

TEMPERATURE CONSTRAINTS ON THE STORAGE AND CURATION OF VOLATILE-RICH SAMPLES FROM THE LUNAR POLES. J. L. Mitchell¹, J. E. Gruener¹, S. J. Lawrence¹, M. D. Fries¹, R. A. Zeigler¹, F. M. McCubbin¹ and J. E. Edmunson². ¹Astromaterials Research and Exploration Science Division, NASA Johnson Space Center, 2101 NASA Pkwy, Houston, Texas 77058 (Julie.L.Mitchell@nasa.gov), ²Jacobs Technology, Inc./NASA Marshall Space Flight Center.

Introduction: NASA's Lunar Exploration Campaign includes lunar sample return efforts beginning in the mid-2020s and human landed missions in the late 2020s-early 2030s [1]. Volatile-rich samples from the lunar poles will be high-priority targets due to their resource potential for human explorers and high science value [2, 3]. In order to precisely characterize the nature of these polar volatile materials upon return to Earth, they will need to be transported and curated under conditions that minimize their chemical and physical alteration.

NASA Policy Directive (NPD) 7100.10F mandates the preservation of existing extraterrestrial samples with minimal alteration, extensive and quantitative documentation of alteration that is provided to investigators, and "the development of long-range plans" for samples yet to be acquired [4]. This abstract summarizes new efforts by the Astromaterials Acquisition and Curation Office at JSC to assess the optimal storage conditions of lunar polar returned samples.

Background: Permanently Shadowed Regions (PSRs) at the lunar poles reach some of the coldest temperatures in the inner Solar System [5]. These cold temperatures are ideal for the accumulation and retention of water ice and other frozen volatiles; previous studies have estimated as much as 10 wt. % water ice at the lunar poles [6]. However, remote sensing instruments searching for water ice in the lunar polar regions have produced ambiguous results [e.g., 7, 8].

The Lunar Crater Observation and Sensing Satellite (LCROSS), launched with the Lunar Reconnaissance Orbiter (LRO) in 2009, impacted the crater Cabeus at the Moon's south pole in an effort to assess the abundance of volatiles within that crater's PSR [6]. LCROSS and LRO detected numerous volatile species after the impact in Cabeus [6], providing a baseline by which to estimate the composition of lunar polar volatiles (Table 1). It is possible that other compounds modeled by Paige et al. (2010) to be stable in PSRs but not detected by LCROSS are also present [5]; among these, some highly reactive species could chemically react with other volatiles and/or the lunar regolith at elevated (>50K) temperatures. For example, the reactivity of formaldehyde to produce polyoxymethylenes is catalyzed by small quantities of ammonia (as low as 0.5% relative to formaldehyde) at temperatures as low as 80K [9]. Additionally, ammonia and water have

been modeled to react with feldspars at temperatures as low as 200K, resulting in alteration of both the volatile compounds and silicate mineral [10]. These previous results indicate that storage temperatures <200K may be needed to prevent alteration of the sample immediately after collection, during transit to Earth, and during curation operations on the ground.

Methods: *Lunar Simulant Development.* A lunar polar sample simulant is being developed that includes a range of volatile compositions. A subset of volatiles detected by LCROSS are included (H₂O, NH₃), while the others (H₂S, SO₂, C₂H₄) are excluded from this initial work for safety reasons. These volatiles are substituted by other compounds that fall within the same thermal stability range as the known compounds based on previous modeling efforts (Figure 1 and Table 1); in the case of CO₂ and CH₃OH, these were detected by LCROSS, but at low abundance (≤2.5% relative to water). The exact volatile simulant composition is shown in Table 1.

Table 1. Volatiles detected by LCROSS and their relative abundances (left) [5]; lunar volatile simulant compounds and relative abundances (right).

LCROSS ^{5,6}		Simulant	
Compound	%	Compound	%
H ₂ O	77.4	H ₂ O	75
H ₂ S	13.0	CO ₂	15
NH ₃	4.7	NH ₃	5
SO ₂	2.5	CH ₂ O	2.5
C ₂ H ₄	2.4	CH ₃ OH	2.5

Remote sensing investigations indicate that volatiles do not exist as clean, distinct layers, but are intimately mixed with lunar regolith [e.g., 1]; we replicate this property by preparing the volatile component of the simulant in the presence of an experimental agglutinate-bearing simulant with an OB-1 base, a lunar highlands-type silicate simulant (Figure 2) [12]. The relative abundances of volatiles in the simulant will be verified by GC-MS.

Storage Tests. Once the volatile/regolith simulant is prepared, aliquots of the simulant will be stored in sealed vials at -20°C and -80°C for one month; this duration is estimated to encompass the time needed for collection, transit, and initial ground characterization of the sample. Silicate-only and silicate-water mixtures

will be prepared using the same procedure and concurrent to the full simulant; these mixtures will serve as control samples for the duration of the test. During the one-month period of time, aliquots will be removed from storage and the volatile composition measured by GC-MS at 0, 1, 5, 10, 15, 20, 25, and 30 days. Particles of the simulant component will be analyzed for compositional and textural changes using FTIR, Raman spectroscopy, SEM, and TEM.

