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Introduction: Zeller et al. 1966 proposed and demonstrated that solar wind protons might react with lunar surface oxygen to produce hydroxyl [1]; this was followed by many studies that supported this conclusion [2]. An infrared absorption due to water or hydroxyl was found widely distributed across the lunar surface by spacecraft observations [3], and later by groundbased observatories [4]. Data from the LAMP spectrometer on LRO showed a UV absorption that is plausibly due to water or hydroxyl [5]. Observations from an airborne observatory show an emission feature due to molecular water is present at high lunar latitudes [6]. Laboratory spectra of lunar soils curated at JSC in dry nitrogen show absorptions at 3 μm due to water or hydroxyl with abundances ~ 1000 ppm inferred [7].

The spacecraft observations show that both the UV and NIR absorptions are strongly temperature dependent, with little evidence for absorption near the subsolar point [3-5]. This has led to the hypothesis that the temperature variations are due to water migrating along temperature gradients. However, models of the exospheric density of water to support this variation far exceed the upper limits provided by LADEE in situ mass spectrometer measurements [5,8].

The absence of an absorption feature near the subsolar point (temperatures ~ 400K) is particularly surprising given the results of Izawa et al. [7] that showed strong spectral features due to water or hydroxyl. However, Izawa et al. cautioned that it is possible that water may have been acquired by the samples during sample acquisition or 50 years of curation.

Core 73001 offered a unique opportunity to spectroscopically examine soils that have been curated differently than the samples examined by Izawa et al. This core was preserved in a Core Sample Vacuum Container (CSVC) sealed on the lunar surface and may have had fewer opportunities for exposure to terrestrial water. This project was aimed at collecting NIR spectral measurements to assess the state of water or hydroxyl on this sample, that may represent the state of hydration on the lunar surface.

A limitation of the core processing in the pristine cabinets at JSC for this work is that the cabinet glass is opaque to IR light beyond 2.5 microns, so remote IR measurements were not possible. However, at the end

of core dissection, the remaining lowest layer of the core (with respect to its processing on its side, not with respect to the lunar surface) was destined to be removed from the pristine processing cabinet for epoxy impregnation and thin section production. This presented the opportunity to introduce a spectrometer into the pristine cabinet and its dry nitrogen environment prior to the removal of the core from dry nitrogen, allowing direct infrared measurement of the core surface.



Figure 1. Photograph of the spectral measurement system positioned over the core. Box with clasps is the FTIR. Cylinder with red leads is the IR illuminator.

Methods: A portable Fourier Transform Infrared (FTIR) spectrometer (Designs and Prototypes Model 102) covering the spectral range from 2 to 14 microns was used to collect spectra from inside the nitrogen purged curation cabinet. An Ion Optics parabolic reflector illuminator with a 900K filament was used to illuminate the sample. The combination of illuminator and spectrometer produced usable spectra from 2 to 5.2 microns. The spectrometer field of view on the core was 13 mm. A sandblasted aluminum surface was used as a semi-diffuse reflectance standard.

The spectrometer is focussed on the surface of the core. During the processing of the last dissection pass, several large clasts were removed leaving cm scale cavities in the core surface. However, six relatively level portions of the core remained at the focus position for infrared spectroscopy.

The ambient temperature of the core does produce thermal emission, so to account for this background, each core position was measured with the illuminator on and off, as were repeated measurements of the standard. Final reflectance spectra were computed as {Core (ON) - Core (OFF)}/{Reference (ON) - Reference(OFF)}.

Spectral measurements were made shortly after introducing the spectrometer into the cabinet, additional measurements the next day, and three hours after the pristine cabinet was vented to room air.

Results: Spectra were obtained of several spots on the core a few hours after introducing the spectrometer into the pristine cabinet (Fig. 2). No obvious water band is present in these spectra. Structure near 3µm are due to low signal to noise ratio of the instrument near 3µm. Spectra obtained the next day feature a prominent, symmetric band centered shortward of three microns. The core cabinet was then vented observe the effect of water adsorbing on the core. Spectra of the core 2 hours after venting show an asymmetric band consistent with adsorbed water.

The occurrence of an hydration band the day following the initial observation of no band was unexpected. This band may have arisen from two potential sources of water contamination. The spectrometer itself has about a cubic foot of volume, and while vented, it is possible some water was retained in the spectrometer case even after 24 hours of nitrogen purging. A second source of water was a liquid nitrogen dewar that was introduced into the cabinet to cool the spectrometer detector. After filling the dewar in the core lab outside the cabinet, it is possible that water condensed onto the inner dewar surfaces, and was released when the dewar warmed overnight. The unusual symmetric band may reflect a very small amount of adsorbed water.

The development of a typical adsorbed water band after cabinet venting was anticipated, and showed that a few hours of exposure is sufficient to produce measurable adsorbed water on regolith surfaces.

Conclusions: These results suggest that lunar regolith does not feature an inherent hydration band. This is consistent with observations from the lunar surface by Chang'E 5. This suggests that the water band observation by [7] was due to water acquired after sample acquisition (e.g., transit to Earth, during curation, or during analysis). However, our

measurements do not explain the appearance of an hydration band on the lunar surface observed remotely, which remains an observation to be explained.

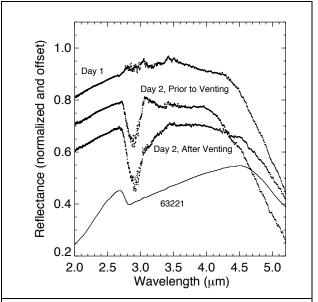


Figure 2. Spectra of the core surface from 2-5 microns. Top, obtained a few hours after introducing the spectrometer into the core cabinet. Second from top, next day. Third from top, after venting cabinet. Bottom, RELAB spectrum of 63221 showing character of terrestrial water contamination.

References: [1] Zeller, E.J., Ronca, L.B., Levy, P.W. (1966). JGR 71, 4855-4860.; [2] Mattern PL, Thomas GJ, Bauer W., J. Vac. Sci. and Tech. 1976 Jan;13(1):430-6.; Ichimura AS, Zent AP, Quinn RC, Sanchez MR, Taylor LA. EPSL 2012 Sep 1;345:90-4. [3] Clark, R. N. (2009). Science, 326(5952), 562-564.; Pieters, C. M., Goswami, J. N., Clark, R. N., Annadurai, M., Boardman, J., Buratti, B., et al. (2009). Science, 326(5952), 568-572. Sunshine, J. M., Farnham, T. L., Feaga, L. M., Groussin, O., Merlin, F., Milliken, R. E., & A'Hearn, M. F. (2009). Science, 326(5952), 565–568. [4] Honniball CI, Lucey PG, Ferrari-Wong CM, Flom A, Li S, Kaluna HM, Takir D. JGR: Planets. 2020 Sep;125(9): e2020JE006484.; [5] Hendrix, A. R., Hurley, D. M., Farrell, W. M., Greenhagen, B. T., Hayne, P. O., Retherford, K. D., et al. (2019). GRL, 46(5), 2417-2424.; [6] Honniball C. I., Lucey, P. G., Li, S., Shenoy, S., Orlando, T. M., Hibbitts, C. A., Hurley, D. M., Farrell, W. M. (2020). Nature Astronomy 10.1038/s41550-020-01222-x; [7] Izawa MR, Cloutis EA, Applin DM, Craig MA, Mann P, Cuddy M. EPSL. 2014 Mar 15;390:157-64.; [8] Benna M, Hurley DM, Stubbs TJ, Mahaffy PR, Elphic RC.. Nature geoscience. 2019 May;12(5):333-8.)