

Decay of Reactivity in Forsterite due to UV Radiation

¹Nathan Wong, ¹John Santarius, ²Lawrence A. Taylor, ³Daniel H. Garrison, ³John T. James, and ³David S. McKay, and ⁴Kimberly R. Kuhlman

¹Department of Engineering Physics, University of Wisconsin, 1500 Engineering Dr., Madison, WI 53706; PH (608) 769-9664; email: nwong@wisc.edu

²Planetary Geosciences Institute, University of Tennessee, Knoxville, TN 37996; PH (865) 974-6013; email: lataylor@utk.edu

³NASA Lyndon B. Johnson Space Center, Houston, TX 77058; PH (281) 483-5048; email: david.s.mckay@nasa.gov

⁴Planetary Science Institute, 1500 East Fort Lowell, Tucson, AZ 85719; PH (520)-622-6300, FAX (520) 622-8060; email: kim@psi.edu

ABSTRACT

The lifetime of reactive sites on the surfaces of irradiated lunar dust grains is of interest to anyone studying human health effects because of the free radicals and toxic compounds that may be formed and may not passivate quickly when exposed to habitat/spacecraft air. One of the major activators of lunar regolith grains may be ultraviolet (UV) radiation, but the contribution of UV radiation to space weathering appears to have been neglected, to our knowledge. The work reported here describes the novel use of time-resolved Raman spectroscopy to measure changes in reactivity caused by UV irradiation. The change in the dominant Raman spectrum peak centers of San Carlos olivine versus time was measured to determine the rate of decay of polished samples exposed to UV radiation in various levels of ambient humidity. The decay time of the reactivity was observed to decrease as the relative humidity increased from 0% to 100%. The chemical reactivity caused by UV exposure appears to passivate after approximately 50 minutes in air containing 45% or higher relative humidity at approximately 25 °C. Experiments such as these will provide guidance in the design and fabrication of living facilities on the Moon.

INTRODUCTION

In returning humans to the Moon, the Lunar Airborne Dust Toxicity Assessment Group (LADTAG) must address many problems faced by the original Apollo astronauts. Major among these is control of the fine dust (<20 μm) that makes up approximately 20 wt% portion of the lunar surface. This ubiquitous, clinging, sharp, abrasive and glassy dust caused a plethora of problems with seals, abrasion, and coatings, in addition to possible health problems, including ‘lunar dust hay-fever’ [1].

Ultraviolet radiation has been measured at Earth’s orbit to be 115 W/m² [2, 3], but, to our knowledge, it has been considered negligible in its contribution to lunar space weathering. The Moon has a hard vacuum of approximately 10⁻¹² torr, allowing direct interaction of UV radiation with the lunar regolith. UV irradiation is

known to cause ionization and has a skin depth of approx. 10 nm, the depth at which space weathering is known to occur.

San Carlos olivine, composed of 90% forsterite – Mg_2SiO_4 (Fo90), is often used to investigate space weathering on the Moon, asteroids and interplanetary dust particles because it is similar to olivine observed in lunar basalts, interplanetary dust particles, and asteroids. Forsterite is one of the major silicate minerals on the Moon, thus it is being used to assess various modes of chemical activation of lunar dust particles [4]. Forsterite has previously been studied using Raman spectroscopy [5] and infrared spectroscopy [6]. It has also been used to simulate shock and ion implantation in interstellar dust grains [7].

EXPERIMENTAL METHOD

Simulation of Photochemical Weathering of Forsterite in a Vacuum.

Raman spectroscopy is used in the present investigation because the spectrum of forsterite contains two very sharp Raman peaks generated by the vibrational modes in the SiO_4 tetrahedra at about 825 cm^{-1} and 856 cm^{-1} , respectively (Figure 1). Samples of single-crystal San Carlos olivines obtained from Gems and Crystals Unlimited were cut into wafers approximately 0.5 mm thick and highly polished with the final polish producing a sample suitable for electron-beam surface diffraction (EBSD). The premise behind using such a high polish was to obtain compositional data using electron probe microanalysis (EPMA) and to remove all mechanical damage that might affect the results. The polished surfaces were exposed to approximately 800 W of UV irradiation in a small vacuum chamber fitted with a quartz window. The vacuum achieved was approximately 10^{-7} torr, but rose to about 10^{-4} torr during UV exposure from a Newport ozone-free quartz xenon lamp 6271 in a Newport 66921 housing. All samples were exposed for 3 hours, equivalent to approximately 4 lunar days [8]. Solar simulators were originally designed for simulating UV exposure at the Earth's surface for lifetime studies in a variety of fields.

