THE HISTORY AND INVENTORY OF WATER ON MARS

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Introduction: The hydrogen isotope ratio (D/H) of H_2O on Mars is fundamental to determining the history of martian water. When compared with terrestial ocean water (VSMOW) a large global enrichment in D is observed on Mars, both within the atmosphere and measured surface sedimentary rocks [e.g., 1-2]. This enrichment can be produced only by escape of a large fraction of hydrogen to space, with H escaping more readily than D. D/H in martian atmospheric water vapor today is enhanced by an average of ~6x relative to VSMOW, but varies seasonally and spatially between ~2-10x, apparently due to wintertime condensation and springtime sublimation of water [1]. The D/H ratio measured in 3 billion-year-old surface mudstone by the SAM instrument onboard the Curiosity rover shows an enrichment of ~3x compared to VSMOW [2]. Assuming the water in this mudstone was in equilibrium with the average martian atmosphere 3 billion years ago, and assuming the original martian atmospheric D/H ratio was similar to that of Earth [3-4], a trend of increasing atmospheric D/H ratio over time is indicated, reflecting the loss of hydrogen to space. In addition, this high D/H ratio in such an old mudstone indicates a rapid loss of hydrogen early in Mars' history, rather than a constant rate of loss over time. This rapid initial hydrogen loss fits well with global observations of an early wet Mars (Noachian) followed by a period of drying (Hesperian) and subsequent ~3 billion years of a relatively dry and inactive surface environment (Amazonian) [e.g., 5].

Martian water inventory based on global observations and surface measurements: Atmospheric water exchanges with non-atmospheric water, and the fraction lost pertains to the sum of water in the atmosphere plus in these exchangeable reservoirs (e.g., polar ice deposits and ground ice). In addition, outgassing by volcanism can affect the D/H ratio in surface water. Carr and Head [6] estimate the total volume of water in current martian exchangeable reservoirs as 20-30 m GEL (global equivalent layer). We can use this value, the current D/H, and the history of D/H to estimate the volume of exchangeable reservoir through time. The present-day average atmospheric enrichment of D/H (6x VSMOW), combined with the present-day exchangeable reservoir of 20-30 m H_2O, yields an initial amount of exchangeable water of ~130-600 m GEL. This requires a loss to space of 110-570 m GEL. Enrichment in D/H by 3x at 3 Ga requires an enrichment between then and now of 2x. In turn, and including outgassing by volcanism that partially resets the D/H, the reservoir at 3 Ga would have been 40-130 m GEL, and the amount lost to space between then and now would have been 25-210 m GEL. Based on the size of this exchangeable reservoir, we provide an observation-based estimate of the water inventory of Mars. The amount at the surface has been as great as 380-970 m GEL H_2O. Of this, 110-570 m has been lost to space, accounting for a large fraction (~30-60 %) of the total water. The majority of the remaining water has been incorporated into surface and subsurface minerals, or been locked up in the crust as ice.

Martian meteorite D/H ratios: This neat story is not reflected in D/H measurements from the martian meteorites, which do not show the expected trend of increasing D/H ratios with decreasing age [e.g., 7-8]. The interpretation of Martian meteorite D/H is complicated by multiple factors, which we aim to disentangle to provide a fuller picture of martian D/H through time: (i) Possible seasonal or spatial variations in the source water at the time of crystallisation, due to condensation and sublimation, as is seen at the present epoch on Mars [1]. These variations could have been driven, especially during earlier epochs, by a seasonal water cycle analogous to that on Earth. This controls whether values measured in a single rock are indicative of global abundances at that time. (ii) Potential later modification on Mars, due to exchange of hydrogen with the Martian environment. For example, episodic or cyclic wetting could result in the development of phyllosilicate veins within surface/subsurface rocks with D/H ratios representative of only the last wetting phase. (iii) Possible changes in D/H resulting from impact. All meteorites have been shocked to some degree by the impact that blasted them from the martian surface, and several meteorites show evidence of more than one impact event (e.g., ALH 84001 [9]). Changes in D/H due to shock pressure are not well studied, but have been observed in laboratory studies of certain hydrous minerals [e.g., 10]. (iv) Potential contamination on Earth after arrival, due to exchange of water with the environment. Exchange has been observed to occur rapidly (years) in at least some instances [e.g., 11].

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