LUNAR SURFACE WATER IN AGGLUTINATES: ORIGIN AND ABUNDANCES. Y. Liu[1] , Y. Guan[2], Y. Zhang[3], G. R. Rossman[2], J. M. Eiler[2], and L. A. Taylor[1], [1]Planetary Geosciences Institute, Department of Earth & Planetary Sciences, University of Tennessee, Knoxville, TN 37996, (yangl@utk.edu) [2]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, [3]Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI 48109.

Introduction: Recent remote-sensing observations have demonstrated surface-correlated OH/H_2O on the regolith of the Moon from high- to mid-latitudes [1-3]. The estimated abundances of lunar surface water from the reflectance spectra ranged from 10-5000 ppm [1-3]. Three sources have been suggested: solar-wind origin; volatile retention from meteoritic impact; and degassing of indigenous water [1-4]. The relative contributions from each of these sources are unclear. In addition, the absolute quantities of OH/H_2O and where in the regolith it is stored remain unknown [5].

In order to investigate the origin and abundance of OH/H_2O, we examined lunar agglutinates, which are aggregates of rock and mineral fragments cemented by melts (agglutinitic glasses) generated by micro-meteorite impacts. These glasses are characterized by numerous vesicles, suggesting vapor presence in their formation. If there is pre-existing surface water, some of it will be volatilized, whereas the rest may be retained in these glasses.

Samples: Lunar agglutinate grains from Apollo 11 soil 10084, Apollo 16 soil 64501, and Apollo 17 soil 70051 were studied. Soil 10084 is a mature soil, whereas soil 64501 is a sub-mature one. Sample 70051 was collected from the surface of the lunar rover at the conclusion of the Apollo 17 mission, and is considered to be immature [6]. The maturity index of lunar soils is defined as I_s/FeO, where I_s is the ferromagnetic resonance intensity from the nanophase metallic Fe and FeO is the total FeO content of the soil [7], which is roughly proportional to agglutinitic contents [8].

H_2 and H_2O and their hydrogen isotope values were obtained on bulk soils in 1970s with step-heating methods [e.g., 9-13]. These studies reported a total H_2 content ($H_2+H_2O+CH_4$) of 35-120 ppm in lunar soils. They also showed that D/H values of released H_2 gas increased with step heating temperatures from near solar-wind values (2×10^{-5}) to terrestrial values ($\sim1.5\times10^{-4}$), which was interpreted as a progressive exchange process between lunar H and terrestrial water [8]. However, Friedman et al. [12] cautioned that some of this H could have a meteoritic origin.

Methods: Paired Fourier Transform InfraRed spectroscopy (FTIR) and Secondary Ion Mass Spectrometry (SIMS) were used to analyze polished impact glasses and agglutinates from the soils. The FTIR measurements were conducted at the University of Michigan. Back scattered electron (BSE) images and the composition of the glasses and minerals were ac-

quired with a Cameca SX-100 EMP at the University of Tennessee.

Analyses for H abundances and D/H values were conducted in two sessions with a Cameca ims-7f GEO ion probe at Caltech. For both sessions, the areas of interest were examined carefully using ion imaging to avoid C and H hotspots (cracks, vesicles). Spots chosen for SIMS analyses are near EMP points. Following a ~3 min sputtering, glassy regions were measured for 20 cycles through the mass sequence of $^{12}C^-$, $^{16}O^1H^-$, [^{18}O-], $^{30}Si^-$, [$^{31}P^-$], $^{32}S^-$, and $^{35}Cl^-$, where the masses in brackets were only measured in the second session. Terrestrial basaltic glasses with 150-260 ppm H_2O [14] were used as standards for H abundances. The instrument H backgrounds of the two sessions were monitored with a dry olivine standard (GRR1017, $<<$1 ppm H_2O, [15]). D/H measurements were conducted on the same spots where H abundances were obtained. The mass sequence of $^1H^-$, $^2H^-$, and $^{16}O^-$ was measured for 15-20 cycles each with 1 s, 15 s and 1 s counting times. One terrestrial rhyolitic glass containing 0.69 wt% H_2O with δD = -69‰$_{VSMOW}$ (MC84-df, [16]) was used to evaluate the instrument mass fractionation (IMF) of D/ H. The matrix effect between basaltic and rhyolitic glasses is insignificant for the results presented in this study.
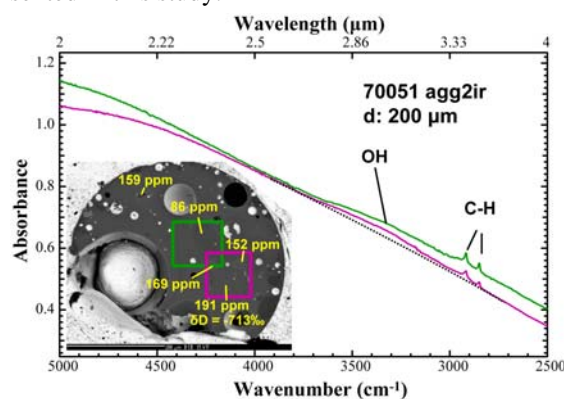
Fig.1. *FTIR spectra of two regions (boxes) in sample 70051 agg2ir. Color of the box corresponds to the color of the spectrum. Estimates using FTIR absorbance yield ~110 ppm H_2O. The dotted curve is a visual fit of the continuum (background) of the spectrum. The OH abundances are labeled for each SIMS spots, and one D/H measurement was conducted.*

Results and Discussion: Agglutinitic glasses in mare soil 10084 and 70051 are relatively uniform in SiO_2 (~41 ±2 wt%) and high in TiO_2 (6-11 wt%). Ag-

glutinitic glasses in the highland soil 64501 are rich in Al_2O_3 (20-35 wt%) with 44-46 wt% SiO_2.

