

HYDROGEN ISOTOPIC COMPOSITION OF TISSINT, THE NEWEST MARTIAN METEORITE FALL. P. Mane¹, R. Hervig¹, M. Wadhwa¹, J. B. Balta², H. Y. McSween Jr.², ¹School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287 (E-mail: Prajkta.Mane@asu.edu). ²Dept of Earth and Planetary Sciences, University of Tennessee, Knoxville.

Introduction: Martian meteorites are the only available subsurface samples to investigate magmatic processes occurring on Mars. The majority of martian meteorites available are finds, complicating geochemical studies due to potential terrestrial alteration. The new martian meteorite Tissint is the first observed martian fall since Zagami in 1962 and it provides a unique opportunity to study Martian subsurface samples minimally altered by terrestrial processes.

Hydrogen isotopes are a very important key to understand the origin and evolution of the Martian hydrologic cycle. Earth-based observations show that martian atmosphere has elevated D/H ratio ~5.2 times than that of the Earth [1]. However, martian meteorites show varying degrees of deuterium enrichment. Proposed mechanisms for the observed variation in D/H ratios in martian meteorites include: isotopic fractionation during degassing of the magma, fractionation during subsolidus diffusion of hydrogen, mixing between two reservoirs having different H isotopic composition, and varying degrees of terrestrial contamination [2-10]. Mixing between two reservoirs is the favored explanation since it is difficult to explain the large variations seen in D/H ratios of martian meteorites by other processes. The mixing hypothesis requires at least two reservoirs differing in their D/H ratio. The one with higher D/H ratio is considered a crustal reservoir, where fluids are in equilibrium with the atmosphere. Rocks in this reservoir will approach equilibrium with the fluids and therefore will have high D/H. The other reservoir with the lower D/H ratio is thought to represent Martian mantle. Due to the absence of plate tectonics on Mars, crustal reservoirs will not be recycled into the mantle and therefore it is assumed that mantle will preserve the primordial D/H ratio. Constraints on the D/H value for the martian mantle are important for inferring the ultimate source of water on Mars.

Apart from the martian mantle, a potential source for low D/H in Tissint is terrestrial contamination. The rapid recovery of Tissint after its fall provides a unique opportunity to analyze hydrogen isotopes in a martian sample with minimum terrestrial exposure. Here, we report the hydrogen isotopic composition of individual phosphate and maskelynite phases from Tissint.

Sample description: Tissint is classified as a depleted basaltic shergottite [11]. The Tissint thin section contains olivine phenocrysts in a fine-grained groundmass of pyroxenes and plagioclase glass

(maskelynite). Olivine phenocrysts are highly fractured. Phosphates (merrillites) are minor phases, ~20-50 micrometer in size (figure 1).

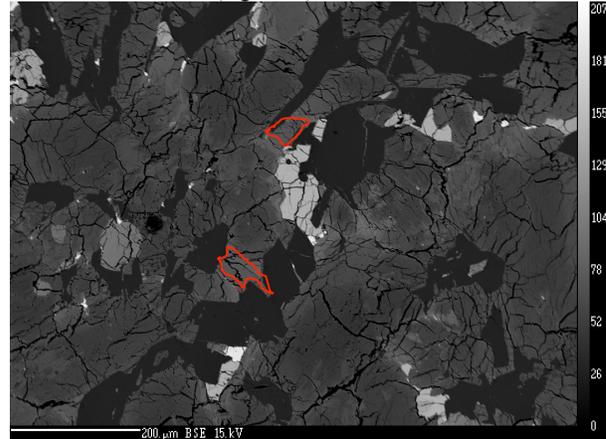


Fig 1: Backscattered electron image of Tissint thin section. Phosphates are outlined in red.

Analytical techniques: The identification of individual mineral phases and determination of mineral chemistry was completed using a Cameca SX-100 electron microprobe at the University of Tennessee. 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, we operated the mass spectrometer at mass resolving power ~300. We measured H (1s) and D (10s) 60 times in each measurement. At the end of the analysis ¹⁸O⁻ was measured, providing H/¹⁸O⁻ ratios used to determine the total H content in the sample (calibrated against Durango apatite). The normal-incidence electron gun was used to neutralize the positive charge build-up in the sputtered crater. We used a GaN sample to align the electron gun using cathodoluminescence.

Standards Analysis: The hydrogen isotopic compositions (δD) of individual analyses are reported relative to Standard Mean Ocean Water (SMOW; D/H=0.0001559).

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

Durango apatite was used a standard, with reported bulk δD value -210‰. 8 spot analyses were made using the Durango apatite standards with raw average D/H ratios corresponding to δD of -276±95.8‰ (2SD). Subsequent analyses of Tissint mineral phases are reported normalized to Durango apatite D/H=-210‰. A

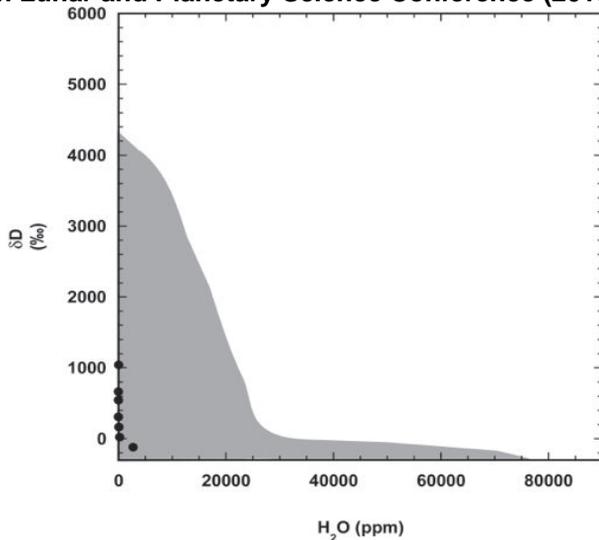


Fig 2: Dark circles represent Tissint Maskelynites. Grey region represents data spread for maskelynites/feldspathic glasses from Shergottites

single spot analysis of nominally anhydrous Lake County plagioclase was performed to measure the hydrogen blank in the Durango apatite standard mount. The resulting $H/^{18}O$ ratio was insignificant and no background correction was applied to the analyses.

