

Proton Induced Hydroxylation on Lunar Soil 78421.38. J. McLain¹, W. Farrell², M. Loeffler³, J. Keller², and R. Hudson². ¹University of Maryland College Park, ²NASA Goddard Space Flight Center, ³Northern Arizona University (jason.l.mclain@nasa.gov)

Introduction: The Dynamic Response of Environments at Asteroids, the Moon and moons of Mars team (DREAM2) is determining the effects of proton implantation and OH creation/retention in lunar soils (specifically lunar soil 78421.38 – Figure 1.A) as a function of temperature, defects, and irradiation. A new MeV proton/electron beam line has been added to the van de Graff accelerator at NASA GSFC Radiation Effects Facility and coupled to a UHV surface science chamber (Figure 1.B). The compressed lunar soils are placed in the UHV chamber and exposed to a low energy 0.1-5 keV hydrogen ion beam to simulate solar wind irradiation and a high MeV beam to simulate solar energetic particles. The exposure rates are varied from 10^{13} particles/cm² to 10^{18} particles/cm².

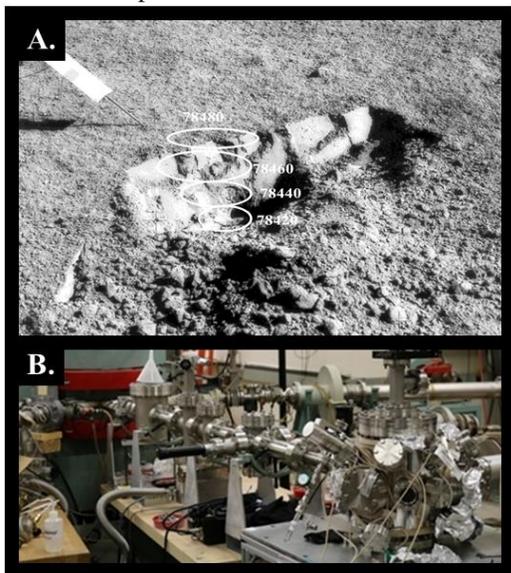


Figure 1. A. Trench at Apollo 17, Station 8 where 78421 was collected, and B. the irradiation chamber and MeV beam line at NASA GSFC Radiation Facility.

Several studies have indicated that proton irradiation at simulated solar wind energies can hydroxylate lunar soils and minerals [1, 2]. However, a more detailed study is needed to understand the OH band structure of irradiated soils, and if the band is effected by thermal cycling or exposure to high energy radiation. With this set of experiments, we can help distinguish between water and OH signatures on the Moon that will compliment several observational studies [3, 4] and provide insight into the wealth of spectral data from M3, LRO, Dawn, Chandrayaan-1, and upcoming Lunar missions.

Experimental Methods and Analysis: Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and evolved gas analysis via mass spectrometry are being used to study the soils before and after irradiation. DRIFTS analysis is performed by removing the sample from the UHV chamber and placing the sample in a Nicolet FTIR spectrometer to monitor the OH and water bands near 3 μm (Figure 2).

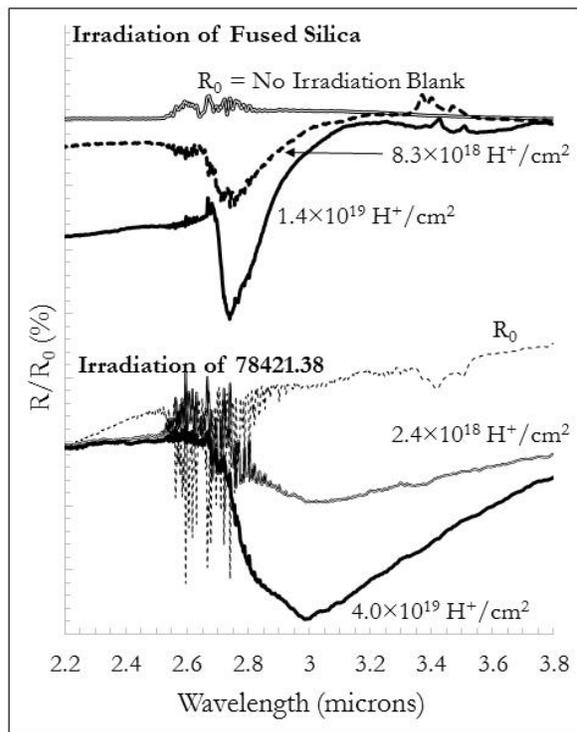


Figure 2. DRIFTS spectra monitoring the evolution of the OH band during proton irradiation of fused silica (top) and lunar soil 78421.38 (bottom).