Time-resolved Raman Spectroscopy with Controlled Humidity. The samples were then taken to the LabRAM Aramis Horiba Jobin Yvon Raman microscope under vacuum and quickly placed into a heating/cooling stage equipped with an HC-610 relative humidity sensor (Ohmic Instruments). The cover was placed on the stage and the sample was brought into focus as quickly as possible. The time between breaking vacuum and first measurement varied from 5-7 minutes. The data were collected using LabSpec 5 with a 532nm green laser, no filter, a 300 micrometer hole, a 1800 grating, and a x50LWD objective lens under four relative humidities controlled by flowing dry air through a bubbler containing MilliQ water. The ambient relative humidity was further controlled by controlling the temperature of the stage.

The experiments reported here describe the novel use of time-resolved Raman spectroscopy. The Raman spectra are collected in a window between 800 cm^{-1} and 900 cm^{-1} to allow for faster data acquisition across the two sharp peaks found at approximately 825 cm^{-1} and 856 cm^{-1} (Figure 2). Three scans of 10 seconds each were averaged with measurements made every minute immediately following focusing on the sample and increased to every 5 minutes, 10 minutes, and 15 minutes as time progressed. Data were collected for approximately 240 min. This method

was used to determine the decay of reactivity in four controlled humidity environments, 1) dry air, 2) 45% relative humidity, 3) 70% relative humidity and finally 4) 100% relative humidity accomplished by placing a drop of MilliQ water on the sample and focusing through it. Once the data were collected, the peaks were fitted using a combination of Gaussian and Lorentzian functions in GRAMS/AI (Thermo Scientific), the standard software used for fitting Raman data. The peaks were then normalized to the lowest peak position for each data set due to the difference in initial position of the Raman peaks between different crystals of forsterite, which may have slightly different compositions.

RESULTS OF TIME-RESOLVED RAMAN SPECTROSCOPY

Raman Spectroscopy of UV-exposed San Carlos Olivine: The normalized peak position for the peak at 825 cm^{-1} is given in Figure 3. The results for the peak at 856 cm^{-1} are given in Figure 4. The authors believe that measurement of the shifts in the main Raman peaks represent a first-order approximation of how lunar soil may react upon entry to the environment of a lunar habitat. Raman spectroscopy is dependent upon the chemical environment surrounding the bond that results in the peak of interest. In this case, it is measuring the environment surrounding the silica tetrahedra that make up the framework of forsterite. Any change such as the preferential loss of an element or change in the bonding in the material can change the position of the Raman peak. The measurement not only accounts for the change in peak center, but also for peak shape through fitting with Grams AI.

Effect of Humidity on Chemical Reactivity of Forsterite: The data resulting from these experiments show a fair amount of scatter, but general trends are apparent. There is an initial very small decrease with time that may indicate a process that passivates very quickly and is lost due to the amount of time required to get the sample from the vacuum chamber to the humidity control stage and focus. A second process is clearly evident in the increase in Raman shift during the interval 50 to 70 minutes. Finally, there is a long slow decrease in peak center until data acquisition ended. We observed the decay time of the reactivity to decrease slightly as the relative humidities increased from 0% to 100%. Experiments such as those used in the present study may provide guidance in the design and fabrication of living facilities on the Moon.

Fitting of Passivation Curves: The data in Figure 3 and Figure 4 were then fitted using piecewise exponential fits, because three processes appear to be active. The break points of the data for the fits were chosen to be near the minimum and maximum data points. An example of one of these fits to the data presented here is given in Figure 5. The results of this analysis indicate that the second process reaches its peak value in approximately 70 minutes at 0% RH while it peaks at 50 minutes at 70% RH.

