# THE HISTORY AND INVENTORY OF WATER ON MARS 

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## Introduction:

Key questions about Mars relate to the history and abundance of water at the surface and the forms that it can take (vapor, liquid, solid). Water interacts with the surface, affecting the geological and geochemical history. And water is intimately connected to the potential for life to exist or have existed.

We use measurements related to the enrichment of $\mathrm{D} / \mathrm{H}$ in $\mathrm{H}_{2} \mathrm{O}$ due to escape to space, surface morphology, and surface and subsurface mineralogy, to derive an observational estimate for the total inventory of water, its current distribution on the planet, and its history.

## Measurements of $\mathrm{D} / \mathrm{H}$ :

The ratio of $\mathrm{D} / \mathrm{H}$ in $\mathrm{H}_{2} \mathrm{O}$ is fundamental to determining the history of water, due to its large enrichment relative to its initial value. D/H in atmospheric water vapor today is enhanced by an average of $\sim 6 x$ relative to its starting point. This value varies seasonally and spatially between $\sim 2-10 x$, apparently due to wintertime condensation and springtime sublimation of water. This large a global enrichment can be produced only by escape of a large fraction of the H to space, with H escaping more readily than D.
$\mathrm{D} / \mathrm{H}$ has been measured in situ in weathering products dated at about 3 b.y. by the SAM instrument on the Curiosity rover. It shows an enrichment of $\sim 3 x$.

The original value of $\mathrm{D} / \mathrm{H}$ on Mars is very close to terrestrial, based on ratios measured within hydrous primary igneous minerals in Martian meteorites. In addition, Martian meteorites show values in weathering products that vary between $\sim 2-6 x$; these values occur in rocks dated throughout Martian history. Interpretation of Martian meteorite $\mathrm{D} / \mathrm{H}$ is complicated by multiple factors, including:
(i) Possible seasonal or spatial variations in the source water at time of incorporation into the minerals, due to condensation and sublimation, as is seen at the present epoch on Mars. Especially during earlier epochs, these variations could have been driven by a seasonal water cycle analogous to that on Earth. This effect can determine whether values measured in a single rock are indicative of global abundances at that time.
(ii) Potential modification on Mars at epochs later than when the weathering products originally formed, due to exchange of water with the Martian environment. For example, episodic or cyclic wetting could result in the development of phyllosilicate
veins within surface/subsurface rocks with $\mathrm{D} / \mathrm{H}$ 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). Changes in D/H due to shock pressure are not well studied, but have been observed in laboratory studies of certain hydrous minerals.
(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.

Due to the large uncertainties in interpretation of meteoritic $\mathrm{D} / \mathrm{H}$, we'll carry out our analysis using the initial $\mathrm{D} / \mathrm{H}$, the Curiosity measurement at about 3 b.y., and the present-day enrichment of $\sim 6 \mathrm{x}$. Our basic results will not change significantly if we use only the initial and present-day values, but we would lose fidelity on the time resolution of the history.

D/H enrichment and exchange with nonatmospheric reservoirs:

H and D are able to escape directly to space by thermal (Jeans) escape. The source of these is $\mathrm{H}_{2} \mathrm{O}$, initially in the lower atmosphere, broken apart primarily by solar UV photons. H is lighter and escapes more readily than D , so the hydrogen remaining in the atmosphere becomes enriched in D. The H and D are reincorporated back into $\mathrm{H}_{2} \mathrm{O}$ by downward mixing and chemical reactions in the middle and lower atmosphere. The relative escape rates of D and H have been calculated, but depend strongly on assumed atmospheric behavior such as warming and mixing during dust storms and the structure of the upper atmosphere, all of which can vary with time. Assuming these relative escape rates, the $\sim 6 \mathrm{x}$ enrichment represents loss of between $\sim 85-95 \%$ of the water in the system.

Atmospheric water exchanges with water not in the atmospheric, and the fraction lost pertains to the sum of water in the atmosphere plus in these exchangeable reservoirs. Exchangeable reservoirs include the polar ice deposits, ground ice identified at high and middle latitudes, and possible low-latitude ground ice. In addition, outgassing by volcanism can affect the $\mathrm{D} / \mathrm{H}$ ratio in surface water.


Fig. 1. Derived size of exchangeable reservoir (top) and fraction of $\mathrm{H}_{2} \mathrm{O}$ remaining (middle) as a function of time, as derived from D/H (bottom).

