CLOUDS IN THE ANCIENT LUNAR ATMOSPHERE

Water Ice Nucleation on Aerosol Simulants

Abstract

Today's moon is vastly different from what it was 3 billion years ago. At that time, it was home to a collisional atmosphere formed through massive amounts of volcanism, releasing enough subsurface gas to sustain surface pressures of up to 1 kPa. Observations of our solar system have taught us that all dense atmospheres are host to clouds and aerosols, and we expect the Moon's to be no different. Knowing when, where, and under what conditions cloud particles form is important for understanding the evolution of the lunar atmosphere, how it reacted to temperature gradients, and how it cycled volatiles. To study this, I investigated the immersion freezing properties of three aerosols: JSC-1A lunar simulant, which is similar in composition and properties to lunar sample #14163 returned by the Apollo 14 Mission; Exolith LMS-1D Lunar Mare simulant, which simulates volcanic deposits on the Moon's surface; and Arizona Test Dust (ATD), a standard for Earth atmospheric studies. A Peltier thermoelectric cooler and droplet freezing array were used to isolate Millipore water droplets with aerosols cooled to temperatures as low as -18^0 C. Aerosol type, aerosol concentration, and droplet size was varied across these experiments. Both lunar simulants were found to nucleate ice less frequently than ATD, with JSC-1A nucleating more droplets than LMS-1D, which exhibited freezing properties similar to pure water. The results indicate that water ice nucleation is possible but highly variable on lunar regolith aerosols, and cloud formation on volcanic dust may have been possible in the ancient lunar atmosphere.

Student Author

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Mentor

Alexandria V. Johnson earned a PhD in Atmospheric Science from Purdue University in 2014 and returned as an Assistant Professor in the fall of 2019. Her research broadly explores the effects of cloud microphysical processes—when, where, and how clouds form and the resultant properties of cloud particles—on the atmospheres of Earth, other solar system bodies, and exoplanets. Her group's work spans a wide range of scientific methods, including laboratory-based experiments to create clouds, observing atmospheres and natural cloud systems, and detailed, microphysics-focused modeling of cloud formation and growth.

INTRODUCTION

Earth's moon has been a central feature of the night sky for billions of years. For all of recorded history, the Moon has been a barren satellite home to an exosphere, where any molecule excited and liberated from the surface by solar radiation is lost to space. Recently, Needham and Kring (2017) proposed that 3 billion years ago, the Moon was host to a collisional atmosphere. If the Moon retained this atmosphere for the estimated 70 million years, it was likely home to complex atmospheric events such as cloud formation, precipitation, and volatile cycling.

This lunar atmosphere is thought to have formed through prolonged periods of pyroclastic eruptions and volcanic outgassing. These processes are known to release substantial amounts of gas from the interior of an astronomical body, as well as ashes and particulates that could remain suspended for long periods of time. It is estimated that on the Moon, these eruptions took place over hundreds of thousands of years, releasing upward of of gas and of material, resulting in a conventional, collisional atmosphere with a surface pressure of 900 Pa (Needham & Kring, 2017). These estimates were created by using the volume of the mare basalt deposits, seen as dark regions on the surface of the Moon (Figure 1) and formed through pyroclastic deposits (Figure 2). While the amount of emplaced mare, outgassed volatiles, properties, and longevity of the lunar atmosphere are currently up for debate (Aleinov et al., 2019; Head et al., 2020; Tucker et al., 2021), this project uses their proposed presence as a starting point to explore further characteristics of the possible, transient lunar atmosphere.

In this paper, I investigate the conditions under which lunar regolith simulants nucleate water ice in the immersion freezing mode. Nucleation is the creation of a new stable phase of a substance, and here I focus on the transition from liquid water to solid water ice with temperature. The regolith simulant acts as a heterogeneous ice nuclei, which reduces the energy barrier to the formation of the new phase and allows the phase transition to occur at temperatures warmer than –40°C. This is an important process in the formation of clouds in the atmospheres of planets with solid surfaces like Earth and Mars. While this heterogeneous ice nucleation has yet to be studied for the ancient lunar atmosphere, I believe it will play an important role and have set out to

