

**COLD TRAPPING OF LUNAR POLAR CRATER VOLATILES: A MODEL OF DESORPTION FROM**

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**Introduction:** In the Lunar Reconnaissance Orbiter (LRO) era, there is now substantial evidence that cold trapping is indeed occurring and possibly may even be of a dynamic nature within lunar polar craters.

LRO's Diviner IR instrument derived annual average temperatures < 100K at the floor of the larger shadowed south polar craters, and these temperatures are cold enough to allow volatiles like water to stay trapped on surfaces for billions of years [1]. Using LRO's Lyman- $\alpha$  Mapping Project (LAMP), [2] reported on a detectable increase in the FUV water-related reflectance above 160 nm in some of the south polar craters, consistent with an water-regolith mix at the surface of about 2% in areal coverage within Shackleton, 1% in Hayworth, 0.3% in Shoemaker and 0.8% in Faustini craters (although the exact spatial distribution to account for the spectral increase in water is not uniquely known).

An increase in the reflected signal from LRO's Lunar Orbiter Laser Altimeter (LOLA) signal at 1064 nm has also been reported from many of the same south polar crater floors, which has been interpreted to be due to the presence of icy-regolith [3, 4]. The LOLA reflectance increase is substantial along the floor and walls of Shackleton crater and has been interpreted to possibly be related to icy-regolith (at ~20% mixture) or newly-exposed surfaces associated with downslope movement along crater wall [5]. The presence of the UV-bright anorthite in Shackleton crater was also suggested to explain the enhanced LOLA signal returns [6]. Fisher et al [4] specifically pointed out that the correlation of volatile signatures and temperature at the lunar poles is generally poor in comparison to ice at Mercury's poles, suggesting other controlling processes.

Hayne et al. [7] combined LRO Diviner and LAMP data over LOLA topography and demonstrated a correlation of maximum temperature and UV water-related reflectance. Their Figure 15 shows the trend of increasing crater-average reflectance with decreasing crater-average temperature as one might expect in the water cold trapping process. They defined the reflectance via an 'Off-On band' ratio: the reflectance in a band centered near 176 nm (high water reflectance) divided by the reflectance in a band centered near 143 nm (low water reflectance), with ratio values between 1.2 and 10 indicative of 1 and 7% water-regolith concentration mix, respectively (see their Figure 3b).

Hayne et al. [7] reported there are many locations with temperatures above 110K with Off/On ratios greater than 1, suggesting surface water molecules are present even above its nominal volatility temperature ( $T > 110\text{K}$ , Off/On > 1).

**The Frosty Grain.** For lunar grains with a surface area of  $0.1 \text{ m}^2/\text{g}$  [8], a 1% wt of surface water corresponds to an average water layer of thickness near ~90 nm covering the grain's surface. However, given the complex irregular shape of lunar grains, it's very likely that this layer thickness represents an average coverage. We might then expect water ice condensation to be 'pooled' in relative minima, like fissures and indentations on the grains. We also might anticipate quasi-dry exposed regions of regolith substrate at relative maxima. We thus consider the substrate at the microscopic grain scales as a heterogeneous water frost on a grain.

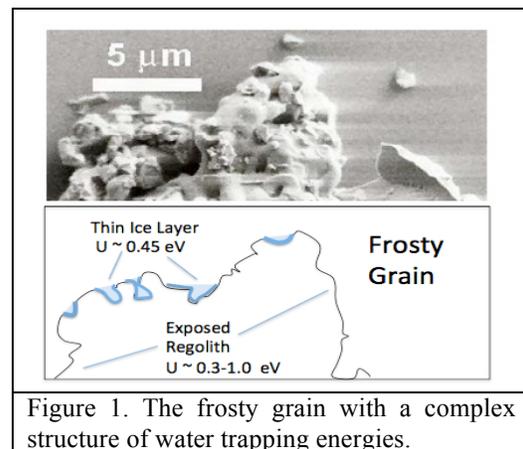


Figure 1. The frosty grain with a complex structure of water trapping energies.

The analog might be the porous activated surfaces found in cryo-pumps [9] that are not yet fully immersed in the condensate, having a sorbent substrate protrude from very thin regions (~100's of nanometers) where the vapor condensate is present. **Figure 1** represents our model 'frosty grain' with any inflowing water molecule having to interact with either an icy or regolith surface.

This frosty-grain model is consistent (but not unique) with the descriptions of intimate water mixtures and water coverage described in Gladstone et al. [2] and Hayne et al. [7]. Also, laboratory work by Poston et al. [8] found that the water activation energies for desorption on grain substrates vary widely at the small (grain) scales. We thus apply the intimate mixture assumption at the smallest grain-level scale, since that is where we have some direct knowledge,

and assume that this mixture is consistent when integrated across the surface to larger kilometers scales within lunar polar craters. Admittedly, we do not have complete knowledge of the patchiness of ice at the meter or kilometer scales in PSRs [10, 11] and thus assume the microscopic model of the frost (Figure 1) integrates across larger scale sizes consistent with the 5 km<sup>2</sup> LAMP observations used by Hayne et al. [7].

