

HYDROGEN ISOTOPE SYSTEMATICS OF MASKELYNITES IN THE SHERGOTTITES ZAGAMI, QUE 94201 AND TISSINT: TERRESTRIAL CONTAMINATION OR DEUTERIC ALTERATION? K. Tucker¹, R. Hervig¹, P. Mane¹, S. Romaniello¹, M. Wadhwa¹, ¹School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287 (E-mail: Kera.Tucker@asu.edu)

Introduction: The known martian meteorites crystallized from melts derived from the Mars mantle, and may hold the key to deciphering the history of water on Mars. Hydrogen isotopes can provide critical information on this complicated history (e.g., [1]). This study reports hydrogen isotopic compositions in three shergottites: the enriched shergottite fall Zagami, and the depleted shergottites QUE 94201 (recovered from the Antarctic) and Tissint (a recently recovered fresh fall). The data shed light on processes that occurred during and shortly after magma emplacement in the crust of Mars.

A fundamental question that has important implications for the origin and evolution of the martian hydrosphere relates to the δD composition of the primordial martian mantle. While martian meteorites are currently the only samples of Mars that can be studied in Earth-based laboratories to address this question, their original water contents and δD compositions have been affected by alteration processes on Mars and the Earth. In this study, we highlight three processes that likely altered the original δD of primary igneous phases in the martian meteorites: interaction with late-stage magma-derived fluids (“deuteric alteration”), interaction with δD -enriched crustal fluids (that exchanged with the Mars atmosphere), and possible terrestrial contamination. While terrestrial contamination has been proposed in previous studies to account for the high water contents and low δD values observed in some phases in the martian meteorites, we show here that it may not be the dominant factor affecting the hydrogen isotope systematics of maskelynite in the shergottites studied here that have very different terrestrial ages. If the martian mantle is characterized by a hydrogen isotope composition similar to that of the Earth, deuteric alteration (i.e., alteration of igneous rocks via interaction with a volatile-rich fluid derived from the magma during the last stages of crystallization) could also account for the hydrogen isotope compositions and water contents of the shergottite maskelynites reported here. As such, we propose here that terrestrial-like hydrogen isotopic compositions observed in some primary igneous phases of the martian meteorites could be due to deuteric alteration rather than terrestrial contamination. Further work with other geochemical tracers will be needed to more rigorously distinguish between these two processes.

Samples and Analytical Techniques: We previously reported hydrogen isotope compositions of maskelynites in a Tissint thin section [2]. This also

included maskelynites analyzed in a thick section of Tissint that was prepared without using any water or epoxy. In addition, for this study, we analyzed another set of polished thin sections of Tissint, Zagami and QUE 94201. Tissint is a depleted olivine-phyric shergottite that fell in Morocco in 2011 and was recovered soon thereafter [3]. It has a crystallization age of ~ 600 Ma [4]. Zagami, which fell in Nigeria in 1962, is a ~ 180 Ma enriched basaltic shergottite [5-7]. QUE 94201 is a coarse-grained depleted basaltic shergottite that was recovered from Antarctica (terrestrial age of 0.29 ± 0.05 Ma), and has a crystallization age of ~ 325 Ma [5-9].

Hydrogen isotopic measurements of individual maskelynite grains were performed using a Cameca IMS 6f ion microprobe at Arizona State University. Each section was gold coated and stored under high vacuum in the ion microprobe sample chamber for at least ~ 4 hours prior to analysis. A Cs^+ primary beam (7-10 nA) was rastered over a $30 \times 30 \mu m^2$ area, and negative secondary ions were accelerated to 5000 eV. The mass spectrometer was operated at a mass resolving power of ~ 400 . H^- and D^- were detected on an electron multiplier, and $^{16}O^-$ on a faraday cup. The area of interest was pre-sputtered for 2-4 minutes to remove surface contaminants. Each analysis cycle consisted of measuring H (1 sec) and D (10 sec) in peak switching mode, with each measurement run consisting of 60-200 cycles; $^{16}O^-$ was measured at the end of each run. Water content was determined using the measured H^-/O^- ratio that was calibrated to determine H_2O concentrations using hydrous rhyolites as standards. Natural obsidian ($\delta D = -150 \text{‰}$ [10]) was used as the standard for the determination of the hydrogen isotope compositions of the shergottite maskelynites.

Results and discussion: In total, 31 spot analyses were conducted on maskelynites in the Tissint thick and thin sections, 15 in the QUE94201 thin section, and 10 in Zagami. The water contents and δD values of maskelynites in the Tissint thick and thin sections show similar ranges (~ 20 -1400 ppm and -200 -+4000‰, respectively). In QUE 94201 maskelynites, these values were ~ 25 -400 ppm and $+160$ -+1800‰, respectively; in Zagami maskelynites, ~ 90 -3600 ppm and ~ 0 -+1100‰, respectively.