FIGURE 1. Left: a high-definition image of the Moon provided by NASA (2019). Dark regions are indicative of mare basalt deposits from pyroclastic eruptions early in the Moon's history. The image has been edited to show the location of the Apollo 14 landing site. Right: Image taken from the Apollo 14 landing site (LPI, 2023) where sample #14163, the basis for the creation of JSC-1A lunar regolith simulant, was collected.
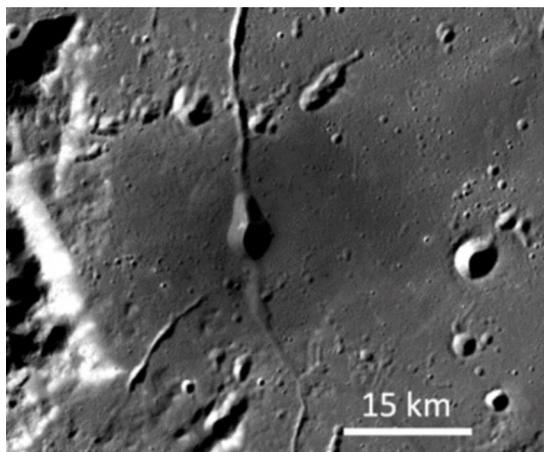
FIGURE 2. Volcanic vent in the Schrödinger Basin located on the far side of the Moon taken from Crawford et al. (2020. Here we see the central peak of an ancient volcano surrounded by dark pyroclastic remains. The eruption of volcanoes like this would have ejected gases and particulate, causing the formation of the lunar atmosphere.

compare the nucleation properties of several different lunar simulants as a means of better understanding the Moon's atmospheric conditions.

In the following section, I describe the methods used and the droplet freezing array for this work. Next, I discuss the results of the immersion freezing experiments across lunar aerosol simulant and control runs. Then I interpret the results and discuss their possible implications for the ancient lunar atmosphere. Finally, I summarize the results and suggest future studies that can help to further elucidate our understanding of the Moon's past.

METHODS

The goal of these studies was to investigate the nucleation properties of several different lunar simulant aerosols by determining the temperatures at which the simulants would initiate freezing of water droplets, whether aerosol concentration played a role in triggering freezing, and how water ice nucleation properties may compare between the moon and Earth.

Droplet Freezing Array

In this work, I expose an array of isolated Millipore water droplets with and without suspended aerosols to temperatures below 0°C as a means to study the ice nucleation properties of these aerosols in the immersion

freezing mode. The experimental design, based on that of Budke and Koop (2015), consists of a thermoelectric cooler, or Peltier, attached with thermal paste to an air-cooled aluminum heat sink. When supplied with a set voltage, electron transfer through the Peltier causes a sharp temperature gradient across the faces of the device, allowing the cold side to reach temperatures down to -18°C after 15 minutes in ambient lab temperatures of 23°C. To track the temperature across the surface of the Peltier with time, seven thermocouple wires were attached to the upward-facing cold surface, with an additional thermocouple attached to the heat sink, using thermal paste (Figure 3).

For each experiment, suspension droplets are isolated from one another with a plexiglass well-plate and glass slides forming individual wells as illustrated in Figure 3. Isolation prevents Wegener-Bergeron-Findeisen water vapor transfer between droplets (Storelvmo & Tan, 2015), which can lead to erroneous freezing events as droplets decrease in size. The microscope slides, on which droplets sit, is pretreated with Rain-X to increase droplet contact angle and reduce the possibility of glass substrate freezing effects. Both sides of the well-plate were coated with Vaseline to create an airtight seal with the glass slides. The Peltier and sealed well-plate were then isolated from the laboratory environment with a styrofoam and plexiglass enclosure to isolate it from ambient temperature changes and reduce condensation of water vapor from the lab environment onto the system.

Lunar Regolith Simulants

The immersion freezing properties of three regolith simulants and aerosols were studied in this work. The two lunar regolith simulants used here were JSC-1A, developed by NASA's Johnson Space Center to mimic the compositional and size characteristics of the mare basalt samples returned by the Apollo 14 astronauts (Figure 1; LPI 2023), and LMS-1D, an extra-fine-grained simulant developed by Exolith Lab to mimic the bulk chemical properties of mare basalt deposits on the Moon (Exolith Lab, 2022). The chemical compositions of each simulant compared to the Apollo 14 sample can be found in Table 1.

