

## Temperature programmed desorption studies of water interactions with Apollo lunar samples 12001 and 72501



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### ABSTRACT

The desorption activation energies for water molecules chemisorbed on Apollo lunar samples 72501 (highlands soil) and 12001 (mare soil) were determined by temperature programmed desorption experiments in ultra-high vacuum. A significant difference in both the energies and abundance of chemisorption sites was observed, with 72501 retaining up to 40 times more water (by mass) and with much stronger adsorption interactions, possibly approaching 1.5 eV. The dramatic difference between the samples may be due to differences in mineralogy and surface exposure age. The distribution function of water desorption activation energies for sample 72501 was used as an initial condition to simulate water persistence through a temperature profile matching the lunar day.

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### 1. Introduction

The presence or absence of hydration on Earth's Moon has been a topic of much discussion dating back to at least the beginning of the space race. Watson et al. (1961) predicted accumulation of water-ice in the cold permanently shadowed regions (PSRs) at the lunar poles. Lunar samples brought to Earth by the Apollo missions were analyzed for hydrogen (Gibson and Johnson, 1971) and were initially found to have hydrogen from the solar wind and water from terrestrial contamination (e.g. Epstein and Taylor, 1974 and Refs. therein). Advanced techniques have more recently found traces of ancient lunar hydrogen deep within grains of lunar samples (Saal et al., 2008; Greenwood et al., 2011a, 2011b; Liu et al., 2012; Hui et al., 2013). Discussion of lunar hydration recently returned to the public eye when observations by several spacecraft-based experiments were interpreted in terms of hydrated species on the Moon. One set of observations was of absorptions near 3 μm in reflected sunlight that are consistent with mineral-bound hydroxyl and possibly water within the first few micrometers of lunar surface materials (Clark, 2009; Pieters et al., 2009;

Sunshine et al., 2009). A second set of spacecraft-based observations were of water-ice particles, water molecules, hydroxyl, hydrogen molecules, and atomic hydrogen in the ejecta plume from the LCROSS impact experiment in a lunar PSR (Colaprete et al., 2010; Gladstone et al., 2010).

Hydrogen can appear on the Moon in three broad varieties: (1) ancient hydrogen incorporated into minerals as hydroxyl or structural water, (2) cold-trapped hydrogen (Starukhina and Shkuratov, 2000) and/or water in PSRs and possibly below the thermal skin depth at high latitudes (e.g. Vasavada et al., 1999), and (3) surficial hydrogen from solar wind implantation seen as H, SiH, SiOH, H<sub>2</sub>, and possibly H<sub>2</sub>O. Each of these reservoirs of hydrogen can have limited exchange with the others via diffusion and migration promoted by thermal cycling, radiation-induced desorption, and impact events. Understanding the abundance and distribution of lunar hydrogen is important for scientific understanding of the history and present workings of the solar system.

Lunar hydrogen is also of great interest to groups seeking to establish permanent lunar bases and interplanetary refueling depots. All forms of hydrogen – including H<sub>2</sub>O, OH, H<sub>2</sub>, and H – are useful for *in situ* resource utilization (ISRU). H<sub>2</sub> is a component of rocket fuel, while H<sub>2</sub>O is necessary for sustaining life at a lunar base or for travel to further destinations. Utilization of lunar hydrogen can reduce the mass of hydrogen that must be brought from the Earth. Oxygen is in plentiful supply on the Moon, but it is incorporated into the silicate minerals and requires energy and

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hydrogen to remove. Hydroxyl and especially water are most sought after for ISRU because it is more energy efficient to produce O<sub>2</sub> or H<sub>2</sub>O from lunar OH/H<sub>2</sub>O than as a byproduct from the reduction of minerals.

In this work, we focus on surficial water, as has been potentially observed by remote sensing of the 2.95 μm band. During reflection, the infrared radiation penetrates up to 10's of microns into the material, sampling not just water adsorbed to the grain surface itself, but also any water trapped inside the mineral or its weathered rim. This work is only considering the adsorbed water, which is capable of migration. General water adsorption behavior on damaged mineral surfaces, such as those found on weathered lunar soil grains, has been reviewed previously (Hibbitts et al., 2011). Water adsorption and desorption from lunar simulant JSC-1A (Goering et al., 2008) and mechanically-micronized JSC-1A and albite (Hibbitts et al., 2011; Poston et al., 2013) have been previously measured. In this work we present results of water adsorption and temperature controlled desorption from Apollo lunar samples.

