

**THE ROLE OF SO<sub>2</sub> IN THE CLIMATE AND GEOCHEMISTRY OF EARLY MARS.** I. Halevy<sup>1</sup>, D. P. Schrag<sup>1</sup> and R. T. Pierrehumbert<sup>2</sup>, <sup>1</sup>Earth and Planetary Sciences, Harvard University, <sup>2</sup>Geophysical Sciences, University of Chicago.

**Introduction:** The prolonged existence of liquid water, perhaps even a northern hemisphere ocean [1], prior to ~3.8 billion year ago [2], and the mineralogy detected on the surface of Mars raise several questions. First, it is unclear how conditions warm enough for the existence of liquid water (or most imaginable brines) were maintained. This is because previous radiative modeling has shown that during the Noachian epoch, when the Sun was only ~75% as luminous as it is today [3], no amount of CO<sub>2</sub> on its own would have been sufficient [4]. This suggests that another atmospheric constituent may have been important during this time, either as a greenhouse agent [5], or as a solar absorber, warming the middle atmosphere and preventing CO<sub>2</sub> condensation [6].

In addition to the problem of getting surface temperatures close to the freezing point of water, an apparent paradox in the mineralogical record is the existence of Noachian clays [7] but the absence of carbonate minerals at exposure abundances anywhere on the planet [8]. The problem with this observation is that under the conditions suitable for clay formation, carbonates are expected to be abundant byproducts of silicate weathering under a CO<sub>2</sub>-rich atmosphere [9].

**The Role of Sulfur Volcanic Emissions:** A possible role for sulfur in resolving these issues is suggested by its prevalence in Martian soils [10]. We have recently proposed that volcanically emitted SO<sub>2</sub> may have played an important role in early Martian climate and in the aqueous chemistry that gave rise to the observed mineral assemblage [11]. We have shown that even small atmospheric concentrations of SO<sub>2</sub> could have inhibited precipitation of carbonate minerals in favor of sulfite (SO<sub>3</sub><sup>2-</sup>) minerals (figure 1) at mildly acidic pH, allowing the formation of clays. Furthermore, we proposed that a negative feedback involving the atmospheric abundance of SO<sub>2</sub> and saturation of sulfite minerals may have regulated early Martian climate instead of the analogous feedback involving CO<sub>2</sub>, which regulates climate on the modern Earth [9].

In a history of Mars based on the above, early volcanic emissions rich in SO<sub>2</sub> and H<sub>2</sub>S depleted the atmosphere of oxidants and resulted in saturation of the surface of Mars with these gases. The resulting higher steady state atmospheric concentration of SO<sub>2</sub> would have augmented a CO<sub>2</sub>-rich greenhouse, helping to maintain surface temperatures close to the freezing point of water. The aqueous chemistry of SO<sub>2</sub> would have resulted in the precipitation of sulfite minerals at

the expense of carbonates, while allowing the formation of clays. When volcanism subsided, the SO<sub>2</sub> was quickly removed from the atmosphere, surface temperatures plummeted and surface weathering arrested. The thick CO<sub>2</sub> atmosphere was subsequently removed by a combination of subsurface weathering, impact erosion and molecular escape following termination of Mars' magnetic field. With continued hydrogen escape, the surface was gradually oxidized and the sulfites transformed to sulfates, releasing acidity in the process. This history is consistent with many observations of Mars, both on the surface and from orbit.

While this analysis may explain the observed mineral assemblage through the role of SO<sub>2</sub> in the aqueous chemistry, it leaves open the question of the actual contribution of sulfur-volatiles to the radiative budget. Here we present a 1-D Monte-Carlo radiative transfer model, which we will use for a rigorous investigation of the role of volcanic sulfur emissions in regulating early Martian climate, and which may be applied to other problems of planetary climate.