Results and Discussion: The hydrogen isotopic composition measurements in Tissint included 8 merrillite grains (9 analyses) and 7 maskelynite grains.

Maskelynites in Tissint are relatively fracture-free glasses showing higher δD values than phosphates (figure 2). However they also show large variations in δD in different grains. The lowest δD value (-123‰) was measured on a fracture and also has the highest water content compared to other maskelynites (~60-300 ppm H_2O). Maskelynites show a weak correlation between their δD value and water content. This effect may be related to shock processes that took place on the surface of Mars during the impact event.

Merrillites in Tissint show a negative correlation between δD and water content (as shown in figure 3). The δD values range from -189 to +440‰. Most previous studies of martian meteorites have reported large variations in the D/H ratios, with a minimum value (martian mantle signature) higher than that inferred for the Earth (martian mantle $\delta D = \sim 275‰$ to $900 \pm 250‰$) [6, 10]. However, other studies (e.g., [4]) have suggested a lower δD of the martian mantle, closer to that of the Earth (Earth's mantle: -40 to -80‰). The hydrogen isotopic composition of Tissint merrillites with $>0.6\%$ H_2O show δD values, between -100 and +200 ‰ which support a lower δD signature for the martian mantle.

Merrillites in Tissint are small and they also contain fractures. Merrillites are commonly thought of as anhydrous minerals; however, we measured 0.4 to 1.2 wt.% H_2O (using Durango with 0.05 % as a standard!). The hydrogen isotopic compositions of the Tissint

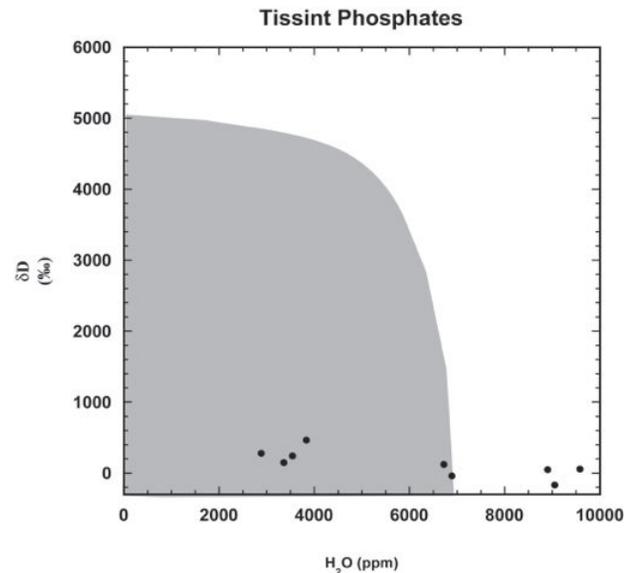


Fig 3: Dark circles represent Tissint phosphates (merrillites), whereas grey region defines data spread from other Martian Shergottites

merrillites exhibit a negative correlation with water content, as previously observed in other martian meteorites and attributed to source reservoir mixing on Mars or the effect of terrestrial alteration. [e.g., 3, 7]. For Tissint, terrestrial contamination is presumed to be less likely. However, because the sample was impregnated with epoxy during thin section preparation, variable contributions of H from terrestrial epoxy in our analyses of phosphates must be considered. To this end, two analyses of a heavily fractured Tissint olivine grain gave apparent H_2O contents of ~ 0.1 wt. %, much less than the phosphates, and showed δD values between -40 and -120‰ (presumed to be from epoxy). An epoxy-free Tissint sample is being prepared to minimize all contaminants and verify the low δD values observed in the Tissint merrillites. Future analyses of existing thin sections should include measurements of ^{12}C or CN^- to test the effect of epoxy in the analyses of meteorite thin sections. Our working conclusion is that δD in H-rich Tissint merrillite is similar to values given in [4] and that terrestrial contamination is minor.

References: [1] Bjoeraker et al. (1989) *Bull. Amer. Astron. Soc.*, 21, 991. [2] Boctor N. Z. et al. (2003) *GCA* 67, 3971-3989. [3] Greenwood G. P. et al. (2008) *GRL* 35, L05203 [4] Hallis L. J. et al. (2012) *EPSL* 359-360, 84-92 [5] De Hoog J. C. M. et al. (2009) *Chemical Geology*, 266, 256-266 [6] Leshin L. A. (2000) *GRL* 27, 2017-2020 [7] Suguira n and Hoshino H (2000) *Meteoritics & Planet. Sci.*, 35, 373-380. [8] Usui T. et al. (2012) *EPSL* 357-358, 119-129. [9] Wang H. et al (2006) *Chinese Science Bulletin* 51, 2001-2005 [10] Watson L. L. et al (1994) *Science* 265, 86-90. [11] Chennaoui Aoudjehan et al. (2012) *Science*, 338, 785-788.