DISCUSSION OF SIMULATED PHOTOCHEMICAL SPACE WEATHERING

The data presented here indicates that photochemical space weathering due to UV radiation is a distinct possibility even though the exposures used here only simulate approximately 4 days of lunar exposure. The main process revealed here

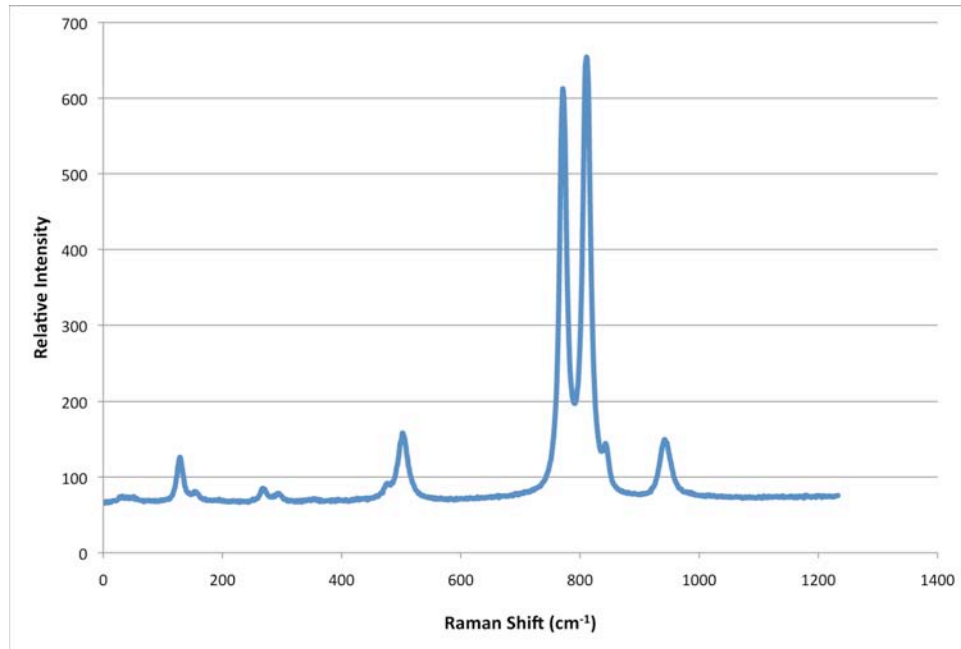


Figure 1 A typical Raman spectrum for San Carlos olivine (FO₉₀). The peaks at approximately 825 cm⁻¹ and 856 cm⁻¹ are due to vibrational modes in the SiO₄ tetrahedra.

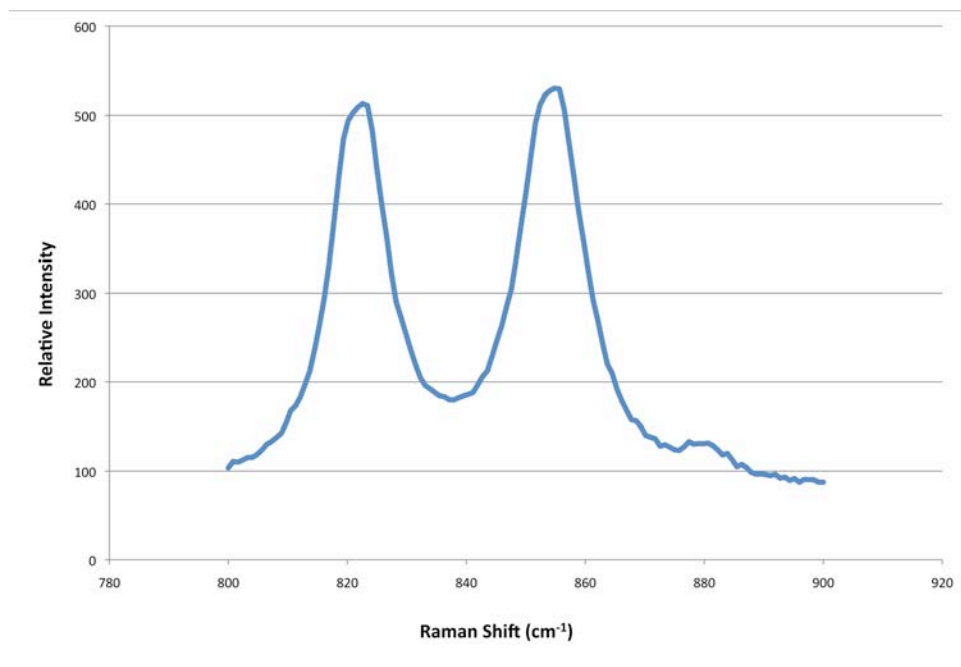


Figure 2. Spectral window of interest for San Carlos olivine (FO₉₀). The peaks were fitted using a combined Gaussian and Lorentzian fit in Grams AI.

