Significant Water Loss during Noachian Era: Constraints from Hydrogen Isotopes in Martian Meteorites

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Introduction: Martian surface morphology implies that Mars was once warm enough to maintain persistent liquid water on its surface [1]. Although the high D/H ratio (~4500 ‰) of the current Martian atmosphere and hydrosphere [1, 2] suggests that significant water should have been lost from the surface during the Martian history, the timing and amount of the water loss have been poorly constrained. Whereas previous studies have focused on the water loss after the disappearance of Martian magnetic field [3], studies for the Noachian (4.5-3.7 Ga) period are limited.

Recent technical developments of ion-microprobe analysis of Martian meteorites have provided more accurate estimation of hydrogen isotope compositions (D/H) of Martian water reservoirs [4-6]. Based on the D/H data from the meteorites, this study determines the amount of water loss during Noachian and post-Noachian periods, and consequently demonstrates that the water loss during early Noachian was more significant than in the rest of the Mars history.

Method: We assume that surficial water is lost in two stages: Stage-1 (4.1-4.5 Ga) and -2 (present-4.1 Ga) (Fig. 1). The boundary (4.1 Ga) is derived from the crystallization age of ALH 84001, the only Martian meteorite formed in Noachian [7]. The amounts of water loss in Stage-1 ($L_{4.5\text{-}4.1\text{Ga}}$) and -2 ($L_{4.1\text{-}0\text{Ga}}$) are calculated backward from the present following the equations of (1) and (2) [3],

$$R = \frac{L}{(I_{t_2}/I_{t_1})^{1/(1-f)} - 1} \quad (1)$$

$$f = \frac{d[\mathrm{D}]/\mathrm{D}}{d[\mathrm{H}]/\mathrm{H}}, \quad (2)$$

where R is the total amount of water in the reservoir, f is a fractionation factor, and I_{t2} and I_{t1} are the D/H ratios before and after the water loss, respectively. We employ f of 0.016, a representative value for Martian present condition [8, 9]. Both water reservoir and water loss are expressed in ocean depth [m] as a global equivalent layer (GEL).

We employ the initial δD of 275 ‰ for the 4.5 Ga primordial Martian water (Fig. 1). This value is derived from analyses of a primitive basaltic meteorite, Yamato 980459, that represents a primary melt from a depleted mantle source formed at ~4.5 Ga [4]. A δD range (1200-3000 ‰) of the near-surficial water reservoir at 4.1 Ga is derived from analyses of magmatic phosphate and secondary carbonate minerals in ALH 84001 [5, 6].

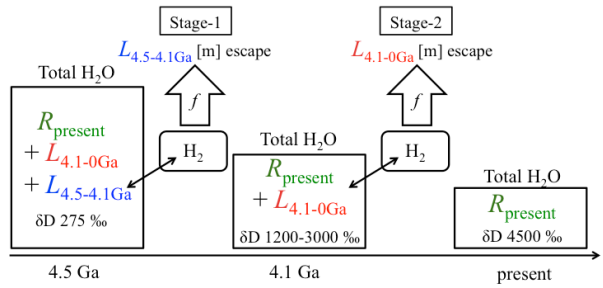

Fig. 1: Schematic illustration of the two stage model for the evolution of the global surface water reservoir on Mars. δD = $[(\mathrm{D/H})_{sample}/(\mathrm{D/H})_{reference}-1]\times1000$, where the reference is Standard Mean Ocean Water (SMOW). $R_{present}$ is the size of the present water reservoir.

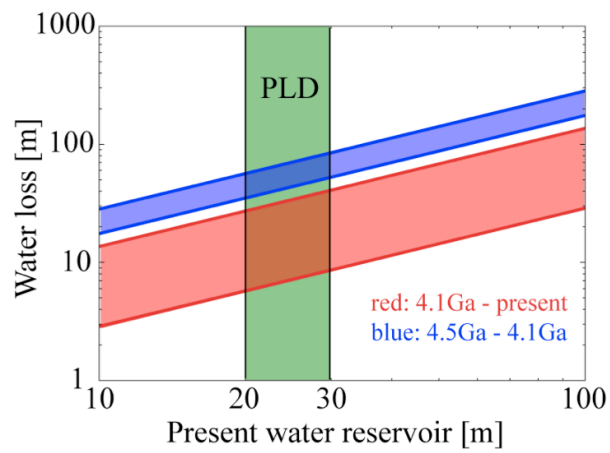

Fig. 2: Water loss during Stage-1 (blue) and Stage-2 (red) as a function of $R_{present}$. The width of the blue and red stripes is derived from the δD uncertainty (1200-3000 ‰) for ALH 84001. An estimated range for the present water reservoir in PLD (green) [10, 11] is also shown.

