CRUSTAL HYDRATION OF OCEAN-SCALE VOLUMES CONTROLLED MARTIAN CLIMATE AND HABITABILITY.

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Introduction: There is abundant geological evidence for large volumes of surface liquid water forming fluvial and potential ocean shoreline features early in Martian history. These approximate a ~100-1500 global equivalent layer (GEL) in meters based on observations of geomorphological features and crustal reservoirs of hydrated minerals [1-2]. Today, most water is stored in the polar cap or subsurface ice and amounts to only 20-40 m GEL of water [3-4]. It is clear based on observation that liquid water availability on Mars has decreased over geological time. However, the processes dictating the size of the atmospheric, liquid, and ice reservoirs of water over Mars' history and water's ultimate fate remain unresolved.

Hydrated phases in meteorite ALH84001 retain hydrogen isotope ratio (D/H) compositions of 2-4 x SMOW for the Early Noachian atmosphere [6-7], while the present-day atmosphere D/H is 5-10 × SMOW (Standard Mean Ocean Water) [e.g. 5]. Previous studies suggested that the fractionation of atmospheric D/H can be explained by significant water loss due to atmospheric escape alone [5,8-9]. These studies model a maximum of 50-240 m GEL water on ancient Mars, which is relatively little in comparison to geological observations [5,8-9]. These models also require much higher past H escape fluxes compared to the current H escape flux ($1\text{-}11\times10^{26}$ H/s; [10]). Hence, this leads to a paradox in which the measured H escape flux, the heavy D/H composition of present-day Mars, and geological estimates of a large, ancient exchangeable reservoir are not compatible with each other.

However, we have abundant evidence for loss of surface water to the crust through formation of globally extensive hydrated minerals early in Martian history [2], which has not been considered in previous studies of water loss. We hypothesize that the inclusion of crustal hydration during the first 1-2 billion years decreases the volume of the exchangeable liquid water reservoir [11]. Consequently, much less atmospheric loss is needed in order to efficiently fractionate the Martian atmosphere to present-day D/H values [11]. This explains both the D/H evolution and loss of water on Mars.

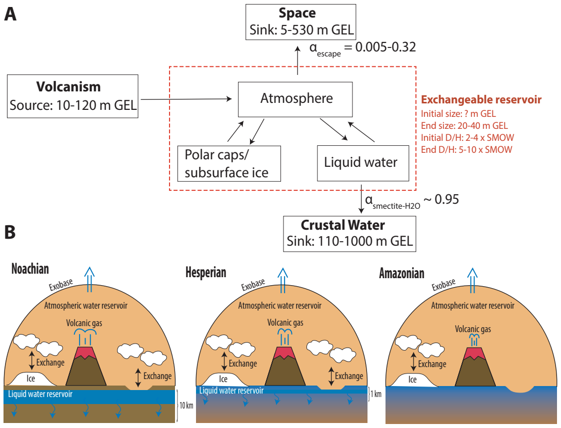

Figure 1: (A) Box model schematic showing source/sink reservoir size ranges. (B) Schematic of time evolution in source/sinks incorporated in the model.

Model methods: To examine this hypothesis, we developed a comprehensive water budget and D/H model that integrates all major water sinks and sources (Fig. 1). We treat surface liquid water, ice, and atmospheric vapor as a single exchangeable reservoir. All simulations are constrained such that the exchangeable reservoir cannot be negative at any point in time. It must reproduce 20-40 m GEL water today as well as D/H composition of the present-day exchangeable reservoir. We determine permitted source and sink fluxes for crustal hydration (F_{crust}), volcanic degassing ($F_{volcanic}$), and atmospheric escape (F_{esc}) for the Noachian, Hesperian, and Amazonian periods based on a literature review of observational and previous model constraints. F_{crust} value ranges are calculated from remote sensing constraints on the size of the crustal reservoir of hydrated minerals and a compilation of orbital remote sensing, rover, and meteorite measurements of water contents in the Martian crust [e.g. 2]. $F_{volcanic}$ value ranges are based on models from [12]. F_{esc} value ranges are adapted from KINETICS [13] photochemical model simulations from this study for the Noachian and Hesperian and observations from MAVEN /MARS Express for the Amazonian [10]. Isotopic equilibrium fractionations are modelled through stepwise Rayleigh distillation with a fractionation factor of atmospheric escape of 0.005-0.32 [14-16]. The fractionation factor between smectite and water of 0.95 [17] is used in the stepwise Rayleigh distillation model to approximate fractionation by crustal hydration. However, such fractionation is minor compared to that caused by atmospheric escape.

