



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

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[1] The present climate of Mars is extremely cold and dry, and is characterized by a very thin CO₂ 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 CO₂ pressure would have been several bars higher. However, the fate of the abundant CO₂ is still unclear. Here we propose a possible scenario for the evolution of CO₂ on Mars. Numerical results suggest that CO₂ in the early atmosphere would have reduced by a runaway condensation to form large CO₂ ice caps. Then, the large CO₂ ice caps should have shrunk by basal melting and most of CO₂ has percolated into subsurface of the ice caps. The CO₂ would have formed clathrate hydrate and carbonate minerals, and may still reside in the subsurface of Mars. This could explain the apparent shortage of CO₂ 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.

1. Introduction

[2] Climate history and atmospheric evolution of Mars have been a matter of debate. Geological evidence suggests that Mars may have been warm and wet in its earliest history [e.g., Carr, 1996; Hynke, 2004]. Greenhouse effect of a dense CO₂ atmosphere could have been responsible for the warm and wet condition, and, at least a few bars of CO₂ atmosphere would have been required, irrespective of formation of CO₂ clouds in a dense CO₂ atmosphere with lower solar luminosity in the past [Pollack et al., 1987; Forget and Pierrehumbert, 1997].

[3] The Martian atmosphere can exchange CO₂ with other two CO₂ reservoirs at the surface, that is, CO₂ ice caps and regolith [Gierasch and Toon, 1973; McKay et al., 1991]. The atmospheric CO₂ pressure is controlled by thermodynamic equilibrium in the surface CO₂ reservoir system (atmosphere-ice-regolith system, hereafter referred to as AIR system). Several studies on the CO₂ reservoir system revealed that such an atmosphere should have collapsed to form large polar caps owing to instability of the CO₂ system on Mars [Haberle et al., 1994; Nakamura and Tajika, 2001, 2002; Yokohata et al., 2002]. There seems to be, however, only a small amount of CO₂ (~0.1 bars equivalent) left in the AIR system at the present [Haberle et

al., 1994; Zent and Quinn, 1995; Mellon, 1996]. On the other hand, although carbonate minerals could be a large CO₂ reservoir [Pollack et al., 1987; Haberle et al., 1994], the Thermal Emission Spectrometer (TES) on the Mars Global Surveyor has not detected large-scale carbonate outcrops at least on the surface of Mars [Christensen et al., 2001].

[4] In this study, a new idea to solve the “missing CO₂” problem is proposed. We consider that most of CO₂ in the AIR system could have been transported to the subsurface of Mars after the collapse of the CO₂ atmosphere. In the following sections, we examine a possibility of melting at the base of the presumed large CO₂ ice caps (that is, basal melting) and transport of CO₂ due to percolation through pore space of the crust.

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 climatological condition and the distribution of CO₂ 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 CO₂ 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 CO₂ 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 CO₂-ice depending on temperature [Durham et al., 1999]. In the ice-sheet model, a uniform temperature field of 180 K in the CO₂ 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 CO₂-ice, H₂O-ice, and CO₂ 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 CO₂ molecules in the ice sheet.

3. Results

3.1. Formation of Large CO₂ Ice Cap

[8] According to our analysis of the Martian AIR system stability using the EBM, most of CO₂ 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 CO₂ in the AIR system

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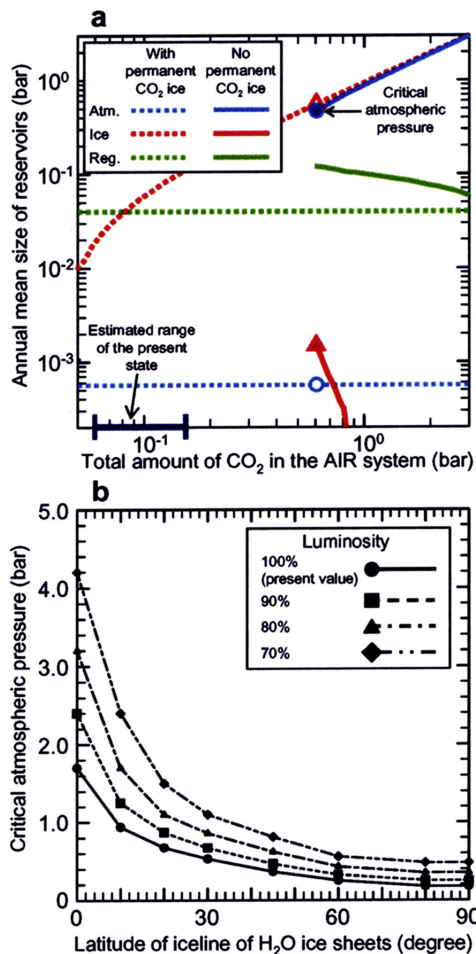


