

## SPECTROSCOPIC STUDIES OF PRISTINE LUNAR REGOLITH UNDER H<sub>2</sub>O, O<sub>2</sub>, AND CO<sub>2</sub> CONTROLLED CONDITIONS. M. R. M. Izawa<sup>1\*</sup>, D. M. Applin<sup>1</sup>, E. A. Cloutis<sup>1</sup>, M. Cuddy<sup>1</sup>, P. Mann<sup>1</sup>

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**Introduction:** Lunar materials are highly susceptible to contamination by Earth's atmosphere and hydrosphere. Many spectroscopic features of lunar regolith that are of high interest, including the effects of nanoscopic Fe<sup>0</sup> particles generated by space weathering processes, and the possible presence of surface hydroxyl and adsorbed molecular water cannot easily be studied in terrestrial laboratories. Further, even trace levels of Fe<sup>3+</sup> produced by terrestrial contamination can significantly alter the spectral properties of lunar materials. In order to provide improved ground-truth for remote sensing data interpretation, we have implemented a range of contamination controls in order to carry out a reflectance spectroscopic study of lunar regolith samples that have been curated in a pristine state since collection and return to Earth by the Apollo astronauts.

**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 97×152×79 cm under a scrubbed, dry N<sub>2</sub> atmosphere. The glovebox also contained Drierite and Chemisorb to further reduce water and CO<sub>2</sub> contamination. Humidity and O<sub>2</sub> levels were monitored continuously with a BW Technologies Gas Alert O<sub>2</sub> Extreme oxygen meter, and an Extech Instruments RH20 humidity/temperature datalogger, and were <<1% throughout the course of the measurements.

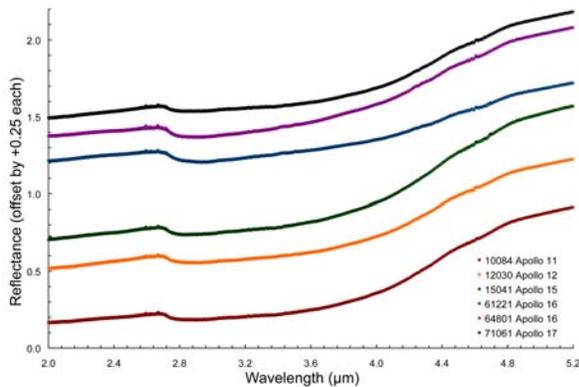
Reflectance spectra from 2.0-5.2 μm were collected with a Designs & Prototypes Model 102F spectrophotometer with 4 cm<sup>-1</sup> spectral resolution. Illumination was provided by an in-house 100 W quartz-tungsten-halogen (QTH) light source directed through an open-air aluminium pipe at 30° from normal. Spectra were acquired relative to an Infragold<sup>®</sup> diffuse gold-coated standard.

Reflectance spectra from 350 to 2500 nm were measured with an Analytical Spectral Devices FieldSpec Pro HR spectrometer with  $i = 30^\circ$  and  $e = 0^\circ$  at a spectral resolution between 2 and 7 nm, internally re-sampled to 1 nm intervals. Data below ~400 nm may be affected by low signal levels and hence data in the 350-400 nm region, particularly abrupt changes in slope, are suspect. Illumination was provided by the same QTH source as above. Spectra were measured relative to Spectralon.

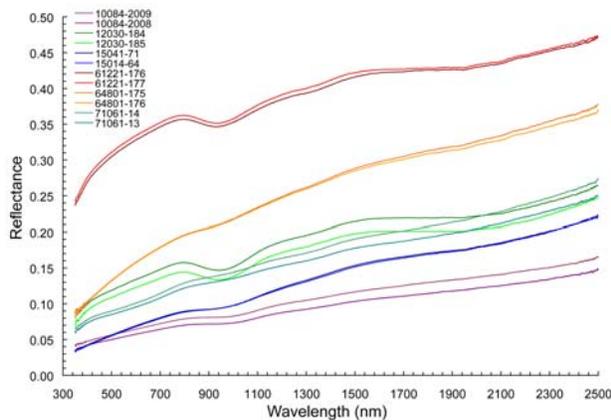
The 200-400 nm spectra were measured with an Maya2000 Pro spectrometer equipped with a grating

