

THERMAL STABILITY OF WATER AND HYDROXYL ON AIRLESS BODIES C. A. Hibbits¹, M. D. Dyar², T. M. Orlando³, G. Grieves³, Dan Moriarty¹, Michael Poston³, Alice Johnson³, ¹JHU-APL, 11100 Johns Hopkins Rd., Laurel, Md., 20723, karl.hibbits@jhuapl.edu, ²Dept of Astron., Mt. Holyoke, ³School of Chem & Biochem, Georgia Institute of Technology.

Introduction: The discovery of water (or hydroxyl) on the illuminated portion of the Moon by three independent spacecraft [1-3], and the excavation of water ice from within a permanently shadowed crater (LCROSS homepage), support the existence of reservoirs of assessable quantities of water. These discoveries are also scientifically intriguing because there are various physical and chemical states that hydrogen can assume in terrestrial bodies in this solar system [4,5] This paper focuses on distinguishing between molecular water (H_2O) and hydroxyl (OH^-) on the illuminated Moon and discusses their thermal stabilities, possible abundances, and mobilities. We also touch upon the relevance of this work to other airless bodies.

It has long been suggested that H_2O or OH^- could be present on the Moon and other airless silicate bodies as the result of chemical interaction between implanted solar wind particles and oxygen atoms in the surface of the silicate or oxide grains in the lunar regolith [6,7]. This ‘water’ now detected on the Moon by an absorption band near 3 μm in reflectance spectra of the surface is currently assumed to be a surface accumulation of solar-wind-generated OH^- or H_2O adsorbed on grains.

H^+ ions from the solar wind with energies ~ 0.2 to 2 keV implant in the upper 10s of nanometers of exposed grain surfaces. These protons will break existing bonds upon implantation and combine with dangling O^{2-} to form OH^- . The efficacy of this process has been demonstrated in the laboratory with MeV and high keV proton bombardment into various oxides and silicates (e.g., [8,9]) with implications detailed by others (e.g., [10]). Although initially surfacial, this OH^- may migrate deep into or around the grain to be protected from UV illumination that would penetrate 1000 times further than the protons from the solar wind. Water and OH^- may also persist in a dynamic equilibrium, being produced, photolyzed, and/or desorbed.

Physical Characteristics of Adsorbed Water: Molecular water (H_2O) and hydroxyl (OH^-) can adsorb onto grain surfaces partially due to electronic attractive interactions originating from the charge redistribution associated with the dipole in the adsorbate (in this case, OH^- or H_2O). Due to hydrogen bonding interactions in the condensed phase, the binding energy of water to itself is ~ 0.5 eV. Using this binding energy, calculations of desorption rates in vacuum indicate that at 130K, ~ 38 nm would sublime over a 2-week period

[11,12]. Thus, water ice is not stable to thermal desorption on dimly lit lunar surfaces.

However, the interaction of the water molecule with the *surface* of a grain can be strong, increasing its resistance to thermal desorption. Molecular water chemisorbed on a mineral surface typically desorbs under laboratory UHV conditions ($<10^{-8}$ torr), beginning around 200K. Stronger dipole interactions between the water molecule and structural defects in a grain surface (such as oxygen vacancies and dangling bonds) result in partial dissociation and higher desorption temperatures. Full dissociation may bind OH^- to the grain surface; with these terminal hydroxyls sites stable up to 500K (see discussion in [4]). Thus, chemisorbed water (or OH^-), can only exist as a monolayer or at most a simple bilayer. Additional layers would be water ice.

Chemisorbed OH^- can desorb only after it recombines with hydrogen or another hydroxyl group. This process, called recombinative desorption requires significant amounts of thermal energy, and forms neutral H_2O , which thermally desorbs. Thermal desorption always involves the ejection of molecular water, in contrast to electron-stimulated or photo-desorption, in which the O-H bond can be broken and H, OH and H_2O are all desorbed (e.g., [13]). The effective grain size (~surface area) is also important, especially for determining absolute abundance of OH^- or H_2O . A monolayer of adsorbant on a 1 μm sphere is equivalent to about 1000 ppm, whereas a onolayer on a 50 μm size particle is only 20 ppm [4]. Lunar soil is very rough at the microscopic scale. All lunar samples are essentially nonporous, but have significant sub-micron surface roughness, with surface areas from ~ 0.2 m^2/g to 4 m^2/g as measured by N_2 , Ar, O_2 , and CO uptake using BET analyses at 77K [14]. For those gases, adsorption is always reversible, consistent with physisorption in which the amount of adsorbed gas is proportional to its overburden pressure [14, 15].