Results: Mixing with depleted volcanically outgassed water vapor (Fig. 2) causes the D/H of the exchangeable reservoir to decrease. Atmospheric escape causes D/H of the exchangeable reservoir to fractionate towards heavier values. The inclusion of crustal hydration during the early part of Mars history increases D/H fractionation because crustal hydration substantially decreases the exchangeable reservoir size and less atmospheric escape is needed to distill the exchangeable reservoir to high D/H compositions.

During the Noachian, decreasing exchangeable reservoir size and increasing D/H are a feature of all model simulations. During the Amazonian, the exchangeable reservoir size is low and its D/H increases slightly in all simulations due to the lack of crustal hydration, low H escape flux, and low volcanic degassing flux. By contrast, the D/H evolution and water levels during the Hesperian is relatively unconstrained because different volcanic outgassing models may result in D/H increasing, decreasing, or staying constant over this period (Fig. 2).

Simulations from our entire parameter space show that ~30-99% of initial exchangeable water reservoir was lost through crustal hydration (Fig. 3). This demonstrates that crustal hydration is as important or even more important than atmospheric escape as a loss mechanism for water on Mars. In fact, certain model solutions do not require an increase in the average atmospheric escape flux compared to present-day to account for the observed increase in D/H and decrease in the exchangeable water reservoir.

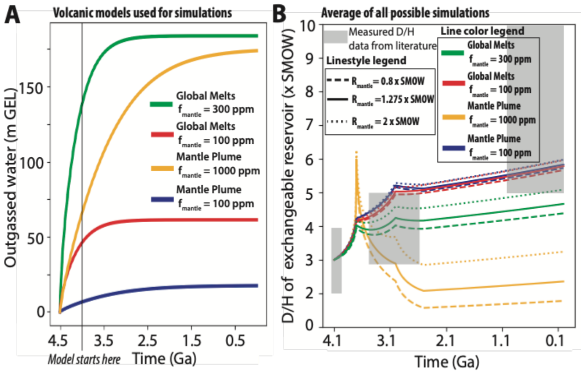

Figure 2: (A) Volcanic degassing models from [12] used in study. F_{mantle} refers to water contents of the mantle, value ranges from [17]. (B) Resulting simulation averages using differing volcanic degassing models from (A) and differing D/H compositions for the mantle (R_{mantle}) as based on meteorites adapted from [19].

Discussion and conclusions: Our model permits a range of early Noachian volumes for the initial exchangeable reservoir of 100-1500 m. Water availability decreased by 40-95% over the Noachian, while Amazonian water availability was similar to today (Fig. 3).

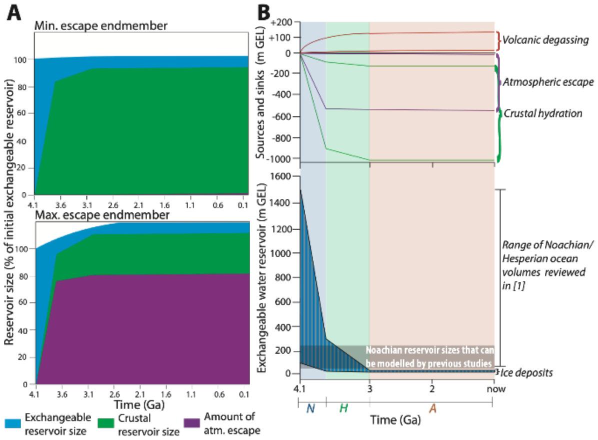

Figure 3: (A) Endmembers of solutions that show the changes in reservoir sizes through geological time. (B) Overview of ranges in flux sizes and all solutions simulating the size of the exchangeable reservoir through time.

Incorporation of water loss by both crustal hydration and atmospheric escape presented in these solutions resolves the major paradox concerning the incompatibilities of the measured H escape flux, the heavy D/H composition of present-day Mars, and geological estimates of a large, ancient exchangeable reservoir [11]. Our modeled early Noachian volumes for the initial exchangeable reservoir (100-1500 m GEL) are compatible with geological estimates of surface water at the time and the lower end of proposed protoatmosphere volumes. The parameter space allows for either a Hesperian exchangeable reservoir that was initially large (≤300 m GEL) and decreased or was similar to present-day levels of 20-40 m GEL. Some simulations are comparable with proposed Hesperian ocean volumes [1]. During the Amazonian period, the modeled low water availability is consistent with geomorphological and mineralogical observations of minimal aqueous activity suggesting the presence of an arid climate. Hence, our modeled evolutionary trajectories explain the major trajectories of Martian climate [11]. This highlights the importance of irreversible crustal hydration in controlling the timescales of planetary habitability as well as the importance of volatile recycling mechanisms, like plate tectonics on Earth, as regulators of the habitability potential of terrestrial planets [11]. Continued examination of D/H in the Martian meteorite record, data from Gale crater, and returned samples collected by the Perseverance rover provide crucial tests of the evolution of water reservoir size and loss.

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