THE EFFECT OF TEMPERATURE ON THE PRESERVATION OF VOLATILE-RICH LUNAR SAMPLES.
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Introduction. The Moon's south pole is a high-priority target for human exploration and scientific study. This interest is, in part, due to the presence of Permanently Shadowed Regions (PSRs), which could contain high concentrations of unique volatiles at cryogenic temperatures **[1]**. Returned samples from PSRs may include a unique combination of rocks, regolith, and volatile species, providing unprecedented insights into the history of the Solar System and the potential for resource utilization on the Moon.

However, because PSR samples are cryogenic upon collection, lunar polar sample return will eventually require cold stowage for the journey from the Moon to Earth. Without cold stowage, PSR sample return will likely result in phase changes and chemical reactions within the volatile component of the sample, which would negatively impact the resulting scientific studies of those samples. This abstract summarizes the initial results from an ongoing characterization of analog PSR samples at a range of temperatures, with the goal of defining the temperatures needed for a flight cold stowage freezer.

Background. Based on remote sensing observations of the Moon **[2]**, south polar PSRs range in temperature from ~120K for small and/or shallow PSRs to ~20K at the most extreme locations in large, deep PSRs. A range of volatiles have been hypothesized to exist at the surface or subsurface of the lunar poles **[3-5** and others**]**. This hypothesis was verified when the LCROSS mission impacted the <50-K PSR in the crater Cabeus, detecting a range of volatiles from water to low condensation temperature species such as H_2S and methane **[6]**. Species such as H_2S and ammonia (also detected by LCROSS) are also highly reactive, and increase the likelihood of chemical reactions at elevated (non-cryogenic) temperatures.

At the Johnson Space Center's Planetary Exploration and Astromaterials Research Laboratory (JSC-PEARL), we have developed a volatile-bearing lunar simulant that incorporates several of the species detected by LCROSS **[Table 1]** mixed cryogenically with the USGS Lunar Highlands Type (LHT) regolith simulant. The new volatile-regolith simulant will be used to assess the degree of sample alteration at room temperature, -20°C, -80°C, and -196°C (liquid nitrogen), over a two-week period. Room temperature samples represent those likely to be returned during initial missions without cold stowage, -20°C provides an analog to Apollo cold curated samples, -80°C is the temperature of multiple flight payload freezers (e.g., MELFI), and -196°C is analogous to lunar PSRs. Two weeks is an approximation of the time between sample collection and Earth return for initial missions. Over this period of time, sample head-space gases will be analyzed using a Universal Gas Analyzer (UGA, a type of mass spectrometer) coupled with a Baratron pressure sensor. After testing, the regolith component of the simulant will be purged of volatiles and preserved for future electron beam and/or FTIR analysis.

Table 1. Five of the volatiles detected by LCROSS (left) and the corresponding volatiles in the JSC full volatile simulant (right), shown as mass % of the total volatile mass. For safety reasons, H_2S in the simulant is limited and methylamine ($MeNH_2$) is used instead of ammonia. Future simulants will include more of the LCROSS compounds than those shown.

LCROSS [6]		**JSC Simulant**	
Compound	Mass %	Compound	Mass %
H_2O	74.9	H_2O	83.3
H_2S	12.5	H_2S	0.4
NH_3	4.5	$MeNH_2$	1.4
CO_2	2.2	CO_2	3.3
CH_3OH	1.6	CH_3OH	11.6

Experimental Procedure. Volatile-regolith simulants will be produced as an initial homogenous batch;

Figure 1. Simulant samples in insulated container. A sample aliquot in a GC vial (inset).

this batch will then be distributed into aliquots (gas chromatography/GC vials or cryo vials), ensuring that each sample has the same starting composition and conditions **[Fig. 1]**. In addition to the "full" simulant shown in Table 1, less complex simulant compositions will be used as baseline and control samples **[Table 2]**. Aliquots will be produced in triplicate for each simulant composition, storage temperature, and date of sampling.

