



Laboratory spectroscopic detection of hydration in pristine lunar regolith



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ABSTRACT

Reflectance spectroscopy of Apollo lunar soil samples curated in an air- and water-free, sealed environment since recovery and return to Earth has been carried out under water-, oxygen-, CO₂- and organic-controlled conditions. Spectra of these pristine samples contain features near 3 μm wavelength similar to those observed from the lunar surface by the Chandrayaan-1 Moon Mineralogy Mapper (M³), Cassini Visual and Infrared Mapping Spectrometer (VIMS), and Deep Impact Extrasolar Planet Observation and Deep Impact Extended Investigation (EPOXI) High-Resolution Instrument (HRI) instruments. Spectral feature characteristics and inferred OH/H₂O concentrations are within the range of those observed by spacecraft instruments. These findings confirm that the 3 μm feature from the lunar surface results from the presence of hydration in the form of bound OH and H₂O. Implantation of solar wind H⁺ appears to be the most plausible formation mechanism for most of the observed lunar OH and H₂O.

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1. Introduction

The prevailing view following analysis of lunar materials returned by the US Apollo and Soviet lunar programs was that the moon is virtually anhydrous, with the possible exception of local cold traps, e.g., near the poles (Urey, 1952; Watson et al., 1961; Nozette et al., 1996; Feldman et al., 1998; Colaprete et al., 2010). Recently, the anhydrous model has been upended by the detection of spectral features near 3 μm in wavelength, attributable to hydroxyl and water by the M³ (Pieters et al., 2009), VIMS (Clark, 2009) and HRI (Sunshine et al., 2009) instruments. In parallel to the remote detection of hydration in the lunar regolith, microanalytical studies of lunar materials using ion microprobe and infrared spectromicroscopy showed unexpectedly high levels of H in lunar minerals and volcanic glasses (Saal et al., 2008; McCubbin et al., 2010; Hui et al., 2013; Saal et al., 2013) and soil agglutinate particles (Liu et al., 2012). Some of the microanalytically-detected H in lunar materials has been ascribed to solar wind bombardment (Liu et al., 2012), and the remainder is ascribed to internal water, though the total concentrations inferred for regolith materials, ranging up to hundreds of ppm in H₂O equivalent (Liu et al., 2012)

are much lower than the values of up to 0.3–0.5 wt.% derived from remote spectral analysis (Clark, 2009; Pieters et al., 2009; Sunshine et al., 2009; McCord et al., 2011). Therefore, some additional hydroxyl and water must be contained in lunar regolith, probably as highly disordered hydroxyl groups at or near grain surfaces, and as strongly hydrogen-bonded adsorbed water. The objective of this study was to provide laboratory confirmation of remote detections of hydrogen in the form of hydroxyl groups and/or bound molecular water in lunar regolith. To accomplish this goal, we have examined six Apollo regolith samples that have remained unopened since collection and return to Earth, under oxygen-, water-, CO₂, and organic-controlled conditions using infrared reflectance spectroscopy. Our results show that these regolith samples, recovered from just below the lunar surface, contain adsorbed water and hydroxyl. The band depths, shapes, and feature positions observed here are similar to those observed for the lunar surface by M³, VIMS and HRI. Implantation of hydrogen by the solar wind has been suggested as the most likely source for lunar hydroxyl and water, a process first suggested by Zeller et al. (1966). Following the M³, VIMS and HRI observations, McCord et al. (2011) presented systematic arguments for the solar wind implantation model. Some contribution of internal (magmatic) hydration may also be remotely detectable in some areas of the lunar surface (Klima et al., 2013).

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Table 1
Sample data for Apollo lunar regolith samples investigated in this study.

Sample	Generic	Specific	Parent	Container	Weight (g)
Apollo 11	10084	2008	162	99425	0.536
Apollo 12	12030	185	7	99440	0.511
Apollo 15	15041	71	20	PV	0.500
Apollo 16	61221	176	25	925444	0.517
Apollo 16	64801	176	4	925454	0.510
Apollo 17	71061	14	5	98990	0.520

2. Samples and analytical methods

Contamination of the Apollo samples with terrestrial water would compromise the goal of this study; therefore special procedures were implemented to preserve their integrity. Spectra were collected in a Plas-Labs 818 GBB glovebox with interior dimensions $97 \times 152 \times 79$ cm; (Plas-labs Inc., Lansing, MI) under a dry N_2 atmosphere, where dry N_2 was passed through a series of Drierite filters. The glovebox also contained Drierite and Chemisorb to remove any remaining water and CO_2 prior to opening of the sample containers. Humidity and O_2 levels were monitored continuously with a BW Technologies Gas Alert O_2 Extreme oxygen meter, and an Extech Instruments RH20 humidity/temperature datalogger, and were $\ll 1\%$ throughout the course of the measurements. Samples were only opened within the glovebox. Additional checks on sample integrity were provided by the inclusion of nanophase iron (50 nm nominal particle size) and calcium sulfide in the glove box, which are extremely sensitive to oxidation, hydration, or adsorption of water. Nanophase iron and CaS samples were monitored spectroscopically throughout the course of the experiment and by X-ray diffractometry (XRD) before and after and no evidence of oxidation, hydration or water adsorption within the glovebox environment was observed. For the XRD analysis, aliquots of nanophase iron and calcium sulfide were removed (through an independently purged airlock) from the glovebox at the beginning of the experiment and immediately analyzed using a Bruker D8 Discover X-ray diffractometer with $Co\ K\alpha_{1,2}$ radiation ($\lambda = 1.78897 \text{ \AA}$) operating at 40 kV and 40 mA. After the entire experiment, aliquots of nanophase iron and calcium sulfide that had remained exposed within the glovebox for the duration were again removed and analyzed by XRD.

