

COLD TRAPPING OF VOLATILES IN THE LUNAR REGOLITH C. A. Hibbitts¹, M. D. Dyar², T. M. Orlando³, G. Grieves³, and J. Szanyi⁴, ¹JHU-APL, 11100 Johns Hopkins Rd., Laurel, Md., 20723, karl.hibbitts@jhuapl.edu, ²Dept of Astron., Mt. Holyoke, ³School of Chem & Biochem, GIT, ⁴EMSL, PNNL.

Introduction: Volatiles released from the interior of the Moon or released by impacts will ballistically migrate across the surface until they either escape to space or are trapped in cold, possibly permanently-shadowed regions and may exist in a physical state other than ice. The question of the presence of H₂O and other volatiles on the Moon is important from scientific and exploration grounds. Extensive cometary volatiles at the lunar poles would offer new opportunities to address important questions on the sources and fluxes of impacting cometary objects on the Moon (and by extension, the Earth) over geologic time. Reservoirs of volatiles, especially water, would also provide resources for sustained human exploration.

On the Moon, the accumulation of water/volatiles will be very different than what is generally tested in laboratory studies. Our experiments have been designed to explore what happens during the accumulation of volatile molecules in the polar regions, in which they would likely first interact with soil particles at cold temperatures and under vacuum (i.e. will the water molecule stick upon hitting a cold regolith grain or will it migrate to form ice?). Our research suggests that adsorption at cryogenic temperatures (cryosorption) onto silicate minerals would occur for water and possibly for other volatiles as well. Additionally, cryosorbed water and other volatiles can potentially be stable at temperatures of the dimly-sunlit lunar polar regions as well as in portions of shadowed craters warmed by nearby sunlit terrain. Thus, cryosorption may be an important mechanism for trapping volatiles in the cold regolith of the lunar polar regions.

Abundance and Detectability: Adsorbed water interacts with the electronic fields of the molecules composing the regolith grains to which it adsorbs. This electronic interaction is extremely short-range and no more than a few layers would be expected to adsorb. However, even this abundance can be significant and detected remotely via infrared spectroscopy. For example, assuming an extinction coefficient for adsorbed water at 3- μm of ~ 0.6 (like water ice) [1], a 2% banddepth would be induced by an equivalent path of only 1.25 μm of adsorbed H₂O. Given a molecular diameter of $\sim 5\text{\AA}$ for H₂O, this would equate to ~ 2500 water molecules, and thus 2500 layers. Even though lunar basalt has a very low surface area of about $1\text{m}^2/\text{g}$ [2], this surface roughness is equivalent in area to spherical particles $\sim 1\ \mu\text{m}$ diameter (compared to clays that have a surface area of $\sim 100\ \text{m}^2/\text{g}$ [3]). Light

would only need to interact with $\sim 2.5\ \text{mm}$ of regolith containing a monolayer of adsorbed water to enable detection. Silicates such as pyroxenes are very weakly absorbing at these longer wavelengths and a path length greater than 2.5 mm may be readily achieved, suggesting that adsorbed water could be detected spectrally in dimly-lit areas on the Moon, if it is present. Accordingly, this research effort is focusing on the ability of silicates to adsorb water under vacuum at temperatures above which ice would sublime and to characterize the infrared spectrum of the adsorbed water.

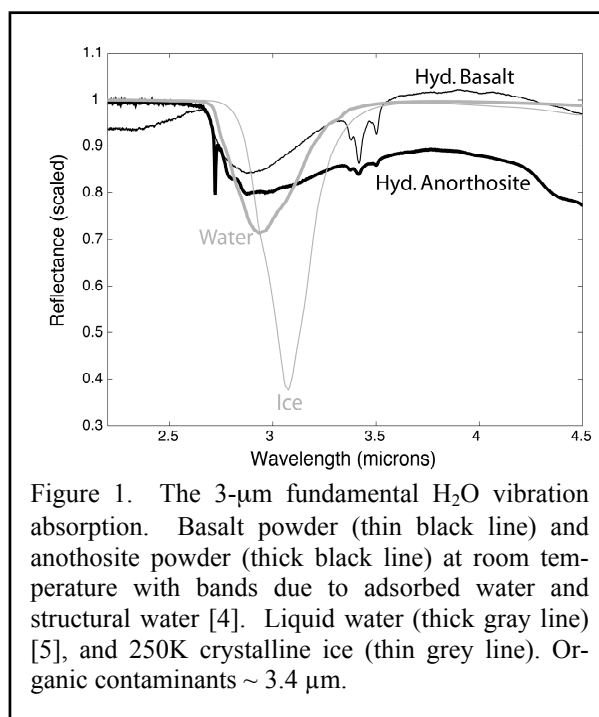


Figure 1. The 3- μm fundamental H₂O vibration absorption. Basalt powder (thin black line) and anorthosite powder (thick black line) at room temperature with bands due to adsorbed water and structural water [4]. Liquid water (thick gray line) [5], and 250K crystalline ice (thin gray line). Organic contaminants $\sim 3.4\ \mu\text{m}$.