The initial experiments involved 2 keV H_2^+ irradiation of olivine and anorthite mineral powders finely crushed and sieved to 45 μm . These analyses did not yield any noticeable increase in the OH bands. However a complimentary proton irradiation study with vacuum baked, ($T = 900^\circ\text{C}$), finely crushed fused silica indicated an increase in the very sharp SiOH feature at 2.74 μm , see Figure 2. The intensity of the reflectance spectra is typically displayed as a ratio (R/R_0) where R_0 is the background or blank spectra and R is the spectra taken after irradiation. The cause of the null result from the mineral experiments was most likely a combination of the large amount of water in the minerals and the lack

of sensitivity of the DRIFTS measurement for the OH band depth due to very few new hydroxyls forming during irradiation. This effect can be visualized when we compare the original fused silica spectra in Figure 3.A. with the irradiation study spectra. The OH band depth for the original fused silica sample is much larger than the small increase of the OH band created during irradiation. The blank in these experiments were initial spectra of the samples before irradiation. Additional blanks were left in the FTIR spectrometer to determine if the samples' exposure to air would also increase the OH bands. However during the time frame of these experiments, the blank showed no spectral changes especially near 2.7 or 3 microns. The 2.7 micron band is very sharp, and the band area increases linearly with total proton flux. In Figure 3, the band from 2.6 to 3.6 microns for the original spectra of fused silica can therefore be split into two surface species, a sharp 2.7 μm SiOH band, and a broad band centered near 2.9 μm for absorbed water molecules. The hydroxyl coverage number density on a fully hydroxylated silanol surface corresponds to $4.6 \pm 0.4 \times 10^{14}$ OH/cm², [5]. We estimate that the rate of proton induced hydroxylation to be on the order of one OH created every 10^6 impinging 1 keV energy equivalent protons.

Lunar Sample 78421.38: The deepest sample from one of the best trenches the astronauts were able to dig is 78421, a very mature mare soil, and contains an abundance of agglutinates (68%), Figure 1.A. The maturity of 78421 is $\text{Is/FeO} = 92$, and the average grain size is 51 microns [6, 7].

Proton Irradiation of Lunar Soil 78421.38: Initial irradiation experiments with unheated lunar soil 78421.38 also showed no increase in the OH band near 3 microns. However after heating the sample to 900°C in vacuum (10^{-5} Torr), proton irradiation produced a broad feature at 3 microns that can be seen in Figure 2 (bottom spectra) which also increases linearly with increasing proton flux. The OH band depth reaches an equilibrium at a flux of $\sim 10^{19}$ H⁺/cm². This equilibrium is far from the OH saturation band depth of the original sample in Figure 3. This is due to the original samples exposure to water in earth's atmosphere and the fact that the proton irradiation is performed with a 1 keV monoenergetic proton beam that has an average penetration depth of only 20 nm while the FTIR beam samples to a 1 μm depth. Once the surface hydroxyls are removed from all of the grains, a wide range of proton energies are required to rehydroxylate down to a 1 μm depth.

We can estimate the proton induced hydroxylation rate by comparing the lunar sample to the fused silica sample. If the total band area for 78421.38 is due to OH formation, then the proton induced hydroxylation rate is

~ 100 times faster, i.e., on the order of one OH created every 10^4 impinging 1 keV protons.

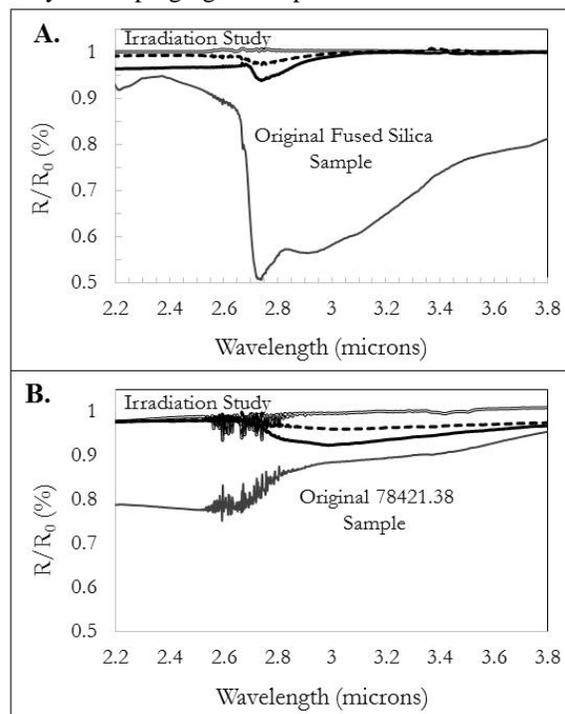


Figure 3. DRIFTS spectra illustrating the evolution of the OH band during proton irradiation of fused silica (top) and lunar soil 78421.38 (bottom) compared to the original untreated sample spectra.

Conclusions: These experiments show that preheating the soils in vacuum to remove OH and adsorbed water is necessary to observe the proton induced OH formation. The OH band locations are markedly different when comparing fused silica to lunar soil 78421.38. The OH feature in the 78421.38 is broad and overlaps with the absorbed water feature in the original fused silica, consistent with spectra in [1]. This implies that IR observations of the lunar surface near 3 μm is from OH and not absorbed water molecules. Preliminary results of MeV irradiation prior to low energy proton irradiation did not show any significant difference in the OH band width or depth in 78421.38. Sample 78421.38 is the first of 7 soils that will be studied. Others include mare soils, 12001, 15271, 70051, and highlands soil types 72501, 62241, and a very immature breccia soil, 73131.

References: [1] Ichimura et al., *Earth and Planet Sci. Let.* 345-348, 2012. [2] Schaible et al., *JGR Planets*, 119, 2014. [3] Milliken, *JGR* 110, 2005. [4] Milliken, Li, *Nat. Geosci.* 10, 2017. [5] Zhuravlev, *Colloids Surf.* 74, 1993. [6] Graf, *Lunar Soils Grain Size Catalog*, 1993. [7] Morris, *Proc 9th Lunar Sci. Conf.*, 1978.