**Desorption and Sublimation from the Frosty Grain.** Figure 2 shows fraction of water retained over 1 billion years from a Monte Carlo surface water sorption model. Specifically, 240000 simulated water molecules are placed on a simulated surface and the desorption activation energy,  $U$ , is defined for each water binding site. We do not use a single  $U$  value, but instead the activation energy at each specific water sorption site is selected by a random weighting from a Gaussian distribution in activation energy having initially a distribution center at 0.45 eV and a distribution width of 0.1 eV – similar to that of a water molecule binding to an icy surface. The retention time of each of these water molecules is  $t = 10^{-13} \exp(U/T)$  seconds and the number retained for  $t > 1$  By is counted as a function of increasing temperature.

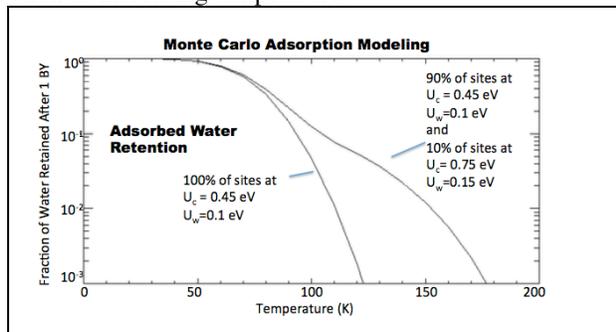


Figure 2. Monte Carlo simulation of water retention after 1 billion years as a function of temperature for sites with a distribution of activation energy centered around 0.45 eV and a Gaussian distribution width of 0.1 eV. Also shown is the effect on water sticking when 10% of the sites have higher activation energy of 0.75 eV.

For the ice-like case having  $U_c = 0.45$  eV and width of  $U_w = 0.1$  eV (the left hand curve in Figure 2) we find that the fraction of water molecules residing on the sorption surface for 1 By drops below 1% at  $T = 110$ K. This case is similar to sublimation from an ice-covered surface [12, 13]

However, if we include a population of water sorption sites with higher activation energy like that found by Poston et al. [8], with 10% of the sites having  $U_c = 0.75$  eV and  $U_w = 0.15$  eV (and 90% at  $U_c = 0.45$  eV and  $U_w = 0.1$  eV), then there is substantially greater water retention with 1% of the sites retaining trapped water even at  $T > 150$ K. This case includes an ice-like surface but also the added effect of the exposed rego-

lith substrate having higher activation energies (deeper water trapping sites).

Thus, if the polar crater floor has a distribution of activation energy similar in nature to the anorthite-rich lunar sample examined by Poston et al. [8], we would expect sorbed water to be retained to relatively high temperatures above 110K.

**Comparison to Observations.** Figure 3 shows the LAMP-derived Off/On ratios as a function of temperature in Haworth crater (from the data set used by Hayne et al. [7]). Figure 3b shows the Off/On ratio values  $> 1.2$ , those indicative of water frost, as a function of temperature. While the peak in the distribution in Figure 3b is below 80K, we note that there is still a population of ‘frost’ values even above 120K.

We thus present the non-unique possibility that the grains in these locations are ‘frosty’ having exposed regolith substrate regions on grain surfaces having activation energy  $> 0.6$  eV. At these locations water can be bound to the surface for  $> 1$  By even at temperatures near 150K (see Figure 2). We suggest the controlling variable is thus  $U/T$  and not  $T$  alone.

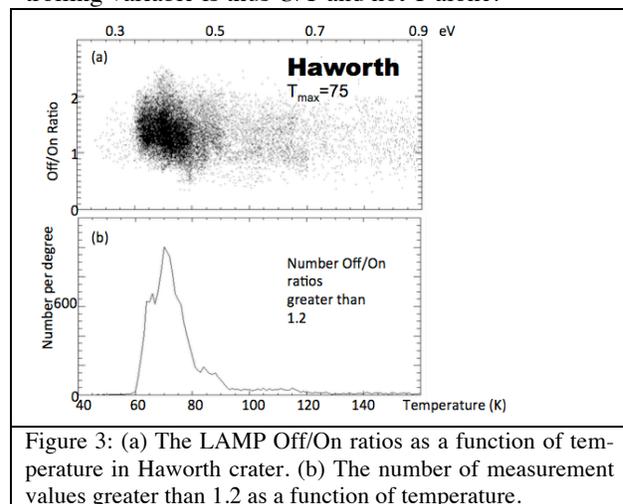


Figure 3: (a) The LAMP Off/On ratios as a function of temperature in Haworth crater. (b) The number of measurement values greater than 1.2 as a function of temperature.

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