Laboratory analogs of Mars clouds: critical saturations for water ice nucleation

Bruce Drury Phebus
San Jose State University

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LABORATORY ANALOGS OF MARS CLOUDS: CRITICAL SATURATIONS FOR WATER ICE NUCLEATION

A Thesis
Presented to
The Faculty of the Department of Chemistry
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Bruce Drury Phebus
August 2009
SAN JOSÉ STATE UNIVERSITY

The Undersigned Thesis Committee Approves the Thesis Titled

LABORATORY ANALOGS OF MARS CLOUDS:
CRITICAL SATURATIONS FOR WATER ICE NUCLEATION

by
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ABSTRACT

LABORATORY ANALOGS OF MARS CLOUDS:
CRITICAL SATURATIONS FOR WATER ICE NUCLEATION

by Bruce D. Phebus

Understanding the current martian climate and water cycle depends on a thorough understanding of water ice clouds, which are modeled based on extrapolation of data relevant to Earth’s atmosphere. These studies show the successful development of a new chamber and experimental protocol for conducting studies of water ice nucleation via vapor deposition. We have performed experiments at cold temperatures and low pressures more representative of Mars. Critical saturation ratios were observed to vary from $1.1 \pm 0.2$ at 185.0 K to $3.3 \pm 0.8$ at 155.1 K on martian dust analogs. Variation in the temperature dependence among different substrates was also observed. The strong temperature dependences observed here for many analogs under water ice nucleation conditions makes it is clear that extrapolation of terrestrial values to martian temperatures is inappropriate. Adsorption/desorption tests with smectite clay and JSC Mars-1 Regolith Simulant were also undertaken to insure that experiments were performed under repeatable conditions. This laboratory work is the first to test martian dust analogs for water ice nucleation under temperatures relevant to Mars ($T = 140 - 210$ K), and it is the first study to examine critical saturations for water ice nucleation on JSC Mars-1 Regolith Simulant under any conditions.
ACKNOWLEDGMENTS

I would like to express my gratitude to my advisor Bradly M. Stone, for including me on this project as well as Laura T. Iraci, for providing day to day council and guidance along with Anthony Colaprete. The guidance, support, and environment to expand my scientific knowledge and skills was never second best along this journey. Also in need of thanks are those who worked on crucial aspects of this project; Alexandra Blanchard, who was deeply involved with the JSC Mars-1, work and Rosi Reed, who helped ready the chamber for use. There are many people who provided needed insight and advice; Cecilia Dalle Ore, Oana Marcu, Rachel Mastrapa, Emmett Quigley, Ted Roush, Max Sanchez, Dave Scimeca, who all were an indispensable part of this work. I would like to thank my committee members Dr. Muller and Dr. Terrill who provided valuable feedback and always pushed for every aspect of this project to be held to the highest standard and gave critical scrutiny. NASA Ames was an environment of such profound positive influence; both the Space and Earth Science branches deserve as much gratitude as I can bestow, for being such an out-of-this-world place to conduct research. Financial support for this work was provided by NASA Planetary Atmospheres and San Jose State Foundation. There are also those who undoubtedly played a vital role, which I cannot quantify or may be unaware of, who also deserve thanks.
DEDICATION

I would like to dedicate this work to my Mother for providing both an environment that allowed creativity to flourish, and the emotional fortitude and zeal needed for the undertaking. I am indebted to my Father who helped instill an interest in science in me, as well as pushed me to do my best in all things. I am humbled by the care shown by my friends and the love and advice they have provided over the course of the work. Thanks goes to all who read drafts and watched presentations of boring things they are never likely to care about besides the care they show me. I can scarcely express my thanks to professors and advisors who provided far more than technical assistance, being a mentor and friend while being a boss who pushes for excellence, must be among the narrowest of paths one can walk.
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1. Introduction

1.1 Characteristics of Mars’s Atmosphere

This study focuses on finding the threshold value needed to start a water ice cloud. Understanding the current martian climate and water cycle depends on a thorough understanding of water ice clouds. This study looks to improve upon previous studies and currently available approximations, to be discussed later in this section, by performing experiments at colder temperatures more indicative of Mars, which may also be relevant for colder clouds on Earth.\(^1\) Results from this work will be of value to modelers looking to include cloud growth and formation in their models, making them more realistic.

Mars, the fourth planet from the sun, differs from Earth, and these differences should be thoroughly covered to firmly ground the reader with an understanding of Mars. As this study is focused on supporting computer modeling of the martian atmosphere, specifically the formation of ice clouds, it is critical to keep the characteristics of the martian atmosphere in mind while moving forward. There is no ocean or standing liquid water on the surface of Mars, allowing for enormous exposed basins. The topography of Mars is dominated by massive features such as vast basins (the northern lowlands), and enormous craters (Hellas and Argyre), as well as the largest mountain (Olympus Mons) and deepest valley (Valis Marinaris) in the solar system.\(^2\) Additional basic information can be found in Table 1.1.

Interest in Mars is likely due both to its similarity to Earth, and its differences. Mars has seasons due to a tilt in its axis of 25 degrees, a day like ours (24.66 h), and ice
at its poles. Differences also abound; two small moons orbit Mars, as opposed to one relatively large one that orbits Earth. Martian polar ice caps are made of dissimilar materials, CO$_2$ at the south and H$_2$O at the north. The atmosphere of Mars has two condensable components, carbon dioxide and water, compared to Earth's one. With interest in developing weather predictions for manned and unmanned exploration, understanding cloud formation under martian conditions will be a considerable step.

**Table 1.1 Basic Comparison of Mars with Earth**

<table>
<thead>
<tr>
<th></th>
<th>Mars</th>
<th>Earth</th>
<th>Ratio (Mars:Earth)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass ($10^{24}$ kg)</td>
<td>0.642</td>
<td>5.97</td>
<td>0.11</td>
</tr>
<tr>
<td>Surface Gravity (m/s$^2$)</td>
<td>3.7</td>
<td>9.8</td>
<td>0.38</td>
</tr>
<tr>
<td>Topographic Range (km)</td>
<td>30</td>
<td>20</td>
<td>1.5</td>
</tr>
<tr>
<td>Solar Irradiance (W/m$^2$)</td>
<td>589</td>
<td>1367</td>
<td>0.43</td>
</tr>
<tr>
<td>Sun-Planet Distance (AU)</td>
<td>1.38-1.67</td>
<td>0.98-1.02</td>
<td>1.53</td>
</tr>
<tr>
<td>Orbital Inclination</td>
<td>25.2°</td>
<td>23.5°</td>
<td>1.06</td>
</tr>
<tr>
<td>Length of Day</td>
<td>24h, 39m, 35s</td>
<td>24 h</td>
<td>1.03</td>
</tr>
<tr>
<td>Revolutions/Year</td>
<td>668.6 sols</td>
<td>365.3 days</td>
<td>1.8</td>
</tr>
</tbody>
</table>

**Basic Comparison of Martian Atmosphere with Earth**

<table>
<thead>
<tr>
<th></th>
<th>Mars</th>
<th>Earth</th>
<th>Ratio (Mars:Earth)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Pressure (Torr)</td>
<td>4.5-6.0</td>
<td>760</td>
<td>0.007</td>
</tr>
<tr>
<td>Scale Height (km)</td>
<td>11</td>
<td>8.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Mean MW (g/mol)</td>
<td>43.4</td>
<td>29.0</td>
<td>1.50</td>
</tr>
</tbody>
</table>

**Martian Atmospheric Composition by Volume**

<table>
<thead>
<tr>
<th></th>
<th>Mars</th>
<th>Earth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide, CO$_2$</td>
<td>95.3 %</td>
<td>320 ppm</td>
</tr>
<tr>
<td>Nitrogen, N$_2$</td>
<td>2.7 %</td>
<td>78 %</td>
</tr>
<tr>
<td>Argon, Ar</td>
<td>1.6 %</td>
<td>0.93 %</td>
</tr>
<tr>
<td>Oxygen, O$_2$</td>
<td>0.13 %</td>
<td>21 %</td>
</tr>
<tr>
<td>Carbon Monoxide, CO</td>
<td>0.07 %</td>
<td>0.2 ppm</td>
</tr>
<tr>
<td>Water, H$_2$O</td>
<td>210 ppm</td>
<td>1 %</td>
</tr>
</tbody>
</table>

Physical characteristics of Mars and Mars's atmosphere compared to those of Earth. Differences and similarities between Mars and Earth are highlighted by the ratio of values. Data taken from Kieffer et al and Pruppacher and Klett.$^{2,3}$
Mars has a dramatically less dense atmosphere than Earth with less than 1 % of the pressure at mean surface elevation on Mars as compared to sea level on Earth. The atmosphere of Mars is composed mostly of carbon dioxide (< 95 %), with water as the second condensable component (< 0.1 %). During seasonal fluctuations, the martian atmosphere reaches temperatures low enough for CO₂ to condense. With as much as 25 % of the atmosphere condensing out each winter, fluctuations in the atmospheric pressure can be dramatic.

Despite the small amount of water, ice clouds form an integral part of the martian hydrological cycle, increasing the transport of water over the planet by a factor of two.⁴ Clouds can also influence the radiative balance of the planet directly, and through their influence on suspended dust as well.⁵,⁶ At least two major water ice cloud types have been observed on Mars, and their prevalence seems to vary with altitude and particle size.⁷ Observations also point to differences in geographic location, with mountain-induced circulation forming clouds,⁸ and clouds observed in the polar night and during summers in the north.⁹

The martian hydrological cycle varies from Earth’s in many respects, including temperature and water partial pressure, which makes relating experiments and measurements of terrestrial clouds to those on Mars difficult. Current experiments studying the formation of cirrus ice clouds on Earth are the nearest approximation for Mars because of the cold temperatures used.¹⁰⁻¹⁵ But even the coldest studies to date have been conducted at temperatures \( T = 194 - 263 \text{ K} \) considerably higher than much of the cloud forming regions of Mars \( T = 140 - 210 \text{ K} \).⁴⁻⁶,⁸,⁹,¹⁶
Ice condensation nuclei, ICN, are central to heterogeneous nucleation of clouds on Earth and Mars. A firm understanding of dusts that could act in this capacity on Mars is crucial. Martian dust has been studied extensively from its distribution in the atmosphere to its composition.

Heterogeneous water ice nucleation is dependent on many factors including particle size, temperature, and composition, with mixed findings regarding the relative importance and effect of each in many studies. Some studies show significant size dependence, with smaller particles being more difficult to nucleate on, many others show temperature dependence, and finally many show mineral dependence. It is also observed that not all particles act equally in supporting nucleation within a given sample. This study is focused on two factors: dust composition and temperature dependence.

