

Climate consequences of CO_2 - SO_2 clathrate hydrate formation on early Mars

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Abstract

It is suggested that the formation of CO_2 - SO_2 clathrate hydrates due to the cooling effect of sulfate aerosols in the potentially CO_2 -rich (a few bar) early atmosphere of Mars may have played an important role through the removal of volcanic SO_2 from the atmosphere and the subsequent enrichment in sulfur of the Noachian cryosphere. For a CO_2 pressure above 2 bar, all the volcanically released SO_2 is converted to clathrates, inhibiting the formation of sulfate particles in the atmosphere. In the 1-2 bar range, only a fraction of SO_2 is converted to sulfate particles, and this mechanism results in some regulation of the surface temperature. At late Noachian/early Hesperian, when the CO_2 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 CO_2 pressure, the surface temperature increases with enhanced level of atmospheric SO_2 at first because of the greenhouse contribution from SO_2 . As the atmospheric SO_2 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 CO_2 clathrate hydrates. The goal of this talk is to assess the potential consequences of CO_2 - SO_2 clathrate formation on the climate of early Mars.

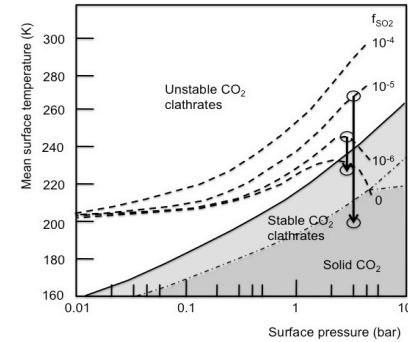


Figure 1: Mean surface temperature as a function of the CO_2 pressure for SO_2 mixing ratios of 0, 1, 10 and 100 ppm (from [1]). The arrows show the cooling effect of SO_2 aerosols at $p_{\text{CO}_2} = 3$ bar and mixing ratios of SO_2 of 1 ppm and 10 ppm. The equilibrium temperatures of CO_2 clathrate hydrate, and CO_2 ice, are plotted as a function of CO_2 pressure (from [2]).

2. Thermodynamic modelling of CO_2 - SO_2 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 CO_2 - SO_2 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 SO₂ 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 CO₂ 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 SO₂ 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, SO₂ 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 CO₂ clathrate equilibrium temperature.

3. Modelling of the combined effects of SO₂ and sulfate aerosols on the surface temperature of Mars

The variation of the surface temperature with respect to the SO₂ mixing ratio has been calculated for p_{CO₂}=3 bar, using a 1-D radiative-convective climate model and a 1-D photochemical model [1]. New calculations have been performed for p_{CO₂} = 1.5, 1.0 and 0.5 bar. From these calculations, we have determined, for each value of the CO₂ pressure, the value of the SO₂ mixing ratio for which the surface temperature is equal to the CO₂ clathrate equilibrium temperature. This “equilibrium” SO₂ mixing ratio is plotted as a function of CO₂ pressure on Fig. 2.

4. Potential consequences of CO₂-SO₂ clathrate formation on the climate of early Mars

Three domains of the CO₂ partial pressure can be distinguished :

- For p_{CO₂} > 2 bars, which could have happened during the Noachian, all the volcanic SO₂ is trapped in the cryosphere, whatever the SO₂ mixing ratio. There is no SO₂ in the atmosphere, and the cryosphere is progressively enriched in SO₂.
- For p_{CO₂} decreasing below 2 bar, but remaining above 1 bar, which could have happened during the late Noachian, the SO₂ level in the atmosphere following a volcanic eruption can reach typically 10 ppm or so. SO₂ in excess is trapped in the cryosphere.

After large volcanic events, the surface temperature is stabilized at the CO₂-SO₂ clathrate equilibrium temperature (≈ 220 K). Some of the SO₂ trapped in the cryosphere at the Noachian may have been released to the atmosphere during this period.

- For p_{CO₂} dropping below 1 bar, which could have happened at late Noachian/ early Hesperian, volcanic activity may result in potentially high levels of SO₂ in the atmosphere, with the resulting formation of sulfate particles in the atmosphere, and sulfate minerals at the surface [4].

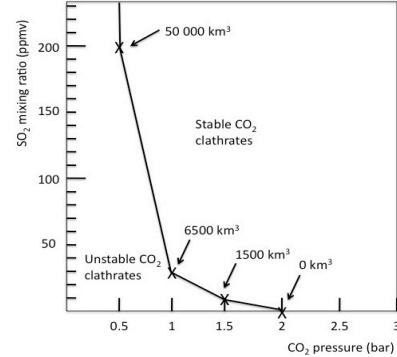


Figure 2: Equilibrium SO₂ mixing ratio as a function of CO₂ pressure. The lava volumes required to give rise to the corresponding SO₂ mixing ratio, calculated by using the same conversion factor as in [5], are indicated on the figure.

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References

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