

SULFUR-RELATED GREENHOUSE WARMING ON EARLY MARS. S. S. Johnson¹, M. T. Zuber¹, T. L. Grove¹, and M. A. Mischna², ¹Department of Earth, Atmospheric and Planetary Science; Massachusetts Institute of Technology; 77 Massachusetts Avenue, 54-810; Cambridge, MA 02139; ssj@mit.edu, ²Jet Propulsion Laboratory, 4800 Oak Grove Drive; Pasadena, CA 91109-8099 M/S 183-401, michael.a.mischna@jpl.nasa.gov

Introduction: A building body of evidence from recent Mars exploration missions suggests 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 now also identified sulfates from orbit on localized layered terrains that extend far beyond these landing sites [3].

Outgassed sulfur volatiles can act as powerful greenhouse gases and may have been important 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 a preliminary model for sulfur delivery to the early Martian atmosphere and its potential warming effects. Degassed sulfur species, and the subsequent formation of sulfuric acid aerosols in the atmosphere, may have been responsible for: 1) producing ubiquitous sulfur-rich dust and widely dispersed sulfate platforms, 2) creating low enough pH levels to allow for jarosite deposition at Meridiani and the prevention of surface carbonate formation on a global scale, and 3) generating short-lived warmer climate conditions that allow for the presence of fluvial features on the Martian surface.

Sulfur Solubility Calculations: A batch melting model, in which decompression melting of the mantle takes place with the solid residue staying with the melt during most of its ascent, is used to assess the sulfur solubility in Martian silicate melts in equilibrium with metal sulfide. 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 [7]. When decompression melting commences, sulfur from immiscible metal sulfide blebs will begin and continue to dissolve directly into the silicate melt. At the base of the lithospheric lid, a final equilibration will take place before the liquid melt is advected to the planet's surface, at which point the remaining metal sulfide blebs will largely be left behind. 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 along cracks and in magma chambers. As

surface temperature and pressure conditions are well beneath the vapor saturation pressures for both H₂S and SO₂ [8], we assume soluble sulfur can be released to the atmosphere.

In calculating the *SSL* in liquid silicate conditions, we use the formula [7]:

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

SSL is in ppm, *T* in Kelvin, and *P* in bars. Constants *A*, *B*, *C* and *D* are derived from a fit to experimental data [1]. The value $a_{FeS}^{sulfide}$ is taken to be ~1 as metallic sulfides are close to stoichiometric FeS in experimental results [1,9]. *nbo/t*, the ratio of non-bridging oxygen anions to tetrahedrally coordinated cations (a measure of the degree of polymerization in the silicate), is found using APXS compositional results from Gusev Crater basalts [10].

Petrology experiments on a Gusev basalt composition document a three-phase multiple saturation of olivine + orthopyroxene + spinel near the liquidus at 10 kbars and 1583 K [11]. This finding suggests that the Gusev basalts either were generated or were last in equilibrium with mantle minerals not far below the ~50 km thick crust [12]. The resulting sulfur solubility, incorporating this temperature and pressure, is ~1400 ppm.

Volatile Release Rate: The volume of the magma associated with the Tharsis igneous province, thought to be largely emplaced by the end of the Noachian, is approximately 300 x 10⁶ km³ [13]. Although degassed volatiles associated with this magma emplacement certainly affected the early climate, it remains unclear to what extent the more deeply intruded magma in the Tharsis province could have communicated with the atmosphere. For this reason we chose to explore the consequences of sulfur volatiles on climate following large, discrete volcanic events. Analyzing dike intrusions associated with Tharsis-radial graben, Wilson and Head [14] estimated that a single giant dike intruded radial to a Tharsis volcano would inject 20,000 to 60,000 km³ of magma over as little as 20 hours. Gases are thought to segregate up to the top of these dikes forming collapse craters and/or generating explosive eruptions, as likely in the Memnonia Fossa region [15]. Convective overturn in wide dikes (>100m) may also enhance the process of volatile release.

We assume degassing occurred on timescales much shorter than the residence time of sulfur volatiles, which is broadly envisaged to be on the order of

one thousand Earth days in a volcanically perturbed Martian atmosphere [5]. The density of the Gusev basalt magma is calculated as 2820 kg/m^3 using the method of Bottinga and Weill [16]. In our atmospheric calculations we consider both H_2S and SO_2 endmembers for exsolved sulfur species (~ 1 to $\sim 3 \times 10^{14} \text{ kg H}_2\text{S}$ or ~ 2 to $\sim 6 \times 10^{14} \text{ kg of SO}_2$) associated with a pulse of 20,000 to 60,000 km^3 of magma emplacement.