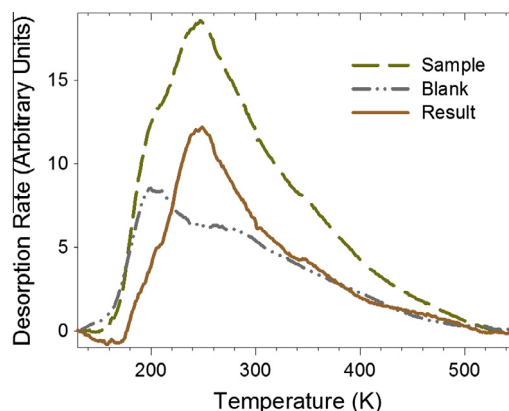
## 2. Experimental

### 2.1. Sample description

A diverse suite of lunar soils was requested from the 'reference suite' of soils sampled by the Apollo and Luna missions (Heiken et al., 1991). The first two samples analyzed are the sub-90 μm fractions of Apollo 17 lunar sample 72501, a mature anorthositic soil, and Apollo 12 lunar sample 12001, a sub-mature low-titanium basaltic soil. For the analysis, 23 mg of sample 72501, and 28 mg of sample 12001, were used. The sub-90 μm fraction was used here to maximize surface area, which maximized absolute signal from the sample. Sample 72501 is relevant to the water adsorption behavior of the lunar highlands, while sample 12001 is relevant to the water adsorption behavior of the mare. Further details regarding the samples may be found in the Lunar Source Book, the Lunar Sample Compendium (Meyer, 2011), the Apollo 17 Sample Catalog (Ryder, 1993), and references therein.

### 2.2. Experimental procedures

The experimental procedures and apparatus have been described previously (Hibbitts et al., 2011; Poston et al., 2013). The standard procedure for temperature programmed desorption (TPD) experiments is to mount the sample in ultra-high vacuum (UHV) and bake the sample to remove any adsorbed gases, cool the sample to the desired dosing temperature, expose the sample to the desired adsorbate, and then heat the sample at a constant rate of temperature in time while monitoring the desorption with a quadrupole mass spectrometer. Briefly, the apparatus consisted of a UHV chamber (base pressure  $<3 \times 10^{-10}$  torr) equipped with: a sample holder and detachable cooling stage capable of cooling the sample to 100 K and heating to 800 K as measured by a type-k thermocouple, a leak valve for exposing the sample to water, an ion gauge to measure chamber pressure, and a Pfeiffer Vacuum Prisma Plus QMG 220 C-SEM mass spectrometer for quantifying the water desorption during the TPD. A computer-controlled heating rate of 0.5 K per second was used and the samples were heated under UHV to 700 K before the first TPD. Gas exposure is quantified by the Langmuir (L) unit, where one Langmuir of exposure represents the statistical expectation of  $10^{15}$  molecules of water arriving at a flat, 1 cm<sup>2</sup> surface. If the sticking probability is unity and no clustering occurs, this would correspond to a water coverage of about a monolayer. In the case of a powdered or porous sample, as is the case here, the  $10^{15}$  molecules per Langmuir are spread



**Fig. 1.** Example of the blank subtraction process showing the relative magnitude of the total signal (dashed line) to the signal from an identical trial performed on the blank sample holder (dashed-dot line) and the result of subtracting the blank from the total signal (solid line). The result is the water desorption intensity that originates from the lunar sample only.

over more than 1 cm<sup>2</sup> of surface area and correspond to much less than a monolayer.

In the previous proof-of-concept work (Hibbitts et al., 2011; Poston et al., 2013), the surrogate samples were rough spheres of average equivalent spherical diameter between 100 and 200 nm. A result of the small size was that the particles adhered well to the sample holder and were placed on both the top and bottom sides of the horizontally-positioned holder. Covering such a large percentage of the holder with sample increased total signal from the sample substantially and eliminated most background signals during the TPD. On the other hand, the lunar samples were highly irregular and of much larger grain size, on the order of 10's of micrometers. Such large particles did not adhere well to the holder, so adjustments were made to the design.

The modified sample holder consisted of a copper bar of about 1 mm thickness wrapped in gold foil to cover the copper bar and form a shallow cup. The purpose of the gold foil was both to form the side walls of the cup and to have a highly hydrophobic holder to reduce water chemisorption background signals. Water-ice can still form on the gold foil at low temperatures, but chemisorption on gold foil is minimal. However, since the sample powders did not adhere well to the gold foil, the sample could only be made to cover about 1–2 cm<sup>2</sup> of the about 10 cm<sup>2</sup> total geometric surface area of the sample holder. This effectively increased the magnitude of the blank desorption intensity by a factor of  $\sim 10$ , and it was seen that the blank signal was about half of the total signal during a TPD (Fig. 1). Therefore, blank TPD's were conducted under the same conditions as each sample exposure and subtracted from the sample trials to isolate signal from the sample. There was also a tail seen at the high temperature end of each TPD, which varied from trial to trial loosely correlated with the experimental history for that day and did not appear to be directly correlated to the water exposure in that trial, nor was it consistent between blank and sample TPDs. It was found that the tail could be fit with an exponential curve and subtracted to reveal the point at which desorption from the sample returned to baseline.

## 3. Results and discussion

### 3.1. Detection of chemisorbed water by TPD

TPD experiments of lunar sample 72501 exposed to water at 165 K are shown in Fig. 2. When water exposure was performed at 110 K, the large quantity of ice desorption from the sample

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