

A MULTI-SIMS INVESTIGATION OF WATER CONTENT AND D/H RATIOS IN ROBERTS MASSIF 04262 WITH INSIGHT TO SOURCES OF HYDROGEN IN MASKELYNITE. J. M. Dudley¹, A. H. Peslier¹, R. L. Hervig², J. A. Tielke³, M. Bose², Z. Jin², ¹Jacobs, NASA-Johnson Space Center, Mail Code XI3 Houston, TX 77058, USA, ²School of Earth and Space Exploration, Arizona State University Tempe, AZ 85287, USA, ³Lunar and Planetary Institute, 3600 Bay Area Blvd. Houston, TX 77058, USA.

Introduction: We want to define the H₂O content ([H₂O]) and hydrogen (H) isotope composition of meteoritic material from Mars [1-3] with motivation to understand Mars' volatile history, constrain geochemical signatures of interior water reservoirs (i.e. the Martian mantle) and explore effects of planetary (e.g. planet formation, magma ocean degassing) and local (e.g. volcanic degassing, impact melting and degassing) processes on H incorporated in minerals. Secondary ion mass spectrometry (SIMS) allows multiple avenues to address these questions. However, application to (1) precious astromaterials and (2) low level H measurements, pose specific challenges that are further complicated when combined. We present preliminary data of a multi-approach (SIMS vs. NanoSIMS) study of H in Roberts Massif 04262 (RBT 04262), an enriched lherzolithic shergottite with non-poikilitic (NP) and poikilitic (P) lithologies [4]. We analyze olivine, pyroxene, and melt inclusions to compare indigenous mantle water, with impact-generated maskelynite to investigate H signatures due to shock.

Methods: Samples and standards were (1) attached to Felsuma Geckskin fabric to polish on lapping film (1 μm) dry without water (2) cleaned with acetone and isopropanol, and (3) pressed into indium. The SX100 Cameca electron microprobe at NASA-JSC was used for major and minor element determination at SIMS targets, and the JEOL 7600F SEM at NASA-JSC for target and crater imaging.

Water contents were calculated from 2 SIMS sessions using Arizona State University's (ASU) Cameca 6f SIMS, and 1 preliminary NanoSIMS session using ASU's NanoSIMS 50L (Fig. 1). Sample D/H ratios were expressed in delta notation ($\delta D = ((D/H)_{\text{Unk.}} / (D/H)_{\text{Std.}}) / (D/H)_{\text{Std.}} \times 1000$, where Std. is VSMOW) for SIMS maskelynite, olivine, pyroxene and melt inclusion data (Fig. 2,4). Although we anticipate results from a second NanoSIMS session to be presented at the meeting, maps of ¹H and ¹²C in an RBT 04262 pyroxene grain from the first NanoSIMS session (Fig. 3) example dense fracture networks in RBT 04262.

Discussion of Results: Mineral and Melt Inclusion Data With Implication for SIMS vs. NanoSIMS. Fig. 1 depicts varied [H₂O] across all analyzed phases with significant overlap. Maskelynite holds the lowest water

content and pyroxene the highest; while olivine and their hosted melt inclusions lie in between.

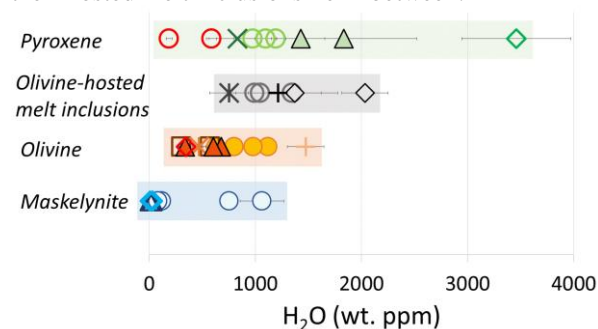


Fig. 1. Water content (wt. ppm H₂O ± 1σ) in maskelynite, olivine, pyroxene, and olivine-hosted melt inclusions measured by SIMS (n=35) and NanoSIMS (in red, n=3). Like symbols correspond to the same grain (Fig. 2 legend). (n = total measurements)

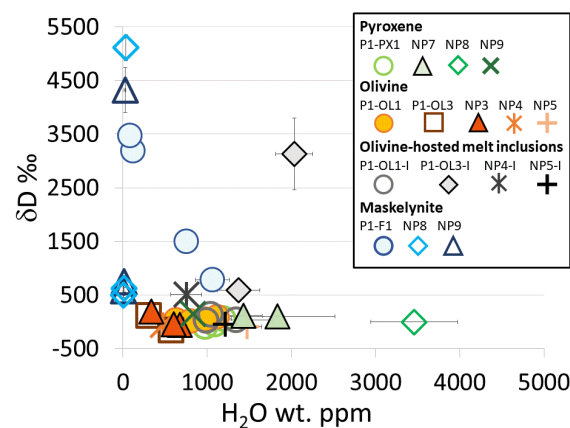


Fig. 2. Water content (wt. ppm H₂O ± 1σ) and δD ± 1σ (‰) in olivine (n=11), pyroxene (n=7), olivine-hosted melt inclusions (n=7), and maskelynite (n=10) measured by SIMS. (n = total measurements)

We note that 3 of the NanoSIMS [H₂O] measurements in olivine and pyroxene are lower (pyroxene) or at the lowest part of the range (olivine) of those measured by SIMS. Although NanoSIMS data are too few to draw conclusions on SIMS vs. NanoSIMS for H determination, these early data hint at differences in inferred [H₂O]. It is possible that the higher lateral resolution of NanoSIMS allows fractures (containing adsorbed water; Fig. 3) to be avoided. However, the fun-

damentally low beam current and ion production in NanoSIMS compared to SIMS is another variable to be considered. Future NanoSIMS measurements of H in RBT 04262 may illuminate differences in the $[H_2O]$ and δD values determined from these two techniques.