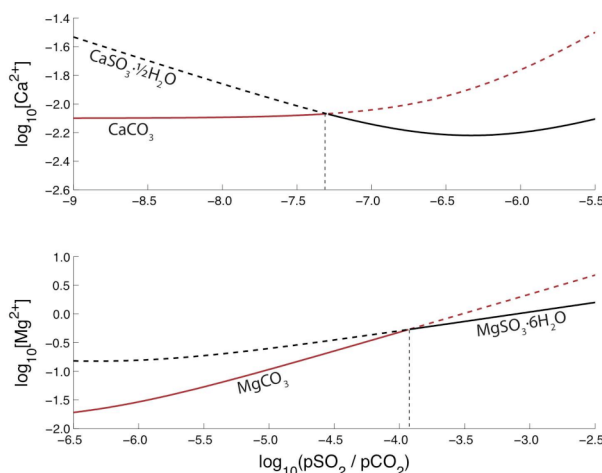


Figure 1: Calcium (top) and Magnesium (bottom) aqueous concentration limits imposed by saturation of sulfite (black) and carbonate (red) minerals as a function of the ratio of the partial pressure of SO<sub>2</sub> to CO<sub>2</sub>. The curves are solid where the mineral represented by them is expected to precipitate, showing that for pSO<sub>2</sub>:pCO<sub>2</sub> ≥ ~5×10<sup>-8</sup> CaCO<sub>3</sub> precipitation is prevented by precipitation of CaSO<sub>3</sub>·½H<sub>2</sub>O and for pSO<sub>2</sub>:pCO<sub>2</sub> ≥ ~1×10<sup>-4</sup> MgCO<sub>3</sub> precipitation is prevented by precipitation of MgSO<sub>3</sub>·6H<sub>2</sub>O.

**1-D Radiative Transfer Model:** Many previous studies of early Martian climate have used various accepted approximations of radiative-convective processes to model the radiative effect of CO<sub>2</sub> [3] as well as other gases, such as CH<sub>4</sub> [5] and SO<sub>2</sub> [6,12,13]. We have constructed a radiative-convective model that does not average molecular absorption over bands (using neither Malkmus or Fels-Goody models [3] nor “correlated-k” [13] methods) and does not assume random overlap between the absorption lines of various atmospheric constituents.

We model radiative transfer with a Monte-Carlo approach, randomly picking a wavenumber within the region of the spectrum important to solar and planetary emission, computing the absorption and scattering cross sections at that wavenumber, integrating the two-stream equations for diffuse radiation and accumulating the fluxes until the error on the estimate is within an acceptable range. The equations include the effect of scattering as well as absorption:

$$\frac{dI_+}{d\tau} = \gamma_2 I_- - \gamma_1 I_+ + \gamma_B \pi B(T(\tau)) + \gamma_+ L_\odot e^{-\frac{\tau_\infty - \tau}{\cos \zeta}} \quad (1)$$

$$\frac{dI_-}{d\tau} = \gamma_1 I_- - \gamma_2 I_+ - \gamma_B \pi B(T(\tau)) - \gamma_- L_\odot e^{-\frac{\tau_\infty - \tau}{\cos \zeta}} \quad (2)$$

where  $I_+$  and  $I_-$  are the upwelling and downwelling diffuse radiation fluxes, respectively.  $\tau$  is the optical depth due to absorption and scattering, increasing from a value of zero at the surface to  $\tau_\infty$  at the top of the atmosphere.  $B$  is Planck’s function,  $L_\odot$  is the incoming solar radiation and  $\zeta$  is the zenith angle. The  $\gamma_i$ ’s are rate coefficients describing the attenuation of radiation due to scattering and absorption and require an assumption about the angular distribution of radiation. A hemi-isotropic approximation was assumed for radiation in the thermal infrared and an Eddington approximation assumed for radiation of shorter wavelength.

The boundary conditions are:

$$I_-(\tau = \tau_\infty) = 0 \quad (3)$$

$$I_+(\tau = 0) = \alpha_s (I_-(\tau = 0) + L_\odot e^{-\frac{\tau_\infty}{\cos \zeta}}) + \pi B(T_g) \quad (4)$$

where  $\alpha_s$  is the surface albedo at the wavenumber considered. Specifically, there is no diffuse downwelling flux at the upper boundary (equation 3), and the diffuse upwelling flux at the lower boundary consists of the reflected diffuse downwelling flux, the reflected solar flux and blackbody radiation from the planetary surface at the ground temperature  $T_g$  (equation 4).

Molecular absorption is computed in the infrared region of the spectrum from the HITRAN [14] line parameters of the atmospheric constituents, including self and foreign pressure broadening. We include continuum absorption of both CO<sub>2</sub> and H<sub>2</sub>O vapor in the infrared. Ultraviolet absorption is calculated by interpolation between measured absorption cross sections [15]. Scattering cross sections are calculated as a function of wavelength from Rayleigh scattering theory.

The spatial divergence of the net flux ( $I_+ - I_-$ ) is used to compute an atmospheric heating rate and drive the atmosphere to radiative equilibrium. A convective adjustment is made wherever the radiative temperature is lower than the moist adiabatic temperature. A similar adjustment is made wherever the radiative or moist adiabatic temperature is lower than the temperature of CO<sub>2</sub> condensation at the local atmospheric pressure.

An advantage of our approach is that the effect of any atmospheric absorber or scatterer, in any region of the electromagnetic spectrum between the ultraviolet and thermal infrared, can be incorporated into the computations by including it as an “atmospheric species”, defining its optical properties and specifying its vertical distribution in the atmosphere (infrared scattering clouds are one such example [16]). Furthermore, the model is applicable to other problems that require a rigorous and careful radiative transfer tool.

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