THE HISTORY OF WATER ON MARS AS CONSTRAINED THROUGH HYDROGEN ISOTOPES.

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Introduction: The history of water on Mars is still an active area of investigation. There is abundant geological evidence for large amounts of liquid water forming fluvial channels and hydrated minerals throughout geological history [1]. Aqueous activity appears to have decreased throughout geological time [1]. Currently, most Mars water is stored in subsurface ice or in the polar cap and amounts to 20-35 global equivalent layers (GEL) [2-4]. It is still unclear how much water was present at different periods in Mars' history and what subsequently happened to that water.

Previous studies have suggested that Mars may have experienced significant water loss due to exospheric escape processes, as evidenced through very high atmospheric D/H isotope ratios [5-6]. However, the current H escape flux (1-11*10^{26} H/s) measured by MAVEN can only account for the loss of 5-30 GEL water and cannot explain the vast amounts of water thought to have been lost through geological time [7]. Estimates of past surface water reservoirs are 150-1000 GEL based on geomorphological features [8]. Elkins-Tanton [9] modelled the catastrophic degassing of a magma ocean and subsequent atmospheric growth in early Mars history, yielding degassing of ~550 GEL for a 500 km deep magma ocean containing 0.05 wt% H_2O [9]. Hence, it is possible that the H escape flux or the effects of non-thermal escape processes may have been higher in the past. In addition, some studies suggest that water could also have been lost due to the production of hydrated minerals within the crust or groundwater reservoirs that have subsequently become part of the undetected subsurface cryosphere [8,10]. However, a detailed model exploring the effects of subsurface ice sequestration or crustal hydration on the evolution of water reservoirs has never been proposed.

In this study, we investigate all of the dominant water-related processes (volcanic degassing, Jeans escape, ice formation, and hydrated crust formation) in an integrated model that simulates the size of water reservoirs on Mars through time. This model is compared to the current size of the water reservoir in polar caps (20-35 GEL [2-4]) and hydrogen isotope compositions of surface water and atmospheric reservoirs from meteorites, Mars rover samples, and the current atmosphere.

Model methods: Hydrogen isotope equilibrium fractionation from Jeans escape can be modelled through Rayleigh distillation: $R = R_0 * \left(\frac{X}{X_0}\right)^{\propto-1}$. Here R is the isotope ratio of the residual reservoir, while R_0 is the isotope ratio of the initial reservoir. X is the size of the residual reservoir, while X_0 is the size of the initial reservoirs. $\propto$ is the fractionation factor. In order to simulate the change in R through time, we evaluate X and X_0 at each million year time step in our model.

Fig. 1 shows a box model of the interacting reservoirs of water in our model. The size of residual surface water reservoir (X) depends on the amount of water released to the atmosphere through volcanic degassing and the amount of water lost from the atmosphere through Jean's escape (Fig. 1). The sizes of these reservoirs can be modelled through time by using measured or calculated escape fluxes and modelled volcanic degassing curves.

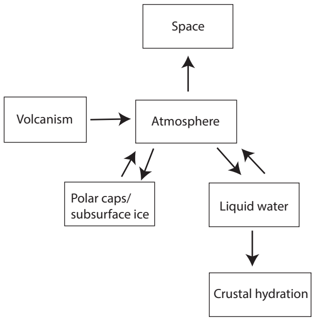

Figure 1: Box model of water reservoirs on Mars .

Model conditions: Initial conditions for the model requires determining R_0 and X_0 from literature. A range of values of R_0 = 2-4 x SMOW can be determined based on SIMS analysis of hydrogen isotopes of water within minerals from the ~4.1 Ga meteorite ALH84001 [11-12]. Consequently, our model starts at 4.1 Ga and does not take into account earlier interactions with a potential magnetic field or how the primordial atmosphere produced a D/H of 2-4 x SMOW, when the mantle has been determined to contain water with δD of 275 ‰ [13].

The Jeans escape flux can be calculated from first principles [14-15]. It depends on the mixing ratio of H_2 and H_2O at the homopause and has likely varied through time. The H_2 is produced photochemically from H_2O in the Martian atmosphere. We performed calculations of the escape flux using the 1D photochemical and transport model, KINETICS [14], for an early 108 km thick Martian atmosphere containing 1 bar CO_2 and 10% N_2 with temperature and diffusion coefficient profiles from [16-17]. These yield an escape flux of 3*10^{25}-3*10^{30} H/s depending on H_2 content (0-10^{-2} H_2). Independently, order of magnitude estimates using the barometric law and equations in [14] yield an estimate of 10^{28} H/s for a 1 bar early Mars atmosphere for comparison with KINETICS results. The current escape flux measured by MAVEN (~$5*10^{26}$ H/s) cannot explain the loss of 150-1000 GEL water (Fig. 2). However, the calculated escape fluxes up to ~4 orders of magnitude higher would generate sufficient water loss (Fig. 2). Further study is required to ascertain the permitted upper and lower limits to the escape flux at different periods in Mars' geological history.

Likewise, estimates for volcanic degassing vary considerably depending on assumptions regarding crustal production rate, surface area fraction for volcanic degassing (f_p), outgassing efficiency (η), and water content within the mantle ($X_{water,mantle}$) (Fig. 2) [18-20]. Different studies provide different model solutions for volcanic degassing. Several models indicate that 40-80% of the initial mantle reservoir may have outgassed resulting in a contribution of 150-250 GEL for an assumed initial water content of 100 ppm with in the mantle (Fig. 2) [18-19,21-22]. However, other models result in outgassing of only 5-10% of the initial mantle (Fig. 2) [18,20]. Table 1 summarizes the range of estimated initial conditions, escape fluxes, and volcanic degassing evaluated that are going to be used in our model.

Initial results and future work: A simple Rayleigh distillation model assuming that the H isotopic composition that is only dependent on Jeans escape, results in an initial surface water reservoir with estimated size of 70-150 GEL depending on fractionation factor [23-25]. This does not align with an escape flux of 10^{26} H/s (~ 10 GEL escaped water), but could be explained by an early Mars escape flux closer to 10^{28}-10^{30} H/s (Fig. 2). In addition, current models of volcanic degassing suggests that >100 GEL of water may have outgassed throughout geological history (Fig. 2).

Geological estimates of larger initial water reservoir sizes in the Early Noachian would therefore necessitate the presence of water in a missing reservoir [5-7]. We propose that such a reservoir could be constituted by deep ices or hydrous minerals in the Martian crust. Remote sensing evidence show that upwards of ~500 GEL of water may be retained within the crust based on detection of smectites in crustal sections of 10 km within Valles Marineris [26]. Future work will consist of running integrated time-dependent models that take into account our proposed estimates of escape flux ranges, volcanic degassing ranges, and remote sensing evidence for ice and hydrated mineral formation.

Table 1: Overview of parameter ranges for initial conditions evaluated for use in future model

(R_0)	2-4 x SMOW	[11-12]
ϕ_{escape}	$1\text{-}11 \times 10^{26} - 8 \times 10^{28}$ H/s	[7], *this study*
($\propto_{escape}$)	0.005-0.32	[23-25]
Degassing models	Grott et al. (2011) Breuer and Tosi (2018) Hauck and Phillips (2002)	[18-20]
f_p	0.01-1	[18]
η	0.4	[18]
$X_{water,mantle}$	1 ppm – 1 wt%	[18-22]

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Figure 2: Models of the range of estimated water amounts related to Jeans escape and volcanic degassing through geological time assuming $X_{water,mantle}$ is 100 ppm [18-20].