Figure 1. (a) Distribution of CO₂ in the AIR system when the 70% luminosity is assumed. The warmer state with no permanent CO₂ ice (solid curves) cannot exist when the atmospheric pressure is lower than the critical pressure. The total amount of CO₂ in the AIR system should have decreased due to impact 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 CO₂ 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 H₂O ice cap, we change the surface albedo of bare ground (that is, without CO₂ ice) in some model runs. The critical pressure is higher for the lower luminosity and the larger H₂O ice cap because these conditions make the CO₂ condensation easier.

should have decreased during the Martian history because the atmospheric CO₂ 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 CO₂ (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 CO₂ 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 CO₂ into permanent CO₂ ice caps, which is called ‘climate jump’. The climate jump corresponds to redistribution of CO₂ in the system (dashed curves in Figure 1a).

[9] There is a threshold level of the atmospheric CO₂ pressure to cause the climate jump at a given solar luminosity (a filled circle in Figure 1a). However, the H₂O ice caps might have formed before CO₂ condensed, if the Martian climate in the past was warm and wet. If H₂O ice caps had existed before the climate jump, the temperature in the polar region would have been lower than that without H₂O ice caps because of their high albedo. Because it makes the CO₂ condensation easier, CO₂ ice caps would have formed under the higher atmospheric pressure (Figure 1b).

[10] According to Figure 1, the CO₂ 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 CO₂ ice caps and the regolith contain rather small amount of CO₂, the total amount of CO₂ in the AIR system should have decreased further after the climate jump (Figure 1a). However, once the atmospheric CO₂ pressure becomes low, it is difficult for CO₂ to escape efficiently to space by the impact erosion [e.g., Melosh and Vickery, 1989]. Loss of CO₂ 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 CO₂ Ice Cap

[11] If the CO₂ ice cap is thicker than a certain critical thickness, the basal temperature of the ice cap exceeds the melting point of CO₂ (which is almost constant at 217 K in the pressure range considered here), resulting in the basal melting of the CO₂ ice cap. The critical thickness as a function of the geothermal heat flow and the surface temperature of CO₂ ice is shown in Figure 2.

[12] On the other hand, we calculated the configurations of the CO₂ ice caps by using the ice-sheet model to estimate the relation between the maximum thickness of CO₂ ice cap and the amount of CO₂ ice (Figure 2). Then, we can obtain the maximal amount of CO₂ which can be contained by thermodynamically-stable CO₂ ice caps. For example, if we assume the geothermal heat flux to be 150 mW/m² [Stevenson et al., 1983] and the surface temperature to be 130 K at 4 Gyr ago, the maximum thickness of ice cap is ~300 m, corresponding to 20–30 mbars of CO₂ (Figure 2). The CO₂ ice caps formed by the climate jump would have contained much larger quantity than this (Figure 1). Therefore, the CO₂ ice caps resulting from the climate jump should have suffered from the basal melting. The typical radius of the CO₂ ice cap is 500–800 km depending on the amount of CO₂ contained. It is comparable to around 10 degrees in latitude.

