



Evolution of water reservoirs on Mars: Constraints from hydrogen isotopes in martian meteorites



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ABSTRACT

Martian surface morphology implies that Mars was once warm enough to maintain persistent liquid water on its surface. While the high D/H ratios (~6 times the Earth's ocean water) of the current martian atmosphere suggest that significant water has been lost from the surface during martian history, the timing, processes, and the amount of the water loss have been poorly constrained. Recent technical developments of ion-microprobe analysis of martian meteorites have provided accurate estimation of hydrogen isotope compositions (D/H) of martian water reservoirs at the time when the meteorites formed. Based on the D/H data from the meteorites, this study demonstrates that the water loss during the pre-Noachian (>41–99 m global equivalent layers, GEL) was more significant than in the rest of martian history (>10–53 m GEL). Combining our results with geological and geomorphological evidence for ancient oceans, we propose that undetected subsurface water/ice (≈ 100 –1000 m GEL) should exist, and it exceeds the observable present water inventory (≈ 20 –30 m GEL) on Mars.

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1. Introduction

Mars is generally considered to be a cold and dry planet, with relatively small amounts of water–ice observed at the polar caps (e.g., Jakosky and Phillips, 2001; Christensen, 2006). On the contrary, a number of geological observations, such as dense valley networks (Scott et al., 1995; Carr and Chuang, 1997; Hoke et al., 2011) and deltas (Cabrol and Grin, 1999; Ori et al., 2000; Di Achille and Hynek, 2010), provide definitive evidence that large standing bodies of liquid water (i.e., oceans and lakes) existed in the early history, the presence of which would have profound implications for the early climate and habitability of Mars (e.g., Carr, 2007; Head et al., 1999; Dohm et al., 2011). The geological observations further include the detection of water-lain sediments and a variety of hydrous minerals (e.g., clays) (e.g., Fialips et al., 2005; Bibring et al., 2006) and evaporites (e.g. gypsum) (e.g., Osterloo et al., 2008) commonly formed by aqueous processes, implying Earth-like hydrologic activities, with Noachian lakes and/or oceans. Despite such compelling evidence for hydrologic conditions that could support oceans and lakes, there are, however, major gaps in

our understanding of the evolution of surface water: e.g., what was the global inventory of martian surficial water/ice, and how did it change through time.

The global inventory of ancient surficial water has been estimated based on the size of reported paleo-oceans (e.g., Head et al., 1999; Clifford and Parker, 2001; Carr and Head, 2003; Ormö et al., 2004; Di Achille and Hynek, 2010). Topographic features of putative paleo-shorelines suggest that large bodies of standing water once occupied the northern lowlands (Head et al., 1999). Shoreline-demarcation studies of the northern lowlands point to several contacts that yield variable sizes of paleo-oceans estimated to range from $\sim 2 \times 10^7$ km³ to 2×10^8 km³ (corresponding to global equivalent layers (GEL) of 130 m to 1500 m, respectively) (Carr and Head, 2003, and references therein). Though the shoreline demarcations (Parker et al., 1989, 1993), supported by Mars Orbiter Laser Altimeter (MOLA) topography (Head et al., 1998, 1999), could not be confirmed using Mars Orbiter Camera (MOC) and Thermal Emission Imaging System (THEMIS) image data (Malin and Edgett, 1999, 2001; Ghatan and Zimbelman, 2006), this variation has been interpreted to reflect the historical change in the ocean volume. For example, two major contacts (contact-1: Arabia shoreline and contact-2: Deuteronilus shoreline) individually represent the larger Noachian and smaller Hesperian

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Table 1

Geologic-mapping-based, time-stratigraphic information, including the Noachian, Hesperian, and Amazonian Periods (Scott and Carr, 1978). The geologic periods have been given estimated absolute age ranges based on impact crater models (Table 1 is modified from Hartmann and Neukum, 2001). Note that we performed comparative analyses among the estimated water amounts of the pre-Noachian, approximately referred to here as Stage-1, and Noachian–Amazonian, approximately referred to as Stage-2, based on recent D/H dataset from martian meteorites.

Stage	Period	Estimated absolute age range [Ga]
2	Amazonian	3.3–2.9 to present
	Hesperian	3.7–3.5 to 3.3–2.9
	Noachian	4.2 to 3.7–3.5
boundary at 4.1 Ga		
1	Pre-Noachian	4.5 to 4.2

oceans, respectively (Parker et al., 1993; Clifford and Parker, 2001; Carr and Head, 2003). Although these geomorphologic studies have provided significant constraints on the history of martian paleo-oceans, they lack information about pre-Noachian (Frey, 2006) oceans because no geologic records are available. Furthermore, the shoreline-demarkation approaches would not be applicable to the youngest Amazonian (3.1 Ga to present) era, during which the surface water would have occurred mostly as ice (Clifford and Parker, 2001; Carr and Head, 2010).

This study endeavors to trace the global inventory of surficial water through time beginning with the embryonic stages of development of Mars (i.e., 4.5 Ga) to present day based on a geochemical approach of hydrogen isotopes (D/H: deuterium/hydrogen). Hydrogen is a major component of water (H₂O) and its isotopes fractionate significantly during hydrological cycling between the atmosphere, surface water, and ground and polar cap ices. Telescopic studies have reported that the hemispheric mean of the martian atmosphere has a D/H ratio of ~ 6 times ($\delta D \approx 5000\%$) the terrestrial values (Owen et al., 1988); $\delta D = [(D/H)_{\text{sample}}/(D/H)_{\text{reference}} - 1] \times 1000$, where the reference is Standard Mean Ocean Water (SMOW). Because the high atmospheric D/H ratio is interpreted to result from the preferential loss of hydrogen relative to the heavier deuterium from the martian atmosphere throughout the planet's history (Lammer et al., 2008), the deuterium enrichment can be used to estimate the amount of water loss due to the atmospheric escape.