that provides coverage from 200 to 859 nm with spectral resolution between 0.48 nm (at 200 nm) and 0.46 nm (at 400 nm). Illumination was provided by an Analytical Instrument Systems Inc. Mini-DTA light source with output from a 30 W deuterium lamp directed through a bifurcated fibre optic bundle consisting of six illumination fibres surrounding a central pick-up fibre feeding into the detector array, producing a biconical geometry with  $i$  and  $e$  centered on ~0° and detector and illumination fields of view of 25.4°. Measurements for each sample were made by first acquiring a dark current spectrum, a reference spectrum of our Puratronic grade BaSO<sub>4</sub> standard, followed by measurement of the samples. The spectra were corrected for irregularities in the BaSO<sub>4</sub> standard using a calibrated deep UV mirror as described by [1].

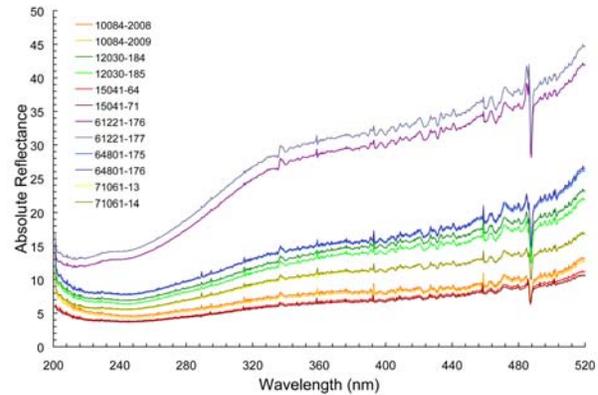
**Results and discussion:** We have detected evidence for hydroxyl and molecular water at concentrations similar to those estimated using three different spacecraft instruments (Chandrayaan-1 Moon Mineralogy Mapper (M<sup>3</sup>), Cassini Visual and Infrared Mapping Spectrometer (VIMS), and Deep Impact Extrasolar Planet Observation and Deep Impact Extended Investigation (EPOXI) High-Resolution Instrument (HRI). We also report high spectral resolution reflectance measurements down to 200 nm wavelength, which reveal features centered near ~260 nm ascribed to <sup>VI</sup>Fe<sup>2+</sup> and to a lesser extent <sup>VI</sup>Ti<sup>4+</sup>, and at 216 nm tentatively ascribed to <sup>VI</sup>Ti<sup>3+</sup>, with a possible contribution from non-octahedral Fe<sup>2+</sup> (e.g., Fe<sup>2+</sup> in the highly-distorted M site of anorthitic plagioclase) The pristine regolith spectra reported here enable the evaluation of compositional-spectral relationships that have been developed for lunar surface compositional mapping using telescopic [3, 4] and spacecraft [5-9] data sets. We find that the methods developed by Lucey and co-workers [5, 7, 8, 10] for FeO and TiO<sub>2</sub> abundance determination are reasonably accurate for most samples, with the exception of the Apollo 17 samples for FeO and with increased errors for very high TiO<sub>2</sub>. Optical maturity parameter (OMAT) correlates reasonably well with physical measures of surface maturity (e.g., I<sub>s</sub>/FeO), again with the exception of the Apollo 17 sample 71061. Possible explanations for the anomalous behaviour of the Apollo 17 regolith include the presence of a pronounced absorption near ~600 nm, which skews the spectral ratios.



**Fig. 1:** Infrared spectra of Apollo regolith samples showing a broad, asymmetric feature between 2.70–4.45  $\mu\text{m}$ . This feature is a mixture of numerous O-H and H-O-H vibrational overtones and combinations, which are poorly resolved because of the vast diversity of possible O-H co-ordination environments in surficial and structural OH and adsorbed  $\text{H}_2\text{O}$ . The weak feature between  $\sim 4.5 \mu\text{m}$  and  $\sim 4.8 \mu\text{m}$  is due to the first overtones of the silicate Si-O fundamental vibrations. Spectra in absolute reflectance, shifted vertically by +0.25 each for clarity.



