

A Sulfur Dioxide Climate Feedback on Early Mars. I. Halevy¹, M. T. Zuber² and D. P. Schrag¹, ¹Earth and Planetary Sci., Harvard University, ²Earth, Atmospheric and Planetary Sci., Massachusetts Institute of Technology.

Introduction: Evidence for abundant liquid water on the surface of early Mars [1], is likely explained by existence of a thicker atmospheric greenhouse, which also had to compensate for an early faint sun [2]. 2–10 bar of CO₂ have been shown to provide sufficient radiative forcing [3], although the existence of a thick CO₂ atmosphere above a liquid surface water reservoir should lead to precipitation of carbonate minerals [4], which have yet to be detected at outcrop abundances on the Martian surface [5]. Suggested explanations for the absence of carbonates include highly acidic environments [6], which would have also prevented the formation of recently detected clays [7].

The abundance of sulfur on the Martian surface [8] suggests a possible solution. We propose that volcanic outgassing of SO₂ and H₂S, during the emplacement of the Tharsis igneous province in the late Noachian [9], exceeded the production of atmospheric oxidants and attenuated the solar UV flux, resulting in dramatically extended residence times of both H₂S and SO₂ in the lower atmosphere and surface environment. Since both are IR absorbers in different regions of the spectrum than CO₂, their addition in modest amounts to a CO₂-rich atmosphere would be more radiatively effective than a doubling of CO₂, perhaps enabling above-freezing surface temperatures. Gaseous-aqueous equilibrium of SO₂ would lead to suppression of carbonate mineral precipitation in favor of sulfite and sulfate minerals, while permitting the formation of clays. A climate feedback analogous to the one involving CO₂ on Earth [4] would have existed, with SO₂ as the dominant control on surface temperature, rainfall and surface water pH and with sulfite mineral precipitation as the terminal SO₂ sink.

An early Martian sulfur cycle: SO₂ and H₂S emitted from volcanoes were removed from the surface environment by a combination of photochemical sinks and precipitation of sulfur minerals. The influx of sulfur gases, based on estimates of sulfur solubility in magma [10] and on the volume of Tharsis [9], could have been $\sim 4 \times 10^{11}$ mole S year⁻¹ if emplacement took 10⁸ years (about twice the present terrestrial sulfur outgassing flux into an atmosphere only a quarter of the volume of Earth's atmosphere).

Of the photochemical sinks, gas-phase oxidation would have been small, because in the absence of a biosphere the only source of oxidizing power is hydrogen escape, which is much smaller than the volcanic and hydrothermal emission of reduced gases [11]. Pho-

todissociation of SO₂ could, in the presence of oxidants, end in recombination [12,13] and little net loss, while in their absence SO₂ would disproportionate, forming sulfate and elemental sulfur [14]. However, the photolysis rate of SO₂ and H₂S would have been smaller than present due to Rayleigh scattering by a thick CO₂ atmosphere and due to SO₂ and H₂S self-shielding [13]. This reasoning suggests a small total atmospheric sink for SO₂ and H₂S and a proportionally attenuated photochemical production of sulfate.

If the rate of volcanic outgassing of SO₂ were higher than both its photochemical destruction rate and the rate of aqueous sulfite disproportionation [15], which is highly uncertain but probably slow at low temperatures, then SO₂ would accumulate in the atmosphere and aquatic environment until the precipitation of sulfite minerals balanced volcanic outgassing. The surface water reservoir would be saturated with the dissolved species of S⁴⁺, leading to a high and stable atmospheric partial pressure of SO₂.

A sulfur dioxide climate feedback: A relatively high atmospheric pSO₂ would have a significant influence on the surface-weathering environment. Sulfurous acid, formed by dissolution of SO₂, is a weak diprotic acid that is much stronger than carbonic acid. Tetravalent sulfur speciation into dissolved SO₂, bisulfite (HSO₃⁻) and sulfite (SO₃²⁻) is pH-dependent and at a pH between 2 and 7 most of the S⁴⁺ is present as bisulfite. Dissolution of SO₂ in rainwater, followed by chemical weathering reactions of silicate rocks, would supply alkalinity to the surface water reservoir, together with the sulfite and bisulfite anions. These could then precipitate sulfite minerals, sequestering SO₂.

The dependence of weathering rates on atmospheric SO₂ through its influence on temperature, rainfall and rainwater pH, combined with the alkalinity-dependent mechanism for the removal of SO₂, creates a climate feedback analogous to the carbon cycle on Earth [4]; should the abundance of SO₂ in the atmosphere rise, an increase in surface temperature would hasten chemical weathering reactions, supplying alkalinity to the surface water reservoir and removing the excess SO₂ through sulfite mineral precipitation.

