

FORMATION AND DETECTION OF OH/OD IN LUNAR SOILS AFTER $^1\text{H}_2^+/\text{D}_2^+$ BOMBARDMENT. A. S. Ichimura¹, A. P. Zent², R. C. Quinn³, L. A. Taylor⁴, ¹Department of Chemistry and Biochemistry, San Francisco State University, 1600 Holloway Avenue, San Francisco, CA 94132, ichimura@sfsu.edu, ²MS 245-3, NASA Ames Research Center, Moffett Field, CA 94035 aaron.zent@nasa.gov, ³MS 239-4, NASA Ames Research Center, Moffett Field, CA 94035 richard.c.quinn@nasa.gov, ⁴Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, TN 37996-1410, lataylor@utk.edu.

Introduction: Absorptions in lunar spectra between 2.8 and 3.0 μm have been reported in Moon Mineralogy Mapper (M^3) data from the Indian Chandrayaan-1 mission [1]. These features are strongest at high latitudes and from fresh feldspar-rich crater ejecta, and have been interpreted as due to OH/ H_2O . This interpretation is supported by neutron [2] and spectral flyby data [3, 4]. Indeed, this water may be a partial-source for the water-ice detected by LCROSS observations [5]. The LCROSS presence of OH/ H_2O had been predicted, with possible sources including cometary impacts [6] and solar wind implantation [7].

It has been speculated by the M^3 team that a feasible explanation for this water that was observed virtually all over the Moon is based upon solar-wind proton implantation. Here we report on a laboratory simulation of this solar-wind hypothesis, and demonstrate that we are able to dehydrate/dehydroxylate lunar samples, expose them to an ion beam of hydrogen or deuterium, and detect the presence of newly formed OH and OD, respectively. Our previous efforts to implant H^+ into lunar specimens utilized a hydrogen plasma with and without a 1keV bias on the specimen holder and met with limited success [8]. For the current study, a commercial ion-beam source proved successful to reproducibly implant hydrogen or deuterium ions into lunar soils.

Experimental: Two lunar specimens were used in this study. One specimen is composed of $<45\mu\text{m}$ fines from a mare region, Apollo 17 soil (70051), and the other is highland material acquired during the Apollo 16 mission (62241; $>45\mu\text{m} < 125 \mu\text{m}$). Dehydroxylation/dehydration of the specimens was accomplished by heating at 500°C at a pressure of 2×10^{-4} Pa for two to four hours. The lunar soil samples were removed to an argon filled glove box (O_2 , $\text{H}_2\text{O} < 0.3$ ppm) for storage. After months of storage, no new signals due to surface hydroxyls were observed under the glove box conditions.

Due to instrument limitations, our protocol required exposure to atmosphere during sample transfers between the glove box, ion-beam, and measurement equipment. A critical part of our experiments utilized deuterium gas $^2\text{H}_2$ (D_2 , 99.8%) in addition to hydrogen ($^1\text{H}_2$) for ion-beam implantation studies. The isotopic shift of OD infrared signals compared to OH allows us

to rule out the possibility that hydroxyl signals resulted from exposure to water vapor. Another advantage of using D_2 for ion-beam studies is that the temporal evolution of the OH signature can be examined simultaneously with the evolution of the lunar soil surfaces.

Ion implantation was accomplished using the etching gun of a Gatan PECS 682 coater-etcher system. The PECS instrument uses high voltage to ionize the gas, which is then accelerated to the desired energy between 1-10 keV. In separate experiments, lunar soils were exposed to $^1\text{H}_2^+$ and D_2^+ ion beams with an energy of 2.3 keV at a pressure of 0.03-0.05 Pa for up to three hours. The beam current was 109 μA . After one hour of exposure, the specimen was removed from the instrument, shaken to expose fresh surface, and the implantation resumed. Samples were immediately transferred to the dry environment of the FTIR for measurement.

Diffuse reflectance FTIR spectroscopy was used to detect the presence or absence of hydroxyl groups in the 4000-1900 cm^{-1} (2.5–5.3 μm) region. Spectra were acquired using a MCT-A detector with 4 cm^{-1} resolution, 256 scans, and were corrected for residual gas phase H_2O and CO_2 .

