

FORMATION, TRANSPORT AND RELEASE OF MOLECULAR WATER ON AND WITHIN LUNAR MATERIALS. T. M. Orlando¹, A. R. Clendenen¹, G. L. Schieber¹, B. M. Jones¹, P. D. Loutenshiser¹, A. B. Aleksandrov¹, C. A. Hibbitts², and M. D. Dyar³, ¹Center for Space Technology and Research, Georgia Institute of Technology, Atlanta, GA, 30332, ²Johns Hopkins University Applied Physics Laboratory, Laurel, MD, 20723. ³Mount Holyoke College, Dept. of Astronomy, South Hadley, MA, 01075. Thomas.orlando@chemistry.gatech.edu

Introduction: In view of the interest in extended missions to near Earth destinations, understanding the presence and persistence of molecular water on the Moon is of both fundamental and applied interest. Ground and spacecraft based spectroscopic studies in the 2.8-micron region imply that up to 10-1000 ppm molecular water and hydroxyl (OH) may exist on or within the regolith on the sun-lit side of the Moon [1-3]. Since the sun-lit side can become too warm for water-ice to be stable and the full optical band expected for molecular water was not resolved, the general presence and persistence of useful amounts of accessible molecular water remains somewhat contested. Permanently shadowed craters, such as parts of Cabeus, are cold enough to capture migrating water molecules for geologic timescales. Indeed, evidence for potentially accessible water on the Moon comes from the LCROSS impact experiment at Cabeus crater. This impact event showed the presence of up to 6% concentration (by mass) of water and ice in the ejecta plume [4]. While this was somewhat expected from previous modeling efforts [5], understanding the sources, sinks and transport of H₂O on the Moon is necessary and requires detailed knowledge of the molecular water binding energies, diffusion constants and transport coefficients. All of these quantities are difficult to obtain from actual regolith and the values will depend on the regolith composition, temperature and space weathering history.

Some modeling efforts use the water-ice sublimation energy to describe the water-regolith interaction even though this is known to be less than the interaction energy of the adsorbed layer [6]. Most of the diffusion and transport coefficients necessary to model the migration and motion of water molecules on and within the regolith are not in the literature and are often approximated or extrapolated from data taken under conditions that may not be representative of the lunar environment.

Recent temperature program desorption (TPD) measurements of water adsorbed on lunar materials under pristine ultrahigh vacuum (UHV) conditions provide values for the activation energy required to desorb water molecules from the regolith surface [7]. TPD measurements also provide binding energies as well as enabling estimates for water adsorption lifetimes. Careful analysis of the TPD profiles and widths can yield diffusion constants. Knudsen

diffusion constants can also be measured directly using mass spectrometric sampling of differentially-pumped packed-beds as a function of flow, regolith porosity and temperature. Finally, thermally activated water formation can be measured from proton irradiated and highly hydroxylated samples using in either TPD and/or mass resolved thermal gravimetric analysis.

Samples: Well controlled TPD experiments were conducted with actual lunar material to obtain desorption activation energies. The lunar samples are low and high-Ti mare soils, KREEPy soil, highland soil, and a mixed lot. This allows for a good sampling of the varied mineralogy from different Apollo landing sites. Details on the sample material mineralogy can be found in Hibbitts et. al. [8], the Lunar Sourcebook [9], and references cited therein. Separately, the Ar, N₂ and H₂O transport and diffusion coefficients, which are mostly dependent on sample bulk permeability, were measured for the lunar simulant JSC-1A.

Experimental Methods: TPD is a well-known surface science technique used to obtain desorption activation energies. TPD is typically carried out under UHV conditions and involves cooling the sample to a desired dosing temperature, dosing the adsorbate such as water at a known dose rate, and controlled sample heating at a constant temperature ramp while recording the number density of molecules released from the surface. This can directly yield the desorption rate. Additionally, flow experiments were performed in a separate specially designed vacuum system [10] over a range of average pressures from 100 to 25,000 Pa at ambient temperature. The chamber was initially evacuated, and the pressure was allowed to stabilize. Controlled N₂, Ar or H₂O flows were introduced into the chamber, and the pressure drops across the packed regolith beds were measured after reaching steady state.

