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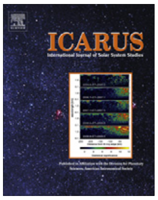

CO_2–SO_2 clathrate hydrate formation on early Mars

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ABSTRACT

It is generally agreed that a dense CO_2-dominant atmosphere was necessary in order to keep early Mars warm and wet. However, current models have not been able to produce surface temperature higher than the freezing point of water. Most sulfate minerals discovered on Mars are dated no earlier than the Hesperian, despite likely much stronger volcanic activities and more substantial release of sulfur-bearing gases into martian atmosphere during the Noachian. Here we show, using a 1-D radiative–convective-photochemical model, that clathrate formation during the Noachian would have buffered the atmospheric CO_2 pressure of early Mars at ~2 bar and maintained a global average surface temperature ~230 K. Because clathrates trap SO_2 more favorably than CO_2, all volcanically outgassed sulfur would have been trapped in Noachian Mars cryosphere, preventing a significant formation of sulfate minerals during the Noachian and inhibiting carbonates from forming at the surface in acidic water resulting from the local melting of the SO_2-rich cryosphere. The massive formation of sulfate minerals at the surface of Mars during the Hesperian could be the consequence of a drop of the CO_2 pressure below a 2-bar threshold value at the late Noachian–Hesperian transition, which would have released sulfur gases into the atmosphere from both the Noachian sulfur-rich cryosphere and still active Tharsis volcanism. A lower value of the pressure threshold, down to ~0.5 bar, could have been sufficient to maintain middle and high latitude regions below the clathrate formation temperature during the Noachian and to make the trapping of SO_2 in clathrates efficient. Our hypothesis could allow to explain the formation of chaotic terrains and outflow channels, and the occurrence of episodic warm episodes facilitated by the release of SO_2 to the atmosphere. These episodes could explain the formation of valley networks and the degradation of impact craters, but remain to be confirmed by further modeling.

1. Introduction

Sulfur dioxide (SO_2) has been proposed as a possible greenhouse gas which worked together with CO_2 to raise the surface temperature of early Mars above the freezing point of water (Halevy et al., 2007; Johnson et al., 2008; Postawko and Kuhn, 1986), allowing liquid water to flow at the surface of the planet and carving the presently observed valley networks and outflow channels. However, the cooling from sulfur gases as a result of sulfate aerosol formation is an observational fact for the current atmosphere of Earth. On early Mars, the cooling effect of sulfate aerosols would also have counteracted efficiently the warming effect due to SO_2 greenhouse effect and sulfur outgassing. After a short period of warming, the presence of sulfate aerosols would have resulted in a colder surface, with a net cooling, instead of warming, of the planet (Tian et al., 2010). No mechanism to keep ancient Mars warm and wet through greenhouse effect has been generally accepted so far, suggesting a cold and wet early Mars. Much of the aqueous activity on Mars could have occurred in subsurface hydrothermal systems powered by magmatic or impact activity (Squyres and Kasting, 1994; Griffith and Shock, 1995; Segura et al., 2002, 2008), rather than at the surface of the planet.

Sulfur, under both oxidized (SO_2) and reduced (H_2S) forms, could have been released in large amount by volcanism during the Noachian. From several 100 millibar to around one bar of sulfur could have been outgassed along martian history, most of which during the Noachian and the Hesperian (see e.g. Craddock and Greeley, 2009; Gaillard and Scaillet, 2009). The reconstructed

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evolution of the cumulated amount of released SO_2 since the early Noachian, shortly after accretion, is shown in Fig. 1. It has been derived from both the CO_2 volcanic release rates calculated from a thermo-chemical evolution model of Mars (Grott et al., 2011) and a photogeological analysis of the martian surface (Craddock and Greeley (2009), referred to as CG09 in this paper). The ratio between SO_2 and CO_2 molar fractions in the volcanic gas f_{SO2}/f_{CO2} is typically in the range from 0.5 to ~1 (see Fig. 5 in Gaillard and Scaillet (2009)). The evolutions of the CO_2 partial pressure (denoted by p_{CO2} in the following) for two values (0.01 and 1) of the surface fraction covered by hot upwellings (f_p) are plotted on Fig. 4b in Grott et al. (2011). By applying the ratio f_{SO2}/f_{CO2} to Grott et al. curves, and taking into account the difference of molar mass between CO_2 (44 g/mol) and SO_2 (64 g/mol), we have plotted in Fig. 1 the corresponding evolutions of the cumulated amount of outgassed SO_2, expressed in pressure units, and the corresponding global equivalent layer (GEL) thickness of the sulfate mineral assuming that all the released sulfur is involved in anhydrite formation. The other plotted curve is obtained from a photogeological analysis of the martian surface yielding a cumulated lava extrusion volume of 0.7×10^8 km^3 (CG09), by assuming that basalts contain 7000 ppm sulfur by mass (an upper range according to Gaillard and Scaillet (2009)), that is 10 times more than assumed in CG09. This curve would be ~3 times lower assuming a lower range of 2500 ppm of S and four times higher assuming a lava extrusion volume of 3×10^8 km^3 (Gaillard and Scaillet, 2009). Both models and observations therefore suggest a cumulated pressure of outgassed SO_2 of typically ~1 bar, corresponding to a ~40 m thick sulfate GEL, within a factor of 3 both ways.