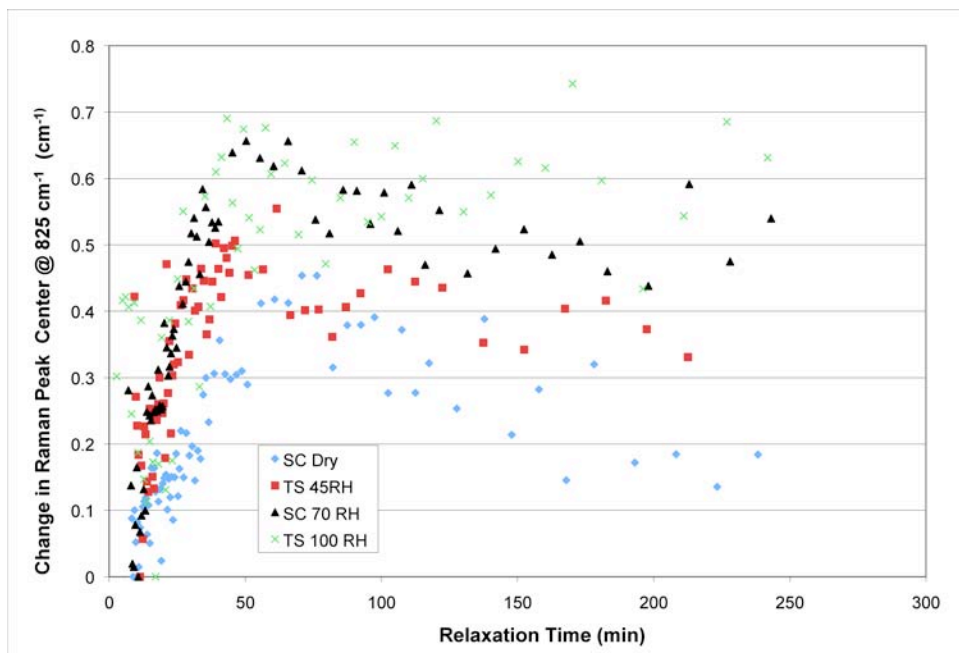


Figure 3. Variation of peak center for the peak at 825 cm^{-1} versus time determined from peak fitting in Grams AI. The data were normalized to the lowest data point in each data set due to the small difference in starting peak position in different samples.

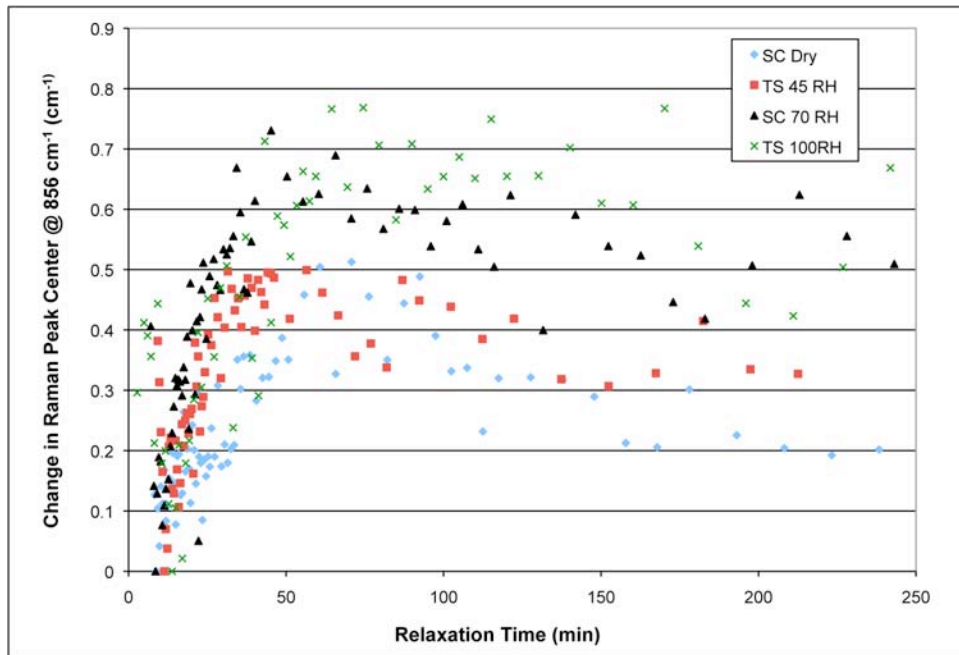


Figure 4. Variation of peak center for the peak at 856 cm^{-1} versus time determined from peak fitting in Grams AI. The data were normalized to the lowest data point in each data set due to the small difference in starting peak position in different samples.