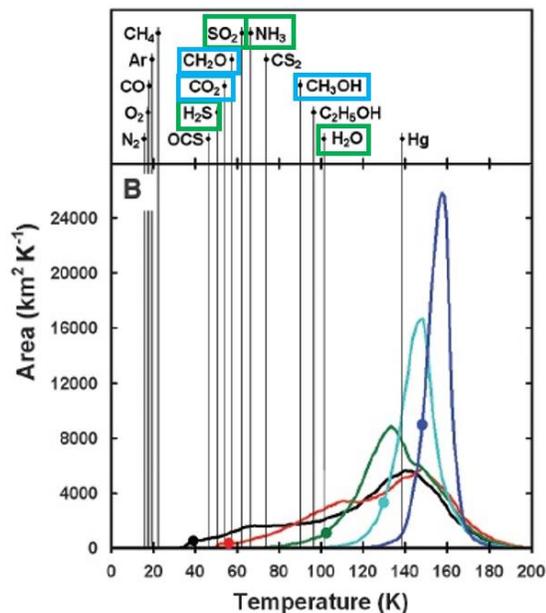


Figure 1. Expected volatiles in lunar PSRs under the temperature range observed by the Diviner instrument (adapted from [5]). Green boxes=volatiles detected by LCROSS at >2.5%; blue boxes=additional volatiles included in lunar polar volatile simulant.

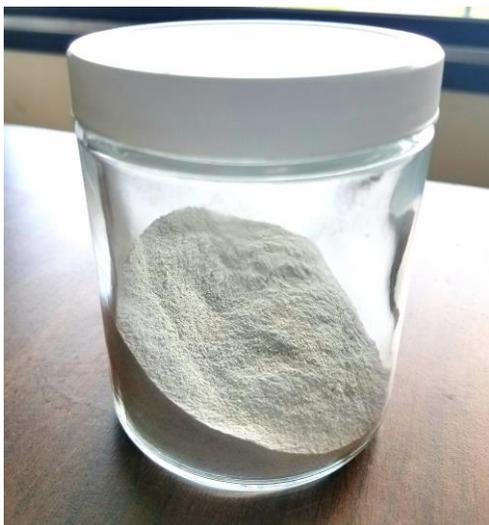


Figure 2. The experimental agglutinate-bearing, OB-1 base lunar highlands-type simulant.

Results and Future Work: Which reaction products are generated, their rates of reaction, and the effect on the silicate fraction of simulant will be quantified. All of these properties will be assessed as a function of temperature. PSRs have significantly lower temperatures than -80°C ; therefore, cryogenic temperatures may be needed for future storage tests. However, the technology for pristine, sterile sample handling at cryogenic temperatures does not currently exist; this study will constrain the timescale at which lunar polar volatile samples can be handled in the laboratory at elevated (up to -20°C) temperatures without significant alteration of the sample.

While feasible for ground storage, achieving cryogenic temperatures in flight for a lunar surface sample return system would be cost-prohibitive. This study will therefore provide insights into sample alteration at higher temperatures (up to -20°C) that could be used to drive future spaceflight hardware requirements.

Future studies will incorporate the full suite of LCROSS-detected volatiles, which includes H_2S , SO_2 , and C_2H_4 . These compounds are highly flammable and/or reactive relative to the other compounds included in this study. Therefore, specific precautions and materials considerations will need to be taken prior to beginning this phase of work.

Once the storage test procedure has been refined and a robust testing protocol developed, future studies will incorporate Apollo lunar regolith instead of simulant to assess the impact of compositional variations between the simulant and lunar highlands regolith (well described in [12]). The results of this work will pave the way for accurately assessing volatile resource availability and maximizing the scientific return of future lunar polar sample return missions.

References: [1] Lunar Exploration Campaign, NASA, 2018. [2] Committee on the Scientific Context for Exploration of the Moon (2007). [3] Spudis, P. D. and Lavoie, A. R. (2011) *AIAA*, 2011-7185. [4] McCubbin, F. M., et al. (2016) *LPSC XLVII*, Abst. #2668. [5] Paige, D. A., et al. (2010) *Science*, 330, 6003. [6] Colaprete, A., et al. (2010) *Science*, 330, 463. [7] Sanin, A. B., et al. (2012) *JGR*, 117. [8] Siegler, M. A., et al. (2016), *Nature*, 531, 7595, 480-4. [9] Schutte, W. A., et al. (1993), *Science*, 259, 5098, 1143-1145. [10] Engel, S., Lunine, J. I., and Norton, D. L. (1994) *JGR* 99, E2. [11] Mitchell, J. L., et al. (2017) *PSS*, in press. [12] Battler, M. M. and Spray, J. G. (2009) *PSS* 57, 2128-2131.