This study utilizes three different dusts: Arizona Test Dust (ATD), JSC Mars-1 Regolith Simulant (JSC Mars-1), and a hand-collected smectite clay from Sedona, AZ. Each dust was chosen such that experimental results would be of value to the modeling community, as well as comparable to previous studies. ATD is often used in nucleation studies and thus provides a comparison with previous lab work performed on the subject of water ice cloud nucleation. Mars dust has been studied (noted above) and an Earth analog has been found using (VIS/NIR) reflectance spectroscopy to match it to its martian counterpart. The JSC Mars-1 is the currently accepted best approximation to actual martian surface material. The clay sample was chosen to act as a lower bound or a “best nucleator” due to its adsorption of water. This study is the first to measure the
water ice nucleation characteristics of JSC Mars-1 Regolith Simulant under any conditions, and the first to measure nucleation under simulated martian atmospheric conditions.

Forming a new phase requires the initial generation of a small portion of the new phase, called a germ, which requires overcoming an energy barrier. Germ formation can occur in two ways homogenous or heterogeneous. Homogenous nucleation is spontaneous generation of a germ from the meta-stable phase, requiring random motion of molecules to bring about a cluster. Heterogeneous nucleation uses a site on some pre-existing material to help aggregate molecules. Formation of a germ is a kinetically governed process; however before it can grow into a stable new phase it must also reach a critical size. Once a critical cluster has formed, additional water molecules increase stability, and growth of the new phase becomes spontaneous.

Formation of drops and snow from vapor in clouds requires nucleation as a precursor. Some general circulation models (GCMs) account for the microphysics of cloud formation using terrestrial values which may not be representative of Mars. The onset conditions required to start water ice growth, which are directly measured in this study, will help improve models by providing values at appropriate conditions allowing the same nucleation mechanisms in the lab as on Mars. Without a clear understanding of the temperature dependence of nucleation conditions, extrapolation of laboratory results focused on Earth’s atmosphere to the temperatures common in the martian atmosphere would be very speculative.
Relative humidity and frost point are commonly used terms for discussing how much water vapor is in the air at a given moment. For experiments concerning high altitude clouds, two new terms come into use when describing the humidity of the air, the saturation ratio, $S$, and supersaturation. For this work the saturation ratio, $S$, will be used exclusively. This value is calculated much like relative humidity. The water pressure, $P_w$, is divided by the vapor pressure over ice at that temperature $VP_{\text{ice}}$, shown in equation (1).

$$S = \frac{P_w}{VP_{\text{ice}}}$$  

(1)

Moving the decimal two places to the right will convert $S$ to the relative humidity for water ice, which is perhaps more familiar to the reader.

The critical saturation ratio, $S_{\text{crit}}$, required to nucleate ice is a factor in the Gibbs free energy of forming the new phase, shown in eq(2). The energy barrier is described by two terms: the surface tension ($4 \pi \sigma r^2$) of the critical cluster and the energy recovered by forming the new phase.

$$\Delta G = 4\pi \sigma r^2 - \frac{4\pi kT \ln S_{\text{crit}}}{3\nu_1} r^3$$  

(2)

In this equation $\sigma$ is the surface tension, $r$ is the radius of the critical cluster. The second term includes the Boltzmann constant, $k$; the molecular volume, $\nu_1$; and temperature, $T$.  

6
With homogenous nucleation requiring extremely high saturations, the presence of ICN allowing for a heterogeneous pathway can lower $S_{\text{crit}}$ considerably.

1.2 Research Objectives

Providing measurements of onset conditions for water ice or critical saturation $S_{\text{crit}}$, under martian atmospheric conditions required the development of a new atmospheric chamber and experimental protocol. This work will cover the experimental method developed to test for these onset conditions as well as results. To directly measure the onset of ice formation we employ a common technique of monitoring for condensed-phase water via infrared spectroscopy. Absorption features for both liquid and solid forms are strong and distinguishable. Although both the OH stretch and bend can be observed in the absorption spectrum, the OH stretch is utilized in this study due to its strength, lack of interference with water vapor, and reduced interference from temperature dependent substrate features.

With the development of a new chamber comes a concern over calibration and control of experimental uncertainty. This work will cover calibration of temperature and pressure measurements used to calculate $S_{\text{crit}}$ for these experiments. Uncertainties arising from those measurements and how they impinge on results will also be discussed. This work reports the threshold saturations needed to initiate water ice on four different substrates. Polished silicon was used as a blank representing an upper experimental bound for results. Three dust candidates were tested: Arizona Test Dust (ATD), JSC Mars-1 Regolith Simulant, and smectite clay. JSC Mars-1 was observed to separate by
gravitational settling upon standing in water after sample preparation, which produced
two fractions that were also tested. With the two fractions, a total of five experimental
substrates were analyzed, with results spanning temperatures 155 – 185 K and pressures
$5.7 \times 10^{-7}$ to $1.1 \times 10^{-4}$ Torr.
2. Experimental Design

2.1 Apparatus Design

The experimental high-vacuum chamber, constructed from stainless steel, was designed in such a way as to minimize volume to ~10 L. Evacuation of the chamber is done using a turbomolecular pump (Pfeiffer TPH 270). A throttle valve (MDC AV-150) and a gate valve (MDC GV-4000VP-PI) control pumping of the chamber. Two KBr (McCarthy Scientific Co. 3-3013 49x6mm) windows allow passage of an infrared beam through the chamber. The infrared beam path is enclosed and purged using dry air (Whatman 75-52). Figure 2.1 has additional components that will be reviewed later.

Figure 2.1: A diagram of the vacuum chamber used for nucleation and adsorption/desorption experiments. The beam path above and below the chamber is enclosed and purged using dried air. The Baratron capacitance manometer used to calibrate the ion gauge is attached just opposite the ion gauge.
A silicon wafer (Dia: 25.0 +0.0 -0.1 mm, Lambda Optics, WI-2502-5 lot #C00021207) is centrally mounted to allow passage of an infrared beam through the center of the chamber. The mount that holds the silicon in a copper ring is attached to a jacketed copper rod imbedded in a vacuum-jacketed liquid nitrogen cryostat. The mount has a resistive heater (Minco HK5228R31.7L12A) held against the end of the jacketed cold finger using a copper clamp, Figure 2.2. The cold finger also has a heater (Minco HK5241R24.7L12A) wrapped around the exposed vacuum jacket and held in place using copper tape (3M Copper Foil Conductive Adhesive 1181). This heater is located as close to the end of the cold finger as possible, covering approximately one third of the jacket.

The silicon substrate is mounted without using any thermal contact paste to prevent contamination; a copper ring/lid sits on top and holds the wafer in place using four stainless steel screws along with twelve stainless steel Belleville conical washers (1/8” 48.0 Pa per square inch when flat), three on each screw. The washers are oriented for maximum travel, with the stack of three washers having alternating orientation: cone down up down. All screws are turned one quarter turn after being tightened finger tight. Thermocouples are often mounted under the bottom washer in the stack, in contact with the copper ring/lid. Thermocouples are also mounted on the vacuum jacket and on the copper ring clamp that holds the control heater in place. All thermocouples used were K-type. Temperature is controlled using a Eurotherm (model#818) temperature controller, using the thermocouple mounted to the copper ring clamp. The jacket heater was set to a single voltage for the duration of an experiment; the voltage between (5-15) V is chosen
to make sure the jacket temperature is between 20 and 45 K warmer than main
monitoring thermocouple, number 1 (Figure 2.2, Section 2.2).

2.2 Measurement of Experimental Variables

Experimental conditions monitored include temperature at various locations on
the mount, total pressure, and the infrared spectrum of the sample. Each of these was
automatically recorded by various methods that will be described in detail.

Temperature was measured using K-type thermocouples and recorded with a Pico
Technology TC-08 USB data logger. Calibration of all thermocouples was done against
the vapor pressure of water in the chamber at the frost point\textsuperscript{33} to account for differences
between the point being measured and the observation region. This calibration will be
discussed in greater detail in Data Analysis. Temperature has been monitored at three
fixed locations in all experiments, and one thermocouple has been adjusted to record
from various locations according to need. The three locations that have consistently had
thermocouples mounted are: 1) under the washer stack top right of the mount, 2) on
copper ring clamp, and 3) on jacket of the cold finger. Locations for the fourth
thermocouple have included: a) below the copper mount bottom left, b) pressed against
the silicon, and c) under the washer stack near left, and imbedded within the silicon wafer
itself (courtesy of KLA Tencor, SensArray Division, Santa Clara, CA). A diagram
illustrating each thermocouple placement follows in Figure 2.2.
Figure 2.2: The mount is shown on the left with a silicon wafer in place. On the right, the copper ring/lid is shown above the mount with a slight recess in the mount and lid. Thermocouples mounted at points “a”, and “2” are attached after the bolt is in place and a nut was back-screwed onto the bolt and tightened to hold the thermocouple in place. When a thermocouple was used at point “b”, a spring was used to hold it in contact with the silicon surface.

Pressure was measured with an ion gauge (Terranova model #934 Ion Gauge I-100-K) that then feeds voltage into Pico Technology ADC-11/12 USB data logger. The voltage output by the ion gauge follows the formula, equation taken from the manual.\(^\text{34}\)

\[
\text{Voltage} = \left( \frac{5}{4095} \right) [(410 \cdot (10 - Z)) + (40 \cdot X.Y)]
\]  
(3)
The equation takes pressure of the form $X \cdot Y \cdot 10^Z$ in Torr; output voltages vary from 0-10 V, with each decade of pressure within a half-volt window. This voltage goes through a voltage divider mounted on an ADC-11 Terminal Board so input voltages vary from 0-5 V. All temperatures and pressure were recorded by PicoLog twice a second. The file start time was recorded by hand into the lab book. Pressure calibration of the ion gauge was accomplished by comparison to a Baratron capacitance manometer (MKS model #127AA, 0.1 Torr full scale, with recent manufacturer's calibration). Calibration of the ion gauge will be discussed further in 3.1 Calculating Critical Saturations.

Infrared spectra were recorded by a Nicolet Nexus 670 FT-IR and MCT-A detector using Omnic software. Both the background and a continuous series of spectra were recorded and time stamped by the software using the computer system clock. The beam path was directed through the center of the silicon wafer. Spectra were taken with frequency ranges of 500-7000 cm$^{-1}$ in most cases; some spectra were taken with frequency ranges of 500-4000 cm$^{-1}$. Gain settings were adjusted according to need all other settings remain constant in this study; resolution 4 cm$^{-1}$, 32 scans averaged per spectrum, aperture 32. Background spectra were taken at temperatures ~14 K ($\sigma = 7$, $N = 65$) above the expected nucleation temperature so that temperature dependant shifts of the silicon and dust absorbance features will be minimized. The primary feature observed in the infrared spectra is the OH stretch of condensed water is observed at 3000-3500 cm$^{-1}$, which can be seen in Figure 2.3 after exposure of smectite clay to water. During the experiment, the integrated peak area (3000-3500 cm$^{-1}$, baseline 2500-3500 cm$^{-1}$) was monitored for ice growth. Other features observed in the spectra include the
OH bend at 1640 cm$^{-1}$, which can be seen in Figure 2.3, however this feature was not used due to interference with water vapor.