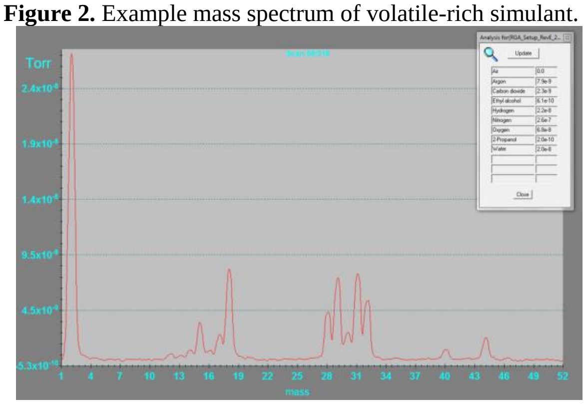
Headspace gases in all Day 0 samples will be analyzed by the UGA immediately. Cold storage samples for future analytical days will be placed in freezers appropriate to their target temperatures (-20°C, -80°C, -196°C). For ambient-temperature samples, regolith and regolith-water samples will be stored in a fume hood, while the full simulant will be stored in a sealed Parr vessel for safety; no other simulants (RWCM/ RWCM+) will be stored at ambient temperature for this test. Samples will be analyzed by UGA in this manner on each Analysis Day outlined in Table 2.

Table 2. Simulant compositions, storage temperatures, and sampling dates for this test. Simulant abbreviations: R = regolith only; RW = regolith and water; RWCM = regolith, water, CO_2, methanol, and methylamine; RWCM+ = regolith, water, CO_2, methanol, methylamine, and formaldehyde; Full = regolith, water, CO_2, methanol, methylamine, and H_2S. "Analysis Day" refers to the number of days after test start.

Simulant	R	RW	RWCM	RWCM+	Full	
Storage Temp. (°C)	+25	-80	-80	-80	-80	
Analysis Day	0	1	3	7	10	14

Analytical Data. The UGA measures the partial pressures in a single sample aliquot over a set mass range of 0-105 atomic mass units (AMU) [**Figure 2**]; this set range was selected to slightly exceed the mass of the highest-mass expected reaction product (H_2SO_4).

Figure 2. Example mass spectrum of volatile-rich simulant.



The Baratron complements the UGA by measuring the total pressure in the headspace of a sample vial. Coupled together, the quantitative abundances of gases will be monitored throughout the test.

UGA analyses of the triplicate samples for each storage temperature, day, and simulant composition will be averaged, and standard deviations for each will be calculated. The compositions of starting species (shown in Table 1) will be characterized as a function of time, and the presence of any new compounds (reaction products) will be monitored as well. Total pressures will be recorded for each sample analysis, and any samples that show signs of leakage (e.g., a significant reduction in pressure or simulant volatiles) will be discarded.

Anticipated Results. Testing is planned to begin in January 2022. The resulting data will allow compositional and phase changes in the volatile component of the simulants to be determined. Both the reduction in initial compounds and the addition of reaction products are expected to be observed. In addition, the relative efficacy of the different temperatures at preserving the initial composition of the simulants will be quantified. Finally, the regolith component of each sample will be argon-purged and stored in a controlled environment for future laboratory analysis. Compositional and morphological changes in the regolith are expected for samples above 0°C. This test will be repeated three times over the course of 2022.

Understanding the effect of temperature on both the volatile and regolith components of analog lunar materials will allow requirements for a cold stowage freezer to be developed. The implementation of cold stowage for lunar polar missions will maximize the preservation of returned samples, enabling ground-breaking lunar and Solar System volatiles science for decades to come.

References: [1] Watson, K., et al. (1961) *JGR*, Vo. 66, No. 9. [2] Paige, D. A., et al. (2010) *Science*, *330, 6003.* [3] Birch, S. (1866) *On The Glacial Condition of the Moon's Surface*, *Geological Magazine*. [4] Arnold, J. (1979) *JGR*, Vol. 84 No. B10. [5] Bussey, B., et al. (1999) *GRL*, Vol. 26, No. 9. [6] Colaprete, A., et al. (2010) *Science*, *330*, *463*.