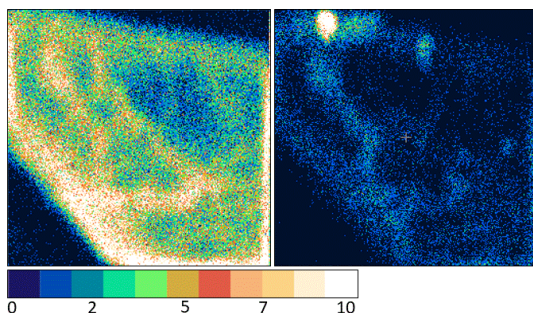


Fig. 3. NanoSIMS 1H (left) and ^{12}C (right) maps of a $20 \times 20 \mu m$ area in a RBT 04262 pyroxene grain.

Maskelynite Water Contents and Potential Hydrogen Signatures. SIMS data show a range of $[H_2O]$ in maskelynite (6 to 1063 ppm wt. H_2O) with elevated δD (504 to 5111‰) compared to olivine and pyroxene (-155 to 197‰) (Fig. 1-2, [3]). Texture plays a role. In *NP* grains, all water contents are below 32 ppm wt. H_2O ($n=6$), with 4 of the 6 measurements clustered at ~ 600 ‰ and 2 at ~ 4700 ‰ (Fig. 4) and no correlation between $[H_2O]$ and δD . In a single *P* maskelynite grain that was enclosed in a 5 mm large pyroxene grain, water contents increase from 81 to 1063 ppm wt. H_2O with decreasing δD from 3475 to 784‰ ($n=4$) (Fig. 4). A similar negative correlation between $[H_2O]$ and δD has been documented in pyroxene [2-3] and impact melt [2,5-6]. Explanations for this relationship include: (1) 1H degassing during crystallization (2) 1H degassing after crystallization (3) mixing between H from Mars' atmosphere (4950‰ [7]) and (A) terrestrial contamination (B) diffused H from the enclosing pyroxene or (C) H recorded in the grain before it was shocked to maskelynite. Since maskelynite is a feldspathic glass produced by shock, preservation of the H crystallization signature is unlikely. Additionally, all measured δD in maskelynite, even the lowest, are significantly higher than expected if the correlation was related to terrestrial water exposure [8-9].

The spread in *P* δD is confined within the range of δD of the *NP* maskelynite. This suggests that the minimum and maximum δD in both lithologies are from the same sources, and that ~ 600 ‰ is inherent to the maskelynite (likely pre-shock). This disfavors hypothesis 3B. However, although H in the maskelynite appears isotopically independent ($\delta D = 784$ to 3475 ‰) from the surrounding pyroxene ($\delta D = -27$ ‰), it is possible that the high-water contents ($>1000 \mu g/g H_2O$) of

this enclosed maskelynite were “trapped” within the host pyroxene.

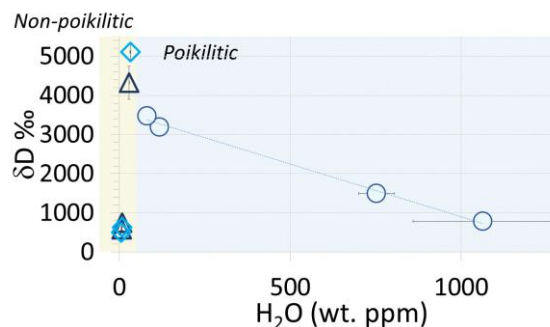


Fig. 4. Water content (wt. ppm $H_2O \pm 1\sigma$) and $\delta D \pm 1\sigma$ (‰) in maskelynite measured by SIMS. Like symbols correspond to individual grains analyzed ($N=3$) within the total number of measurements ($n=10$). *NP* measurements are shaded in yellow, and *P* in blue.

One scenario could be that varied amounts of atmospheric H were incorporated in some of the maskelynite during shock, producing a range from the igneous δD (600‰) to >3500 ‰ as mixing increased. Alternatively or concurrently, as maskelynite was generated during shock, igneous H (600‰) degassed and δD values increased (>3500 ‰) as 1H was preferentially lost. Evolution from low to high δD , whether from degassing or atmospheric mixing, cannot be discerned and will be modeled in future work.

Conclusions: Preliminary data suggests that water contents derived by NanoSIMS are lower in RBT 04262 olivine and pyroxene than by SIMS. This investigation will be continued. Likewise, H in maskelynite appears to be sourced from 2 endmembers that require further study. We argue that the low-end H source (600‰) is igneous, and hypothesize that the high-end is either due to atmospheric mixing, or loss of 1H during shock driven degassing. Numerical modeling will be performed to compare measured data.

References: [1] Peslier A. H. et al. (2019) *Geochim. Cosmochim. Acta*, 266, 382-415. [2] Dudley J. M. et al. (2019) *LPSC L*, Abstract #2971. [3] Dudley J. M. et al. (2019) *Goldschmidt 2019*, Abstract #863. [4] Usui et al. (2010) *Geochim. Cosmochim. Acta*, 74, 7283-7306. [5] Usui T. et al. (2015) *Earth Planet. Sci. Lett.*, 410, 140-151. [6] Liu Y. et al. (2018) *Earth Planet. Sci. Lett.*, 490, 206-215. [7] Owen et al. (1988) *Science*, 240, 1767-1770. [8] Hoefs J. (2015) *Stable Isotope Geochemistry*, 229-432. [9] Stephant A. (2018) *Scientific Reports* 8, 12385.