Atmospheric collapse and transport of carbon dioxide into the subsurface on early Mars

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1. Introduction

[1] The present climate of Mars is extremely cold and dry, and is characterized by a very thin CO$_2$ atmosphere. On the other hand, geological evidence suggests that the Martian climate in the past might have been warm and wet, suggesting that the atmospheric CO$_2$ pressure would have been several bars higher. However, the fate of the abundant CO$_2$ is still unclear. Here we propose a possible scenario for the evolution of CO$_2$ on Mars. Numerical results suggest that CO$_2$ in the early atmosphere would have reduced by a runaway condensation to form large CO$_2$ ice caps. Then, the large CO$_2$ ice caps should have shrunk by basal melting and most of CO$_2$ has percolated into subsurface of the ice caps. The CO$_2$ would have formed clathrate hydrate and carbonate minerals, and may still reside in the subsurface of Mars. This could explain the apparent shortage of CO$_2$ on the present Martian surface. Citation: Kurahashi-Nakamura, T., and E. Tajika (2006), Atmospheric collapse and transport of carbon dioxide into the subsurface on early Mars, Geophys. Res. Lett., 33, L18205, doi:10.1029/2006GL027170.

2. Model

[5] We used three numerical models in this study. First is a time-dependent latitudinally-one-dimensional energy balance climate model (EBM) with the AIR system of Mars, which is similar to that used by Nakamura and Tajika [2003]. We used this model to simulate the climatic condition and the distribution of CO$_2$ in the AIR system. In this study, the obliquity for the present Mars (25.2°) is assumed.

[6] The second model is an ice-sheet model coupled with the EBM to determine the configurations of the CO$_2$ ice caps (see Section 3.2). The ice-sheet model adopted here is based on work by Birchfield et al. [1981]. We considered a local CO$_2$ budget at the surface via condensation and sublimation, and ice flow due to deformation of ice and the basal slide. We use the rheological property of CO$_2$-ice depending on temperature [Durham et al., 1999]. In the ice-sheet model, a uniform temperature field of 180 K in the CO$_2$ ice caps is assumed for simplicity.

[7] The third is a time-dependent one-dimensional heat conduction model. This model is used in Section 3.3 to estimate the timescale of the thermal evolution of an ice sheet composed of CO$_2$-ice, H$_2$O-ice, and CO$_2$ clathrate hydrate. The geothermal heat flux for the past time is given at the base of the ice sheet. Latent heat and change in thickness by phase change are considered in the model. We also consider a diffusion of CO$_2$ molecules in the ice sheet.

3. Results

3.1. Formation of Large CO$_2$ Ice Cap

[8] According to our analysis of the Martian AIR system stability using the EBM, most of CO$_2$ should have been kept in the atmospheric reservoir when the atmospheric pressure was high (see solid curves in Figure 1a). However, the total amount of exchangeable CO$_2$ in the AIR system

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would have escaped to space owing to ice condensation easier. Melosh and Vickery ice caps and which can be contained by ice cap is thicker than a certain critical \( T \). Then, we can obtain ice \( K _ { \text{CURAHASHI-NAKAMURA AND TAJIKA: TRANSPORT OF CO}_2 \text{IN EARLY MARS} } \). Figure 2. \( \text{IN EARLY MARS} \) ice (solid curves) cannot exist when the \( T \) ice caps resulting from the climate jump would have formed under the higher atmospheric pressure (Figure 1b).

According to Figure 1, the \( \text{CO}_2 \) ice caps formed by the climate jump would have contained several hundreds mbars at least. They would have contained even more than 1 bar in some cases. Because the present \( \text{CO}_2 \) ice caps and the regolith contain rather small amount of \( \text{CO}_2 \), the total amount of \( \text{CO}_2 \) in the AIR system should have decreased further after the climate jump (Figure 1a). However, once the atmospheric \( \text{CO}_2 \) pressure becomes low, it is difficult for \( \text{CO}_2 \) to escape efficiently to space by the impact erosion [e.g., Melosh and Vickery, 1989]. Loss of \( \text{CO}_2 \) by the sputtering (<0.2 bar during the past 3.8 Gyr) would be also insufficient [Haberle et al., 1994; Luhmann et al., 1992].