**Figure 2.3:** Infrared spectra of a nucleation experiment, Si-14, on silicon. Each spectrum is labeled with the collection time in min, which relates to Figure 2.7. Note the OH stretch between 3000-3500 cm$^{-1}$ is not affected by water vapor. The OH bend was occluded by water vapor, observed between 1500-2000 cm$^{-1}$ and 3000-4000 cm$^{-1}$. Nucleation of water ice in this experiment occurred at ~270 min. *Absorbance for gas phase CO$_2$.

Spectral differences between adsorbed water and ice are observed, allowing for a distinction between the two phases. Adsorbed water has a broad rounded peak with what appears to be two overlapping absorbance bands between 3500-3000 cm$^{-1}$, whereas ice
has three distinct features observable in the same region, these can be observed in Figure 2.4.

**Figure 2.4:** Infrared spectra of a nucleation experiment, Clay-04 on smectite clay. Each spectrum is labeled with the collection time, which relates to Figure 2.9. Nucleation of water ice occurred at ~151 min. Note the OH bend for non-crystalline water can be clearly seen in this between 3000 and 3500 cm\(^{-1}\), which has a distinctly different absorbance than water ice. Also the OH bend is clearly visible between (1600-1710 cm\(^{-1}\)).
2.2.1 Sample Mount Handling Procedure

The silicon substrate experiments all started with properly opening the chamber. To minimize pump downtime, the turbo pump is closed off from the sample side of the chamber by closing both the gate valve and the throttle valve. A full diagram of the chamber can be seen in Figure 1.1. The chamber is slowly leaked up to 1 atmosphere by bleeding air through the H₂O line, by opening the leak valve (Varian 951-5014) slightly. Once the chamber is at room pressure, bolts holding the cryostat are removed so the cryostat can be pulled back, exposing the cold finger. The chamber opening is inspected for contamination then covered using aluminum foil. Screws holding down the copper cover are all loosened to finger tight and then removed to prevent cracking of the silicon wafer. Once the wafer has been removed the dust, if there is any, can be scraped off and weighed and or observed.

Reassembly is preceded by careful cleaning of the mount with acetone followed by a wipe with water, same as used for sample preparation. All components are cleaned, including the bolts, washers, mount, cover, and silicon wafer. Once all components are clean, the silicon wafer is placed back in the mount with the copper ring/lid on top. Screws are tightened to finger tight and then turned one quarter turn past in an X pattern. With the cover secured, substrates can now be added to the surface, if desired.

The MCT-A interferogram response (peak-to-peak voltage) allows a rough comparison of the light reaching the detector from one experiment to another. With salt windows and silicon wafer in the beam path, a peak to peak voltage of approximately 7 V is observed with a gain of 1. All spectra used for these experiments share identical
aperture 32 (iris diameter 5.08mm), resolution 4 cm\(^{-1}\), and number of averaged spectra 32, regardless of substrate.

### 2.2.2 Preparing Arizona Test Dust

Arizona Test Dust (ATD) samples were of ultrafine grade (ISO 12103-1, Powder Technology Inc., Burnsville, MN). The dust had a volume mean diameter of 5 \(\mu\)m, by number half are smaller than 1.2 \(\mu\)m, with a total specific surface area of 1.721 m\(^2\)mL\(^{-1}\), a composition of 68-76% SiO\(_2\), 10-15% Al\(_2\)O\(_3\), and 2-5% Fe\(_2\)O\(_3\), 2-4% Na\(_2\)O, 1-2% MgO, 0.5-1% TiO\(_2\), 2-5% K\(_2\)O by weight. Three separate applications of dust were used. For the first sample was \(~3\) g in \(~30\) ml acetone (Fisher, ACS certified grade lot#963772) for experiments ATD-01 through ATD-05, ATD-07 and ATD-09. For the second and third samples, \(~2\) g of ATD was mixed with \(~20\) ml acetone, and used for experiments, ATD-08, ATD-10, and ATD-11. Samples are deposited from acetone slurries and allowed to air dry. The peak-to-peak voltage observed with the sample in the beam path for the first deposition was 7.6 V (gain = 4), the second 6.6 V (gain = 2), the third 8.9 V (gain = 4). Achieving complete spatial coverage of the wafer along with keeping peak-to-peak voltage high was the chief goal of the application, not constraining the mass. The quantity of ATD used was too small to be weighed accurately.
2.2.3 Preparing Smectite Clay

Smectite clay samples were generated from a smectite-rich, hand-collected soil sample from Sedona, Arizona. Approximately 1 g was rinsed with reagent grade water (Sigma-Aldrich 320072-2L) after which ~1/2 g was then ground for one minute in a mortar and pestle. This was then added to ~5 mL of water. Approximately 1 ml of thoroughly-mixed sample was then pipetted from the slurry onto the silicon substrate. For ice nucleation experiments, approximately 1 ml of slurry was used for all experiments except Clay-05 and Clay-07. Spectrometer maintenance was carried out during this run of experiments and source lamp was replaced. Experiments Clay-01 through Clay-04, had detector voltages of ~8 V, gain = 4; after source replacement, experiment Clay-06 showed 10.2 V, gain = 4; experiments Clay-06, Clay-08 and Clay-09 showed 8.0 V, gain = 2. For experiments Clay-07 & Clay-05, 1 ml of slurry was applied, (8.2 V, gain = 4), and after experiments were complete weighed and found to be 24 mg. Samples were dried at temperatures between 20 and 50° C, followed by pumping to pressures lower than 1x10^-6 Torr. For adsorption/desorption experiments on clay, 1 ml of slurry was pipetted onto the surface and allowed to settle for a minute before excess water was wicked away using a Kimwipe. The detector voltage for this sample was 2.3 V. Samples were always dried till they appeared only slightly moist.

Micrographs taken of the Sedona clay sample (Figure 2.5) show that approximately half the dust particles are less than 1.5 μm in size, with another quarter of the sample between 1.5 and 3 μm. The surface area of the sample is dominated by 5-10% of the particles observed to have at least one axis longer than 10 μm. The largest particle
observed was 45 x 70 µm. The smectite-rich clay sample from Sedona, AZ is a close spectral (IR) match to SAz-1, with likely contributions from calcite and gypsum (T. Roush, personal communication). Adsorption of water by SAz-1 has been conducted for temperatures and pressures more representative of earth using infrared spectroscopy\textsuperscript{35,36} showing it to adsorb considerable amounts of water up to 70 % of its own weight.

\textbf{Figure 2.5:} Micrographs of smectite dust taken under 100x magnification. Both images are focused on the same sample, however the focal point is shifted to enhance the detail of larger grains left and smaller grains right. A 0.5 mm bar is located in the top left of each image.
2.2.4 Preparing JSC Mars-1 Regolith Simulant

JSC Mars-1 Regolith Simulant was the third type of dust material used. Our study utilized the < 1 mm size fraction of JSC Mars-1. The composition of the JSC Mars-1 surrogate has been studied by [28] and is characterized as a mix of ash particles that have alteration rinds of various thicknesses, as well as altered ash particles. SEM images show a composition of finely crystalline composite of feldspar, Ti-magnetite, olivine, pyroxene, and glass. X-ray diffraction spectra of the dust show a composition of 43.5% SiO$_2$, 23.3% Al$_2$O$_3$, and 15.6% Fe$_2$O$_3$, 6.3 CaO, 3.4% MgO, 2.4% Na$_2$O, 3.8% TiO$_2$, 0.6% K$_2$O, 0.9% P$_2$O$_5$, and 0.3% MnO by weight, with volatiles removed [28].

For experiments carried out on samples of Whole JSC Mars-1, ~1 ml of dust was ground for one minute along with ~1 ml water. All dust was rinsed into a vial with ~10 ml of water (Sigma Aldrich, lot # 0034HC). Settling of the dust was observed after less than 10 min, which will be discussed further below. For all ice nucleation experiments conducted on Whole JSC Mars-1, approximately 0.25 ml was pipetted immediately after agitation onto the surface of the silicon substrate, creating as uniform a distribution as possible. The sample used for nucleation studies was dried using a heat gun at ~35 °C, but always less than 50 °C. It was dried until it appeared only slightly moist. For adsorption/desorption experiments, the same procedure was used to deposit the dust. A Kimwipe was used to remove excess water for adsorption/desorption experiments prior to full understanding of the settling phenomena. The chamber was reassembled in the same manner detailed previously.
Gravitational settling after grinding JSC Mars-1 was observed to produce multiple layers; after two days the smallest particles still had not fully settled. Three layers were distinctly observable in the sample; a lightly colored tan top layer, a darker tan layer in the middle, and a dark grainy layer that settled within a few seconds. The possibility that the middle layer was a composite of the top and bottom layers was considered likely, and so a method for isolating the top and bottom layers was devised. For a control, two samples were prepared identically. Each sample containing 1.1 g of JSC Mars-1 was ground for 1 minute along with 1.5 ml water, rinsed into vials for a total volume of 12 ml. Samples were allowed to sit for 2 h and then centrifuged for 45 min at 4,500 RPMs. The top fraction was then gently disturbed and removed by pipetting, and will be referred to as the light fraction. The middle portion, which we believe to be a mixture of the light and bottom components, was removed by adding water, shaking and pipetting the suspended particles repeatedly, leaving the purified bottom fraction, which will be referred to as the dark fraction. Micrographs taken of these two fractions can be viewed in Figure 2.6 B & C. The un-fractionated sample is believed to be a combination of the light and dark fraction with micrographs shown in Figure 2.6 A.
Figure 2.6: All micrographs are taken at 20x magnification with a 1 mm scale bar along the top of each image. Whole JSC Mars-1 Regolith Simulant (A) shows moderate clumping after being scraped from the wafer. The light fraction of JSC Mars-1 (B) showed clumping as well as small and large free particles. The Dark Fraction of JSC Mars (C) shows no clumping only free particles. The light fraction was also observed to have articles as large as ~0.5 mm in size, the dark fraction had some small particles ~0.01 mm in size.
2.4 Measuring Ice Nucleation Conditions

With dust present or blank silicon, the chamber is sealed and is evacuated by mechanical pump, with the turbo pump closed off from the roughing line to prevent back pressure from harming the pump. Once the chamber is below 50 mTorr, the turbo pump is opened to the roughing line and the chamber is then allowed to pump down for a minimum of two days, with both gate valve and throttle valve open, prior to any experiments reaching pressures in the $1 \times 10^{-6}$ Torr at a minimum.