Interestingly, all sulfate minerals detected at the surface of Mars by OMEGA/Mars Express have been emplaced during the Hesperian, a relatively late epoch in martian history (Bibring et al., 2006). Later observations of CRISM on MRO have revealed additional sulfate deposits, a few of them under the form of interbedded phyllosilicate and sulfate layers in sediments of Noachian craters (Terra Sirenum) in the Southern hemisphere (Murchie et al., 2009). These intracrater deposits are relatively widespread, far from those mapped by OMEGA and at higher elevation, excluding that they have been transported from equatorial regions (Wray et al., 2011). Although a younger age for these sediments cannot be excluded, they are suspected to have formed by evaporitic processes in an acidic context at the Noachian. Such formations associating phyllosilicates and sulfates are also found in terrestrial acidic saline lake deposits (Baldridge et al., 2009). Most of sulfate deposits are observed in Hesperian terrains. They consist of several kinds of formations: (i) Hesperian layered sulfates under the form of extended deposits in Terra Meridiani, (ii) Interior Layered Deposits (ILD) throughout the Valles Marineris trough system consisting of massive mounds of layered material up to several kilometers thick, (iii) gypsum deposits in north polar dune field (Gaillard et al., 2013). Sulfur is also part of soil and dust at the global scale at an average level of ~6.8% (King and McLennan, 2010). It has been suggested that some sulfates could have been formed by evaporitic processes in the Valles Marineris region prior to Tharsis formation, then redistributed by fluvial transport to Meridiani Planum, where they are now observed, during the elevation of the Tharsis uplift (Fan et al., 2008). If so, sulfates detected in Hesperian terrains could have been formed in the Noachian. The question of the origin of sulfates is debated, and at least some of the observed deposits could have formed in the late Noachian. In the present paper, we make the hypothesis that most of the sulfates observed in equatorial regions (layered deposits, ILD) have been formed at the Hesperian (not excluding a start at the late Noachian), and propose an explanation for the scarcity of sulfates in Noachian terrains, and their apparently massive deposition at the Hesperian.

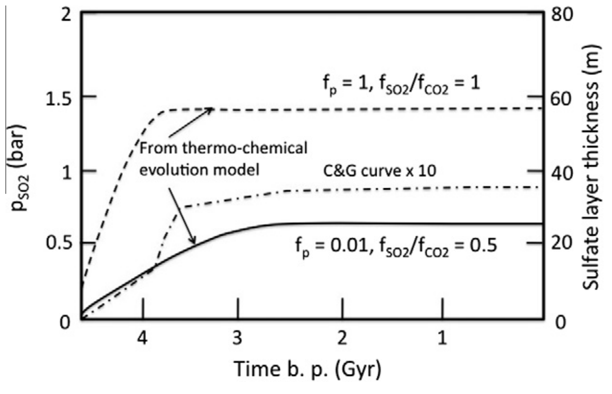

Fig. 1. Evolution of the cumulated amount of volcanically released sulfur in terms of SO_2 pressure (left vertical scale) and thickness of the corresponding sulfate mineral GEL (right vertical scale), assuming full conversion of sulfur into sulfate minerals. The "C&G" curve (dotted-dashed line) is obtained by multiplying by 10 the curve proposed in CG09 from a photogeological analysis of surface morphology (Greeley and Schneid, 1991). The two other curves are derived from CO_2 evolution curves proposed by Grott et al. (2011), as explained in the main text. These curves give the amount of CO_2 released from mantle carbon and do not include a possible contribution of superficial carbon (e.g. carbonates) to the volcanic CO_2.

The evolution of CO_2 on Mars is poorly constrained. Despite the discovery of carbonates in SNC meteorites and the recent orbital and in situ observations of carbonate rocks at some locations on the surface of Mars (see e.g. Niles et al., 2013), carbonates are not proved to be extensively present on Mars. The lack of global carbonate outcrops on Mars, which seems to contradict a massive presence of CO_2 in its early atmosphere, could be explained by either the action of sulfuric or sulfurous acids in large, standing bodies of water suppressing the formation of carbonates (Fairén et al., 2004; Halevy et al., 2007), or a rapid escape of early martian CO_2 atmosphere (Tian et al., 2009, referred to as T09 in this paper), or both.

According to an early Mars upper atmosphere model (T09), the timescale for 1 bar of CO_2 to be removed through thermal escape would have been ~1 Myr at 4.5 byr ago (Ga) and ~10 Myr at 4.1 Ga. Note that at first stages, during typically the first 100 Myr, carbon escape may have been slowed down by water hydrodynamic escape, which is not taken into account in T09. If Mars was endowed with amounts of CO_2 similar to those found on Venus and the Earth (~100 bar), and according to the model of T09, most of its initial CO_2 inventory would have been lost within the first 100 Myr after its formation. A mechanism that can possibly help Mars to keep its CO_2 inventory is carbonate formation through weathering of basalt (Pollack et al., 1987). The same authors proposed that a dense CO_2 atmosphere (1–5 bar) could have been maintained during the Noachian by constant recycling of CO_2 back into the atmosphere through rapid burial and thermal decomposition of carbonate minerals. They calculated a typical cycling time of CO_2 at 273 K of ~10 Myr, decreasing to ~1 Myr at larger temperatures of 300 K for a CO_2 pressure of 1 bar, a temperature easily achievable in the subsurface even if the surface was cold. If the formation of carbonate through weathering has occurred at a rate comparable to that of carbon thermal escape, substantial amounts of carbon could have been trapped in the format of carbonates and cycled through the subsurface-hydrosphere–atmosphere system. If so, a significant atmosphere of CO_2 could have survived until 4.1 Ga. The combination of a rapid formation of carbonate and a rapid thermal escape of carbon on Noachian Mars could have decreased the atmospheric pressure of Noachian Mars even more rapidly, resulting in shorter warm periods and longer, more frequent cold periods on Noachian Mars. It is important to note that the timescales of carbonate formation and their further destabilization are still poorly understood.