### 3.2. Possibility of Basal Melting of \( \text{CO}_2 \) Ice Cap

If the \( \text{CO}_2 \) ice cap is thicker than a certain critical thickness, the basal temperature of the ice cap exceeds the melting point of \( \text{CO}_2 \) (which is almost constant at 217 K in the pressure range considered here), resulting in the basal melting of the \( \text{CO}_2 \) ice cap. The critical thickness as a function of the geothermal heat flow and the surface temperature of \( \text{CO}_2 \) ice is shown in Figure 2.

On the other hand, we calculated the configurations of the \( \text{CO}_2 \) ice caps by using the ice-sheet model to estimate the relation between the maximum thickness of \( \text{CO}_2 \) ice cap and the amount of \( \text{CO}_2 \) ice (Figure 2). Then, we can obtain the maximal amount of \( \text{CO}_2 \) which can be contained by thermodynamically-stable \( \text{CO}_2 \) ice caps. For example, if we assume the geothermal heat flux to be 150 mW/m\(^2\) [Stevenson et al., 1983] and the surface temperature to be 130 K at 4 Gyr ago, the maximum thickness of ice cap is \( T \approx 300 \) m, corresponding to 20–30 mbars of \( \text{CO}_2 \) (Figure 2). The \( \text{CO}_2 \) ice caps formed by the climate jump would have contained much larger quantity than this (Figure 1). Therefore, the \( \text{CO}_2 \) ice caps resulting from the climate jump should have suffered from the basal melting. The typical radius of the \( \text{CO}_2 \) ice cap is 500–800 km depending on the amount of \( \text{CO}_2 \) contained. It is comparable to around 10 degrees in latitude.

Although the age when the climate jump occurred is uncertain, the high efficiency of impact erosion of the atmosphere during the heavy bombardment period [Melosh and Vickery, 1989] and the geological evidence of the warm and wet climate on the ancient terrain [e.g., Carr, 1996] should have decreased during the Martian history because the atmospheric \( \text{CO}_2 \) would have escaped to space owing to impact erosion [Melosh and Vickery, 1989] and pick-up ion sputtering [Luhmann et al., 1992] of the atmosphere. It would have resulted in decrease in the atmospheric pressure (solid curves in Figure 1a). However, when the total amount of exchangeable \( \text{CO}_2 \) (or the atmospheric pressure) became lower than a certain critical value, the energy income onto the poles by the solar radiation would have fallen below the outgoing energy by the long-wave radiation. Therefore, the atmospheric \( \text{CO}_2 \) would have condensed and released the latent heat to compensate for the deficit of energy. The condensation would have continued until the steady-state energy balance was achieved again. This results in runaway condensation of atmospheric \( \text{CO}_2 \) into permanent \( \text{CO}_2 \) ice caps, which is called 'climate jump'. The climate jump corresponds to redistribution of \( \text{CO}_2 \) in the system (dashed curves in Figure 1a).

There is a threshold level of the atmospheric \( \text{CO}_2 \) pressure to cause the climate jump at a given solar luminosity (a filled circle in Figure 1a). However, the \( \text{H}_2\text{O} \) ice caps might have formed before \( \text{CO}_2 \) condensed, if the Martian climate in the past was warm and wet. If \( \text{H}_2\text{O} \) ice caps had existed before the climate jump, the temperature in the polar region would have been lower than that without \( \text{H}_2\text{O} \) ice caps because of their high albedo. Because it makes the \( \text{CO}_2 \) condensation easier, \( \text{CO}_2 \) ice caps would have formed under the higher atmospheric pressure (Figure 1b).

Figure 1. (a) Distribution of \( \text{CO}_2 \) in the AIR system when the 70% luminosity is assumed. The warmer state with no permanent \( \text{CO}_2 \) ice (solid curves) cannot exist when the atmospheric pressure is lower than the critical pressure. The total amount of \( \text{CO}_2 \) in the AIR system should have decreased due to impact erosion and pick-up ion sputtering (see text). The filled and open circles represent the sizes of the atmospheric reservoir just before and after the climate jump, respectively. Similarly, the filled triangle represents the amount of \( \text{CO}_2 \) in the seasonal ice caps just before the climate jump, and the open triangle corresponds to that in the permanent ice cap after the climate jump. (b) Critical atmospheric pressure for the climate jump. To simulate the effect of the change in the surface albedo by \( \text{H}_2\text{O} \) ice cap, we change the surface albedo of bare ground (that is, without \( \text{CO}_2 \) ice) in some model runs. The critical pressure is higher for the lower luminosity and the larger \( \text{H}_2\text{O} \) ice cap because these conditions make the \( \text{CO}_2 \) condensation easier.
suggest that the climate jump might have occurred probably during the late Noachian or the early Hesperian.