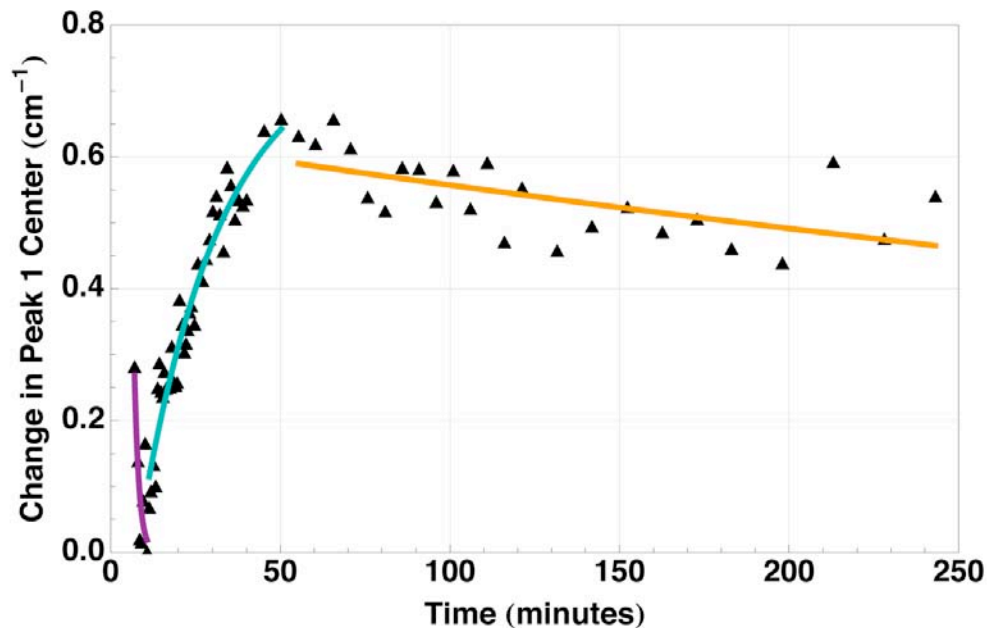


Figure 5. Padé approximation plus piecewise exponential fits to the Raman peak at 825 cm^{-1} of the data taken at 70% RH.

appears to passivate within 50-70 minutes depending upon the ambient humidity. These data have important ramifications for the design of ingress procedures for astronauts returning to a lunar habitat. The data for all samples do not appear to reach a steady state in the 240 minutes of data acquisition, but this can be expected since the UV radiation is likely causing disorder in the lattice and may even be reducing iron or magnesium. The Si-O bond energy is 6.44 eV [9], while UV radiation varies from 3 eV to 124 eV. If enough bonds are broken, O_2 may form and diffuse out of the damaged layer. The skin depth of UV penetration into minerals is approximately 10-20 nm and roughly matches the depth of solar wind proton and alpha particle implantation. Thus, it should be considered as a potential mechanism of space weathering on airless bodies. Transmission electron microscopy is needed to assess the amount of damage and species produced by UV radiation. The rate of change after 50-70 minutes slows dramatically and may not be important for astronaut health. The amount of UV radiation, while demonstrating an effect, only simulates 4 days of lunar UV exposure. Thus, longer exposures are planned. Simulation of geological timeframes is impractical with the solar simulators available.

FUTURE WORK

A better understanding of the chemical or physical changes that cause the Raman peaks to change is currently being investigated using X-ray photoelectron spectroscopy (XPS), UV-visible reflectance spectroscopy and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. Additional experiments will be run using analogs of the other major lunar minerals such as

plagioclase and pyroxenes. Terrestrial analogs are not the ideal materials to be using due to the differences in oxygen fugacity under which they formed. However, the techniques described here must be demonstrated on terrestrial analogs before requesting actual lunar samples from the Curation and Analysis Planning Team for Extraterrestrial Materials (CAPTEM).

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