We also ran control experiments with Arizona Test Dust (ATD), a widely used simulant for terrestrial water cloud nucleation studies, to allow for a comparison with Earth-based water ice nucleation at the same temperatures. Bulk visible differences between JSC-1A, LMS-1D,
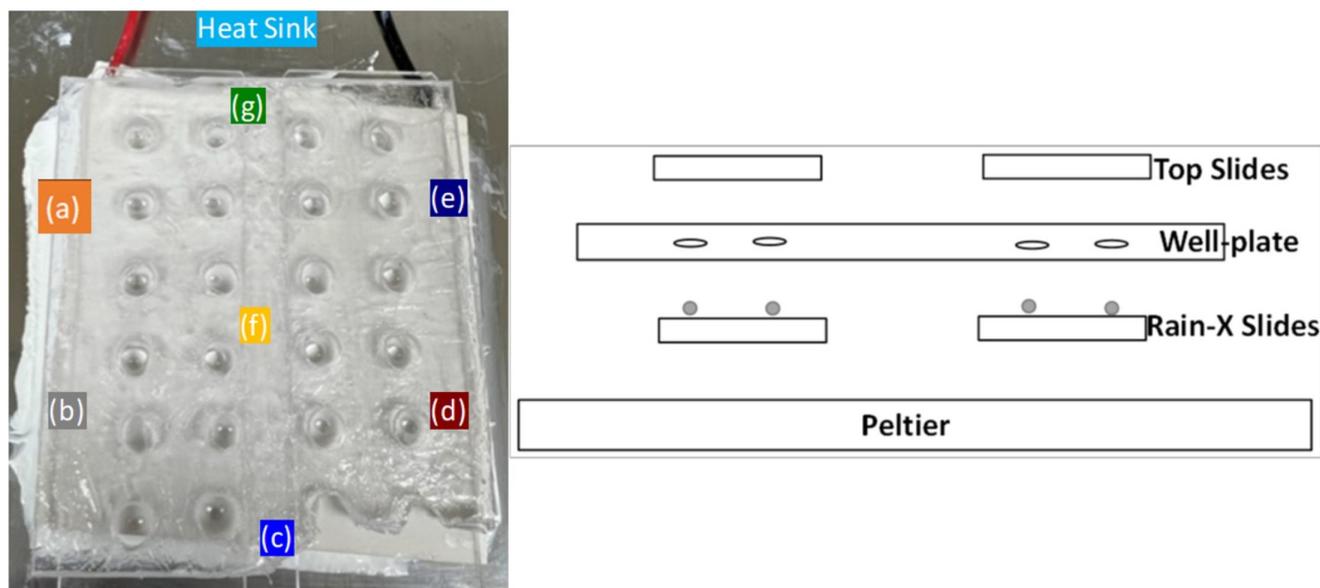
FIGURE 3. Left: The Peltier Droplet Freezing Array built for and used in the studies presented here. This setup is modeled on that of Budke and Koop (2015). The locations of individual thermocouple wires used to collect Peltier surface temperature data are identified by letter with line colors as represented in Figure 5. Right: Enlarged diagram of the droplet well setup.

TABLE 1. Composition of lunar simulants compared to authentic mare.

Compound	Authentic Lunar Mare (76.5 g/mol)	JSC-1A Mare (69.0 g/mol)	Exolith Mare (64.86 g/mol)
	% of Mass		
SiO_2	47.3	47.7	46.9
Al_2O_3	17.8	15.0	12.4
CaO	11.4	10.4	7.0
FeO	10.5	7.4	8.6
MgO	9.6	9.0	16.8
TiO_2	1.6	1.6	3.6
Fe_2O_3	—	3.4	—
K_2O	0.6	0.8	0.7
Cr_2O_3	0.2	—	—
MnO	0.1	0.2	0.2
Na_2O	—	—	1.7
P_2O_5	—	0.7	0.2

FIGURE 4. Images of bulk aerosol dusts used in this work. Left: Arizona Test Dust (ATD) simulant dust. Middle: Image of Johnson Space Center lunar mare simulant (JSC-1A) created at NASA (Cannon, 2023). Right: Exolith Mare LMS-1D simulant dust.

and ATD aerosols can be seen in Figure 4. Pure Millipore water droplets were also studied to compare the efficiency of heterogeneous and homogeneous nucleation (freezing without the presence of a nuclei) in our droplet freezing array.