Mineralogy: A consequence of gas-aqueous equilibrium of sulfite is the suppression of carbonate mineral precipitation. Simplified thermodynamic calculations show that hannebachite (CaSO₃·½H₂O) precipitates before calcite (CaCO₃) if pSO₂/pCO₂ ≥ $\sim 5 \times 10^{-8}$ and that MgSO₃·6H₂O precipitates before magnesite

(MgCO_3) if $p\text{SO}_2/p\text{CO}_2 \geq \sim 4 \times 10^{-7}$ (figure 1). Despite the insolubility of siderite (FeCO_3), kinetic barriers for its precipitation may mean that on a reducing early Martian surface the concentration of Fe^{2+} were limited by the precipitation of sulfide minerals. Although a more rigorous thermodynamic approach is necessary to accurately predict which minerals precipitate, these preliminary calculations suggest that the proposed climate feedback is plausible, as is inhibition of carbonate mineral precipitation at only mildly acidic to neutral pH, consistent with the recent detection of clays [7].

Transition to modern Mars: When volcanism ceased on Mars, continued oxidation of the surface due to hydrogen escape quickly scrubbed the sulfur species from the atmosphere. Without the radiative effect of SO_2 and H_2S , the surface water froze, weathering arrested and mineral precipitation ceased to sequester carbon and sulfur in sediments. The frozen surface water was redistributed over time, as the seasonal cycle and changes in obliquity periodically raised local temperatures enough to mobilize it. In the shallow subsurface, an early high geothermal gradient kept the water circulating. Interaction of the hot water with silicate rocks caused weathering reactions that sequestered the CO_2 atmosphere in carbonate minerals precipitated in crustal pores and fractures. As the planet cooled, the water percolated deeper into the crust, where geothermal circulation and subsurface weathering persisted. The present thin CO_2 atmosphere is the result of 3–4 billion years of this subsurface weathering.

During the last 3.5 Ga, episodic stability of liquid water at the highly oxidized surface would have created extremely acidic and highly concentrated solutions, mostly by dissolution and oxidation of sulfite minerals to sulfate and less so by rapid weathering of basalt, as previously suggested [6]. The aqueous chemistry that occurred when these small, transient water bodies refroze or evaporated would, however, be similar to that previously discussed by Tosca et al. [6]. Another possible consequence of this acidification is the dissolution of any siderite that may have formed.

The geochemical sequence of events we describe is consistent with the stratigraphic interpretation of mineral distribution on the surface of Mars [16] and, perhaps more importantly, provides a mechanistic explanation for the observed mineralogy. It successfully explains the evidence for liquid water and the formation of clay minerals with no detectable precipitation of carbonate minerals early in Martian history, as well as the transition to a cold, arid, oxidizing, acid-sulfate dominated Mars ~ 3.5 Ga. Detection of sulfite minerals on Mars would provide unequivocal proof of this hypothesis, as there is no other way for their formation.

Although the vulnerability of sulfites to post-depositional oxidation and disproportionation makes it unlikely that they would remain in direct contact with the atmosphere, their existence in sedimentary formations is possible.

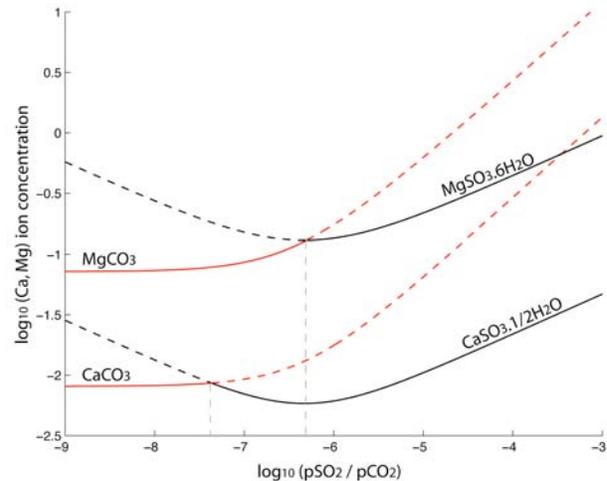


Figure 1: Cation concentrations limited by mineral saturation. The upper set of curves shows Mg-mineral saturation and the lower set shows Ca-mineral saturation. In both sets, the red curve denotes a carbonate mineral and the black curve a sulfite mineral. The solid part of the curves is the region of $p\text{SO}_2/p\text{CO}_2$ where the mineral represented by the curve precipitates. A thin grey, dashed line marks the critical value of $p\text{SO}_2/p\text{CO}_2$ for each of the cations.

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