *JGR*, 107, 5020. [16] Mischna, M.A. *et al.*, 2nd MAtMO Conf, Granada (2006). [17] Wood, B. E. *et al.* (2002) *Astrophys. J.*, 574, 412-425. [18] Pavlov, A. A. *et al.*, (2000), *JGR*, 105, 11,981-11,990. [19] Pavlov, A. A. *et al.*, (2001), *JGR*, 106, 23,267-23,287. [20] Pavlov, A.A and Kasting, J.F., (2002) *Astrobiology*, 2(1), 27-41. [21] Giorgi, F. and Chameides, W.L. (1985), *JGR*, 90, 7872-7880. [22] Ribas, I. *et al.*, (2005), *Astrophysical Journal*, 622, 680-694.