Results: TPD: We recently reported TPD data and simplified modeling of water interactions on lunar samples [7]. Spectra contained evidence for both a broad distribution of molecularly chemisorbed water and bulk-water ice formation. A numerical analysis method was used to obtain the distribution function of the measured molecular chemisorption sites, *however, this technique does not take into account i) the coverage dependence of the activation energy, ii) diffusion on and between the grains, iii) the fractal nature of the grain and iv) the overall heterogeneous*

coverage. Note some diffusion and trapping occurs to a limited extent in even the thinnest films studied. Data on the low-Ti mare soil show similar TPD spectra to the simulants however, the mare sample consistently adsorbs less water than the highlands. The highest binding energy site is ~ 0.9 eV though this is present in $< 1\%$ of the overall surface sites.

Diffusion/Transport: Transport measurements in JSC-1A found viscous permeabilities for Ar and N₂ between $1.6\text{--}3.5 \times 10^{-12}$ m² in the slip flow regime [10]. This is consistent with existing literature values. The Klinkenberg slip parameter ranged from 6877–8998 Pa for Ar, and 2511–5621 for N₂. [10]. The JSC-1A permeability measurements were for porosities of about 0.4. The transport values for water are currently being measured but are expected to be different due to the stronger interaction potential. These pressure ranges and transport numbers are relevant to *in situ* volatile extraction technologies. Measurements at lower pressure are on-going and will be useful for modeling migration and transport on the surface.

Water Formation and ISRU Lunar Maps: We have recently shown that molecular water can be formed in highly hydroxylated lunar samples that have been exposed to the solar wind via a thermally activated process known as recombinative desorption (RD) [11]. This process is particularly important for minerals containing Mg, Fe, Ti and Ca hydroxides. The temperatures required for this to occur can be as low as 325–350K and is within the temperature excursion of the equatorial portion of the sun-lit side of the Moon. Thus, a natural water production rate is expected in the hottest regions of the Moon, especially in zones with high Mg and Ca content.

The Moon has an abundance of solar power and thus a possible way to “produce water” from the lunar regolith is to use concentrated solar light. In fact, the moon is an ideal location for utilizing solar resources, because a lunar day is ~ 14 earth days and the Moon has a declination of $\sim 1.5^\circ$ (compared to Earth’s $\sim 23.5^\circ$) [12]. Since there are very limited seasonal changes to light conditions and no atmosphere to reduce the amount of solar radiation, the extraterrestrial solar radiation incident on the Moon is ~ 1365 W/m² (compared to Earth’s surface ~ 1000 W/m²). Using the data on the lunar topography and permanently illuminated or shadowed regions from the Lunar Reconnaissance Orbiter, we are creating a map of solar resources on the Moon as a function of both space and time. This can then be correlated with the known reflectance spectra and mineralogical resources on the Moon surface. Theoretically, this lunar resource map could be used to find locations and times where the solar and mineralogical conditions are ideal for producing useful volatiles.

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References: [1] Clark, R. N. (2009) *Science*, 326, 562-564. [2] Pieters, C. M., et al. (2009) *Science*, 326, 568-572. [3] Sunshine, J. M., et al. (2009) *Science*, 326, 565-568. [4] Colaprete, A., et al. (2010) *Science*, 330, 463-468. [5] Watson, K., et al. (1961) *JGR*, 66, 3033. [6] Crider, D. H. and R. R. Vondrak (2000) *JGR*, 105 (E11), 26773. [7] Poston, M. J., et al. (2015) *Icarus*, 255, 24-29. [8] Hibbitts, C. A., et al. (2011) *Icarus*, 213(1), 64. [9] Heiken, G., D. Vaniman, and B. M. French, eds. (1991) *Lunar Sourcebook*, New York, Cambridge Univ. Press. [10] Schieber, G. L., et al, submitted, *Icarus* (2018). [11] Jones, B. M. et al, (2018), *GRL* [12] Burke, J. D. (2012). *Moon: Prospective Energy and Material Resources*. V. Badescu: 335-345.