OH abundance. Among eight doubly polished agglutinates from soil 10084 and 70051, five samples display noticeable FTIR absorption in the 2.9-3.2 μm range, typical for OH groups (Fig. 1). Most grains also display absorption at ~3.4 μm for C-H bands, possibly due to organic contamination attached to vesicle walls. Although the optical path of IR beam included minerals and vesicles, estimates using the 3500-cm^{-1}-band intensity (relative to the continuum baseline, dotted black curve) suggest 100-190 ±60 ppm H_2O in these agglutinates.

Thirteen agglutinates and four impact glasses were examined with SIMS. Results indicate that the agglutinitic glasses contain 27 ±4 to 458 ±12 ppm H_2O by weight (Fig. 2), whereas the impact glasses are as dry as the dry olivine standard. These H contents in agglutinates are consistent with those obtained with the step-heating method on the same Apollo 11 soil 10084 [8]. Most mineral fragments (plagioclase and pyroxene) in these agglutinates contain low H, similar to or slightly above that of the dry olivine standard. Our results demonstrate that agglutinitic glasses, not minerals, host the OH/H_2O in the samples.

H isotope compositions. Visible contaminates in vesicles and cracks display δD of about -50 to -200‰. Most agglutinates from three soil samples contain δD of -845 ±30‰ to -562 ±40‰ for 240-76 ppm H_2O (Fig. 2), consistent with the result of [9]. One sample (10084agg8ir) contains small positive δD (+190 to +267‰) for ~190 ppm *H_2O* (Fig. 2). Different regions of 10084agg2 *display strong D enrichment with δD = +5413 ±350‰ for 27 ppm H_2O and +4206 ±150‰ for 458 ppm H_2O* (red dots in Fig. 2).

Using a spallation production rate of D at the surface $(1.5 \times 10^{-10}$ $moleD_2/g/10^8$-yrs in [13]) and solar-flare exposure age of the sample (100 Ma, [17]), we obtained 6×10^{-10} g of spallation-D per gram of soil. This amount of spallation D could contribute to the observed D in some agglutinates (e.g., -845‰ with 240 ppm H_2O and -562‰ with 72 ppm H_2O). However, D contents in other samples are too high to be solely caused by spallation. If D contents are solely from terrestrial water, mixing of solar-wind H with 16-44 wt% terrestrial water can generate the measured OH contents for samples with δD <-560‰. However, if terrestrial contamination plays a role in these samples, we would expect D/H values increasing toward the Earth value with increasing H contents. Such a trend is not evident in Fig. 2 (green triangles). The large D/H values in 10084agg2 are higher than lunar apatite [18] and cometary water [19], but are comparable to chondrites [19] and lunar volcanic glasses with much lower H contents (0-70 ppm H_2O in [20]). The highly

enriched D in 10084agg2 may represent: 1) loss of H_2 and retention of spallation-D during repeated impact melting; 2) magmatic origin (?); 3) meteoritic origin with D enrichment by subsequent impacts.
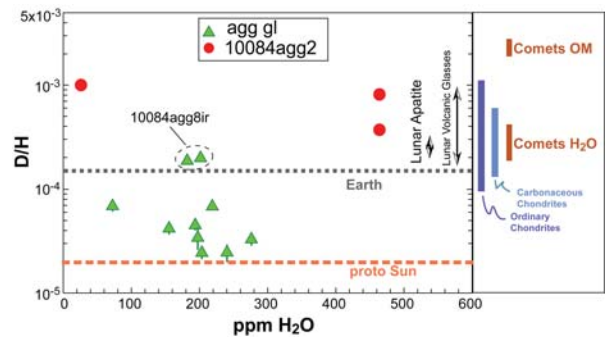
Fig. 2. *D/H values versus OH contents (in ppm H_2O) of lunar agglutinitic glasses. D/H is corrected for IMF and OH is calculated after subtracting background values. Error bars are shown if they are larger than the symbol size. Values for proto Sun, Earth, Comets, and chondrites are from [19] and for lunar samples from [18, 20].*

Conclusions: Paired FTIR and SIMS measurements of lunar agglutinates have shown that: 1) the major reservoir of OH/H_2O is mainly in agglutinitic glasses produced by micrometeorite impact; 2) mineral fragments have negligible OH; 3) H isotope compositions of OH in agglutinitic glass suggest solar-wind origin with a second source for D. The primary formation of OH in these glasses is most likely due to solar-wind proton bombardment, as demonstrated by Ishimura et al. [21]. In which case, the volatiles in lunar soil could be a direct function of the agglutinitic-glass contents – increasing with the maturity of a soil. The OH/H_2O in agglutinitic glasses may partially account for the remotely-sensed OH/H_2O [1-3]. The solar-wind implanted H on the surface of the grains may have been lost during sample collection and storage. The detected OH in agglutinates represents a distinct reservoir of OH/H_2O in lunar regolith.

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