The concentration of aerosol suspended in droplets was varied to provide freezing data on high and low aerosol concentrations, ranging from 2.06 10⁻³ mg/µL to 3 10⁻⁴ mg/µL, which is equivalent to $10^4 – 10^5$ particles/3µL droplet and $10^3 – 10^4$ particles/3µL droplet, respectively. The volume of individual droplets was also varied with 1, 3, and 6 µL droplets tested for each high and low aerosol

concentration. Finally, for each set of experimental conditions, three full droplet arrays were created and the nucleation conditions were extracted, allowing for anywhere from 0 to 72 frozen droplets to be tested per experimental condition.

Data Collection

During each experiment, temperature and nucleation events were recorded as a function of time, with collected data being dependent upon the aerosol's nucleating properties, aerosol concentration, and droplet size as

discussed in the previous section. A LabView program was written to automatically display and log temperature data from the eight thermocouples (Figure 3) throughout an experiment. Experimental runs started at room temperature and lasted for 15 minutes after voltage was applied to the Peltier. As the system temperature decreased, manual inspection of droplets was performed and the time at which a freezing event took place was recorded, identified as when droplets appeared matte rather than shiny. In postprocessing, the time of each freezing event was used to identify the temperature at which each droplet froze, and the number of droplets frozen in total was recorded.

RESULTS

Results obtained during these experiments are dependent on each aerosol's nucleating properties, the concentration of simulants present, and the size of the droplets used. It was hypothesized that as the size of the droplets increased, more droplets would freeze due to statistical effects; and that with higher aerosol concentrations, the probability of an aerosol with the appropriate nucleation site being present would increase proportionally. Both conditions would lead to more frozen particles, freezing at warmer temperatures, and decreased time to freeze. Similarly, it was predicted that decreasing the concentration would cause a proportionate decrease in the quantity of frozen droplets, colder nucleation temperatures, and longer time to freeze.

Peltier Temperature Variations

As noted in the Methods section, temperature measurements from across the Peltier were recorded over the course of each experiment. Figure 5 shows a representative example of temperature data collected for a single experimental run. Here we see that the central thermocouple (wire label: f) consistently measures the coldest temperatures, while the thermocouple at the bottom right corner of the Peltier (wire label: d) also regularly measures the warmest temperatures.
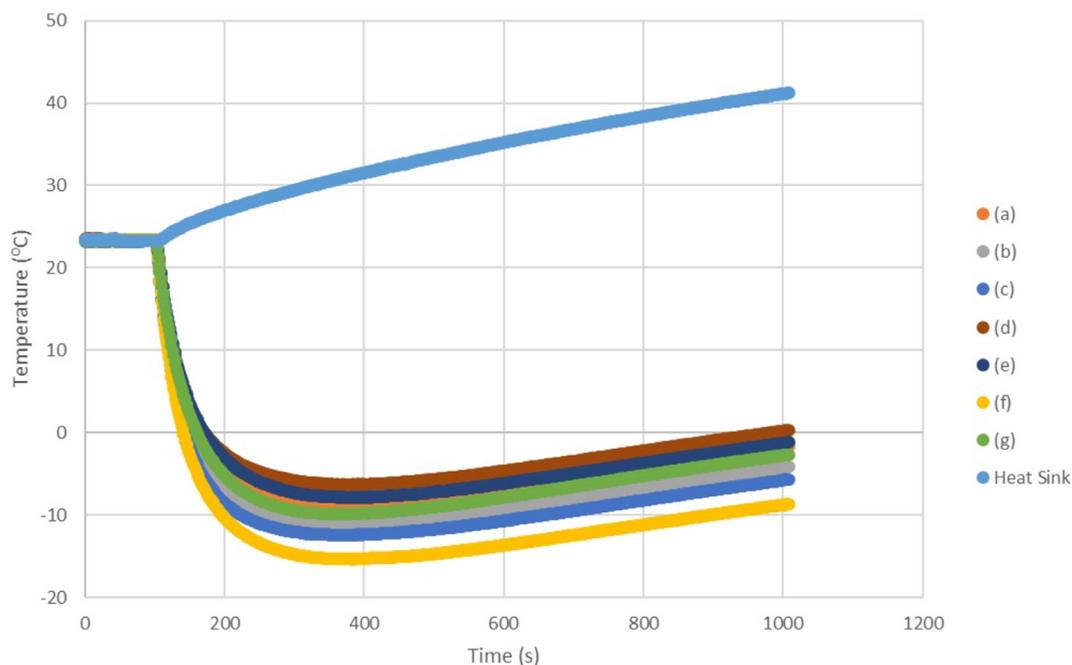
FIGURE 5. Time (s) vs. temperature (°C) data for a single experimental run. Voltage is supplied on the Peltier at around 100 seconds, after which an immediate drop in the temperature of the Peltier's top surface and an immediate (but smaller) increase in temperature of the heat sink is observed. Each line corresponds to a thermocouple wire location shown in Figure 3, with an additional line for the temperature of the heat sink. Lowest system temperatures are typically reached 4–5 minutes after voltage is applied, in the center of the Peltier, with temperature rising in pace with the heat sink temperature rise thereafter.