An important issue which is not within the control of the experimenters is that of pre-analysis contamination of the samples, either during their return to Earth or subsequently, either during the 40–43 years of curation or during shipment to the laboratory. The samples investigated in this study are splits of material that (to the best of our knowledge) were not exposed to air or water during either return or curation. The specific sample identities and parentage of the materials investigated here are summarized in Table 1. The samples were delivered to HOSERLab in sealed sample vials (packed under high-purity N_2 atmosphere at NASA Johnson Space Center) held in heavy plastic, within airtight steel containers further wrapped in heavy plastic, all held within a steel briefcase. There was no sign of damage to any of the packaging materials when they were removed from the case within the purged glovebox. We also opened the successive layers of packaging material with the O_2 and RH meters nearby, to observe any spike in either O_2 concentration or relative humidity at the moment of opening (which could indicate the presence of contamination), no such spike was observed.

Reflectance spectra from 2.0 to 5.2 μm were collected with a Designs & Prototypes Model 102F spectrophotometer (Designs & Prototypes, Simsbury, CT). Samples were illuminated with an

HOSERlab in-house 100 W quartz–tungsten–halogen light source directed through an open-air aluminum pipe at 30° from normal. The spectrometer is equipped with a Designs & Prototypes customized optical assembly that allows a spot size of ~ 7 mm to be viewed by the instrument. The spectrometer uses a Michelson interferometer which contains the infrared optics, beam splitter, and the scanning mirror assembly. The internal mirrors are servo driven at a constant speed to produce the interferograms. Spectral resolution for all measurements in this study was 4 cm^{-1} . The thermo-electrically cooled detector (77 K) consists of InSb over mercury cadmium telluride (MCT). The servo, electronics, and wavelength calibration are referenced to a temperature controlled laser diode. Samples were placed on an adjustable stage and were placed into focus, aided by a removable Modicam 10 video camera (Camea, Brno, Czech Republic) directed into the optical assembly. Reflectance spectra were acquired relative to a 35 mm diameter Infragold[®] diffuse gold-coated standard (Labsphere, North Sutton, NH). Reference spectra were acquired with the same viewing geometry and illumination as the samples and with the same number (100) of co-adds.

3. Results and discussion

Spectra of pristine lunar regolith have spectral features due to water and hydroxyl that are similar to those detected by M^3 , VIMS and HRI, displaying a broad asymmetrical feature centered near $\sim 3 \mu\text{m}$ and extending from $\sim 2.70 \mu\text{m}$ to $\sim 4.45 \mu\text{m}$ (Fig. 1). A weak feature between $\sim 4.5 \mu\text{m}$ and $\sim 4.8 \mu\text{m}$ is ascribable to the first overtones of the silicate Si–O fundamental vibrations. The rise in reflectance towards longer wavelengths is due primarily to rising reflectance approaching the principle Christiansen feature, which occurs near ~ 7.5 – $9.0 \mu\text{m}$ for many silicates (e.g., Conel, 1969; Prost, 1973; Logan et al., 1978; Cooper et al., 2002). Because the Infragold[®] standard and the regolith powders were held within the same environment, and a standard spectrum was measured prior to each sample run, it is expected that temperature differences between the sample and standard were small, of the order of a few $^\circ\text{C}$. Nevertheless, there may be a minute contribution of thermal excess affecting these spectra, the primary effect of which would be to reduce the band depths. The precise location of the band centers of the hydration features, near $2.957 \mu\text{m}$ are indicative of a high degree of hydrogen bonding, as would be expected for adsorbed water remaining in material exposed to the hostile lunar surface environment (Clark, 2009). Continuum-removed spectra show that in detail, the 3- μm band in these samples consists of a sharp inflection near $\sim 2.80 \mu\text{m}$, attributable to structural hydroxyl, and a pair of features with local minima near $\sim 2.95 \mu\text{m}$ and $\sim 3.14 \mu\text{m}$ attributable to bound water and hydroxyl (Fig. 2). These feature locations are very close to the values of $\sim 2.81 \mu\text{m}$, $\sim 2.95 \mu\text{m}$ and $\sim 3.14 \mu\text{m}$ observed by HRI (Sunshine et al., 2009). The feature near $3.14 \mu\text{m}$ is similar to that due to structurally bound water in silicate minerals (Farmer, 1974). The apparent band depths (calculated as depth below a linear continuum anchored on the short-wavelength side of the band, following the method described by McCord et al., 2011) at $2.8 \mu\text{m}$ and $3.0 \mu\text{m}$ in our spectra of Apollo samples are very similar to those observed by M^3 near the lunar equator (Fig. 3A).

Quantification of the water content of the lunar regolith samples in this study is subject to many uncertainties due to the mineralogical and textural heterogeneity of the samples. Using the Normalized Optical Path Length (NOPL) method of (Milliken and Mustard, 2005) we calculate between ~ 0.08 and $\sim 0.16 \text{ wt.}\%$

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