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Ultraviolet photodesorption as a driver of water migration on the lunar surface

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A B S T R A C T

We have studied the photodesorption of monolayer coverage of water ice coating amorphous carbon by 193 nm photons. We found that the column density of water decreases exponentially with fluence during irradiation at 120 K and obtain a desorption cross-section of $(7.4\pm0.5)\times10^{-19}$ cm^2. We estimate the lifetime for photodesorption to be ~14 h for average solar activity at the sub-solar point on the Moon. The photodesorbed molecules, based on other experiments, are expected to be slower than the escape velocity and to be re-adsorbed on the surface, contributing to water migration. For comparison, we determine the effect of 4 keV He^+ on water-coated Apollo 16 soil (65901) under similar experimental conditions. We find a sputtering cross-section of $(1.2\pm0.4)\times10^{-16}$ cm^2. We calculate that photodesorption by solar UV is four orders of magnitude more effective than sputtering by the solar wind in causing migration of adsorbed water on the lunar surface.

1. Introduction

This work was motivated by recent reports of remote sensing of surficial OH/H_2O on most of the lunar surface. Analysis of infrared spectroscopic measurements of the Moon obtained by three independent space instruments, the Moon mineralogy mapper (M^3) on Chandrayaan-1, the visual and infrared mapping spectrometer (VIMS) on Cassini and the high-resolution instrument (HRI) infrared spectrometer onboard deep impact (DI), indicate the existence of H_2O (and OH groups) within the uppermost layers of the lunar surface. Pieters et al. (1999) observed that the infrared OH band depth varied with the mineralogy and location across the lunar surface. Sunshine et al. (2009) observed a diurnal dependence of the infrared absorption band, suggesting that the regolith undergoes a dynamic H_2O loss (perhaps by photon-stimulated desorption, PSD) and rehydration cycle over the lunar day. A suggested alternative explanation has been that variations in band depth are due to surface topographic effects on reflectance (Clark, 2009). The three reports agree in that H_2O or OH is spatially distributed across the entire lunar landscape, with larger abundances observed at higher latitudes and the poles.

The presence of water on the lunar surface is surprising considering that many potential removal mechanisms exist, such as photodesorption (followed by photodissociation), thermal desorption, meteorite impact, radiation damage, and sputtering. The mechanism for water production or delivery to the lunar surface is unknown. However, some possible sources include: cometary or meteoritic delivery combined with surface diffusion, water/ice beneath the lunar source diffusing from the interior, or chemical effects due to solar wind impact on the lunar regolith (Arnold, 1979). An often-considered hypothesis is that OH and H_2O are formed by the interaction of the solar wind with silicates and other oxygen-bearing minerals within the lunar basalt. Ion irradiation over a range of energies (0.5-3 keV) can lead to the breaking of chemical bonds within various minerals. Implanted or trapped protons from the solar wind may attach to those broken bonds and form OH and subsequently H_2O. Such a mechanism is implied by Sunshine et al. (2009) to explain the apparent rehydration of the entire lunar surface, which requires a daily renewal source to propagate OH/H_2O production.

We investigated this hypothesis in our laboratory (Burke et al., 2011) using Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and secondary ion mass spectroscopy (SIMS). The outcome was the absence of significant formation of either OH or H_2O, which was ascribed to the preferential depletion of oxygen by sputtering during proton irradiation. This depletion was confirmed by *in situ* post-irradiation surface analysis using XPS and SIMS. Our results provided no evidence to support the formation of significant amounts of H_2O in the lunar regolith via implantation of solar wind protons as a mechanism responsible for the strength of OH absorption in recent spacecraft data. We determined an upper limit for the production of surficial OH on the lunar surface by solar wind irradiation to be 0.5% (absorption depth) (Burke et al., 2011), much less than the 3–14% in the alluded 2009 reports on lunar infrared reflectance. Recent reports by Managadze et al. (2011) and Ichimura et al. (2012) show OH/OD

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formation from irradiating simulants or lunar soil with hydrogen (H, D) ions. Managadze et al. (2011) used SIMS to detect sputtered water ions from lunar simulants but did not correlate them to IR measurements. SIMS is orders of magnitude more sensitive than IR absorption and thus a small SIMS signal may not give an observable signal in IR. Ichimura et al. (2012) used high pressures (not ultrahigh vacuum) and multiple exposures to air. Furthermore, the possible contamination of the ion beam with OH^+ (OD^+) ions in both studies makes it difficult to assert that ion irradiation under lunar conditions can produce sufficient OH to account for the remote infrared observations of lunar soil.

Whatever the origin of lunar water, it is important to establish the stability of the water molecules, the migration from or to the polar cold traps, and the cause of the diurnal variations in infrared water signatures. In particular, it is of interest to determine the role of solar radiation and the solar wind in altering surficial water. Here we report measurements of photodesorption of adsorbed water on amorphous carbon and sputtering of adsorbed water from lunar highland soil (65901) at 120 K.