Temperature variations of around 10°C were regularly seen across the face of the Peltier, indicating a temperature gradient across its surface. For simplicity, the temperature was measured at the central thermocouple, which was the coldest and regularly reached –18°C, to indicate the temperature at which a droplet froze. In most cases, this will be an overestimation of the reduction in temperature required for ice nucleation and droplets will have frozen at warmer temperatures. Temperature data was also collected on the air-cooled heat sink, as there is a maximum temperature differential across the faces of the Peltier that can be maintained. To this end, average temperature differences were observed between the center thermocouple and heat sink of about 40°C, which falls within the operating characteristics of the Peltier.

Nucleation Through Immersion Freezing

For each aerosol type droplet sizes of 1, 3, and 6 μL were tested and the concentration of suspended aerosol varied between 2.06 10^{-3} g/cm^3 and 3 10^{-4} g/cm^3, which are equivalent to 10^4 – 10^5 particles/3μL droplet and 10^3 – 10^4 particles/3μL droplet, respectively.

For each aerosol type, concentration, and droplet size, three experimental runs were completed, or 54 experiments in total. This resulted in accumulated totals of 380, 381, and 402 droplets for experiments conducted with ATD, JSC-1A, and LMS-1D, respectively (Table 2). These cumulative values vary slightly due to droplet loss to the well walls. In these experiments, ATD, our terrestrial analog, was found to be the most efficient nucleator, freezing 36.6% of droplets. This was followed by the lunar regolith simulants with JSC-1A, which froze 12.9% of droplets, and LMS-1D, which froze only 3.2% of droplets. Control experiments with pure Millipore water were also conducted for the three droplet sizes, resulting in the testing of 190 droplets and a freezing rate of 4.2%.

TABLE 2. Droplets frozen.

Simulants	# Frozen / Total	Percentage Frozen
ATD	139 / 380	36.6%
JSC-1A	49 / 381	12.9%
Exolith	13 / 402	3.2%
Water	8 / 190	4.2%
Total	209 / 1353	15.4%

For each freezing event, the time at which the particle froze with respect to the start of the experiment and the temperature of the central thermocouple were recorded; this data has been plotted in Figure 6. It was determined, based on the results, that many of the 3μL droplets containing JSC-1A or LMS-1D took longer to freeze than ATD, but also did so at warmer temperatures. The 6 μL droplets containing lunar simulants generally froze later than ATD and at colder temperatures. The 1 μL droplets were in general the fastest to freeze, with little variation between JSC-1A and ATD, but there were no freezing events for pure water or LMS-1D for this size. Note that only slight variations in freezing time or temperature were seen across the different aerosol concentrations.