The time required for the basal melting can be estimated by solving a time-dependent heat conduction problem. For this case, we simply consider a vertically one-dimensional problem on CO$_2$ ice. The results suggest that it takes several thousands years before the base of CO$_2$ ice begins to melt after the climate jump. This timescale is longer than a timescale of the runaway condensation of CO$_2$ to form the large ice caps in the model (~$10^5$ years, which is obtained from the EBM), but much shorter than that required for the ice flow (~$10^5$ years, obtained from the ice-sheet model). This means that large CO$_2$ ice caps could be formed, but the ice flow process would be too slow to avoid the basal melting. That is to say, the CO$_2$ ice caps formed by the climate jump would have undergone the basal melting.

3.3. Transport of CO$_2$ Into Subsurface

It is generally considered that the Martian crust would have been modified by impact processes and it is abundant in pores and fractures. The pore space in the Martian crust is estimated to be very large (~$10^8$ km$^3$) [Clifford, 1993], allowing the storage of a large amount of CO$_2$. The transport of H$_2$O from the surface into the crust via basal melting has been suggested [Clifford, 1993]. We propose a similar process could have played a role to transport CO$_2$ into the subsurface.

Possible evolutions of ice caps obtained from the heat conduction model are shown in Figure 3. After the formation of the large CO$_2$ ice caps, liquid or gaseous CO$_2$ produced at the base of ice cap would have permeated and

![Figure 2](image-url) Critical thickness of CO$_2$ ice cap for basal melting, obtained as a steady state of heat conduction problem. The surface temperature is assumed to be 130, 140, and 150 K, corresponding to the temperatures at the surface of permanent CO$_2$ ice caps for various solar flux (~148 K for the present luminosity, and ~132 K for the 70% luminosity). The geothermal heat flow as a function of time is adopted from the thermal evolution model of Mars [Stevenson et al., 1983]. Relation between the critical thickness of CO$_2$ ice cap and the amount of CO$_2$ contained in the ice caps at both poles is shown on the right of the figure.

![Figure 3](image-url) Schematic illustration of the evolution of ice caps based on the heat conduction model. The initial thickness and thermal structure are based on results of the EBM and the ice-sheet model. (a) If H$_2$O ice cap did not exist before CO$_2$ condensation (a0), CO$_2$ ice cap by the climate jump would have formed on the ground (a1). When temperature at the bottom of CO$_2$ ice cap reached to the melting point, the CO$_2$ ice would have begun to melt (a2). Liquid or gaseous CO$_2$ would have permeated into the subsurface as the basal melting progresses (a3). (b) If H$_2$O ice cap existed before CO$_2$ condensation (b0), CO$_2$ ice cap by the climate jump may have formed on the H$_2$O ice cap (b1). After basal melting, CO$_2$ molecules would have diffused through the H$_2$O ice to form CO$_2$ clathrate hydrate (CO$_2$ 6H$_2$O) (b3). The clathrate layer would have been thickened as the diffusion progresses. Finally, CO$_2$ molecules might have reached the ground, resulting in infiltration into the subsurface (b4).
diffuse directly into the subsurface through cracks and pores in the crust (Figure 3a). If the pressure in the pores was lower than the saturation vapor pressure of CO$_2$, gaseous CO$_2$ would diffuse according to a pressure gradient. Even if the diffusion of gas was so slow that the pressure may have reached to the saturation pressure, CO$_2$ would have percolated downward owing to the gravity in liquid phase. The average permeability of the Martian crust is estimated to be $10^{-2}$–$10^{-5}$ m$^2$ [Clifford, 1993]. Because the flux of liquid-CO$_2$ percolation ($10^{-3}$–$10^{-5}$ kg/m$^2$s) estimated from Darcy’s law is much larger than the amount of CO$_2$ produced by the basal melting per unit time ($10^{-4}$–$10^{-5}$ kg/m$^2$s), the liquid CO$_2$ could have been successfully transported. By the process in Figure 3a, it would have taken $\sim 10^5$ years to transport 1 bar of CO$_2$. The timescale is controlled by the speed of the melting of CO$_2$ ice at the base of the ice cap.