Maskelynite is diaplectic glass formed by shock. Experimental studies suggest that the hydrogen isotope compositions in shergottite phases could be shifted to heavier values (perhaps by up to $\sim 100\text{‰}$) and that wa-

ter contents could be enriched during shock (e.g., [11]). Nevertheless, such studies also highlight the uncertainty of determining how an actual impact under Mars ambient conditions would effect these parameters. Our analyses show that δD is variable among the maskelynite grains in each of the shergottites investigated here, and also within individual grains. This variability could be due to zoning during crystallization, post-magmatic alteration (including shock), or terrestrial contamination. Many of the maskelynites have relatively low water contents similar to those in terrestrial volcanic plagioclase, but a significant number have >200 ppm H_2O . If terrestrial contamination can be ruled out, and if the measured water content in these maskelynites is assumed to be magmatic in origin, the estimated H_2O abundance in coexisting melt (using plagioclase-melt partition coefficients [12]) ranges from as low as ~ 0.2 wt.% to well over 10 wt.%. The latter value is too high compared to recent estimates of the water content of shergottite magmas (e.g., [13]). As shown by [14], terrestrial plutonic plagioclase is strongly affected by deuterium alteration that results in enrichment of their water content. This alteration can often be patchy, as evidenced by partially sericitized terrestrial plagioclase [15]. It is possible that a similar sericitization (deuterium alteration) process affected the original plagioclase in the shergottites prior to the maskelynitization event.

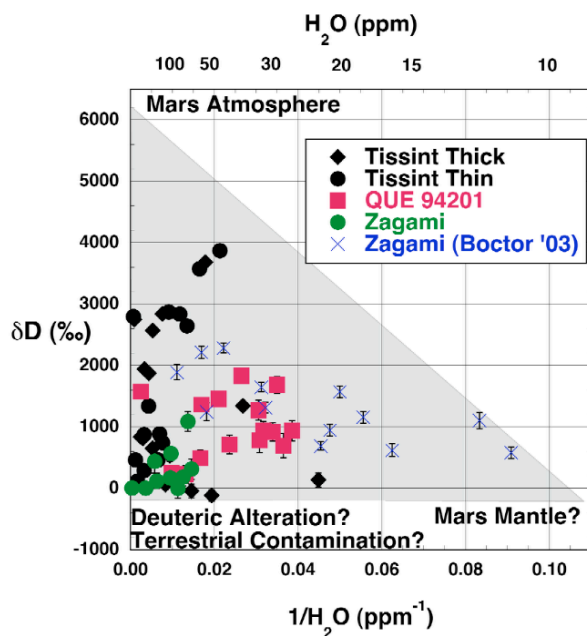


Figure 1: Water contents (shown as $1/H_2O$ on lower x-axis or as H_2O content on upper x-axis) versus δD for maskelynites in Tissint, QUE94201 and Zagami analyzed in our laboratory ([2] and this study; solid symbols); maskelynite data of [18] are also shown (crosses). Errors are $\pm 2SD$.

The hydrogen isotope data obtained in this study are shown in Fig. 1. At least three end-members are required to account for the spread in the data and are represented by the apices of the triangular shaded area in Fig. 1. The top of the triangle (with highly elevated δD) likely represents the martian atmospheric end-member. The δD composition of this end-member is in the range of values reported recently for martian atmosphere and fines by experiments aboard the Mars Curiosity Rover [16,17]. As such, shergottite maskelynites with high δD values most likely interacted with groundwaters on Mars that exchanged with a D-enriched atmosphere. The lower-right corner of the triangle (near-terrestrial δD , low water content) likely represents a martian mantle end-member while the lower-left corner (near-terrestrial δD , high water content) represents either terrestrial contamination or deuterium alteration (or some combination of the two).

Previous studies have ascribed low δD and H_2O -rich compositions of some phases in the martian meteorites to terrestrial contamination [1,2,18]. While this process likely affected the heavily fractured phosphates and mafic silicates in these shergottites (as was also recently demonstrated by [19]), the maskelynites show few fractures. Furthermore, hydrogen isotope compositions of maskelynites in all three shergottites investigated here (which have very different terrestrial ages ranging from essentially ~ 0 to $\sim 300,000$ yrs) generally fall within the same compositional space (defined by the shaded triangle in Fig. 1). As such, although unable to definitely rule out terrestrial contamination, we propose that the terrestrial-like hydrogen isotopic compositions of the maskelynites with relatively high water contents are due to late-stage deuterium alteration of the original plagioclase. A further implication of this work is that the martian mantle has a near-terrestrial hydrogen isotope composition.

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