In general, most droplets froze within the first 6 minutes of the experiment start, regardless of the aerosol type or concentration. It was also determined that larger droplets froze more often. Droplets tended to freeze at temperatures of around –11°C or colder. The ATD control was the most efficient nucleator, followed by JSC-1A and then LMS-1D. A clear demonstration of this nucleation efficiency can be seen in the temperature vs. volume data for the 6 μL droplets (Figure 6), where ATD started freezing at warmer temperatures (around –11°C), followed by JSC-1A at lower temperatures (around –12°C), and then LMS-1D and water at lower temperatures still (around –14°C). ATD froze earlier overall compared to the simulants for this droplet size.

DISCUSSION

Within each lunar simulant tested, the 3 μL droplets froze at warmer temperatures, as warm as –9°C, with some taking upward of 9 minutes into the run to freeze, resulting in a wide spread of values as shown in Figure 6. Compared to the 1 μL or 6 μL droplets, this is both warmer and longer. More robust statistics from an increased number of experimental runs are needed to get a better understanding of the effects of droplet size on nucleation and of what the conditions, particularly temperature, of water ice formation through immersion freezing may be. The data also shows that the time to freeze and the temperature at which freezing took place were essentially independent of the concentration of suspended aerosols within a droplet. That is, the increase or reduction of suspended aerosols did not have a
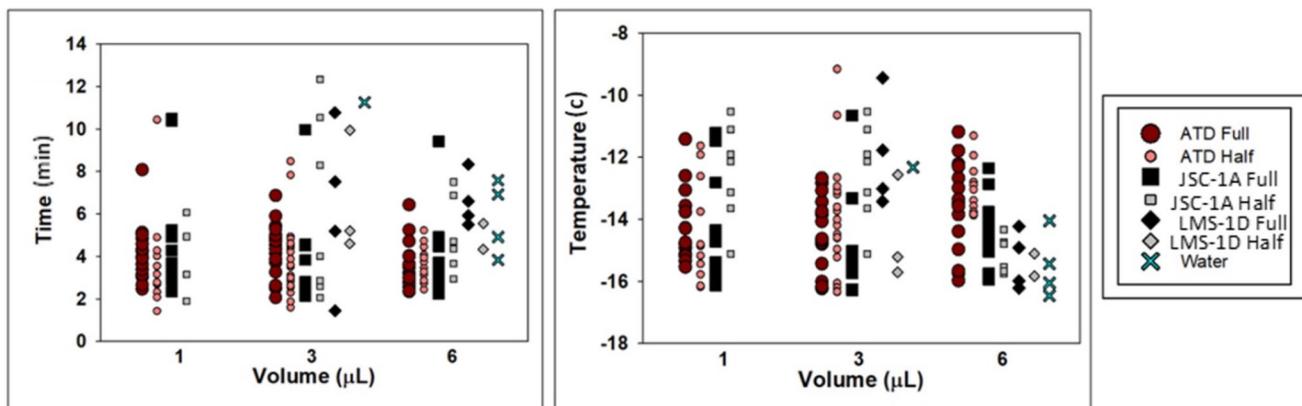
FIGURE 6. Left: Volume vs. time data for each concentration of simulant used. Right: Volume vs. temperature data for each concentration of simulant used. High and low concentration data is plotted for each droplet size. If a marker is not shown for a given droplet size and simulant type or pure water, no freezing event was observed.

significant effect on immersion freezing. With these results, it can be hypothesized that the lower concentration of suspended particles was no more limiting to the phase transition than the higher concentration. Further testing at lower suspended aerosol concentrations is needed to obtain information on chances for nucleation efficiency with availability of lunar aerosols formed through volcanism.

It was found that ATD, at all concentrations and droplet sizes, was more efficient at triggering water ice nucleation than either of the lunar regolith simulants. This is likely due to ATD particle morphology and nucleation site availability, allowing water molecules to better bind onto the aerosol surface, enhancing the freezing chain effect. These results imply that immersion freezing of water ice and cloud formation may be more efficient on Earth than in the ancient lunar atmosphere at Earth-relevant atmospheric conditions.