Results: The results show that water losses in Stage-1 ($L_{4.5\text{-}4.1\text{Ga}}$) and Stage-2 ($L_{4.1\text{-}0\text{Ga}}$) are positively correlated with the amount of the present water reservoir ($R_{present}$), and that $L_{4.5\text{-}4.1\text{Ga}}$ is always greater than $L_{4.1\text{-}0\text{Ga}}$ at any $R_{present}$ (Fig. 2). This indicates that the water loss is more significant in Stage-1 than in Stage-2. This is simply because more water loss is required to change the D/H ratio of larger water reservoir. Present water reservoirs exist mainly as polar layered deposits (PLD), which corresponds to 20-30 m GEL [10, 11]. By taking this value into account, $L_{4.5\text{-}4.1\text{Ga}}$ and $L_{4.1\text{-}0\text{Ga}}$ are 35-85 m and 5.7-41 m, respectively (Fig. 2). The sum of these values ($L_{4.5\text{-}4.1\text{Ga}}$, $L_{4.1\text{-}0\text{Ga}}$, and $R_{present}$)

yields 82-120 m GEL for the total water reservoir at 4.5 Ga (Fig. 3).

Discussions: We employ the fractionation factor f = 0.016, which is valid under the present cold Mars. This fractionation involves two mechanisms: (i) D-H exchange between H_2O and H_2 and (ii) escape-induced fractionation of H against D. Geological evidence suggests that Noachian Mars was warmer than the present [1]. Such a warmer condition reduces the former D/H fractionation between H_2O and H_2 (i.e., larger f). High extreme UV (EUV) radiation of younger Sun, which induces high exobase temperature [12], also reduces the latter D/H fractionation by the atmospheric escape as a result of intense escape of both H and D. Thus, because the f of 0.016 employed in this study is likely to be minimum (i.e., largest fractionation), our model yields the minimum estimate on the water loss. Even if it is granted, f is thought to be greater in older Stage-1 than in younger Stage-2 because of warmer near-surface and hotter exobase conditions in Stage-1 than in Stage-2. Thus, our main conclusion, more water loss in Stage-1 than Stage-2, would not change.

If more realistic f value is taken into account, water loss and initial water reservoir become larger. [12] showed that Martian thermospheric temperature was ~10^4 K under the high solar EUV radiation. Assuming that Noachian Mars was as warm as ~273 K, then f increases as high as ~ 0.3 [13], and our model provides $L_{4.5\text{-}4.1\text{Ga}}$ and $L_{4.1\text{-}0\text{Ga}}$ values of 8.5-71 m and 79-180 m, respectively. This results in the total water reservoir of 150-220 m at 4.5 Ga, which is consistent with the ~150 m Noachian ocean inferred from the geomorphologic evidence [14].

The "bottleneck" to restrict the water loss is remaining oxygen as a result of the hydrogen escape. Two mechanisms have been proposed to remove the remaining oxygen from the system: (i) escape to the space and (ii) oxidation of surface material. Water loss estimated by oxygen escape models [3, 15] are shown in Fig. 3. [3] calculates an amount of water loss after the disappearance of Martian magnetic field (i.e., equivalent to Stage-2), whereas [15] provides a water loss around 4.5 Ga (i.e., equivalent to Stage-1); note that [15] yields the maximum estimate because [15] assumes no magnetic field during the first 0.15 Gyr. These oxygen escape models are basically consistent with our results at f = 0.016.

If f was actually greater than 0.016 in the past, more oxygen should have been removed and the oxidation of surficial materials is required to lose more water from the planet. However, [16] indicates that the contribution of sulfur oxidation to water loss was ~10 m GEL, which is significantly smaller than the amounts of water loss estimated by the oxygen escape models [3, 15]. Thus, different oxidation processes such as sarpentinization [16] might have occurred to facilitate the efficient water loss.

Water supply by comets could have possibly changed the D/H ratio of the Noachian Martian water reservoir without significant hydrogen escape, because comets have typically higher D/H ratios (~1000 ‰) [17] than that of the Martian primordial water (< 275 ‰) [4]. For example, supply of ~10^{19} kg comets, which corresponds to ~100 m GEL, increases the D/H ratio of the surface water reservoir by ~1000 ‰. However, comets are typically enriched in noble gases. ~10^{19} kg comets with a probable Xe/H_2O ratio of ~10^{-5} [18] result in 10^{14} kg of Xe, which is 10^6 times Martian atmospheric Xe. Thus, such a significant supply of comets is unlikely.

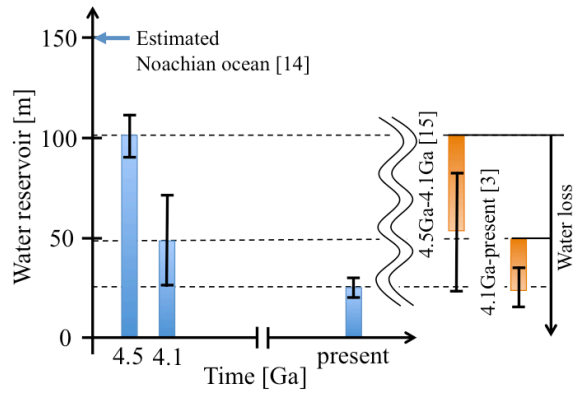

Fig. 3: Evolution of Martian water reservoir estimated in this study (blue), compared with water losses estimated by oxygen escape calculation models [3, 15] (orange).

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