Water vapor over a liquid water (Sigma Aldrich, lot # 0034HC) is leaked into the chamber from a bulb in an ice bath. The water source is freeze pumped at least once at the start of the day. The bulb is frozen in ethanol and dry ice (or occasionally over liquid nitrogen), and then evacuated to less than 25 mTorr to remove volatile impurities.

To measure the base pressure for the day’s experiments, the line connecting the water bulb to the chamber is evacuated, as air leak through the leak valve (Varian 951-5014) is the dominant leak for the chamber. Once the water vapor line is evacuated to less than $2 \times 10^{-6}$ Torr, the leak valve is closed and the pressure is observed. Once the pressure in the chamber is stable for longer than one minute, that pressure is recorded as the base pressure for the chamber that day. Error in the measurement of this value will be discussed in detail in Data Analysis section 3.2.

Setting the experimental water pressure is done by opening the leak valve, pumping out the water line below $2 \times 10^{-6}$ Torr and then reclosing the leak valve partially to remove air from the line. The water bulb is then opened and the leak valve is adjusted
until the desired pressure is reached. The pressure is monitored for drifting; once the pressure is observed to remain constant for 10 min or more the experiment is continued.

Temperature and pressure collection was begun prior to taking the infrared background. All temperatures & pressures are recorded twice a second by automatic data loggers; for temperature readings, a Pico Technology TC-08 USB using K type thermocouples, for pressures a Pico Technology ADC-11/12 USB is used. The time stamp for the file is recorded by hand. The cryostat is always cooled after the pressure has stabilized; liquid nitrogen was added to the cryostat and once the jacket temperature has begun to fall, the jacket heater was turned on as the heater may overheat if it is turned on prior. The Eurotherm controller automatically adjusts the heater output to maintain a constant temperature at the thermocouple attached to the copper ring clamp. Once the system has reached the desired temperature it is allowed to equilibrate for at least 10 min.

Backgrounds for “series” spectra collection are taken at times when temperature and pressure conditions are as stable and steady as possible in order to observe changes once the chamber conditions are altered. The settings for backgrounds are: gain is variable, aperture of 32 (iris diameter 5.08mm), resolution 4 cm\(^{-1}\), 7000-500 or 4000-500 cm\(^{-1}\), and 32 averaged scans. At two points in time during nucleation experiments the temperature and pressure were stable for background spectra. A background spectrum could be taken at room temperature to observe adsorption of water as it is introduced and as the temperature is decreased. Once a stable pressure has been established by opening and setting the leak valve, the cryostat is cooled by adding liquid nitrogen and setting a temperature for the Eurotherm controller to hold. A temperature chosen approximately
20 K warmer than the expected saturation temperature is held for ten or more minutes to allow for equilibration prior to a background spectrum being taken. The temperature observed at thermocouple 1 cools to approximately ten degrees colder than the set point of the Eurotherm, observing thermocouple 2. When a background is taken while the sample is cold and has finished equilibrating, it minimizes temperature effects from subsequent cooling. Strong absorbance features for the dusts studied are centered primarily between 500 - 2000 cm\(^{-1}\). Small shifts in the dusts absorbance features due to changes in temperature, interfere with the OH bend as well. Although no distinct features are noted in the OH stretch region, the dust and silicon undoubtedly absorb some light which may have some temperature dependence. The background for series collection always includes the silicon wafer and any dust present for the experiment, and thus we are blind to both.

Series collection begins as soon as possible after the background is taken, which is at most two minutes. Series spectra are taken 12.75 s apart with the same parameters as mentioned previously. With the series collection running the experiment can continue.

Temperature is decreased in steps, checking for nucleation at each step. Early experiments were conducted with a faster protocol than later experiments, with times between steps being held steady for a minute compared with several minutes for later experiments. Experiments done with faster protocols were repeated with slower protocols. The length of the temperature step prior to nucleation is noted in the table associated with each substrate. The time required for the mount to equilibrate at a new temperature, observed at thermocouple 1, depends on the step size. For half degree
temperature steps, the most common step size used, equilibration takes place in ~1 minute; for a two degree temperature step equilibration takes place in ~1.5 min.

Once nucleation is observed through a sharp rise in integrated peak area, 3000 to 3500 cm$^{-1}$ with a baseline of 2500 to 3500 cm$^{-1}$, the nucleation pressure is averaged over 60 s. The nucleation temperature is defined as midway between the ultimate and penultimate steps, and the uncertainty defined as the difference between the two. An experiment is shown in Figure 2.6 with corresponding spectra in Figure 2.3. Uncertainty in the nucleation temperature is dominated by the size of the temperature step. Error propagation will be discussed in detail in Data Analysis Section 3.2. Samples with strong water uptake prior to nucleation required a different method for defining post-nucleation temperature steps.
Figure 2.7: A typical experiment, Si-14, involves stepping down the temperature (gray diamonds, right axis) until the integrated infrared peak area (3500-3000 cm$^{-1}$ black squares, left axis) begins to increase sharply, indicating ice nucleation and growth. In this example, ice growth on silicon occurred near 275 min, with $P_n = 1.8 \times 10^6$ Torr, $T_n = 160.0$, $S_{crit} = 3.1$. Around 290 min, the temperature was reduced to grow a significant ice layer to allow for calibration of the thermocouple at the equilibrium point, as shown ~316 min.

Finding the absorption spectrum of water ice in the presence of non-crystalline water requires looking at changes in integrated peak area per unit time, $dA/dt$, as well as spectral subtractions. A spectral subtraction is done by taking the last spectrum in a temperature step and subtracting the spectrum observed earliest in the same step. By subtracting the spectrum taken earliest in the temperature step, features changing due to changes in temperature are minimized and previously adsorbed water is ignored. Two
spectral subtractions for experiment Clay-01 are shown in Figure 2.8 along with the four spectra used to create the subtractions. The sharp rise in integrated peak area corresponds with water ice observable in the second subtraction spectrum; the first subtraction only has adsorbed water present, both spectra correspond to the experiment shown in Figure 2.8.

Figure 2.8: Each spectrum is labeled with the collection time in min, which relates to Figure 2.9. Changes in the sample's spectrum, experiment Clay-01, can be better viewed by taking spectral subtractions. The subtractions on the right, B, are labeled with which spectra were used shown left, A. The subtraction spectrum on the right labeled 120.0 – 114.0 makes the absorbance due to ice easier to view with the adsorbed water removed. The subtraction spectrum labeled 112.0 – 104.0 only shows that more water has adsorbed to the sample during the penultimate temperature step. Spectral subtractions were done using the equation of $A - k \times B = \text{subtraction}$, $k = 1$ for all subtractions shown.
Figure 2.9: Experiment, Clay-01, conducted on clay showed uptake resulting in a non-negligible integrated infrared peak area (3500-3000 cm\(^{-1}\) black squares, left axis) prior to nucleation which increases sharply after 115 min indicating ice growth. \(P_n = 8.4 \times 10^6\) Torr, \(T_n 170.4\) K, and \(S_{\text{crit}} = 1.5\). Around 137 min, the temperature was reduced to grow a significant ice layer to allow for calibration of the thermocouple at the equilibrium point, as shown ~180 min.

2.5 Identifying Nucleation Temperature

To clearly define nucleation, a rise in dA/dt must be observed. Defining inflection was done both by eye and by using a forecasting test. The forecast test used a least-squares fit line of two hundred data points forecasted forward 10 min; the fit moves forward for each successive data point. When all integrated peak areas are observed to be
greater than the forecasted value, the first spectrum is noted to have a change in \(\frac{dA}{dt}\). A small number of data points that scatter high can fool the forecast test into observing a change in integrated peak area one step early. The first step where a change in integrated peak area is observed, by eye or forecast test, and where ice can be observed via spectral subtraction is deemed to be the step of nucleation. For experiments Whole JSC M-01 and Whole JSC M-02, a change in \(\frac{dA}{dt}\) observed both by eye and using the forecasting test was used to identify ice before it could be conclusively identified in the spectrum.

Once temperature steps have been defined prior to and after nucleation, temperatures within each step must be chosen. Average temperatures were not used, as small temperature fluctuations could cause nucleation, and should not be averaged out. Any distinct small dip in temperature in the post nucleation step is used as the post nucleation temperature, an example of just such a choice is shown in Figure 2.9 at \(\sim115\) min. A representative data point is chosen for the temperature step to make certain that a pre-nucleation temperature is chosen that does not bias results by choosing the coldest or warmest temperature present in the step.

Calibration of thermocouples is crucial, as there is no means of measuring the temperature directly in the beam path. Accounting for the slight difference between the temperature in the observing region and the temperature at the thermocouples is crucial, as even small errors in temperature lead to large errors in calculated \(S_{\text{crit}}\). Thermocouple 1 mounted near the silicon wafer is calibrated by using the frost point of ice as described by equation 8 from Murphy and Koop.\(^{33}\) With enough ice present the temperature can be adjusted until the infrared spectrum remains constant. With a known pressure and stable
ice, the temperature in the beam path can be calculated. The calculated temperature can be used to correct the observed temperature, with an average correction of -0.7 K for all experiments reported in this study. There is an example of the equilibrium just discussed observable near the end of the experiment shown in Figure 2.9.

Once the thermocouples have been calibrated, the expected vapor pressure over ice at the nucleation temperature is calculated using equation 7 from Murphy and Koop. The critical saturation ratio, $S_{\text{crit}}$, at the nucleation temperature is then defined at the observed water vapor pressure divided by the calculated equilibrium vapor pressure.

\begin{equation}
S_{\text{crit}} = \frac{P_v}{P_{\text{eq}}}
\end{equation}

2.6 JSC Mars-1 & Clay Adsorption/Desorption Experiments

Both smectite clay and JSC Mars-1 were observed to adsorb water. To be sure that all adsorbed water would be observed, a room temperature background was recorded, while the system was pumped down, and series collection was started prior to introduction of water vapor and cooling. This was done to make certain all water which adsorbed would be observed in subsequent IR spectra. This did result in shifts in spectral features of the dust. However OH stretch features are far stronger and high sensitivity was not as crucial. Calibration of thermocouples was accomplished a few days prior to adsorption/desorption experiments; a small offset, $a = 0.39$ K, (see section 3.1 for further details) was found for the mount at the temperature to be used for the experiments. With
both the temperature and pressure known, conditions near nucleation could be approached and maintained without generating ice.

Adsorption was done at the upper pressure limit of the experimental system, \(~7 \times 10^{-4}\) Torr. This was done to provide as much water vapor as possible to answer possible questions about saturation of the dust and to aid comparison with similar studies. Experiments on both smectite clay and JSC Mars-1 were made as identical as possible to aid in comparison.