Spectral Characteristics: Due to the very low absolute abundance (<1000 ppm) of hydrogen on the moon, the only detectable absorption band due to H is the ~ 3 μm stretching fundamental, present for molecular H_2O and OH^- , and even H_3O^+ . The OH^- ion is responsible for the position of the “3- μm ” band when centered near or shortward of 2.9 μm . When the OH^- is tightly bound to the surface the shortened bond length causes the the band position to shift to higher energy and thus shorter wavelength. A broad band is

consistently detected for the OH⁻ absorption on the Moon. This broad range of vibrational energies is consistent with OH⁻ adsorbed over a wide range of sites and is commonly seen in water adsorbed onto terrestrial minerals [3].

Current Results: To date, our work demonstrates that the strength of the adsorption of water on a lunar analog grain surface depends on the crystallinity, surface defects, and composition of the adsorbate.

We have conducted Temperature Programmed Desorption (TPD) experiments on a variety of lunar analogs, including Fe-rich, low-water-content, anorthositic-composition glasses (Figure 1). We have found that these glasses, in contrast to minerals, do not readily adsorb water; in fact, the water-water bond is stronger than the glass-H₂O interactions. Thus, these glasses appear hydrophobic. Similarly, early results from pristine lunar mare soils show a low affinity for water [16,17,18,19]. It is also possible that the Fe-rich glasses, like the mare on the Moon and the surface of some asteroids such as Vesta, do not adsorb as much water as Ca-rich glasses (analogous to lunar highland compositions).

We have also obtained bi-directional infrared reflectance spectra of the same materials in the 2-5-μm region. Results are consistent with the TPD spectra. Water does not adsorb onto basaltic and Fe-rich anorthositic composition glasses to create a 3-micron band > 1%, whereas minerals such as anorthoclase, do possess a band [3]. Unlike these analogs, Lunar glasses have surface defects from solar wind irradiation and micrometeorite bombardment. These defects are likely necessary for the uptake and persistence of water under lunar conditions. Future work will need to investigate the adsorption of water onto irradiated glasses of lunar composition.

Acknowledgments: We are grateful for support of this project from LASER grant # NNX08AZ01G and Lunar Science Institute grant # NNH08ZDA008C.

References : [1] Pieters et al. (2009), *Science*. [2] Sunshine et al., (2009), *Science*. [3] Clark, (2009) *Science*. [4] Dyar et al. (2010), submitted, *Icarus*; [5] Hibbitts et al. (2009) *LPSC*; [6] Hapke, B. (1965) NY Acad. Sci. [7] Keller et al., 1966 [8] Mattern et al. (1976), *J. Vac. Sci. & Tech*; [9] Gruen et al. 1976 [10] Starukhina and Shkuratov, 2000 [11] Vasavada et al., (1999), *Icarus* [12] Grieves et al., this LPSC [13] Lane et al., (2007), *J. Phys Chem*. [14] Cadenhead et al., 1972, *LSC 3* [15] Fanale et al., (1971) *JGR* [16] Holmes et al., (1973) *LSC 4*, [17] Holmes et al., (1974) *LSC 5* [18] Cadenhead and Stetter, (1974) *LSC 5*.

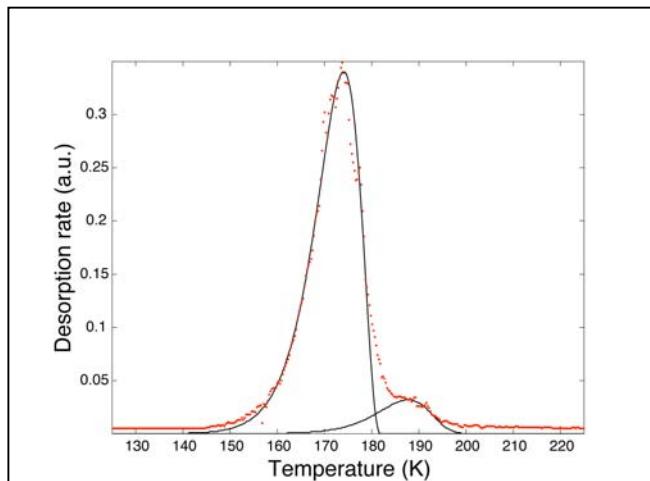


Figure 1. TPD spectra of water-ice desorbing from an Fe-rich lunar basalt analog glass. (red) data. (black) models: one 0th-order model for ice desorption at 170K and a smaller peak due to adsorption of water onto the cryostat/sample mount. This glass (and others) are hydrophobic because the surface lacks defects that facilitate bonding of OH⁻. True lunar glasses would have surface defects due to irradiation to provide sites for those bonds.