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Early Evolution of Martian Atmosphere and Hydrosphere: Constraints from Isotopic Compositions

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Current Mars has a cold and dry surface environment with a small amount of water-ice observed at the polar regions (Christensen, 2006). On the contrary, increasing evidence suggests that the early Mars once sustained a warm climate with a large amount of liquid water (e.g., Di Achille & Hynek, 2010). Though impact erosion and thermal/nonthermal escape are accepted to have possibly contributed to the loss of the early atmosphere and hydrosphere (Lammer et al., 2008), the timing of the escape and the relative importance of each process are poorly constrained.

The thermal/nonthermal escape induces isotopic fractionation that leaves behind heavier isotopes in the atmosphere and hydrosphere, whereas the impact erosion removes a fraction of atmosphere without the isotopic fractionation. The early evolution of the atmosphere and hydrosphere is constrained by the isotopic data of the martian meteorite Allan Hills 84001 (ALH 84001), which records a high hydrogen isotope ratio (D/H = $\sim$2-4 times the Martian primordial water) of 4.1 Ga surface water (Boctor et al., 2003; Greenwood et al., 2008). The high D/H ratio suggests that a larger amount of water was lost during the first 0.4 billion years than the later periods by the thermal/nonthermal escape (Kurokawa et al., 2014). On the other hand, the isotope ratios of noble gases at 4.1 Ga show unfractionated values, implying that the atmosphere was lost after 4.1 Ga (Mathew & Marti, 2001; Jakosky & Phillips, 2001). Estimates of atmospheric nitrogen isotope composition of ALH 84001 varies in previous studies (Miura & Sugiura, 2000; Mathew & Marti, 2001).

We calculate the evolution of the total amounts of the atmosphere and hydrosphere and their isotopic compositions individually, considering the impact erosion and thermal/nonthermal escape. First, we calculate the evolution of the total atmospheric pressure due to the impact erosion using a stochastic bombardment model (Kurosawa et al., 2013). We calculate the surface age using the cumulative number of impacts and an empirical curve obtained from the lunar craters (Chyba, 1991). The erosion efficiency at each impact is calculated using a modified sector blow-off model (Vickery & Melosh, 1990). The momentum of an expanding silicate vapor is calculated using the entropy method (e.g., Ahrens & O'Keefe, 1972; Kurosawa et al., 2012) and thermodynamic data for forsterite (Sekine et al., 2012). Second, we calculate the evolution of the isotope ratios of the minor volatile elements (D/H, $^{15}N/^{14}N$, $^{38}Ar/^{36}Ar$) due to the thermal/nonthermal escape following the evolution of the total pressure. We assume the escape rates of the ion pick-up, sputtering, and photochemical escape given by Jakosky et al. (1994) and Pepin (1994) for oxygen, nitrogen, and argon. Hydrogen is lost by the Jeans escape whose escape rate is regulated by the loss of oxygen (Liu & Donahue, 1976). The fractionation factor of hydrogen is assumed to be 0.016 (Krasnopolsky et al., 1998; Krasnopolsky 2000). We adapt the fractionation factors of other species (nitrogen and argon) tabulated in Jakosky et al. (1994).

The total pressure decreases in several orders of magnitude during the first several hundred million years which corresponds to the heavy bombardment period, whereas the degree of pressure reduction is relatively insignificant after this period. The nitrogen and argon isotope ratios start to increase as the total pressure decreases. On the contrary, the D/H ratio increases independently of the total atmospheric pressure because the major reservoir of hydrogen is the hydrosphere.

Comparing our results with the isotopic data at 4.1 Ga recorded in the martian meteorite ALH 84001, we propose a scenario that the loss of atmosphere and hydrosphere had proceeded before 4.1 Ga. An efficient isotopic fractionation of atmospheric nitrogen and noble gases due to the thermal/nonthermal escape started after the impact erosion of the thick early atmosphere during the heavy bombardment period.

Keywords: Mars, atmosphere, hydrosphere, isotope, impact, atmospheric escape