It was also found that JSC-1A and LMS-1D lunar simulants had very different overall nucleation results. Table 2 shows that JSC-1A had a total of 12.9% of droplets freeze compared to only 3.2% for LMS-1D, even though the chemical and mineral compositions of the simulants are similar, and they were created to mimic the same regions on the Moon. While meant to be chemically similar, their physical differences—including color, particle size, and suspension properties—are clear upon observation, as shown in Figure 4. While physical differences from visual inspection alone cannot explain the differences in nucleation properties, they can hint at what part of the chemical

makeup is causing the increase or reduction in nucleation efficiency. I speculate that this might be due to considerable differences in concentrations of MgO, Al_2O_3, and CaO between JSC-1S and LMS-1D as shown in Table 1.

From these results, it can be reasoned that the formation of water ice in clouds on the moon through heterogeneous nucleation is directly linked to the chemical makeup of the aerosols, their available nucleation sites, and the temperature at which the droplets are cooled, which all follows directly from nucleation theory. In turn, the extent of water ice cloud formation on the ancient Moon would depend on the amount of volcanic outgassing and aerosols present to act as heterogeneous ice nuclei, and the chemical makeup of that nuclei, which has yet to be fully explored. Additionally, it can be seen that ATD is a more efficient ice nuclei than of the lunar simulants, within which JSC-1A was more efficient than LMS-1D. Even though these results may indicate that cloud formation on the Moon may not be as extensive compared to that on Earth, any amount of freezing in the ancient lunar atmosphere would play a key role in volatile cycling and climate. In other words, it could be inferred that there was an active lunar hydrological cycle on the Moon and that its surface was directly affected by solid or liquid precipitation.

CONCLUSION

Researching the ancient lunar atmosphere can provide planetary and atmospheric scientists with valuable

information relevant to both current day and past astronomical bodies. Let's take, for instance, Titan, Saturn's largest moon, where clouds and precipitations are composed of methane-ethane-nitrogen mixtures and a robust hydrological cycle has led to the creation of vast lakes and subsurface oceans. This is all possible due to the dense nitrogen-dominated atmosphere protecting the surface of Titan. Investigating the properties of the ancient lunar atmosphere can help us infer how atmospheres on small bodies form, the histories of these bodies, and how such an atmosphere is lost over time.

Starting with Needham and Kring's (2017) estimates of an ancient lunar atmosphere, and through experiments on the nucleation properties of lunar regolith simulants, this project determined that lunar regolith simulants can facilitate water nucleation in the immersion freezing mode under Earth-based conditions, suggesting that clouds could have formed within the atmosphere of the Moon and may have played into a hydrological cycle. Additionally, it was found that the chemical makeup of aerosols plays a large role in the immersion freezing properties of water droplets. This in turn can be linked to the degree of outgassing and eruption properties during the formation of the transient atmosphere. Finally, in comparing the nucleation properties of lunar simulants to an Earth control, we see that water ice clouds on Earth may form more readily than those on the moon. These results will be impactful for planetary and atmospheric sciences as they provide unique context to the properties of the ancient Moon and insight into lunar cloud formation billions of years ago. I believe that the conclusions emerging from this work will provide the foundations for future lunar atmospheric studies.

I plan to continue this research by investigating the nucleation property differences between JSC-1A and LMS-1D simulants by testing the freezing properties of individual minerals, such as TiO_2, Al_2O_3, MgO, CaO, and Fe_2O_3. This will provide information about which compositional fractions contribute, or not, to the difference in nucleation behaviors between the two simulants. I am also in the process of designing and creating a new experimental setup with better temperature and automated features to determine the exact moment of freezing. To round out this study of lunar regolith simulants, I will be testing the immersion freezing properties of Exolith Highland Simulant,

LHS-1D, which simulates the higher elevation, brighter regions on the Moon, as these aerosols also could have been present within the atmosphere. Finally, I aim to perform atmospheric chemical equilibrium modeling for the ancient Moon to determine what the final equilibrated atmosphere would be composed of and how it would have affected cloud formation and surface properties of the Moon.

ACKNOWLEDGMENTS

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