## Hydrodynamic escape of a reduced proto-atmosphere on early Mars

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The short growth time of proto-Mars inferred from analyses of Martian meteorites implies that the proto-Mars likely gravitationally maintained both the solar nebula component and the impact degassed component as a proto-atmosphere. Planetary building blocks containing metallic iron should induce production of reduced volatiles such as  $H_2$ ,  $CH_4$  and CO because metallic iron acts as a reductant for the degassed component (Kuramoto and Matsui, 1996). Atmospheres with reduced compositions are promising sites for photochemical production of organic matters precursory for life (Schlesinger and Miller, 1983). If a reduced proto-atmosphere was formed and maintained on early Mars, it may be important as a field for synthesis of organic matters linked to the emergence of life organisms.

However, the reduced proto-atmosphere once possibly formed on a rocky planet has been considered to be rapidly lost by hydrodynamic escape. Hydrodynamic escape occurs when radiative heating of an atmosphere accelerates a radial outflow of an atmosphere against the planetary gravity and it is possibly induced by the extreme ultraviolet (EUV) flux of the young Sun. Previous numerical studies (Lammer et al., 2013; Erkaev et al., 2014) estimate the atmospheric escape rate of an oxidized Martian proto-atmosphere, suggesting that the proto-atmosphere with the amount equivalent to ~100 bar could have been lost per 10 Myr under the EUV flux 100 times the present. But their result likely depends on the assumption that molecules are fully dissociated into atoms. Since the gravity on Mars is small, it is likely that a considerable fraction of molecules stays undissociated in the escape outflow. If infrared active molecules are included in the atmosphere, they may reduce the atmospheric escape rate by radiative cooling. If the atmospheric escape rate decreases, the reduced environment that is suitable for producing organic matters likely continues for a long time. So far, the effect of radiative cooling on hydrodynamic escape remains poorly understood. Here, we develop a one-dimensional hydrodynamic escape model which include radiative cooling processes and photochemical processes for a multi-component atmosphere. We calculate the escape rate of a reduced Martian proto-atmosphere and estimate the duration of the reduced environment on early Mars.

We solved the fluid equations for a multi-component gas assuming spherical symmetry considering radiative processes and photochemical processes. These equations are solved by numerical integration about time until the physical quantities settle into steady profiles. We use the UV spectrum 100 Myr after the birth of the Sun estimated by the observations of solar-type G stars. We consider CO and CH<sub>4</sub> as radiative coolant, and consider their energy transitions with high emissivity. We calculate the radiative cooling rate by using the photon escape probability. In this modeling, a hybrid-type atmosphere in which the degassed component and solar nebula component are mixed is supposed with 18 chemical components including photolysis products.

The mass escape rate decreases more than one order as the mixing fraction of CO and  $CH_4$  increases > 10% because of the energy loss by radiative cooling of CO and  $CH_4$ . Concurrently, the mass fractionation between  $H_2$  and other heavier species occurs more remarkably. Time scale for  $H_2$  loss may be longer than 100 Myr when the the degassed component is larger than  $^{\sim}1.0 \times 10^{21}$  kg equivalent to  $^{\sim}100$  bar atmosphere. In many simulation cases, CO and  $CH_4$  are left behind implying that the reduced environment further continues until these reduced species are oxidized by photolysis. Our result suggests

a reduced environment on early Mars may have continued more than 100 Myr and played an important role producing organic matters.

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