

**FORMATION, TRANSPORT AND RELEASE OF VOLATILES FROM PACKED LUNAR REGOLITH GRAINS** B. M. Jones<sup>1</sup>, T. M. Orlando<sup>1</sup>, A. Alexandrov<sup>1</sup>, C. A. Hibbitts<sup>2</sup> and D. Dyar<sup>3</sup>, <sup>1</sup>Georgia Institute of Technology, Atlanta GA (Thomas.Orlando@chemistry.gatech.edu), <sup>2</sup>Applied Physics Laboratory, Johns Hopkins University, Laurel, MD and <sup>3</sup>Mt. Holyoke College, South Hadley, MA

**Introduction:** Water on the moon has been a source of scientific exploration and debates regarding the quantity of water present on the moon have oscillated throughout the years. Initial analysis of Apollo samples indicated that water was absent and that previous observations of water were a result of atmospheric contamination<sup>1</sup>. Several simultaneous yet independent observations of OH/H<sub>2</sub>O by the Moon Mineralogy Mapper (M<sup>3</sup>), Visual and Infrared Mapping Spectrometer (VIMS), and Deep Impact Extended Investigation (DIXI)<sup>1-3</sup> have yielded compelling but ambiguous evidence for surficial H<sub>2</sub>O. More definitive molecular water detection came from the Lunar Crater Observation and Sensing Satellite (LCROSS) impact experiment in the permanently shadowed region of the Cabeus crater. This impact liberated ~155 kg of water ice and significant amounts of hydrogen in the ejecta plume.<sup>4</sup> Water was also observed in the lunar exosphere by the neutral mass spectrometer onboard the Lunar Atmosphere and Dust Environment Explorer (LADEE) following impacts from micrometeoroids in the lunar regolith.<sup>5</sup> Most recently, Honnibal et. al.<sup>6</sup> provided the first unambiguous optical detection of molecular water on and within the Moon surface by observing the 6 micron band using the SOFIA observatory. This work reported molecular water abundances of about 100 to 400  $\mu\text{g g}^{-1}$  and suggested the majority of the water was likely stored within or between the glassy grains. In this work we report controlled measurements of the formation, transport and release of molecular water and hydrogen from lunar regolith grains.

**Approach:** The experimental apparatus and methods for measuring the formation and release of H<sub>2</sub>O and H<sub>2</sub> from heated Apollo samples were slightly modified from those described previously. Briefly, the technique is known as temperature program desorption (TPD) and utilizes an apparatus that consisted of a small (~10 liter) ultra-high vacuum (UHV) chamber held at  $< 2 \times 10^{-9}$  torr, a quadrupole mass spectrometer, and small (0.1 mm  $\times$  15 mm  $\times$  20 mm) stainless steel sample holder strip. A mass of  $5 \pm 1$  mg of the Apollo sample was placed on the strip under atmospheric conditions and transferred to the UHV chamber. A controlled heat ramp was applied to the sample of  $0.5 \text{ K s}^{-1}$ . Current for heating the sample holder was supplied via a Stanford Research Systems (CS580) and the temperature of the sample was controlled from 300 – 1000 K via a PID algorithm and a type K thermocouple. Desorbing neutrals were mass selected, detected and quantified

with a calibrated residual gas analyzer (Pfeiffer Vacuum Prisma Plus QMG 220 C-SEM). Control experiments without lunar samples were conducted under the identical conditions to isolate and subtract signal from background (chamber walls and sample holder).

The sample analyzed was Apollo 15 lunar sample 15221. Sample 15521 is considered a highland reference with a maturity index  $I_s/\text{FeO} = 63$ .

**Results and Discussion:** Significant amounts of H<sub>2</sub>O and H<sub>2</sub> were observed evolving from Apollo sample 15221 during temperature program desorption. Considering the high temperatures at which molecular water and hydrogen were desorbing, we interpret the majority of observed water and hydrogen to originate following recombinative desorption (RD) of hydrogen implanted defects (i.e. primarily M-OH hydroxyl groups) created through solar wind bombardment of protons. Our analytical treatment considered desorption from the vacuum grain interface and transport through the void space of both molecular adsorbed species (1st order) and species desorbing following a reaction between neighboring hydroxyl groups (2nd order). In addition, activated sub-surface diffusion was considered. The kinetic model involved a set of modified Polanyi-Wigner based differential equations that were solved simultaneously while optimizing parameters ultimately reproducing the experimental TPD signal. The water TPD signal (not shown) displayed three individual peaks. The first low temperature peak corresponds to second order RD of neighboring hydroxyl groups at the vacuum grain interface and within the buried void space of the regolith. Finally, the last high temperature peak corresponds to sub-surface hydroxyls diffusing to the surface where RD occurs however, delayed from diffusion. Likewise, H<sub>2</sub> formation occurs from a reaction between subsurface hydroxyls and metastable hydrogen atoms that diffuse to the surface and are released into the gas phase.

The results, when compared to observational data, support the contention that the observed 2.8 micron signal is dominated by OH which can be moderated by the thermally induced formation of water via RD. Though RD is a minor H<sub>2</sub>O source term during a normal lunation, it can become appreciable during impact events. For example, approximately  $2 \pm 0.3 \times 10^{16}$  molecules of water were formed and detected following heating of an Apollo regolith sample 15221 up to 1200 K. This temperature is easily surpassed in the thermal

spike of an impact event and can lead to the production and release of  $0.6 \pm 0.1$   $\mu\text{g}$  of water or 120 ppm of the regolith mass by weight. If  $\text{H}_2\text{O}$  formation occurs deep enough, some water may undergo a complicated multiple scattering/transport process and eventually become trapped within the cooling vitrified glass and/or between densely packed grains. Similar amounts ( $8 \pm 0.6 \times 10^{15}$  molecules or  $0.02 \pm 0.01$   $\mu\text{g}$ ) of  $\text{H}_2$  are also produced and detected. In view of the high mobility of  $\text{H}_2$ , most is expected to be released and not trapped.

**Summary and Conclusion:** Our results indicate that recombinative desorption contributes a minor amount to a general water source term during a normal lunation. It is also a minor source term for the water released in the LCROSS impact event. However, it can be a significant persistent source of translationally hot migrating water molecules that can form via micrometeorite collisions in sunlit regions which are normally void of water. Water can also undergo multiple scattering in the impact zone and potentially become trapped in the glass or between annealed grains.  $\text{H}_2$  will also be formed during these impact events in sun-lit regions. Since the trapping probability is low, most will likely be released. Since a large amount of  $\text{H}_2$  was observed in the LCROSS ejecta plume, the release from cold regions may contain sources that are signatures of molecular hydrogen production via electron radiolysis of physisorbed or trapped water via solar wind electrons penetrating the PSR.

**References:** [1] Sunshine J. M. et al. (2009) *Science* 326, 565-568. [3] Pieters C. M. et al. (2009) *Science* 326, 568-572. [4] Clark R. (2009) *Science* 326, 562-564. [5] Colaprete, et al., (2010), *Science* 330, 463-468. [6] Honniball, C.I., Lucey, P.G., Li, S. Orlando, T. M. et al. *Nat Astron.* doi.org/10.1038/s41550-020-01222-x (2020), [7] Benna et. al., , et al. *Nat. Geoscience.* (2019) May;12(5):333-8, [8] Morris, R., 1978. *Lunar and Planetary Science Conference Proceedings*, pp. 2287-2297.