To desorb water, the water source was simply removed from the system by closing the valve, as controlled reduction in pressure is unreliable. This is an extreme shift in conditions and not perfectly representative of natural martian environment. The temperature is also lowered so that the change in saturation conditions is less extreme. Desorption temperatures used are representative of atmospheric temperatures of Mars (\(~180\) K).

To allow as much time as possible for adsorption and desorption, no equilibration step was completed the day of the adsorption/desorption experiments. Thus the temperature uncertainty was estimated from experience with nucleation experiments. Behavior of both smectite clay and JSC Mars-1 will be discussed qualitatively in Results Section 4.2 under Adsorption/Desorption Experiments.
3. Data Analysis and Error Propagation

3.1 Calculating Critical Saturations

The saturation ratio is defined as the vapor pressure, $P_n$, divided by the equilibrium vapor pressure of bulk ice at the same temperature, $VP_{ice}$. The critical saturation ratio, $S_{crit}$, describes the conditions required to initiate ice nucleation. The final value of $S_{crit}$ has no units, as it is calculated as pressure over pressure, as shown in equation (4).

$$S_{crit} = \frac{P_n}{VP_{ice}}$$

Calculation of the critical saturation ratios, $S_{crit}$, requires calibrated measurements of temperature and partial pressure of water. Temperature at the time of nucleation is used to calculate $VP_{ice}$; uncertainty in this term will be discussed first starting with temperature calibration. Calibration of thermocouples which is done with ice in equilibrium as observed via FTIR of the OH stretch (3500-3000 cm$^{-1}$). With ice neither subliming or depositing, it is in equilibrium with the vapor, defined as $P_{eq}$. The temperature, $T_{eq}$, in the beam path can be calculated from equation 8 from Murphy and Koop$^{33}$ shown as equation (5) in this work. This equation requires pressures be in Pa and returns values in K.

$$T_{eq} = \frac{1.814625\ln(P_{eq}) + 6190.134}{29.12 - \ln(P_{eq})}$$

(5)
This value is then used to correct the observed temperature, $T_{\text{eqobs}}$, at the time of equilibrium using equation (6).

$$a = T_{\text{eqobs}} - T_{\text{eq}}$$  \hspace{1cm} (6)

The resulting correction, $a$, is used to then correct thermocouple measurements taken at the time of nucleation.

With temperature being stepped down successively looking for nucleation during each step, the nucleation temperature is between the temperature of the final step and the step just prior. An average, $T_{\text{ave}} = \frac{1}{2}(T_{\text{post}} + T_{\text{pre}})$, of the temperature observed during of the ultimate, $T_{\text{post}}$, and the penultimate, $T_{\text{pre}}$, steps are corrected using $a$, to give the nucleation temperature, $T_n$.

$$T_n = T_{\text{ave}} - a$$  \hspace{1cm} (7)

With the temperature at the time of nucleation, $T_n$, calibrated, the denominator of $S_{\text{crit}}$, can be calculated. The final calculation of $V P_{\text{ice}}$ can then be done using $T_n$, as the input to equation 8 from Murphy and Koop\textsuperscript{33} shown here as equation (8), which requires values in K and returns values in Pa.

$$V P_{\text{ice}} = e^{\left\{9.550426 - \frac{5723.265}{T_n} + 3.53068 \ln(T_n) - 0.00728332 T_n\right\}}$$  \hspace{1cm} (8)

In addition to calculating the true temperature of nucleation, the pressure, $P_n$, at the time of nucleation must be calculated. Pressure is measured and then converted to
voltage by the ion gauge that feeds to the PicoLog, as noted in section 2.2 Measurement of Experimental Variables. Measurement offsets from the automatic data collection must be corrected this is done to correct values recorded to values shown by the ion gauge on the front panel. The voltage from one minute of the PicoLog data is averaged; the result is corrected by adding 0.007 V and multiplied by 1.0033, to account for electronic losses, to become the final voltage used by the look up function.

Calibration of the ion gauge itself was done using purified water (Sigma Aldrich, lot # 0034HC) and a Baratron capacitance manometer (MKS model #127AA, 0.1 Torr full scale, with recent manufacturer’s calibration). This final voltage is then used as a look-up value to find the pressure from a table generated from equation as provided by the ion gauge manufacture.

\[
\text{Voltage} = \left( \frac{5}{4095} \right) \left[ (410 \times (10 - Z)) + (40 \times X.YY) \right]
\]  

Equation (9) is nearly identical to equation to that found in the manual noted in section 2.2, where the pressure is input in Torr as X.Yx10^2. However one additional digit has been added to generate a look-up table with one additional significant figure in order to remove the rounding error in the look-up function in Microsoft Excel 2003. Two corrections remain before this value from the look up table can be used: the residual air that could not be pumped away must be subtracted, and the biased response of the ion gauge to water must be accounted for.
Half of the base pressure is estimated to be air and half water. A new value, \( \omega \), is introduced that represents this ratio of water to air, defined in equation (10); we estimate \( \omega = 0.5 \).

\[
P_{bw} = \omega(P_{bw} + P_{bair}) \tag{10}
\]

\( P_{bw} \) represents the base pressure due to water, \( P_{bair} \) represents the base pressure due to air. Subtraction of \( P_{bair} \) will be discussed further once a second correction is introduced.

Ion gauges do not respond linearly to all gases, and a correction factor (or gas factor, \( GF \)), must be used to account for the differences in ionization of water vapor and \( N_2 \) for which the ion gauge is calibrated. The measured gas factor for water, \( GF_w \), for our system was 1.312 with a discussion of this value and error found in the next section. We have taken gas factor for air to be, \( GF_{air} = 1.00 \).

The observed base pressure, \( P_{obs} \), includes two components \( P_{bw} \) and \( P_{bair} \); also \( P_{obs} \) also includes the differences in detector response.

\[
P_{obs} = \left( \frac{P_{bair}}{GF_{air}} + \frac{P_{bw}}{GF_w} \right)
\]  

(11)

With equation (10) above, two equations and two unknowns allow for \( P_{bair} \) and \( P_{bw} \) to be individually solved for in terms of \( P_{obs} \), a measured value. \( P_{bair} \) can then be subtracted away from subsequent measurements, leaving only the pressure of water at any point in time.

The pressure observed at the time of nucleation retrieved from the look up table is corrected by subtracting \( P_{bair} \) then multiplying by \( GF_w \). The resulting pressure, \( P_n \), is in
Torr and represents all the water in the chamber. The final calculation of \( S_{\text{crit}} \) is simply a division of \( P_n \) by \( V_{P_{\text{ice}}} \) converted to Torr.

### 3.2 Uncertainties and the Propagation of Errors

Uncertainty in critical saturation ratios will be discussed in this section with an explanation of the propagation of errors used in calculating \( S_{\text{crit}} \). A diagram of equations used in the propagation of errors\(^{38} \) is shown in Figures 3.1 & 3.2. The uncertainty in \( S_{\text{crit}} \) \((\delta S_{\text{crit}})\) has roughly equal contributions coming from uncertainty in precision of our thermocouple measurements, \( \delta T \), and uncertainty in the ion gauge calibration factor for water, \( \delta G_{F_{\text{air}}} \). Starting with the equation for \( S_{\text{crit}} \), equation (4), the partial derivatives for each of the terms are shown as equations (12&13).

\[
\frac{\partial S_{\text{crit}}}{\partial P_n} = \frac{1}{V_{P_{\text{ice}}}} \quad \frac{\partial S_{\text{crit}}}{\partial V_{P_{\text{ice}}}} = \frac{-P_n}{V_{P_{\text{ice}}}}^2 \quad (12&13)
\]

The uncertainty in \( V_{P_{\text{ice}}} \), \((\delta V_{P_{\text{ice}}})\), will be discussed first. The uncertainty in this value is dominated by the reproducibility of the thermocouple calibration. As the vapor pressure over ice is calculated from equation 8 from Murphy and Koop\(^{33} \) (shown in this work as equation (8)), \( \delta V_{P_{\text{ice}}} \) was evaluated from the uncertainty in the input value, \( T_{\text{eqobs}} \).

Calculating the uncertainty in \( V_{P_{\text{ice}}} \) was done by taking \((T_{\text{eqobs}} + \delta T_{\text{eqobs}})\) and \( T_{\text{eqobs}} \), as inputs into equation (8) and using the difference as \( \delta V_{P_{\text{ice}}} \). This was done rather than differential error propagation, as equation (8) is a fit equation and will not accept inputs outside of the allowed range. Uncertainty in \( T_{\text{eqobs}} \) is estimated to be the difference
between the final temperature observed with no change in integrated peak area over time, and the nearest temperature showing a $\text{d}A/\text{d}t$ not equal to zero.

$T_{\text{ave}}$ and the calibration factor ($a$) are the two values used in calculating $T_n$, shown in equation (7). The uncertainty in $a$ ($\delta a$) is dominated by the reproducibility of the calibration factor, (0.5 K). The calculation for $\delta a$ is shown in equation (14).

$$\delta a = \sqrt{(0.5)^2 + (\delta T_{\text{eqobs}})^2}$$  \hspace{1cm} (14)

With the difference between $T_{\text{pre}}$ and $T_{\text{post}}$ dominating for larger steps, $\delta T_{\text{ave}}$ is non-negligible. The two values input values, $T_{\text{pre}}$ and $T_{\text{post}}$, have uncertainties that must also be accounted for along with the step size itself. The calculation for $\delta T_{\text{ave}}$ is shown below as equation (15).

$$\delta T_{\text{ave}} = \sqrt{\left(\frac{\partial T_{\text{ave}}}{\partial T_{\text{pre}}} \cdot \delta T_{\text{pre}}\right)^2 + \left(\frac{\partial T_{\text{ave}}}{\partial T_{\text{post}}} \cdot \delta T_{\text{post}}\right)^2 + \left(\frac{1}{2} \left(T_{\text{pre}} - T_{\text{post}}\right)^2\right)}$$  \hspace{1cm} (15)

$\delta T_{\text{pre}}$ and $\delta T_{\text{post}}$ represent the temperature drift during a temperature step, 0.1 K.

Uncertainties in $P_n$ are dominated by the ion gauge calibration factor for water ($GF_w$), which was found by making 7 measurements over the course of 11 months and averaging them. Four terms go into calculating $\delta P_n$, as shown in equation (16).

$$\delta P_n = \sqrt{\left(\frac{\partial P_n}{\partial P_{\text{nobs}}} \cdot \delta P_{\text{nobs}}\right)^2 + \left(\frac{\partial P_n}{\partial P_{\text{air}}} \cdot \delta P_{\text{air}}\right)^2 + \left(\frac{\partial P_n}{\partial GF_{\text{air}}} \cdot \delta GF_{\text{air}}\right)^2 + \left(\frac{\partial P_n}{\partial GF_w} \cdot \delta GF_w\right)^2}$$  \hspace{1cm} (16)
\( \delta P_{\text{obs}} \), was found to be 4% of the pressure measured. This value was found by averaging one minute of pressure data at the time of nucleation for each experiment and taking those values averaging them. This value is used as the error for \( \delta P_{\text{obs}} \) for all experiments; this was done to average out intermittent electronic noise. The uncertainty \( \delta G F_{\text{air}} \) is deemed to be 0. The difference between literature values for \( G F_w \) and the measured value for our system is deemed to be \( \delta G F_w \). The uncertainty in the base pressure due to air, \( \delta P_{\text{air}} \), will be covered below.