Estimates of the total volume of water in these exchangeable reservoirs today are $20-30 \mathrm{~m}$ GEL (global equivalent layer). We can use this value, the current $\mathrm{D} / \mathrm{H}$, and the history of $\mathrm{D} / \mathrm{H}$ to estimate the volume of exchangeable reservoir through time, as follows:
(i) Present-day enrichment of D/H by $6 x$, combined with the present-day exchangeable reservoir of $20-30 \mathrm{~m} \mathrm{H}_{2} \mathrm{O}$, yields an initial amount of exchangeable water of $\sim 130-600 \mathrm{~m}$ GEL. This requires that loss to space over time would have to have been 110570 m GEL.
(ii) Enrichment in $\mathrm{D} / \mathrm{H}$ by 3 x at 3 b.y.a. requires an enrichment between then and now of $2 x$. In turn, and including outgassing by volcanism that partially resets the $\mathrm{D} / \mathrm{H}$, the reservoir at 3 b.y. would have to have been $40-130 \mathrm{~m}$ GEL, and the amount lost to space between then and now would have been 25210 m GEL.

Fig. 1 shows the inferred size of the exchangeable reservoir through time. Note that the amounts required to have been lost to space are much larger than would be derived by taking the present-day loss rate as constant through time; this would have resulted in loss of only 3-30 m GEL.

## Global inventory of water:

Table 1 shows the inferred inventory of water, based on the present work and a number of recent analyses. Amounts are as follows, all given as GEL m $\mathrm{H}_{2} \mathrm{O}$ :
(i) Water lost to space, $110-570 \mathrm{~m}$, with values likely to be nearer to the high end based on our current understanding of relative escape rates of D and H.
(ii) Water incorporated into minerals at the surface and in the subsurface. These have been identified from orbit and from the ground, and estimates of their total volume have been made based on extrapolation to what cannot be directly observed. Best estimate is $130-260 \mathrm{~m}$, but amounts as large as 500 m
cannot be ruled out.
(iii) Present-day exchangeable water ice, 20-30 m . This includes the polar caps and other ice deposits that have been identified and mapped.
(iv) Potential buried ice from an early ocean, 110 m . Although there is no universal agreement as to whether it existed, its volume can be estimated if it filled the northern-lowlands (and if it still resides there as ice).
(v) Water inferred to be in the crust and that did NOT debouch in floods, $400-1000 \mathrm{~m}$. This estimate is based on the source region for the flood channels, the volume of water necessary to carve the channels, and the assumption that the rest of the global crust also contained additional water that was not released to the surface.
(vi) Water released by volcanic eruptions or intrusions. Estimates vary from 5-120 m, depending on degassing efficiency and the role of intrusive volcanism. This water is counted as lost elsewhere, so is not listed explicitly in the table.

There may be other potential sources or sinks of water through time, but we have listed all for which there is good direct or indirect evidence for their existence. Note that only $370-970 \mathrm{~m}$ has been at the surface subsequent to the earliest Noachian.

| Water Sink | Amount $\left(\mathrm{m} \mathrm{H}_{2} \mathrm{O}\right.$ GEL) |
| :--- | :---: |
| Lost to space | $110-570$ |
| Surface/subsurface <br> minerals | $130-260$ |
| Polar/non-polar ice | $20-30$ |
| Possible residual from <br> early ocean | 110 |
| Remaining within crust | $400-1000$ |
| Total amount of water | $770-1970$ |

Table 1. Global water inventory based on volume of the different sinks available.

## Issues:

These estimates depend on a number of assumptions or issues that cannot be evaluated at this time. These include:
(i) Is the atmospheric $\mathrm{H}_{2} \mathrm{O}$ well mixed with nonatmospheric ice deposits, such that they have a uniform or constant $\mathrm{D} / \mathrm{H}$ ?
(ii) What happens to the water cycle, dust-storm behavior, and the H and D escape rate at other obliquities?
(iii) Are extrapolations of present-day behavior to early epochs valid given the potential for a very different seasonal behavior and hydrologic cycle?
(iv) To what extent do the different $\mathrm{D} / \mathrm{H}$ values in meteorites reflect real spatial or temporal variations, and how can we use them to determine global average values at each epoch?
(v) Is there free water or ice in the crust, has it
been at the surface subsequent to the Noachian, and has it exchanged on any timescale with near-surface water?
(vi) Have we accounted for all sources and sinks of water and, especially, to what extent have they equilibrated with each other in $\mathrm{D} / \mathrm{H}$ throughout time?

## Summary:

We provide an observation-based estimate of the water inventory of Mars. The amount at the surface has been as great as $370-970 \mathrm{~m}$ GEL $\mathrm{H}_{2} \mathrm{O}$. Of this, $110-570 \mathrm{~m}$ has been lost to space, accounting for a large fraction ( $\sim 30-60 \%$ ) of the total water. Most of the rest has been incorporated into surface and subsurface minerals or been locked up in the crust as ice. A small amount ( $20-30 \mathrm{~m}$ ) is accessible today at the surface as ice in the polar regions or near the surface as ground ice.