[13] 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]

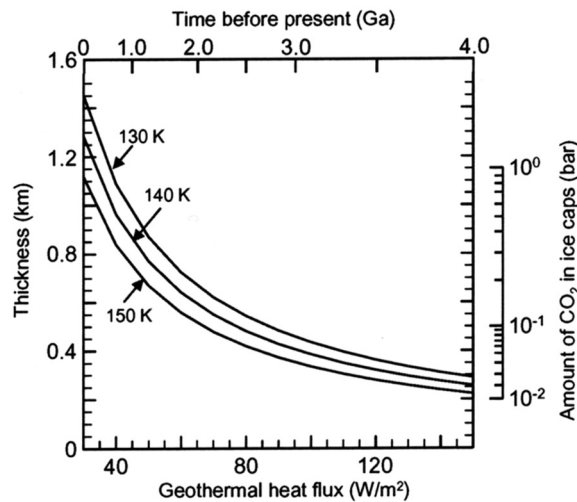


Figure 2. Critical thickness of CO₂ ice cap for basal melting, obtained as a steady state of heat conduction problem. The surface temperature is assumed to be 130, 140, and 150 K, corresponding to the temperatures at the surface of permanent CO₂ ice caps for various solar flux (~ 148 K for the present 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 CO₂ ice cap and the amount of CO₂ contained in the ice caps at both poles is shown on the right of the figure.

suggest that the climate jump might have occurred probably during the late Noachian or the early Hesperian.

[14] 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 CO₂ ice. The results suggest that it takes several thousands years before the base of CO₂ ice begins to melt after the climate jump. This timescale is longer than a timescale of the runaway condensation of CO₂ to form the large ice caps in the model ($\sim 10^2$ years, which is obtained from the EBM), but much shorter than that required for the ice flow ($\sim 10^5$ years, obtained from the ice-sheet model). This means that large CO₂ ice caps could be formed, but the ice flow process would be too slow to avoid the basal melting. That is to say, the CO₂ ice caps formed by the climate jump would have undergone the basal melting.

3.3. Transport of CO₂ Into Subsurface

[15] 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 ($\sim 10^8$ km³) [Clifford, 1993], allowing the storage of a large amount of CO₂. The transport of H₂O 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 CO₂ into the subsurface.

[16] Possible evolutions of ice caps are shown in Figure 3. After the formation of the large CO₂ ice caps, liquid or gaseous CO₂ produced at the base of ice cap would have permeated and