Solving for \( P_{\text{air}} \) using equation (11) and substituting \( P_w \) and \( \omega \) for \( P_{\text{air}} \) using equation (10) gives equation (17).

\[
P_{\text{air}} = G F_{\text{air}} \cdot P_{\text{obs}} \left[ 1 + \frac{P_{\text{obs}}}{G F_w} \left( \frac{\omega}{1 - \omega} \right) \right]^{-1}
\]

(17)

This equation is in terms of previously mentioned variables: \( G F_{\text{air}} \), \( G F_w \), \( P_{\text{obs}} \), and \( \omega \). The first of two additional values that are needed to calculate \( \delta P_{\text{air}} \) is \( \delta P_{\text{obs}} \), which we estimate to be \( 5 \times 10^{-8} \) Torr. The final value \( \delta \omega \), is estimated to be 0.25.
3.1 Equation Schematic 1

\[ S_{\text{crit}} = \frac{P_n}{V_{P_{\text{ice}}}} \]  
\[ \text{eq}(4) \]

\[ \delta S = \sqrt{\left( \frac{\partial S}{\partial P_n} \cdot \delta P_n \right)^2 + \left( \frac{\partial S}{\partial V_{P_{\text{ice}}}} \cdot \delta V_{P_{\text{ice}}} \right)^2} \]

\[ \delta P_n \text{ see next page} \]

\[ \delta V_{P_{\text{ice}}} = \text{eq}(8)[T_n + \delta T] - \text{eq}(8)[T_n] \]

\[ T_n = T_{\text{ave}} - \alpha \]

\[ \alpha = T_{\text{eqobs}} - \text{eq}(5)[P_{\text{eq}}] \]

\[ T_{\text{ave}} = \frac{1}{2}(T_{\text{pre}} + T_{\text{post}}) \]

\[ \delta T_{\text{ave}} = \sqrt{\left( \frac{\partial T_{\text{ave}}}{\partial T_{\text{pre}}} \cdot \delta T_{\text{pre}} \right)^2 + \left( \frac{\partial T_{\text{ave}}}{\partial T_{\text{post}}} \cdot \delta T_{\text{post}} \right)^2 + \left( \frac{T_{\text{pre}} - T_{\text{post}}}{2} \right)^2} \]

\[ \delta T_{\text{pre}} = 0.1 \text{ K} \quad \delta T_{\text{pre}} = 0.1 \text{ K} \]

\[ \delta T_{\text{eqobs}} \text{ see table of results} \]

**Figure 3.1:** A diagram of the equations used in the propagation of error in calculating \( \delta V_{P_{\text{ice}}} \) is shown above. Values used in calculating \( \delta V_{P_{\text{ice}}} \) can be found in the table of results for each experiment. Partial derivatives, see Appendix B, are used in calculating uncertainties.
3.2 Equation Schematic 2

\[
\frac{\Delta S_{\text{crit}}}{\Delta P_n} = \frac{1}{VP_{\text{ice}}}
\]

\[
P_n = \left( P_{\text{obs}} - P_{\text{air}} - \frac{1}{GF_{\text{air}}} \right) \cdot GF_{w}
\]

\[
\Delta \delta P_n = \sqrt{\left( \frac{\partial P_n}{\partial P_{\text{obs}}} \cdot \Delta P_{\text{obs}} \right)^2 + \left( \frac{\partial P_n}{\partial P_{\text{air}}} \cdot \Delta P_{\text{air}} \right)^2 + \left( \frac{\partial P_n}{\partial GF_{\text{air}}} \cdot \Delta GF_{\text{air}} \right)^2 + \left( \frac{\partial P_n}{\partial GF_{w}} \cdot \Delta GF_{w} \right)^2}
\]

\[
\Delta P_{\text{obs}} = 0.04 \cdot P_{\text{obs}}
\]

\[
\Delta GF_{\text{air}} = 0
\]

\[
\Delta GF_{w} = 1.312 - 1.1
\]

\[
P_{\text{obs}} = \frac{P_{\text{air}} + P_{\text{bw}}}{GF_{\text{air}} \cdot GF_{w}}
\]

\[
P_{\text{air}} = GF_{\text{air}} \left( P_{\text{obs}} - \frac{P_{\text{bw}}}{GF_{w}} \right)
\]

\[
P_{\text{bw}} = \omega \left( P_{\text{bw}} + P_{\text{air}} \right)
\]

\[
P_{\text{air}} = GF_{\text{air}} \cdot P_{\text{obs}} \left[ 1 + \frac{P_{\text{obs}}}{GF_{w}} \left( \frac{\omega}{1 - \omega} \right) \right]^{-1}
\]

\[
\Delta P_{\text{air}} = \sqrt{\left( \frac{\partial P_{\text{air}}}{\partial GF_{\text{air}}} \cdot \Delta GF_{\text{air}} \right)^2 + \left( \frac{\partial P_{\text{air}}}{\partial GF_{w}} \cdot \Delta GF_{w} \right)^2 + \left( \frac{\partial P_{\text{air}}}{\partial P_{\text{obs}}} \cdot \Delta P_{\text{obs}} \right)^2 + \left( \frac{\partial P_{\text{air}}}{\partial \omega} \cdot \Delta \omega \right)^2}
\]

\[
\Delta GF_{\text{air}} = 0
\]

\[
\Delta P_{\text{obs}} = 5 \times 10^{-8}
\]

\[
\Delta GF_{w} = 0.212
\]

\[
\Delta \omega = 0.25
\]

Figure 3.2: A diagram of the equations used in the propagation of error in calculating \(\Delta P_n\) is shown above. Values used in calculating \(\Delta P_n\) can be found in the table of results for each experiment. Partial derivatives, see Appendix B, were used in calculating uncertainties.
4. Experimental Results

4.1 Water Ice Nucleation Studies

4.1.1 Water Ice Nucleation on Silicon

Due to the pressures and temperatures of the experiments, heterogeneous nucleation on the silicon substrate itself is an unavoidable experimental constraint. The nucleation conditions for ice growth on the silicon wafer form an upper bound on the $S_{\text{crit}}$ values that can be observed on surrogate dust materials. Results for nucleation experiments from fourteen experiments on a total of three silicon wafers are shown in Figure 4.1. Experimental calculations, and results for each experiment are shown in Table 4.1. Observed values of $S_{\text{crit}}$ range from 1.7 at 178.8 K to 3.1 at 160.0 K. Taken with results from other studies, our observations point to higher $S_{\text{crit}}$ values at lower temperatures. A cluster of 9 experiments, performed between 174 and 177 K (Figure 4.1) shows the reproducibility of $S_{\text{crit}}$ values that were taken over the course of all nucleation experiments.
Figure 4.1: Nucleation threshold saturation ratios measured for water ice nucleation on silicon as a function of temperature (open circles). The black dotted line shows a linear best fit through the data ($S_{\text{crit}} = -0.0644 T_n + 13.3$). This fit line will be repeated on subsequent plots.

The $S_{\text{crit}}$ values are inversely related to the nucleation temperature, with an empirical fit of $S_{\text{crit}} = -0.0644 T_n + 13.3$ ($R^2 = 0.7$). This fit is not intended for extrapolation outside the experimental region, as there will be an asymptotic approach to $S = 1$ at warmer temperatures, and there is no data colder than 160 K. All nucleation results in this study are fit linearly, as there is insufficient information to constrain alternative functional forms. The fit for ice nucleation on silicon will serve as a baseline.
for comparison for further experiments on dust making comparisons between data sets
simpler.

Water ice is has three visible features in the region 3000-3500 cm$^{-1}$, some
temperature dependence in both peak positions and amplitude. This temperature
dependence for the OH stretch has been noted for hexagonal ice.$^{39,40}$ We also observe
variations in spectra for some experiments with absorption features shifting to longer
wavelengths and broadening, which can be seen in Figure 4.2 for experiment Si-05.
Similar spectral features were observed for ice aerosols generated in the lab by Clapp et
al.$^{40}$ who attribute these spectral shifts to Mie scattering and temperature dependent
changes to the OH stretching absorbance. These distortions to the OH stretch of water
ice are observed with other substrates, notably ATD, and Whole JSC Mars-1. Smectite
clay and Light fraction JSC Mars-1 were not observed to display this phenomenon. No
systematic relationship causing these distortions has been noted; neither temperature nor
pressure appears to be the cause.
Figure 4.2: All spectra shown above are from the same experiment Si-05 conducted on silicon, with collection times labeled in min. Water is not observed to significantly adsorb to silicon so no distortion of the spectra can be attributed to adsorbed water. All spectra above are of water ice after the time of nucleation which occurred at (134.5 min). The conditions for this experiment were $P_n = 3.5 \times 10^5$ Torr, $T_n = 175.6$, and $S_{cm} = 2.0$.