Greenhouse Warming Effects: The simulations used to evaluate the consequences of sulfur volatiles on greenhouse warming were performed using a one-dimensional radiative transfer model adapted for the early Martian atmosphere.

The model atmosphere is comprised of 25 layers with the greatest resolution occurring near the surface. The overall radiative equilibrium is determined by the transmission spectra of these different atmospheric layers. Arrays of absorption coefficients for chosen gas mixtures across a predetermined matrix of temperatures and pressures are calculated off-line and stored in look-up tables (LUTs). The LUTs then describe the atmospheric properties associated with carbon dioxide atmospheres having small amounts of SO_2 or H_2S . (Other components of the Martian atmosphere, including nitrogen and argon, are not significantly active in the visible-IR region of the spectrum.) Because traditional line-by-line radiative calculations are computationally intensive, we use the “correlated-k” method to approximate absorption within discrete spectral bands covering the entire visible-IR spectrum [17].

The model takes into account the effects of convective overturning and vertical mixing. Initial and surface conditions are from [18], and represent typical mid-latitude conditions. A conservative figure of 75% luminosity was incorporated into our model although recent work suggests that solar luminosity may have been higher [19]. A conservative surface pressure, 50 mbar of CO_2 into which our sulfur gases are released, was chosen for this study. Results suggest that large-scale sulfur volatile release in the early Martian atmosphere may have generated up to a 20K greenhouse warming effect, depending on the amount and species of sulfur gas (see Figure 1).

Conclusions and Implications: There is striking evidence for stable liquid water and/or near-surface groundwater on ancient Mars in the form of high erosion rates during the Noachian and the presence and early age of dendritic valley networks. We hypothesize that large, episodic releases of sulfur volatiles early in the history of the planet, a scenario that accords well with recent Mars mission findings, may have contributed to the generation of sufficient warming for this to occur. The Martian sulfur cycle

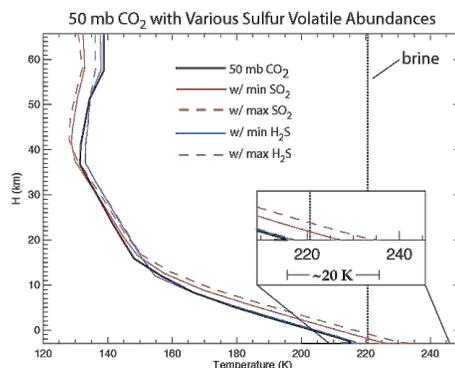


Figure 1. Annually averaged surface temperature for a 50 mb CO_2 atmosphere with and without an SO_2 or H_2S contribution. Included for reference is the freezing point of a possible Martian brine [20].

appears to play a focal role in our understanding of the planet, particularly its geology, climate, and even life: it has been postulated that the subsequent deposition of oxidized sulfur species from the atmosphere could establish chemical potential gradients in the near surface environment, serving as a possible energy source for chemolithoautotrophic organisms [6]. Areas for future work include more detailed climate modeling, alternative avenues of magma delivery, and the incorporation of water, both in the melt and in the atmosphere.

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] Holzheid, A. and Grove, T.L. (2002) *American Mineralogist*, 87, 227-237. [8] Lemmon, E.W. *et al.* (2005) NIST Standard Reference Database Number 69, (<http://webbook.nist.gov>). [9] Mavrogenes, J.A. and O'Neill, H.St.C. (1999) *Geochimica et Cosmochimica Acta*, 63, 1173-1180. [10] McSween, H.Y. *et al.*, (2006) *JGR*, 111, E02S19. [11] Monders, A.G. *personal communication*. [12] Zuber, M.T. (2001) *Nature*, 412, 220-227. [13] Phillips, R.J. *et al.* (2001) *Science*, 291, 2587-2591. [14] Wilson, L. and Head, J.W. (2002) *JGR*, 107, 5057. [15] Scott, E.D. and Wilson, L. (2002) *JGR*, 107, 5020. [16] Greeley, R. *et al.* (2005) *JGR*, 110, E05008. [17] Lacy A.A. and Oinas, V., (1991), *JGR*, 96, 9027-9063. [18] Haberle, R.M. *et al.* (1993) *J. Atmos. Sci.*, 50, 1544-1559. [19] Wood, B. E. *et al.* (2002) *Astrophys. J.*, 574, 412-425. [20] Burt, D.M. *et al.* (2002) *LPS XXXII*, Abstract #1240.