

**EFFECTS OF DESERT WEATHERING ON METEORITIC HYDROGEN ISOTOPE SYSTEMATICS: INSIGHTS FROM TISSINT.** A. Stephant<sup>1,2</sup>, P. Mane<sup>1,2,3</sup>, L.A.J. Garvie<sup>1,2</sup>, R. Hervig<sup>2</sup>, and M. Wadhwa<sup>1,2</sup>, <sup>1</sup>Center for Meteorite Studies, <sup>2</sup>School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-6004, <sup>3</sup>Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721-0092.

**Introduction:** The hydrogen isotopic composition of meteorites and their components can provide insights into the source of water on their parent bodies and secondary processes that may have occurred on these bodies. As such, determining the indigenous D/H ratio of meteorites and their constituent phases is crucial. Nonetheless, terrestrial weathering can affect many of the properties of meteorites, such as their chemistry, mineralogy, composition of organic matter, as well as the isotopic compositions of a range of elements including H, C, O and noble gases [1]. For example, the Holbrook meteorite shows a significant  $\delta^{18}\text{O}$  shift over the 99 years of sample recovery from its fall location in Arizona [2]. Approximately 98% of meteorites in collections are finds and have been subjected to varying degrees of terrestrial weathering. Even if the effects of weathering on meteorites are broadly similar for a variety of terrestrial environments (e.g., oxidation of metal, formation of carbonates), the modification of a meteorite's specific physicochemical characteristics is a function of the terrestrial residence time, climate, and soil composition at the recovery site [1,3-4]. Therefore, determining the effects of terrestrial exposure on meteorites recovered from a variety of terrestrial environments is important since this information would allow us to deconvolve such effects from their indigenous characteristics [5].

Water in the liquid and vapor state in the terrestrial environment can be added to, and exchanged with, the indigenous water in a meteorite and can overprint its indigenous D/H ratio. One approach used to evaluate such effects is to conduct laboratory experiments involving isotopically spiked water [6,7]. However, such experiments are of short duration compared to the much longer exposure typically experienced by the majority of meteoritic finds and did not result in significant changes in the D/H ratio (i.e.,  $\leq 15\%$ ). An alternative approach is to assess the effects of terrestrial contamination based on the hydrogen isotope analyses of natural meteoritic samples that have experienced varying degrees of terrestrial exposure. In particular, the D/H ratio has been used to distinguish between secondary aqueous alteration occurring under martian versus terrestrial conditions, because the martian surface water reservoir that may have interacted with the shergottites and nakhlites is thought to be significantly D-enriched relative to terrestrial reservoirs (e.g., [8,9]). Thus, measuring the D/H ratios of individual phases in relatively fresh martian meteorite falls could provide a

measure of the rate of hydrogen isotopic exchange in the terrestrial environment.

In this study, we report the results of experiments that we conducted using the most recent martian meteorite fall, Tissint, to assess the effects of weathering on hydrogen isotope systematics resulting from different residence times in a desert environment.