**Fig. 2:** Reflectance spectra of Apollo lunar regolith samples in the ultraviolet, visible, and near-infrared (UV-Vis-nIR) range, 350–2500 nm. All spectra show a substantial ‘red’ spectral slope (i.e., an increase in absolute reflectance with increasing wavelength). Various spectral features are discernable. Bands centred near  $\sim 950 \text{ nm}$  and  $\sim 2000 \text{ nm}$  are dominantly ascribable to  $\text{Fe}^{2+}$  in the octahedral sites of silicate minerals and glasses. The  $\sim 950 \text{ nm}$  feature is due primarily to the less-distorted M1 site in pyroxenes, and the  $\sim 2000 \text{ nm}$  feature to the more highly distorted M2 site in pyroxenes. A weaker feature centred near  $1250 \text{ nm}$  is due primarily to trace levels of  $\text{Fe}^{2+}$  substituting for  $\text{Ca}^{2+}$  in the highly-distorted M site of plagioclase. The Apollo 17 samples 71061-14 and 71061-13, and the Apollo 12 samples 12030-184 and 12030-185 show a broad, shallow feature centred near  $600 \text{ nm}$  that is ascribable to a combination of  $\text{Fe}^{2+}$ - $\text{Ti}^{4+}$  charge transfer features in ilmenite, mafic glasses, and other (Fe,Ti)-bearing phases, possibly with a contribution from  $\text{Ti}^{3+}$ .



**Fig. 3:** Ultraviolet reflectance spectra of pristine Apollo lunar regolith. All spectra show a general increase in reflectance with increasing wavelength. A broad band centred near  $\sim 260 \text{ nm}$  is ascribable to  $\text{VI}\text{Fe}^{2+}$ , with a lesser contribution from  $\text{VI}\text{Ti}^{4+}$ . Both  $\text{VI}\text{Fe}^{2+}$  and  $\text{VI}\text{Ti}^{4+}$  occur in a wide variety of specific sites, including the M1 and M2 sites in pyroxene, the M site of plagioclase, octahedral sites in ilmenite and other Fe-Ti oxides, and octahedral sites in silicate glasses; this produces a correspondingly broad absorption feature. A weaker feature near  $216 \text{ nm}$  is tentatively ascribed to  $\text{VI}\text{Ti}^{3+}$ . Trivalent Ti is known to occur in many lunar materials [2]. Small, sharp features are due to imperfect correction for  $\text{D}_2$  molecular lines in spectrum of the deuterium lamp light source.

**References:** [1] E. A. Cloutis *et al.*, *Icarus* **197**, 321 (2008). [2] D. J. Vaughan, R. G. Burns, *Phil. Trans. of the Royal Society A* **285**, 249 (1977). [3] D. E. Melendrez, J. R. Johnson, S. M. Larson, R. B. Singer, *JGR -Planets* **99**, 5601 (1994). [4] J. R. Johnson, S. M. Larson, R. B. Singer, *GRL* **18**, 2153 (1991). [5] P. G. Lucey, D. T. Blewett, B. L. Jolliff, *JGR* **105**, 20297 (2000). [6] P. G. Lucey, D. T. Blewett, G. J. Taylor, B. R. Hawke, *JGR* **105**, 20377 (2000). [7] P. G. Lucey, D. T. Blewett, B. R. Hawke, *JGR* **103**, 3679 (1998). [8] P. G. Lucey, G. J. Taylor, E. Malaret, *Science* **268**, 1150 (1995). [9] M. S. Robinson *et al.*, *GRL* **34**, (2007). [10] D. Blewett, P. G. Lucey, B. R. Hawke, B. L. Jolliff, *JGR* **102**, 16319 (1997).

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