

HYDROGEN ISOTOPE FRACTIONATION DURING IMPACT DEGASSING OF PYROXENE AND MASKELYNITE IN SHERGOTTITE LARKMAN NUNATAK 06319. J. M. Dudley¹, A. H. Peslier¹, and R. L. Hervig², ¹Jacobs, NASA-Johnson Space Center, Mail Code X13, Houston TX 77058, USA, ²School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA

Introduction: Hydrogen in nominally anhydrous minerals (NAMs) in meteorites provides insight to mantle sources of indigenous water on differentiated bodies: e.g. Peslier et al. 2017 [1], including Mars [2-4]. However, all meteorite samples, including Martian shergottites, record impact events as fractures, deformation, silicate darkening, shock melt veins and pockets, etc. The effect of shock on hydrogen in NAMs is poorly constrained, and must be understood prior to using these data to infer planetary indigenous water. Here we present water contents and D/H ratios (calculated as δD , i.e. the variation of the D/H ratio relative to a standard, in this case sea water "SMOW") in pyroxene, olivine and maskelynite in the olivine-phyric shergottite Larkman Nunatak 06319 (LAR 06319) as a function of proximity to impact melt. While the results suggest impact may have a role in fractionating H isotopes, the magmatic signature of H₂O in Mars can be preserved in some pyroxene.

Methods: Introduction of terrestrial contamination during sample preparation poses a great challenge to accurate water and D/H measurement of meteorites. To minimize terrestrial lab contamination to LAR 06319, water, glue, epoxy, and polishing solvents were avoided in sample preparation in this study. Samples were attached to adhesive-free, Felsuma Geckskin fabric and doubly polished dry, and cleaned with acetone and isopropanol. Fourier Transform Infrared Spectroscopy (FTIR) and Secondary Ion Mass Spectrometry (SIMS) were used to measure water content and D/H ratios in pyroxene, maskelynite, and impact melt in one meteorite piece and 2 individual olivine and pyroxene grains. A Hyperion microscope of a Bruker FTIR at NASA-JSC was used to assess the presence of water in minerals before co-mounting samples and standards in indium. SIMS target locations were identified and characterized for major element concentrations with the SX100 Cameca electron microprobe at NASA-JSC, as transects across pyroxene, olivine, maskelynite, and impact melt. Water contents and δD were measured with the Cameca 6f SIMS at ASU. The JEOL 7600F SEM at NASA-JSC was used to image the SIMS craters to verify that no fractures or inclusions were analyzed.

Results: Water contents in LAR 06319 range from 29 to 750 $\mu\text{g/g}$ H₂O (n=14) in pyroxene, 92 to 1354 $\mu\text{g/g}$ H₂O in olivine (n=4), 19 to 1032 $\mu\text{g/g}$ H₂O (n=5)

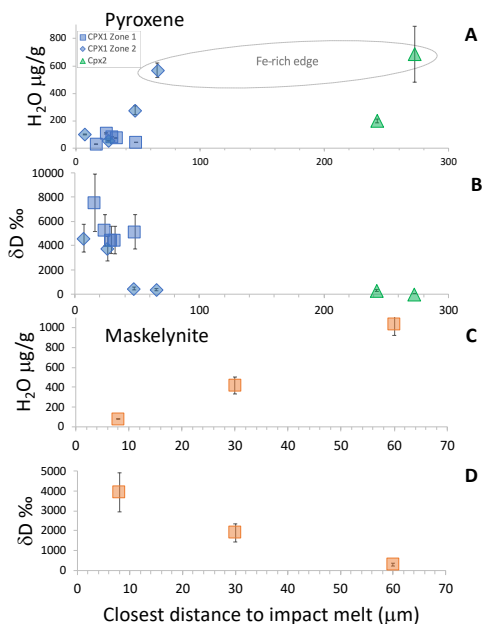


Fig. 1. Profiles of LAR 06319 (A) pyroxene water content ($\mu\text{g/g}$) (B) δD ‰, and (C) maskelynite water content ($\mu\text{g/g}$) and (D) δD ‰, plotted with distance from impact melt. Measurement locations are labeled in Fig. 2.

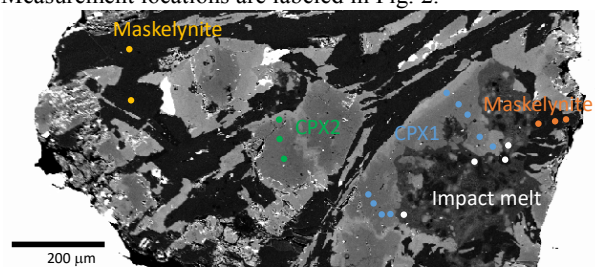


Fig. 2. Back-scattered electron image of an aliquot of LAR 06319 showing the locations of SIMS measurements. Traverses of pyroxene (blue and green) and maskelynite (orange) in contact with impact melt are plotted in Fig. 1. CPX = clinopyroxene

in maskelynite, and 90 to 209 $\mu\text{g/g}$ H₂O (n=4) in impact melt. Corresponding δD values range from 95 to 7534‰ in pyroxene, -14 to 2622‰ in olivine, 298 to 4245‰ in maskelynite, and 3253 to 4615‰ in impact melt. Pyroxene and maskelynite exhibit lower water contents and higher δD near (<50 μm in pyroxene and <10 μm in maskelynite), compared to far away from (>50 μm in pyroxene and >30 μm in maskelynite), the impact melt (Fig. 1 and 2). Pyroxenes located away from impact melts have higher water content (up to