Compared to a number of geomorphologic studies (e.g., Scott et al., 1995; Head et al., 1999; Clifford and Parker, 2001; Carr and Head, 2003; Di Achille and Hynek, 2010), only a few geochemical investigations have been conducted (Chassefière and Leblanc, 2011; Lammer et al., 2003). This is partly because there have been a limited number of reliable D/H datasets for martian meteorites, and the martian meteorites typically have younger ages (typically, < 1.3 Ga) (Nyquist et al., 2001). However, recent technical developments of ion-microprobe analysis of martian meteorites including the 4.1 Ga ALH 84001 pyroxenite have provided more accurate and comprehensive datasets for D/H ratios of martian water reservoirs (e.g., Greenwood et al., 2008; Usui et al., 2012; Hallis et al., 2012a, 2012b), yielding new information helpful for unraveling the origin and evolution of water on Mars. Furthermore, although martian meteorites were derived from limited and highly biased regions of the surface of Mars (McSween et al., 2009; Usui et al., 2010; Christen et al., 2005), their radiometric ages are more accurate and precise than crater counting ages.

Based on the recent D/H dataset from martian meteorites, we estimate the amount of water loss during 4.5 Ga to 4.1 Ga, which we refer to here as Stage-1 in our analysis (approximating the pre-Noachian; Table 1), and consequently demonstrate that the water loss during 4.5 Ga to 4.1 Ga was more significant than in the rest of the Mars history (4.1 Ga to present, approximating Noachian–Amazonian; Table 1), which we refer to as Stage-2 in

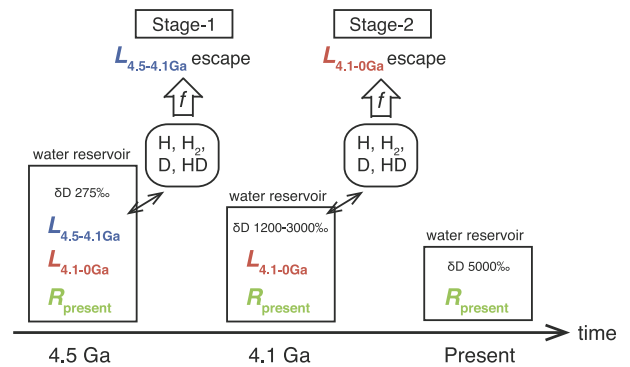


Fig. 1. Schematic illustration of the two-stage model for the evolution of the global surface water reservoir on Mars. R_{present} is the size of the present water reservoir, $L_{4.5-4.1\text{Ga}}$ and $L_{4.1-0\text{Ga}}$ are the water loss during Stage-1 and -2, and f is the fractionation factor (see text).

our analyses. Combining our results with geological estimates for the volume of martian paleo-oceans, we propose that unidentified surficial water–ice reservoirs should currently exist and the volume (≈ 100 – 1000 m GEL) should exceed the estimated present water inventory (20–30 m GEL, Christensen, 2006) on Mars.

2. Calculation

The amount of water loss due to the atmospheric escape between time t_1 and t_2 can be calculated from an assumed amount of present water reservoir using the following equations:

$$L_{t_1-t_2} = R_{t_1} - R_{t_2} = R_{t_2} \times \left[\left(\frac{I_{t_2}}{I_{t_1}} \right)^{\frac{1}{1-f}} - 1 \right], \quad (1)$$

and

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

Here $L_{t_1-t_2}$ is the amount of water loss due to the atmospheric escape during the time from t_1 to t_2 , R and I are an amount of water reservoir and a D/H ratio at each time, respectively, f is the fractionation factor, and $[H]$ and $[D]$ are the abundances of H and D in the combined reservoirs in atoms cm^{-2} (Lammer et al., 2003). Both the volumes of water reservoir and water loss are expressed in ocean depth [m] as a global equivalent layer (GEL). Using the density of water of 10^3 kg m^{-3} and the surface area of $1.4 \times 10^{14} \text{ m}^2$, 1 m GEL corresponds to $1.4 \times 10^{17} \text{ kg}$ of water. Eq. (1) can be rewritten as:

$$\frac{R_{t_1}}{R_{t_2}} = \left(\frac{I_{t_2}}{I_{t_1}} \right)^{\frac{1}{1-f}}, \quad (3)$$

which gives a ratio of the amount of water for t_1 and t_2 . Eq. (3) is used in Sections 3.2, 3.3, and 3.4 to discuss the evolution of the amount of water through time.

We employ the fractionation factor f of 0.016, a representative value reported for the present martian condition (Krasnopolsky et al., 1998; Krasnopolsky, 2000). Since the D/H fractionation due to magmatic outgassing is relatively insignificant (e.g., $f = 0.9$, Pineau et al., 1998), we consider the D/H fractionation to be solely due to atmospheric escape. We calculate surface water loss in two stages: Stage-1 (4.5–4.1 Ga) and -2 (4.1 Ga–present), as shown in Fig. 1. The boundary (4.1 Ga) is derived from the crystallization age of ALH 84001, the only martian meteorite which records a Noachian crystallization age (Lapen et al., 2010), though there has been a very recent reporting of a martian meteorite NWA 7533 with an extremely ancient (≈ 4.4 Ga), pre-Noachian age (Humayun et al., 2013).

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