HYDROGEN ISOTOPIC COMPOSITION OF THE MARS MANTLE INFERRRED FROM THE MOST RECENT MARTIAN METEORITE FALL, TISSINT.

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Introduction: Determining the primordial hydrogen isotopic composition of a planet is important for constraining the sources of volatiles on that planet. Dynamic models of Solar System formation suggest that water was accreted on parent bodies beyond ~1 to 5 AU, and the inner Solar System was relatively depleted in volatiles [1]. As such, the terrestrial planets that accreted in the inner Solar System are expected to be depleted in water whereas giant planets would be relatively enriched. Whereas Jupiter’s D/H ratio is close to the Solar value [2], that of the bulk Earth is significantly higher (D/H = 1.49 (± 0.03) × 10^{−5}; [3]). Therefore, Earth’s water is thought to have been delivered post-accretion by comets and/or asteroids (e.g., [1, 4]). In fact, since CI chondrites have hydrogen isotope compositions similar to that of the Earth, they are considered to be the primary source of water on the Earth [4]. Similarly, if the D/H ratio of the primordial martian mantle can be determined, the source of volatiles on Mars can be identified.

The hydrogen isotopic compositions of distinct planetary reservoirs can also provide insights into the evolution of hydrological cycle on a planetary body. Mars shows strong evidence of atmospheric loss during its early history. Earth-based observations show that the martian atmosphere has an elevated D/H ratio that is ~5.2 times that of the Earth [5]. This has been confirmed by more recent higher precision analyses by instruments on the Mars Science Laboratory Curiosity rover [6]. Furthermore, high and variable D/H ratios (δD ~4000-7000‰) were reported for volatiles released from heating of martian fines from the Rocknest aeolian deposit suggesting that surface rocks have exchanged hydrogen with the Mars atmosphere [7].

The observed deuterium enrichment in the martian atmosphere is thought to be the result of loss of the martian atmosphere over geological timescales (e.g., [8-10]). The ubiquitous presence of valley networks [11] and lake deposits [12] on ancient martian terrains is evidence for the presence of surface water and of a thicker atmosphere in the early history of Mars. However, the present-day relatively dry conditions on Mars, with its thin CO₂-dominated atmosphere, suggest that a significant quantity of volatiles were subsequently lost. There are varied estimates of how much water was originally present in martian reservoirs, and questions relating to how and when this water may have been lost remain controversial. Knowing the initial D/H ratio of Mars would allow us to estimate the amount of water lost from that planet over its geological history, and how much water may still be remaining in its subsurface reservoirs.

Martian meteorites potentially provide a means of understanding the origin and evolution of the hydrologic cycle on Mars. Although martian atmospheric D/H ratios have undoubtedly evolved over time, because of the absence of plate tectonics the martian mantle is expected to have preserved its primitive isotopic composition. The hydrogen isotopic composition of magmatic minerals in these meteorites can provide constraints on the composition of the primordial mantle reservoir on Mars, as well as on the processes and timescales of volatile loss from this planet.

Investigations of D/H ratios in minerals of the martian meteorites have shown that they record varying degrees of deuterium enrichment [13-17]. Tissint is the first observed martian meteorite fall since 1962. It has been classified as a depleted basaltic shergottite, and contains olivine phenocrysts in a fine-grained groundmass of pyroxenes and glass of plagioclase composition (maskelynite) [18]. The rapid recovery of this meteorite and its minimal residence time in the terrestrial environment implies that it is one of the most pristine samples of Mars available for laboratory investigations. As such, it provides a unique opportunity to study the hydrogen isotopic composition of martian magmas.

Analytical techniques: The analysis of hydrogen isotopic composition was performed using a Cameca IMS-6f secondary ion mass spectrometer at Arizona State University using a Cs⁺ primary beam (10kV), a primary current from 7 to 10 nA, and detection of negative secondary ions (accelerated to 5 keV from the sample). Since H₂ has never been detected in our analytical setup, we operated the mass spectrometer at mass resolving power ~300. Each analysis run is composed of 60 cycles of measuring H (1s) and D (10s). At the end of each analysis run, ¹⁸O was measured, providing H/¹⁸O ratios that were used to determine the total H content in the sample. The hydrogen isotopic compositions (δD) of individual analyses are reported relative to Standard Mean Ocean Water (SMOW; D/H=0.001559), as follows:

$$\delta D = \frac{[(D/H)_{\text{Sample}}/(D/H)_{\text{SMOW}}] - 1 \times 1000}$$

Durangoapatite and silicate glasses were used as standards to determine the δD values of phosphates and silicates in Tissint.
Results and Discussion: The phases analyzed for their hydrogen isotopic compositions in Tissint included phosphates (merrillites) and silicates (olivine, maskelynites and a melt inclusion) (Figure 1). Tissint olivines have a limited range in δD values, from +12% to +470‰. Merrillites show a large variation in their δD values, which range from +118% to +2427‰. Maskelynites show the largest variation in δD values (from -116% to +3682‰) of any phase analyzed in Tissint. A single devitrified melt inclusion in an olivine phenocryst has δD values of +900 to +1400‰.

The likely causes for δD variation in these phases include isotopic fractionation caused by degassing of the magma [19], hydrothermal alteration by crustal fluids with high δD (e.g., [13, 14]), post-crystallization shock and/or shock implantation of the martian atmosphere (e.g., [20]), as well as terrestrial contamination (e.g., [16, 17]). While one or more of the processes mentioned above are likely to have contributed to the δD variation, it is difficult to disentangle the effects of individual processes. It is important to note that all of the above-mentioned processes, with the exception of terrestrial contamination (and possibly magma degassing), would result in an increase in the original (magmatic) δD value.

Since we believe that the Tissint analyses reported here have been minimally affected by terrestrial contamination (in a natural or laboratory environment), it may be reasonable to hypothesize that the lowest δD values measured in Tissint phases correspond to upper limits on the magmatic values, possibly following open-system degassing. If this is correct, the hydrogen isotopic composition of the martian mantle is similar to that of the Earth’s mantle [3]. This suggests that the sources of water on both these terrestrial planets were similar and that this water was delivered following initial accretion. Moreover, if the primordial martian mantle had a D/H ratio similar to that of the Earth, Mars would have to lose ~80-90% of its original crustal water content to achieve its present day atmospheric D/H ratio [21].