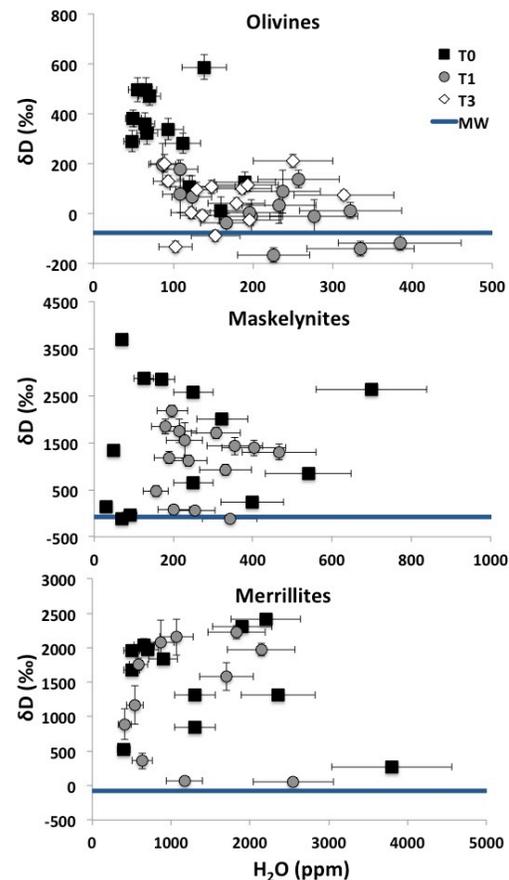


Figure 1. Plots of  $\delta\text{D}$  (‰) vs.  $\text{H}_2\text{O}$  (ppm) in olivines (top), maskelynites (middle) and merrillites (bottom) for the three sections of Tissint; see text for details. The blue line represents meteoric water (MW) in Grand Canyon, Arizona [10].

**Samples:** Tissint fell 18<sup>th</sup> July 2011 in southern Morocco; many pieces totaling over 7 kg were recovered within a few months. As the freshest martian meteorite fall, it is one of the least terrestrially altered martian samples in our meteorite collections. A 1.85 g interior piece of Tissint was dry cut into three slices, and designated as T0 (0.43 g), T1 (0.70 g), and T3 (0.72 g). The cut surfaces were subsequently ground and then polished with 1  $\mu\text{m}$  diamond polish: all preparation was done without liquids. The T0 sample is the

same anhydrously prepared thick section on which hydrogen isotope analyses were conducted and recently reported [9]; we conducted additional analyses of this section. The other two slices, T1 and T3 were placed on the ground in the Sonoran desert at 32° 58.195'N, 112° 30.768'W, ~18 km east of Gila Bend, Arizona. Precipitation at Gila Bend is ~15 cm/yr. T1 and T3 were removed from the desert after one and three years, respectively. The two slices retrieved from the desert were cleaned with a brush to remove dust, but were not re-polished prior to hydrogen isotope analyses.

**Analytical methods:** Secondary ion mass spectrometry (SIMS) measurements of D/H ratios and H<sub>2</sub>O concentrations were performed on the Cameca IMS 6f at Arizona State University. Olivines, maskelynites, and merrillites were analyzed in T0 and T1; only olivines were analyzed in T3. Analyses were conducted using methods similar to those for the T0 slice described in [9]. A Cs<sup>+</sup> primary beam (~10 nA) was rastered over a 30×30 μm<sup>2</sup> area. A field aperture set the analyzed area to 15 μm diameter, which reduced background associated with the crater edges. Each measurement comprised 50 cycles H<sup>-</sup> and D<sup>-</sup> measurements, with counting time of 1 s and 10 s, respectively. At the end of each measurement, <sup>16</sup>O<sup>-</sup> was measured. The H<sup>-</sup>/<sup>16</sup>O<sup>-</sup> ratio was used to determine the total H<sub>2</sub>O content. Vacuum in the analysis chamber was ~5-10×10<sup>-10</sup> torr. Following analyses, SIMS crater depths in some T3 olivines were measured by stylus profilometry.

**Results:** The H<sub>2</sub>O contents and D/H ratios, expressed as δD, measured in individual phases in the three sections are shown in Fig. 1; for the T0 sample, the data shown are from [9] and this study. The H<sub>2</sub>O contents range from 48±10 to 190±38 ppm for olivines; 30±6 to 699±140 ppm for maskelynites; and 400±80 to 3800±760 ppm for merrillites. The δD values range from 12±53 to 586±49 ‰ for olivines; -116±94 to 3682±40 ‰ for maskelynites; and 272±28 to 2418±15 ‰ for merrillites [9]. In the T1 sample, the H<sub>2</sub>O contents range from 86±17 to 384±77 ppm for olivines; 156±31 to 466±93 ppm for maskelynites; and 416±83 to 2549±510 ppm H<sub>2</sub>O for merrillites. The δD values range from -166±29 to 197±84 ‰ for olivines; -110±37 to 2171±128 ‰ for maskelynites; and, 55±34 to 2222±97 ‰ for merrillites. In the olivines measured in the T3 sample, H<sub>2</sub>O ranges from 89±18 to 314±63 ppm and δD from -135±22 to 210±26‰. Five depth profiles in olivine grains were performed; one example is shown in Fig. 2, although all exhibit the same trend, with H<sub>2</sub>O content decreasing with depth from the surface (approaching an asymptotic value at ~25 microns depth), while δD keeps increasing.