750 $\mu\text{g/g H}_2\text{O}$) and lower δD (down to 15 ‰) at their Fe-rich edge compared to their center (up to 200 $\mu\text{g/g H}_2\text{O}$ and 300‰). The individual olivine grain records the same trend as the pyroxene not affected by impact melt from its center to its rim, with high water content and low δD at its Mg# 71 core and low water and high δD at its Mg# 62 rim. However, without petrographic context, proximity to impact melt is not known. Although spatial context is lacking for the individual pyroxene grain measured, its low δD (~112‰) and high water content ~580 $\mu\text{g/g H}_2\text{O}$) is consistent with a location far from any impact melt.

We observe a negative correlation between δD and $1/[\text{H}_2\text{O}]$ in the impact melt (Fig. 3), consistent with other studies of impact melt in LAR 06319 [5], and in impact melt and groundmass glass in shergottites Tissint [6], Elephant Moraine 79001 (EETA 79001) [4,5], and Yamato 980459 [5]. This trend was argued to record mixing between a D-enriched and a D-poor component, corresponding to surficial or sub-surface water on Mars and the Martian mantle respectively [4-6].

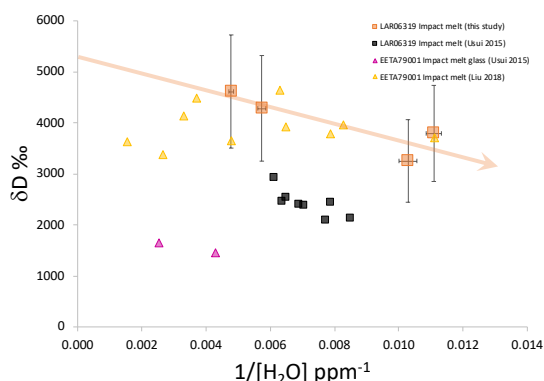


Fig. 3. $1/[\text{H}_2\text{O}]$ vs. δD in LAR 06319 impact melt. Measurements collected at point locations labeled in Fig. 2.

Discussion: The exposure age of LAR 06319 (2.24 Ma, [7]) is too small to correct H_2O and δD for spallation. Terrestrial contamination is also unlikely because high H_2O and low δD (towards ≤ 0 ‰) would be expected. However, the edges of pyroxene near impact melts record high δD and low water contents while the edges of the pyroxene far from the impact melt record higher H_2O contents and lower δD . Furthermore, the water content of the impact melt (~143 $\mu\text{g/g H}_2\text{O}$) is similar to [6] (~150 $\mu\text{g/g H}_2\text{O}$), with higher δD (3253-4615‰ in this study vs. 2096-2528‰ in [6]), providing strong evidence against contamination.

The lower water content in maskelynite near the impact melt vein (Fig. 2) is in contrast to the observa-

tion of [4] in EETA 79001, of higher water content closest to the impact melt. However, increases of δD in maskelynite towards the impact melt is evidenced here (δD reaching values >3000 ‰) and in EETA 79001. One difference between the two studies is that we show a systematic traverse in maskelynite, while [4] analyzed separate grains, losing petrographic context.

We argue that the variation in δD and H_2O in LAR 06319 maskelynite and pyroxene relative to an impact melt vein is evidence for hydrogen degassing from these nominally anhydrous minerals during impact. Decreases in water contents accompanied by large increases in δD during degassing has been evidenced experimentally in a garnet [8] and in nakhlite pyroxenes [3]. Pyroxene δD values reach ~7500 ‰ near the impact melt, well above Martian atmospheric δD (4950 ‰ [9]). Moreover, the presence of bubbles in the impact melts of LAR 06319 indicates degassing during localized impact melting [10]. Our findings indicate that shock effects on H content and isotopes of NAMs are significant and need to be assessed prior to interpreting H analyses in term of magmatic and mantle source processes.

The increase of water content at the Fe-rich edge of the pyroxenes far from impact melt is consistent with crystallization from a differentiating melt, a process during which H is incompatible [11]. H isotopes, however, are not fractionated during crystallization, and the slight decrease in δD towards the pyroxene edge could indicate that the melt from which the Fe-rich edges crystallized from was degassing. Degassing in a melt containing water speciated as H_2O and OH indeed results in δD decreases [12]. The interior of pyroxenes may record signatures of Martian magmatic water, pre-volcanic and pre-impact degassing.

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