Results and Discussion: Figure 1 shows reflectance spectra for the Apollo 17 mare soil reported as the ratio of R/R_0 with the specimen heated under vacuum serving as the reference. The effect of temperature is to dehydroxylate the lunar soil as shown by the

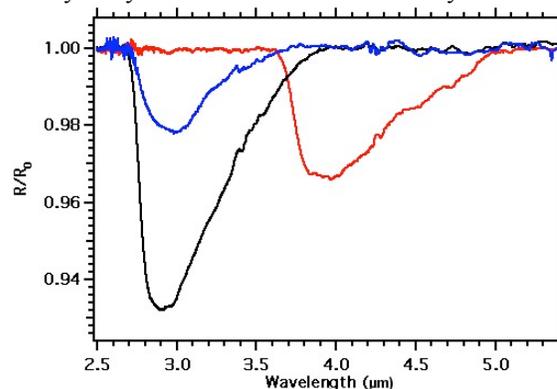


Figure 1. Diffuse reflectance spectra of the Apollo 17 sample before (black), after 500°C and exposure to the D_2^+ (red) and H_2^+ ion beams (blue).

broad band at 2.91 μm (Fig. 1, black) of the specimen before any treatment. Exposure of a heated sample to hydrogen or deuterium ion beams produces absorptions at 2.96 and 3.92 μm , respectively. The isotope shift of the OH fundamental vibrational stretching frequency from 3442 cm^{-1} to 2551 cm^{-1} during D_2^+ exposure shows that ion implantation was successful and not due to reaction of the mare soil surface with water vapor during sample transfer.

After initial measurements, all specimens were stored under ambient conditions. Figure 2 presents IR spectra that were acquired after 5-10 days exposure to air. The mare soil specimen implanted with D^+ (red) shows an additional feature at 2.91 μm while the OD signal has decreased slightly in intensity. The specimen heated to 500°C under vacuum acquires an absorption at 2.91 μm during the same period (black). The newly formed OH signal is ascribed to reaction of the mare soil surface with atmospheric water. The H^+ implanted specimen (Fig. 2, blue) also increases in intensity commensurate with formation of additional OH by reaction with water vapor.

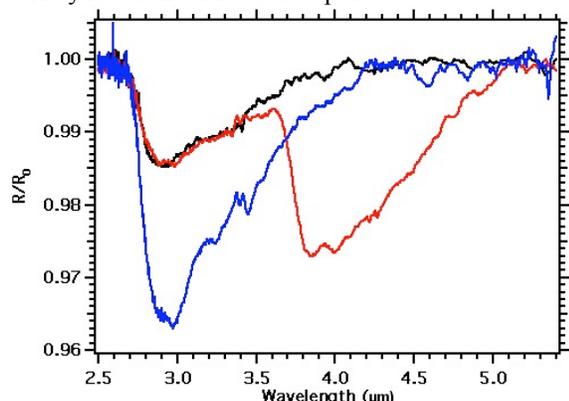


Figure 2. Temporal dependence of OD and OH signals of the mare soil exposed to D_2^+ (red) and H_2^+ (blue) after 10 and five days at ambient, respectively. After 10 days at ambient, the reference specimen (black) acquires characteristic OH signals.

The evolution of the specimen surface during exposure to ambient conditions is important for two reasons. Firstly, it provides evidence that D^+ and by analogy H^+ , were indeed implanted into the lunar soil. If the newly formed OD signals were due only to surface species, then exchange with water vapor would decrease the OD signal over time. Instead, we observe that the loss of OD signal intensity is not commensurate with the gain of OH due to reaction with water vapor. Measurements over longer periods show that the OD signal does not decline significantly after 10 days. A kinetic energy of 1.15 keV per D^+ (H^+) ion

permits access to subsurface regions of the lunar soil that are inaccessible to water vapor. Secondly, this study shows that the rate of OH reformation is relatively slow for the heated mare soil sample. Transfer of specimens in air between instruments while not ideal, does not seriously undermine our protocol and justifies the continued examination of other lunar and terrestrial samples by this method.

Conclusions: Evidence for newly formed OH and OD signals in Apollo 17 mare soil after exposure to H_2^+ and D_2^+ 2.3 keV ion beams, respectively, has been presented. The IR signals are attributed to surface and subsurface hydroxyl groups that formed during reaction of H^+ and D^+ with silicates in agglutinitic rims and subsurface minerals. Our observations support the hypothesis that solar wind implanted protons may be responsible for the OH/ H_2O infrared bands observed by M3, VIMS, and EPOXI. Our results contrast with those of Burke et al. who carried out a series of carefully controlled proton implantation experiments on polished ilmenite [9]. While the difference may be due to a matter of surface area – powders have more surface area than polished sections – the issue is still one of open debate. Nevertheless, our additional work on H^+ and D^+ implanted Apollo 16 highland soil is consistent with the evidence presented here [10].

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