2. Experimental methods

2.1. Photodesorption experiments

Experiments were performed in an ultrahigh vacuum chamber cryopumped to a base pressure of $\sim 2\times10^{-9}$ Torr with a setup described in detail in Raut et al. (2012) and Fulvio et al. (2012). The chamber houses a quartz-crystal microbalance (QCM) cooled by a closed-cycle He-refrigerator. The QCM does not function when coated with lunar soil because the non-uniform soil with large grain size (more than a few microns) causes excessive mechanical damping. We coated the crystal with readily available amorphous carbon foil (~50 nm thick), which was the substrate for the water deposition. The advantage of carbon over the gold electrode of the QCM is that its electronic properties are closer to those of a non-metallic regolith. The carbon-coated QCM was irradiated with 100 keV Ar^+ ions to fluences of $\sim 10^{14}$ ions cm^{-2} to sputter-remove a few monolayers of impurities that coat the foil before transferring to the vacuum system. The surface was cooled and water was deposited from a microcapillary array doser at normal incidence to the substrate. The experiments were done at 120 K, the highest temperature at which adsorption of a monolayer becomes possible. The QCM measures the areal mass of the water film condensed on the carbon substrate, which is converted to column density. The column density of the deposited ice film was 1.6×10^{15} H_2O cm^{-2}, or about one monolayer, considering the roughness of the carbon foil.

The film was irradiated at normal incidence with 193 nm (6.41 eV) ultraviolet photons from an ArF excimer laser. Using a MgF_2 lens ($f=50$ cm), the beam was defocused to a rectangular spot (~25 mm × 75 mm) on the target, larger than the sensitive diameter of the QCM (∅=6 mm). This ensured the absence of heating effects or multi-photon processes, in agreement with similar experiments by Wolf et al. (1991). The laser output was measured with an Ophir power meter placed in the path of the beam. The 10 ns laser pulses had an average fluence of (1.24 ± 0.14) mJ cm^{-2} at 1 Hz, or equivalently, $\sim 1\times10^{15}$ photons cm^{-2}/pulse. Our results are independent of photon flux. The column density of water adsorbed on the carbon substrate was monitored via QCM during laser irradiation up to a fluence of $\sim 4\times10^{18}$ photons cm^{-2}.

2.2. Sputtering experiments

Using XPS, we measured the sputtering cross-section for water vapor deposited on mature Apollo 16 highland soil (sample 65901) under 4 keV He^+ irradiation. In these experiments, a small (~0.1 g) sample of lunar soil was deposited in a 10 mm diameter × 1 mm deep copper cup and placed on a LN_2-cooled sample holder. The soil was neither compressed nor held with a bonding agent such as carbon tape. These ion irradiation experiments were conducted in an ultra-high vacuum (base pressure $\sim 10^{-9}$ Torr) Physical Electronics 560 XPS/SAM system, equipped with an X-ray source mounted perpendicular to the double-pass, cylindrical-mirror electron energy analyzer (CMA). XPS is a quantitative surface analytical technique that uses mono-energetic X-rays that penetrate the sample surface, ejecting electrons of a characteristic binding energy (BE) with respect to the Fermi level. These photoelectrons have a kinetic energy in the spectrometer, $E_x–BE–\Phi$, where Φ is the measured work function of the spectrometer and E_x is the energy of the incident X-ray. The XPS signal is provided by those photoelectrons that leave the sample surface without energy loss, originating from a thin surface layer (2–4 nm on average, depending on the photoelectron energy). Elemental composition is obtained by incorporating the instrument sensitivity for each element, providing quantitative information with an accuracy of ~15%. The CMA was operated at an energy resolution of 3.2 eV to provide high sensitivity, ensuring that all the surface constituents on each mineral were identified to be <1% level. Data were taken using primarily Al ($K\alpha_{1,2}$) X-rays to minimize the overlap of Auger and photoelectron spectra.

Before water growth, adventitious carbon and atmospheric water were removed from the surface by irradiating the sample using 1 keV Xe^+ ions to a fluence of 2×10^{16} ions cm^{-2}. The removal of the atmospheric species was identified with XPS as a decrease in the atomic percentage of carbon present on the surface and in the oxygen to silicon ratio. The sample was then cooled to ~80 K and dosed with water at normal incidence through a capillary array. The water deposit was thermally stable during the experiments at 120 K and desorbed completely at 180 K.

As mentioned above, we could not use a QCM for these experiments with non-uniform granular soil. Thus, the amount of water on the soil, ~2 monolayers, was determined by the increase in atomic percentage of oxygen on the surface relative to Si (the increase in the O:Si ratio). The soil was irradiated with 4 keV He^+ ions rastered uniformly over an area larger than that sampled by XPS and XPS data were taken after each irradiation period as a function of integrated fluence. The beam was positioned at an angle of 25.3° to the surface normal, but the roughness of the soil means that the local incidence angles varied. Irradiation was done at a flux of $\sim 10^{14}$ ions cm^{-2} s^{-1}, as measured with a Faraday cup. This flux is seven orders of magnitude larger than at the Moon but, at 0.064 W cm^{-2}, the power density is insufficient to cause detectable heating.

3. Results

For photon irradiation, the H_2O column density decreased exponentially with fluence F during irradiation as expected from a single process that removes a monolayer or less of water in proportion to coverage (Fig. 1). An exponential curve was fit to the data:

$$\eta=\eta(0)\exp(-\sigma_d F),$$

with

$$\eta(0)=1.6\times10^{15}\ H_2O\ cm^{-2}$$

From this curve, we obtained a cross-section $\sigma_d=(7.4\pm0.5)\times10^{-19}$ cm^2, which describes the amount of water