If Mars had a warm and wet climate, H$_2$O ice cap(s) could have formed before the formation of the CO$_2$ ice caps due to the climate jump (Figure 3b). In this case, a H$_2$O ice may have underlain the CO$_2$ ice. CO$_2$ molecules would diffuse through the H$_2$O ice to form CO$_2$ clathrate hydrate. Then, CO$_2$ molecules diffused through the CO$_2$ clathrate layer and reached the ground, resulting in infiltration into the subsurface. In this way, the permeation of CO$_2$ also occurs in the case of CO$_2$-H$_2$O ice cap evolution as shown in Figure 3b. If the pores in the subsurface were initially filled with H$_2$O ice, similar processes would operate on the CO$_2$ ice cap on the underground H$_2$O ice. Time required for this process is controlled by the progress of the diffusion of CO$_2$ molecules, and thus depends on the diffusivity of CO$_2$ molecule and the initial thickness of the H$_2$O ice. Although the diffusivity of CO$_2$ is uncertain, it would be $10^{-9}$–$10^{-10}$ m$^2$/s as that of other various kinds of molecule [e.g., Livingston et al., 2002]. The initial thickness of H$_2$O ice is limited by the basal melting like the CO$_2$ ice. Moreover, the basal melting of H$_2$O ice would be further promoted by the cover with CO$_2$ ice. This effect would make the required time short. Even if we assume the maximum thickness of H$_2$O ice as the initial condition, the timescale of the process in Figure 3b is estimated to be $10^3$–$10^4$ years.

4. Discussion and Conclusions

If the basal melting of CO$_2$ ice caps occurs, a portion of liquid CO$_2$ might coalesce and ascend due to buoyancy. The upward migration and refreezing of liquid CO$_2$ would realize more efficient heat transport, resulting in more gradual temperature gradient. Consequently, the possible thickness of CO$_2$ ice cap in dynamic equilibrium can be thicker than the critical thickness in Figure 2. Even if it were the case, however, CO$_2$ would be also transported downward by the process discussed in Section 3.3 as long as the base of the CO$_2$ ice cap is wet with liquid CO$_2$. In other words, the CO$_2$ ice cap would continue to shrink until the basal melting stops.

The CO$_2$ transported to the underground might diffuse and spread out through networks of fractures and pore space within the subsurface of Mars. It is shown that a large quantity of groundwater could be transported through the subsurface networks of fractures [Clifford, 1993]. Therefore, liquid CO$_2$ in the subsurface could also have been transported laterally because the viscosity of liquid CO$_2$ is much lower than that of water. Because pore space in near-surface crust at latitudes other than the polar regions might have been sealed up by the ground ice layer [Clifford, 1993], the CO$_2$ molecules which entered the subsurface could not come back to the atmosphere. A part of CO$_2$ might have fixed as clathrate and/or carbonate minerals through reactions with H$_2$O ground ice and/or groundwater. The rest of CO$_2$ might remain to be gaseous and/or liquid CO$_2$ phases in the pore space of the subsurface.

Geomorphologic features such as a chaotic terrain might have formed by explosive pulverization of ground materials when clathrate in the subsurface decomposed and released a large quantity of gas [Komatsu et al., 2000; Hoffman, 2000]. Carbonate minerals in the Martian meteorite (ALH84001) is enriched in $^{13}$C, suggesting the source of carbon being CO$_2$ in the atmosphere [Romanek et al., 1994]. The oxygen isotopic composition of the carbonates indicate that they precipitated from a fluid in the Martian crust [Romanek et al., 1994]. These features suggest exchange of CO$_2$ between the atmosphere and the crust [Romanek et al., 1994; Jakosky and Jones, 1997].

This scenario explains the fate of a large quantity of CO$_2$ which might have existed as an ancient atmosphere of Mars. Ongoing or future missions, such as Mars Express, Mars Reconnaissance Orbiter, or NetLander, to explore the subsurface of Mars, may provide evidence for a large amount of CO$_2$ in subsurface of Mars.

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References


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