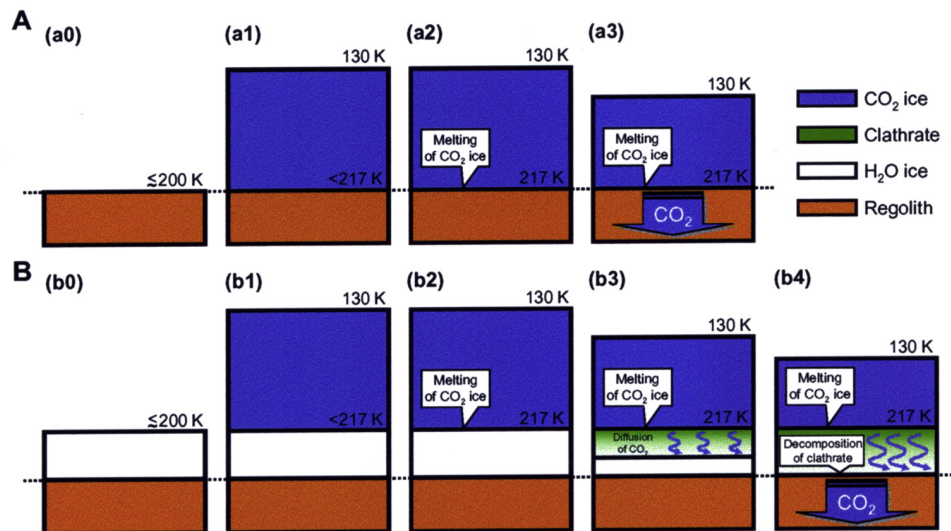


Figure 3. Schematic illustration of the evolution of ice caps based on the heat conduction model. The initial thickness and thermal structure are based on results of the EBM and the ice-sheet model. (a) If H₂O ice cap did not exist before CO₂ condensation (a0), CO₂ ice cap by the climate jump would have formed on the ground (a1). When temperature at the bottom of CO₂ ice cap reached to the melting point, the CO₂ ice would have begun to melt (a2). Liquid or gaseous CO₂ would have permeated into the subsurface as the basal melting progresses (a3). (b) If H₂O ice cap existed before CO₂ condensation (b0), CO₂ ice cap by the climate jump may have formed on the H₂O ice cap (b1). After basal melting, CO₂ molecules would have diffused through the H₂O ice to form CO₂ clathrate hydrate (CO₂ 6H₂O) (b3). The clathrate layer would have been thickened as the diffusion progresses. Finally, CO₂ 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 CO₂, gaseous CO₂ 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, CO₂ would have percolated downward owing to the gravity in liquid phase. The average permeability of the Martian crust is estimated to be 10^{-9} – 10^{-14} m² [Clifford, 1993]. Because the flux of liquid-CO₂ percolation (10^2 – 10^{-3} kg/m²s) estimated from Darcy's law is much larger than the amount of CO₂ produced by the basal melting per unit time ($\sim 10^{-6}$ kg/m²s), the liquid CO₂ could have been successfully transported. By the process in Figure 3a, it would have taken $\sim 10^5$ years to transport 1 bar of CO₂. The timescale is controlled by the speed of the melting of CO₂ ice at the base of the ice cap.

[17] If Mars had a warm and wet climate, H₂O ice cap(s) could have formed before the formation of the CO₂ ice caps due to the climate jump (Figure 3b). In this case, a H₂O ice may have underlain the CO₂ ice. CO₂ molecules would diffuse through the H₂O ice to form CO₂ clathrate hydrate. Then, CO₂ molecules diffused through the CO₂ clathrate layer and reached the ground, resulting in infiltration into the subsurface. In this way, the permeation of CO₂ also occurs in the case of CO₂-H₂O ice cap evolution as shown in Figure 3b. If the pores in the subsurface were initially filled with H₂O ice, similar processes would operate on the CO₂ ice cap on the underground H₂O ice. Time required for this process is controlled by the progress of the diffusion of CO₂ molecules, and thus depends on the diffusivity of CO₂ molecule and the initial thickness of the H₂O ice. Although the diffusivity of CO₂ is uncertain, it would be 10^{-9} – 10^{-10} m²/s as that of other various kinds of molecule [e.g., Livingston *et al.*, 2002]. The initial thickness of H₂O ice is limited by the basal melting like the CO₂ ice. Moreover, the basal melting of H₂O ice would be further promoted by the cover with CO₂ ice. This effect would make the required time short. Even if we assume the maximum thickness of H₂O ice as the initial condition, the timescale of the process in Figure 3b is estimated to be 10^7 – 10^8 years.

4. Discussion and Conclusions

[18] If the basal melting of CO₂ ice caps occurs, a portion of liquid CO₂ might coalesce and ascend due to buoyancy. The upward migration and refreezing of liquid CO₂ would realize more efficient heat transport, resulting in more gradual temperature gradient. Consequently, the possible thickness of CO₂ ice cap in dynamic equilibrium can be thicker than the critical thickness in Figure 2. Even if it were the case, however, CO₂ would be also transported downward by the process discussed in Section 3.3 as long as the base of the CO₂ ice cap is wet with liquid CO₂. In other words, the CO₂ ice cap would continue to shrink until the basal melting stops.

[19] The CO₂ 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 CO₂ in the subsurface could also have been transported laterally because the viscosity of

liquid CO₂ 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 CO₂ molecules which entered the subsurface could not come back to the atmosphere. A part of CO₂ might have fixed as clathrate and/or carbonate minerals through reactions with H₂O ground ice and/or groundwater. The rest of CO₂ might remain to be gaseous and/or liquid CO₂ phases in the pore space of the subsurface.

[20] 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 ¹³C, suggesting the source of carbon being CO₂ 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 CO₂ between the atmosphere and the crust [Romanek *et al.*, 1994; Jakosky and Jones, 1997].

[21] This scenario explains the fate of a large quantity of CO₂ 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 CO₂ in subsurface of Mars.

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