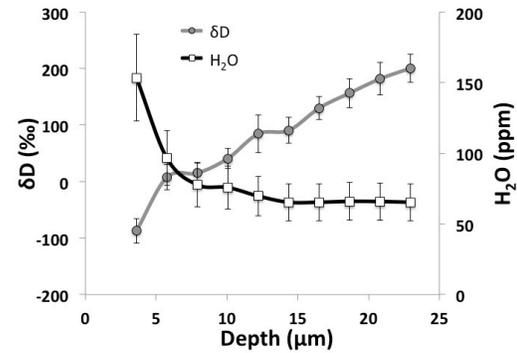


Figure 2. SIMS depth profile on one olivine grain from T3.

**Discussion:** The H<sub>2</sub>O contents and δD values for maskelynites and merrillites in T1 overlaps the T0 values. In contrast, olivines in T0 and T1 show marked differences, with T1 olivines having higher H<sub>2</sub>O contents and approaching terrestrial-like δD values (Fig. 1, top). However, olivines in the T1 and T3 sections show similar ranges (within the analytical errors) for the H<sub>2</sub>O contents and δD values. This similarity suggests that this mineral, which typically has very low indigenous water content, is measurably altered after only one year of exposure to desert weathering, but that longer exposure (up to ~3 years) does not further affect the H<sub>2</sub>O-δD systematics to a significant degree. Moreover, depth profiles on olivines in the T3 section (Fig. 2) demonstrate that the effect of terrestrial alteration on H<sub>2</sub>O-δD systematics decreases with depth, with interiors being less affected.

Under desert weathering conditions and with only a year of exposure, olivines in Tissint exhibit significant changes in H<sub>2</sub>O contents and δD values, and these effects are depth dependent, as illustrated by the depth profile in an olivine after 3 years of exposure. However, phases with higher indigenous water contents, such as maskelynites and merrillites are not significantly affected, even after a year of exposure. Results from this study highlight the importance of sample selection and preparation in investigations of H<sub>2</sub>O-δD systematics in nominally anhydrous phases of meteorites. Specifically, while meteorite falls (with immediate recovery) are best for such studies, the effects of terrestrial alteration may be mitigated by sampling the interiors of finds.

**References:** [1] Bland P.A. et al. (2006) *MESS II*, 853-867. [2] Pillinger C.T. et al. (2013) *LPSC 44<sup>th</sup>*, #2883. [3] Al-Kathiri A. et al. (2006) *Meteoritics & Planet. Sci.*, 41, 8, A217-A230. [4] Zurfluh F.J. et al. (2011) *X-Ray Spectrom.*, 40, 6, 449-463. [5] Abreu N.M. and Brearley A.J. (2005) *Meteoritics & Planet. Sci.*, 40, 4, 609-625. [6] Robert F. and Deloule E. *LPSC 33<sup>th</sup>*, #1299. [7] Engrand C. et al. (1999) *Meteoritics & Planet. Sci.*, 34, 773-786. [8] Hallis L.J. et al. (2012) *Geochim. Cosmochim. Acta*, 97, 105-119. [9] Mane P. et al. (2016) *Meteoritics & Planet. Sci.*, 51, 11, 2073-2091. [10] Pendall E. (2000) *Global Change Biol.*, 6, 287-301.