Laboratory Measurements: Following upon our work investigating the adsorption of CO₂ onto nonice materials under vacuum at cryogenic temperatures, we have begun to investigate the cold trapping (cryosorption) of water onto non-ice materials, with an emphasis on lunar analogs as the absorbants. We directly dose cold samples under high vacuum ($<10^{-7}$ torr) and monitor the sample with infrared spectroscopy and mass spectroscopy for evidence of volatile trapping and release. The IR spectrum of adsorbed water on clay (Figure 2) is obtained by dividing the transmission spectrum of the clay after being exposed to water vapor at $\sim 150\text{K}$ by the transmission spectrum of the wa-

ter-free clay (desiccated under vacuum at 200°C for 24 hrs). The steep slope and sharp band $\sim 2.7 \mu\text{m}$ in the room-temperature montmorillonite is due to OH in the crystal structure. Volatile/adsorbate molecular interactions at cryogenic temperature are weaker than the chemical interactions that occur at warmer temperatures. Water and CO_2 can remain present, adsorbed onto the samples, at several 10s of degrees above which the ices would sublime, but not at or near room temperature. Thus, the 150K -160K near-surface and surface temperatures of the sunlit lunar polar regions [7] may be sufficiently cold to allow adsorbed water to remain stable at the poles over geologic time.

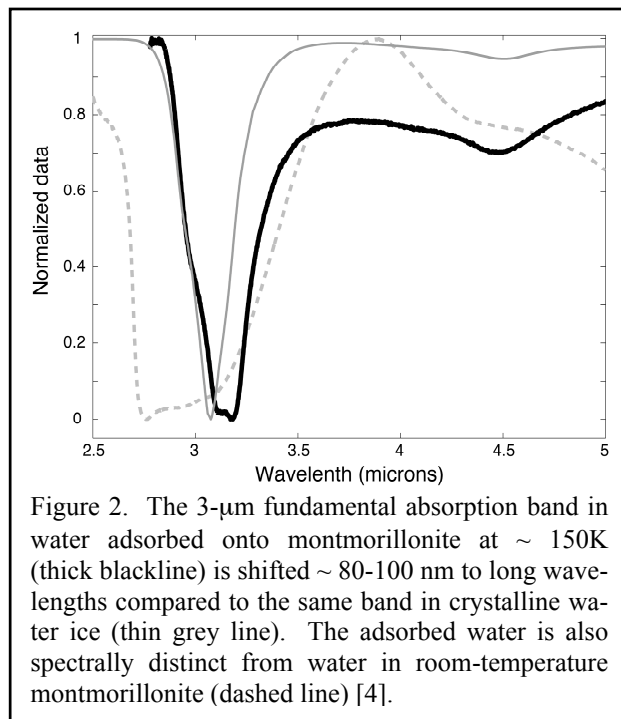


Figure 2. The 3- μm fundamental absorption band in water adsorbed onto montmorillonite at $\sim 150\text{K}$ (thick blackline) is shifted $\sim 80\text{-}100 \text{ nm}$ to long wavelengths compared to the same band in crystalline water ice (thin grey line). The adsorbed water is also spectrally distinct from water in room-temperature montmorillonite (dashed line) [4].

Spectral Characteristics of Trapped Water: In work currently funded under the LASER program and similar to work under the OPR program, we are investigating the stability and IR spectral characteristics of volatiles including water adsorbed onto silicates, including lunar analogs, under conditions very similar to the lunar poles ($\sim 100\text{-}200\text{K}$, and high vacuum). We have begun with clay minerals in order to refine our procedures and for those materials have found that volatiles that do not adsorb under high vacuum at room temperature (CO_2 , CO , H_2O) can adsorb at low temperatures, high vacuum, through a process akin to physisorption and is probably due to a weak (sometimes induced) electrostatic attraction [6]. The infrared transmission spectra of these volatiles are distinct from that of their solid and gas phases.

H_2O strongly affects the 2.7-3- μm region (Figure 1). In hydrous minerals, H_2O that is included in the crystal structure has a strong, but narrow absorption band near 2.7 μm . This band is due to the OH-cation stretch vibration. Decreased crystallinity can tend to broaden this feature (as with oxyhydroxides) so it is spectrally similar to molecular water. H_2O ice, whether amorphous or crystalline, has its stretching vibrational fundamental absorption band centered near 3.1 μm . This is a very strong feature that is usually quasi-metallic reflective, but it is adsorbing at very low abundances (as modeled here) or micron grain sizes. Temperature effects are minimal. The 3- μm absorption of ice will only be slightly weakened at low temperatures (e.g. Zhang et al., 2007), and there should be no shift in position of the band.

For adsorbed water, its fundamental 3- μm band shifts $\sim 80\text{-}100 \text{ nm}$ to longer wavelengths, suggesting the vibration of the adsorbed water is lower energy than for ice. This is consistent with electronic interaction between the H_2O molecule with the heavier montmorillonite molecule inducing a lower frequency to the vibration.

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References : [1] Denevi B.W. et al. (2007) *J. Geophys. Res.*, 112, E05009 ; [2] Cadenhead et al. (1972) *LSC III*, 2243-2257; [3] Chiou C. T. (2002) *J. Wiley & Sons*, pp 86-105; [4] Salisbury J. W. et al. (1991) *Johns Hopkins Univ. Press, Baltimore, MD*. [5] Wieliczka et al. (1989) *Appl. Opt.* 28, 1714-1719; [6] Hibbitts, C.A. and J. Szanyi, *Icarus*, 191, 371-380; [7] Vasavada et al. (1999) *Icarus*, 141, 179-193.