Water ice has always been observed to display three distinct overlapping features within the OH stretching region. Three features can be observed in all the spectra shown in Figure 4.2. Instances where the more traditional spectrum appears overlaid with spectra that show scattering have been also been observed. Experiments where spectra were observed to transition from having significant scattering to less scattered and back, have been observed (Si-05 & Si-03).
The reproducibility of experimental results is of paramount importance in any scientific endeavor. Re-testing of $S_{\text{crit}}$ on silicon in a narrow temperature range was done over the course of all experiments conducted in this study. A total of nine experiments were carried out at temperatures between 174 and 177 K, which provided comparison with literature results\textsuperscript{1} and showed consistent behavior of the apparatus. The observed variation of 1.7 to 2.6 in $S_{\text{crit}}$ shows repeatability within the calculated uncertainty. Three silicon substrates were tested and no dependence was observed; the wafer used for each experiment has been listed in Table 4.1. These results are in agreement with nucleation studies on silicon done at warmer temperatures by Fortin et al. and Trainer et al.\textsuperscript{1,41} These studies found values for $S_{\text{crit}}$ of 2.3 $\pm$ 0.3 at 170 K for Fortin and 3 $\pm$ 1 for Trainer. Results observed by Trainer et al.\textsuperscript{41} at 165 K show $S_{\text{crit}}$ values as high as 5 with an uncertainty of 1, required to nucleate on silicon which is higher than predicted by this study ($S_{\text{crit}} = 2.6 \pm 0.7$). As only two data points in this set are colder than 165 K, additional measurements would likely improve our understanding of $S_{\text{crit}}$ at colder temperatures.
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<th>$T_{\text{exp}}$ [K]</th>
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<td>1.7E-08</td>
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</table>

A description of all column headers is found in Appendix A: List of Calculated and Observed Variables.
4.1.2 Water Ice Nucleation on Arizona Test Dust

The goal of this work is to make measurements of onset conditions for water ice nucleation under martian conditions for analogs of martian dust particles. Arizona Test Dust (ATD) chosen because of its use in previous $S_{\text{crit}}$ studies.\textsuperscript{10,13,27} Saturation ratios required to nucleate water ice on ATD were similar to those observed for nucleation on silicon, as shown in Figure 4.3. When measurement uncertainty is taken into consideration the two fit lines are similar with results from one data set overlapping the other. Results for ATD ranged from $S_{\text{crit}} = 1.1$ at 185.0 K to $S_{\text{crit}} = 2.3$ at 160.7 K and $S_{\text{crit}} = 3.2$ at 163.3 K. The fit line through the eleven data points has an equation of $S_{\text{crit}} = -0.0720 * T_n + 14.4$, $R^2 = 0.8$. Table 4.2 shows conditions, and calculations, and results for these experiments. Note that Figure 4.3 retains the fit line for silicon but not the data points; the data points shown are for ATD. Subsequent plots will follow this pattern of retaining the fit line from previous results and showing only data points from the dust under discussion. The similarity between the results for ice nucleation on ATD and silicon was of considerable surprise, as was the temperature dependence in nucleation results. Studies point to ATD as being a relatively good deposition mode nucleator with $S_{\text{crit}} = 1.0 - 1.3$ at 230 K,\textsuperscript{13} and $S_{\text{crit}} = 1.0 - 1.1$ at 197 K,\textsuperscript{10} with both studies showing little to no temperature dependence. However these studies looked at saturation values on ATD at higher temperatures more representative of Earth and so would not necessarily predict higher $S_{\text{crit}}$ values at lower temperatures more representative of Mars.
Figure 4.3: Nucleation threshold saturation ratios measured for water ice nucleation on Arizona Test Dust as a function of temperature (solid diamonds). The black dashed line shows a linear best fit through the data \( S_{\text{crit}} = -0.0720 \times T_{\text{nuc}} + 14.4 \). The black dotted line shows the best fit through the data from Figure 4.1 for ice nucleation on silicon.

Experiments performed with ATD showed absorbance features for ice similar to that seen in Figure 2.3 for most experiments. Variation in the OH stretch like that observed in Figure 4.4A was observed for experiments ATD-03, ATD-05 and ATD-06, further data about each experiment can be found in section 2.3.2 and Table 4.2. Spectra from experiments ATD-05 and ATD-09 are shown in Figure 4.4, which shows absorbance shifted to longer wavelengths (lower frequency). ATD has been observed to show moderate distortion of the ice stretching region prior to nucleation, it is most likely
due to scattering, however this feature is weak. Qualitative comparison between peak areas for adsorbed water on ATD and smectite/JSC Mars-1 suggests that ATD adsorbed considerably less water. However note that identical weights of dust were not used, constrained by the need to cover the wafer as uniformly as possible while maintaining strong signal to the detector.

**Figure 4.4:** Experiments ATD-05 (A), and ATD-09 (B), were both conducted on Arizona Test Dust. Note that all spectra are labeled with collection times in min. The first spectrum shown for each plot was taken prior to nucleation, with all subsequent spectra containing water ice.

Repeatability of results on dust that could be altered by exposure and so be pre-activated was addressed by performing two repeat experiments. Results for experiments ATD-03 ($S_{\text{crit}} = 1.5 \pm 0.3$, 5.2x10^{-5} Torr, 179.1 K) and ATD-02 ($S_{\text{crit}} = 1.5 \pm 0.3$, 5.2x10^{-5} Torr, 179.2 K), which were performed consecutively with the same water partial pressure and a drying step between, are indistinguishable within the calculated errors. The drying between experiments ATD-03 and ATD-02 consisted of $S_{\text{crit}} < 0.1$ being held for 5 min before re-cooling. With no significant reduction in $S_{\text{crit}}$ observed for the second experiment, pre-activation of dust was not observed. Drying could possibly have
deactivated the dust, in which case all experiments would have been performed on
deactivated dust, as drying is done overnight on other runs and to higher temperatures (room temperature). It is also possible that all experiments were performed on active dust, with no observation of deactivation.
A description of all column headers is found in Appendix A: List of Calculated and Observed Variables.

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<th>Designation</th>
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4.1.3 Water Ice Nucleation on Smectite Clay

Smectite clay proved to be a much better nucleator than the silicon substrate alone or ATD. Observed values for eleven nucleation experiments are shown in Figure 4.5, with temperatures ranging from 156 to 174 K. These results also showed temperature dependence, $S_{\text{crit}} = -0.105T + 19.3$ with $R^2 = 0.7$. Table 4.3 shows experimental conditions, calculations, and results for these experiments. With the strong uptake of water observed before ice nucleation in most experiments, observation of temperature dependent $S_{\text{crit}}$ values were unexpected. With clay showing the steepest slope in $S_{\text{crit}}$ for any of the substrates, it seems temperature dependent behavior might become more of a factor at lower temperatures for better nucleators, possibly due to switching to a new mechanism at lower temperatures.
Figure 4.5: Nucleation threshold saturation ratios measured for water ice nucleation on smectite clay as a function of temperature (black squares). The black solid line shows a linear best fit through the data \( S_{\text{crit}} = -0.105 \times T_{\text{nuc}} + 19.3 \). The black dashed line is the best fit to the data for ATD, and the black dotted line is the fit for results on Silicon.

Definite uptake of water by clay was observed prior to nucleation. Figure 4.6 and the corresponding Figure 4.7 for experiment Clay-04 show spectra with adsorbed water prior to nucleation and the subsequent change in absorption features that occur when ice has formed. As discussed previously, adsorbed water has a distinctly different peak shape, exhibiting only one or two features, compared to three in the well-characterized peak shape of water ice seen later in the experiment. The times noted for each spectrum in Figure 4.7 correspond to time on the X-axis in Figure 4.6. Note in this figure when
integrated peak area rises (~160 min) the spectra begin exhibiting water ice features, and the change in total peak area per minute increases. Nucleation experiments were not carried out on clay samples that had been allowed to saturate with adsorbed water. Full saturation was never observed for any sample of clay. Adsorption will be discussed further in 4.2.1 Adsorption/Desorption Experiments on Smectite Clay.

![Graph showing time and peak area data](image)

**Figure 4.6:** Experiment Clay-04 has temperature (gray, right axis) stepping down until the integrated infrared peak area (3500-3000 cm\(^{-1}\), black, left axis) begins to increase sharply, indicating ice nucleation and growth. In this example, ice growth on silicon occurred ~151 min, with \(P_n = 5.3 \times 10^6\) Torr, \(T_n = 168.6\), and \(S_{\text{crit}} = 1.3\). Around 163 min, the temperature was reduced to grow a significant ice layer to allow for calibration of the thermocouple at the equilibrium point, as shown ~211 min.
Figure 4.7: Infrared spectra of a nucleation experiment, Clay-04. Spectra shown are the same as shown previous in Figure 2.4, spectra here are shown only from 2500-4000 cm$^{-1}$. Each spectrum is labeled with the collection time in min, which relates to Figure 4.6. Nucleation of water ice occurred after $\sim$151 min. Note the OH stretch for non-crystalline water can be clearly seen in this between 3000 and 3500 cm$^{-1}$, which has a distinctly different shape than water ice.

Two experiments Clay-03 and Clay-04 were carried out at nearly identical pressures to test repeatability and for pre-activation. They were carried out on consecutive days, and although the second day did result in a reduced $S_{\text{crit}}$ value (1.5 then 1.3 both with an uncertainty of 0.3), results are well within experimental uncertainty. Experiment Clay-01 was performed after experiment Clay-04 and resulted in a higher $S$ value at a higher temperature, which is the opposite of the behavior expected if pre-
activation occurred. Thus, we conclude that our experiments are likely conducted uniformly on non-pre-activated or completely pre-activated dust.
A description of all column headers is found in Appendix A: List of Calculated and Observed Variables.

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Table 4.3 Smectite Clay Experimental Conditions: Observed and Calculated Variables
4.1.4 Water Ice Nucleation on Whole JSC Mars-1

Separation of JSC Mars-1, as discussed in section 2.3.4, Preparing JSC Mars-1 Regolith Simulant, produced two fractions, a light colored top layer and a darker bottom layer, which were tested independently for their nucleation properties. Results for fractionated JSC Mars-1 will be discussed in the next section.

In experiments performed on un-fractionated (whole) JSC Mars-1 samples, the results showed strong temperature dependence and required lower saturation ratios than either ATD or silicon, but not quite as low as for ice nucleation on smectite clay (Figure 4.8). With experiments spanning from 155 to 180 K on un-fractionated JSC Mars-1, empirically fitting nucleation results for thirteen experiments gives an equation of $S_{\text{crit}} = -0.0920T + 17.6$ $R^2 = 0.9$. Table 4.4 shows experimental conditions, calculations, and results for these experiments. The slope of this data set is intermediate between ATD and smectite clay with definite temperature dependence.
Figure 4.8: Nucleation threshold saturation ratios measured for water ice nucleation on whole JSC Mars-1 as a function of temperature (black triangles). The solid gray line shows a linear best fit through the data ($S_{\text{crit}} = -0.0920 \cdot T_{\text{nuc}} + 17.6$). The black solid line is the best fit for data from smectite clay, black dashed line is for ATD, black dotted line is for Silicon.

Spectra from a representative experiment are shown in Figure 4.9. Adsorption of water is seen prior to nucleation, similar to the behavior seen for smectite clay, with corresponding Figure 4.10 showing temperature steps and integrated peak area.

Discerning if whole JSC Mars-1 takes up more or less water than the smectite samples was impossible in these experiments. It is difficult to compare quantities of adsorbed water without known masses of material and controlled distribution on the wafer which
was not achieved. One experiment, Whole JSC M-06, was observed to show scattering like that in Figure 4.2.

Figure 4.9: Infrared spectra of a water ice nucleation on Whole JSC Mars-1, experiment Whole JSC Mars-12 is shown. Each spectrum is labeled with the collection time in min, which relates to Figure 4.10. Nucleation of water ice occurred ~157 min. Note the OH stretch feature (3000 and 3500 cm\(^{-1}\)) for adsorbed water prior to nucleation can be observed as well as crystalline water ice after nucleation.
Figure 4.10: Experiment Whole JSC M-12 has temperature (gray, right axis) stepping down till nucleation, when the integrated infrared peak area (3500-3000 cm$^{-1}$ black, left axis) begins to increase sharply, indicating ice nucleation and growth. In this example, ice growth on Whole JSC Mars-1 nucleation occurred ~157 min, with $P_n = 7.0 \times 10^{-7}$ Torr, $T_n = 155.4$, and $S_{crit} = 3.8$. Calibration of the thermocouple at the equilibrium point is shown at ~262 min.

