

Climate consequences of CO₂-SO₂ clathrate hydrate formation on early Mars

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Abstract

It is suggested that the formation of CO₂-SO₂ clathrate hydrates due to the cooling effect of sulfate aerosols in the potentially CO₂-rich (a few bar) early atmosphere of Mars may have played an important role through the removal of volcanic SO₂ from the atmosphere and the subsequent enrichment in sulfur of the Noachian cryosphere. For a CO₂ pressure above 2 bar, all the volcanically released SO₂ is converted to clathrates, inhibiting the formation of sulfate particles in the atmosphere. In the 1-2 bar range, only a fraction of SO₂ is converted to sulfate particles, and this mechanism results in some regulation of the surface temperature. At late Noachian/early Hesperian, when the CO₂ pressure dropped below 1 bar, this mechanism would not have been efficient any longer, and the sulfur injected by volcanism in the atmosphere, first converted to suspended sulfate particles, could have been involved in the formation of sulfate minerals at the surface.

1. Introduction

The cooling effect of sulfate aerosols on the early Mars climate has been recently pointed out through a detailed photochemical/ microphysical model of ancient Mars' atmosphere [1]. Under certain CO₂ pressure, the surface temperature increases with enhanced level of atmospheric SO₂ at first because of the greenhouse contribution from SO₂. As the atmospheric SO₂ concentration keeps increasing, photochemistry leads to the formation of sulfate aerosols which can reflect sunlight and cause surface cooling. The amplitude of the cooling effect due to sulfate aerosols may reach up to 60 K (Fig. 1). At 3 bar, cooling by sulfate aerosols results in a surface temperature low enough to allow the formation of CO₂ clathrate hydrates. The goal of this talk is to assess the potential consequences of CO₂-SO₂ clathrate formation on the climate of early Mars.

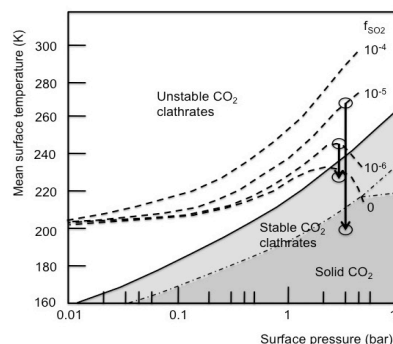


Figure 1: Mean surface temperature as a function of the CO₂ pressure for SO₂ mixing ratios of 0, 1, 10 and 100 ppm (from [1]). The arrows show the cooling effect of SO₂ aerosols at pCO₂ = 3 bar and mixing ratios of SO₂ of 1 ppm and 10 ppm. The equilibrium temperatures of CO₂ clathrate hydrate, and CO₂ ice, are plotted as a function of CO₂ pressure (from [2]).

2. Thermodynamic modelling of CO₂-SO₂ clathrates in Martian atmospheric conditions

The van der Waals and Platteeuw [3] model describes the equilibrium of hydrate phases by means of a convergence between a statistical thermodynamics approach implementing Kihara parameters and a classical approach implementing reference state parameters. Using this approach, a model has been used to extrapolate to low temperatures existing data on the composition of CO₂-SO₂ clathrates. A domain of Kihara and other parameters fitting these data has been defined. Through a sampling of this domain, a beam of extrapolated curves has been generated describing

the full space of parameters compatible with existing data. At 200-220 K, the enrichment factor of SO_2 in the clathrate with respect to gas is found to be very high, at least ≈ 100 . It results that the conversion of only 1% (or less) of the CO_2 present in the atmosphere in clathrates, easily achieved due to the large amounts of water available in the early Mars hydro-cryosphere, is efficient enough for removing all the atmospheric SO_2 from the atmosphere. As soon as the surface temperature falls below the clathrate formation equilibrium temperature due to the formation of sulfate aerosols in the atmosphere, SO_2 is removed to the surface/subsurface through clathration of the cryosphere, resulting in a decrease of the sulfate formation rate and therefore an increase of the surface temperature, with a subsequent active stabilization of the surface temperature at a value close to the CO_2 clathrate equilibrium temperature.

3. Modelling of the combined effects of SO_2 and sulfate aerosols on the surface temperature of Mars

The variation of the surface temperature with respect to the SO_2 mixing ratio has been calculated for $p_{\text{CO}_2}=3$ bar, using a 1-D radiative-convective climate model and a 1-D photochemical model [1]. New calculations have been performed for $p_{\text{CO}_2} = 1.5, 1.0$ and 0.5 bar. From these calculations, we have determined, for each value of the CO_2 pressure, the value of the SO_2 mixing ratio for which the surface temperature is equal to the CO_2 clathrate equilibrium temperature. This “equilibrium” SO_2 mixing ratio is plotted as a function of CO_2 pressure on Fig. 2.

4. Potential consequences of CO_2 - SO_2 clathrate formation on the climate of early Mars

Three domains of the CO_2 partial pressure can be distinguished :

- For $p_{\text{CO}_2} > 2$ bars, which could have happened during the Noachian, all the volcanic SO_2 is trapped in the cryosphere, whatever the SO_2 mixing ratio. There is no SO_2 in the atmosphere, and the cryosphere is progressively enriched in SO_2 .
- For p_{CO_2} decreasing below 2 bar, but remaining above 1 bar, which could have happened during the late Noachian, the SO_2 level in the atmosphere following a volcanic eruption can reach typically 10 ppm or so. SO_2 in excess is trapped in the cryosphere.

After large volcanic events, the surface temperature is stabilized at the CO_2 - SO_2 clathrate equilibrium temperature (≈ 220 K). Some of the SO_2 trapped in the cryosphere at the Noachian may have been released to the atmosphere during this period.

- For p_{CO_2} dropping below 1 bar, which could have happened at late Noachian/ early Hesperian, volcanic activity may result in potentially high levels of SO_2 in the atmosphere, with the resulting formation of sulfate particles in the atmosphere, and sulfate minerals at the surface [4].

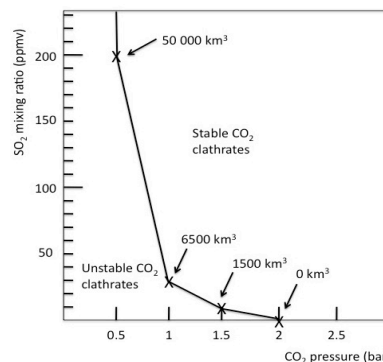


Figure 2: Equilibrium SO_2 mixing ratio as a function of CO_2 pressure. The lava volumes required to give rise to the corresponding SO_2 mixing ratio, calculated by using the same conversion factor as in [5], are indicated on the figure.

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References

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