Three experiments (Whole JSC M-04, Whole JSC M-05, and Whole JSC M-06) were carried out to test repeatability on un-fractionated JSC Mars-1. Results were very repeatable, $1.7 \leq S_{crit} \leq 1.8$; temperatures ranged between 170.3 and 170.7 K and pressure between $1.1\times10^{-5}$ to $1.0\times10^{-5}$ Torr.
A description of all column headers is found in Appendix A: List of Calculated and Observed Variables.
4.1.5 Water Ice Nucleation on Fractionated JSC Mars-1

Nucleation conditions for two fractions of JSC Mars-1 Regolith Simulant (JSC Mars-1) were tested independently. Results from a total of seven experiments done on the fractionated JSC Mars-1 are shown in Figure 4.15, with data and fits for the light fraction shown. Lighter and darker colored dust fractions have been observed in the Gusev crater by the Mars rover Spirit.42

Our light and dark fractions of JSC Mars-1 were both observed to adsorb water prior to nucleation of water ice. Relative amounts of adsorbed water are difficult to compare, but the signal for adsorbed water was considerably stronger for the light fraction. Results from the light fraction showed absorption spectra similar to those for water uptake on smectite clay, with a continuous adsorption of water. However some experiments showed changes in the adsorption rate that corresponded to each change in temperature. Thus the forecasting technique used for identifying ice nucleation on other dust analogs was used less rigorously for ice nucleation on the light fraction.

Fluctuations in dA/dt can be observed in the experiment shown in Figure 1.11.
Figure 4.11: Experiment Light JSC M-05 involves stepping down the temperature (gray, right axis) and observing the integrated infrared peak area (3500-3000 cm$^{-1}$ black, left axis). In this experiment identification of ice was done using spectral subtractions. There are slight fluctuations in dA/dt that correspond to changes in temperature that prevent accurate application of the forecasting test. Nucleation was determined to occur at \( \sim 104 \) min, using spectral subtractions shown in Figure 4.12. Pressure at the time of nucleation was \( 7.2 \times 10^{-6} \) Torr, with \( T_n = 169.9 \) and \( S_{\text{crit}} = 1.4 \).

Spectral subtractions were required to identify ice nucleation on the light fraction. The absorbance for crystalline ice can be identified in the subtraction spectrum below.

The light fraction also showed better nucleation properties than the unfractionated sample, which was unexpected. A fit to the seven experiments, for temperatures between 159.6 to 182.0 K, gives an equation of \( S_{\text{crit}} = -0.0469T_n + 9.38 \) $R^2 = 0.8$. This fit shows less temperature dependence than other analogs tested as well as being a better nucleator.
(lower $S_{\text{crit}}$ values) across the range of temperatures tested. The fit and data are shown in Figure 4.15. The lower threshold required to nucleate on the light fraction was unexpected and puzzling. How could a fraction have better nucleation properties than the whole sample from which it was derived?

**Figure 4.12:** Infrared spectra of water uptake on the light fraction of JSC Mars-1, experiment Light JSC M-05 is shown (A). Each spectrum is labeled with the collection time in min, which relates to Figure 4.11. Changes can be better viewed by taking spectral subtractions (B). Each subtraction is labeled with the spectra used. The subtraction spectrum labeled 100.1 - 91.0 shows only that more water has adsorbed to the sample during the penultimate temperature step. The subtraction on the right, labeled 109.1 - 101.1, makes the absorbance due to ice easier to view with the adsorbed water removed. Spectral subtractions were done using the equation of $A - kB = \text{subtraction}$ with $k$ values shown in the legend. Adsorption of water is likely occurring concurrently with ice growth, using a $k = 1.05$ for subtraction 109.1 - 101.1, shows water ice more clearly. A small additional amount of adsorbed water has likely been adsorbed after spectrum 109.1 was collected.

Experiments conducted on the dark fraction showed significant scattering, distorting the absorption spectra and in all cases making identification of the onset of crystalline water impossible. Four experiments were performed between temperatures of 165 and 180 K. Figure 4.13 shows an example experiment on Dark Fraction JSC, where
scattering was observed to create a dip in the absorbance spectrum at ~3500 cm\(^{-1}\), increasing the integrated peak area between 3000 and 3500 cm\(^{-1}\). The uptake of adsorbed water in all previous experiments was observed to be steady and continuous, whereas this phenomenon was observed to initiate upon a reduction in temperature like that of water ice. Because this behavior was so different than that observed for the integrated peak area for water deposition on silicon, ATD and clay, the described nucleation experiment protocol using dA/dt inapplicable for experiments on the dark fraction.

Figure 4.13: Infrared spectra of a nucleation experiment on dark fraction JSC Mars-1. Each spectrum is labeled with the collection time in min, which relates to Figure 4.14. A change in dA/dt occurred at ~80 min. Note the region between 3500-3000 cm\(^{-1}\) does not show sharp features like those shown previously for water ice in Figure 2.3.
Figure 4.14: With the temperature (gray diamonds, right axis) stepping down until the integrated infrared peak area (3500-3000 cm⁻¹ black squares, left axis) begins to increase sharply. The distinct change in dA/dt at ~80 min does not correspond to spectra that can be identified as water ice. The water pressure at the time was $2.0 \times 10^{-5}$ Torr, in contrast to all previous experiments. Calibration of the thermocouple is not shown at ~230 min.

The rounded features in the absorption spectra (Figure 4.13) do not rule out adsorbed water being responsible for the scattering. The difference in absorbance may also point to another form of ice other than hexagonal. The possibility that there is a sudden onset of water uptake also cannot be ruled out.
Figure 4.15: Nucleation threshold saturation ratios measured for ice nucleation on Light Fraction JSC Mars-1 as a function of temperature (open squares). The gray dashed line shows a linear best fit through the data ($S_{\text{crit}} = -0.0469\times T_{\text{nuc}} + 9.38$). The dark closed circles are the retest of Whole JSC Mars-1, with error bars not shown; errors are listed in Table 4.6. The solid gray line is the best fit for data from Whole JSC Mars-1; black solid line is for smectite clay; black dashed line is for ATD; black dotted line is for silicon.

4.1.6 Water Ice Nucleation on Re-Test JSC Mars-1

To evaluate the surprising observation that the light fraction of JSC Mars-1 (open squares and dashed gray line Figure 4.15) appeared to nucleate ice at lower $S_{\text{crit}}$ values than observed for the Whole JSC Mars-1 (gray solid line Figure 4.15), a re-test using the control sample was undertaken. To address the concern that the experiments on the light fraction were more sensitive to ice onset conditions due to a higher fraction of incident
infrared radiation (measured by peak to peak voltage of the interferogram) passing through the dust and reaching the detector. Experiments were designed to test for bias that could result.

We returned to the control sample, which underwent the same grinding and centrifuge procedure as the fractionated JSC Mars-1 samples. The sample was remixed prior to application, just as the Whole JSC Mars-1 was remixed prior to application. The control sample was applied sparingly to the silicon wafer, permitting a larger fraction of light from the infrared beam to reach the detector. The dust was deposited to mimic previous peak-to-peak signal values for the light fraction and un-fractionated experiments so that detection limits would not be influenced by infrared throughput. Peak-to-peak voltages and gain settings are listed in Table 4.6 for these experiments. Uniform coverage was maintained by cleaning and reapplication of dust if a uniform application was not obtained.

Five re-test experiments (Re-test JSC M-01 through Re-test JSC M-05), were performed on control samples of JSC Mars-1. These re-test experiments found $S_{\text{crit}}$ values (black circles Figure 4.15) more similar to those of the light fraction (open squares, and gray dashed line Figure 4.15) than to the values seen with original whole JSC data (solid gray line, Figure 4.15). Two experiments (Re-test JSC M-02 and Re-test M-04) had detector voltages (~14 V, gain = 2) similar to that of the light fraction data set (~7 V, gain 1 & ~12 V, gain = 2). The three remaining experiments (Re-test JSC M-01, Re-test JSC M-03, and Re-test JSC M05) had detector voltages (~14 V, gain 8) similar to those of the first set of Whole JSC Mars-1 (~10 V, gain 8). All five new data points
show consistent behavior and temperature dependence, similar to that displayed by the light fraction data, indicating that the throughput of light does not affect the observation of the onset of water ice in the infrared spectra (Figure 4.15). Although the temperature range of the second set of Whole JSC Mars-1 data is limited (159.6 to 164.0 K), this control set does suggest that differences in sample handling could have affected results, making the control sample of JSC Mars-1 sample a more efficient nucleator than the original whole sample.

Differences between the first set of Whole JSC Mars-1 and the control (re-mixed) experiments include: the person preparing the sample and the centrifuge process. Sample application and chamber reassembly for Whole JSC Mars-1 was carried out by the same individual (B.P.) for both the Whole JSC Mars-1 and re-mixed control. Results were consistent despite changes in dust quantity (heavy application of un-fractionated JSC Mars-1 did little to change $S_{\text{crit}}$ value). The only consistent difference between the Whole JSC Mars-1 and the re-mixed control was sample centrifugation step and preparer.

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A description of all column headers is found in Appendix A: List of Calculated and Observed Variables.
4.2 Adsorption/Desorption Experiments

With the observation of water adsorbing to the smectite clay and JSC Mars-1 regolith simulant, experiments were designed to understand how adsorption was affecting the dust over the course of the experiment and to directly assess if saturation of the substrate could be affecting results. Quantification of the water uptake was not attempted because the mass and specific surface area of the samples was not determined.

4.2.1 Water Adsorption/Desorption on Smectite Clay

Smectite clay showed uptake of water not when the sample was initially exposed to water vapor, but only when temperatures were reduced. Both uptake and desorption steps can be seen in Figure 4.16. Two distinct adsorption rates can be seen: an initial fast uptake that occurs during the cooling step, followed by a slow continuous uptake of water (~75 to ~200 min). As distribution and quantity of dust over the wafer is not perfectly even, comparison with a second dissimilar sample would be invalid, only the relative behavior will be discussed.

The initial adsorption accounts for the majority of water taken up, which happens during roughly the first hour after cooling for this experiment. It should be noted that the clay is not observed to saturate even after 3 h of exposure to approximately $S_{\text{crit}} = 0.95$. Observation of adsorbed water in the infrared spectrum has bearing on nucleation experiments because the OH stretch absorption is in the same location for water. Adsorbed water also likely plays a role in nucleation. Steady uptake observed by infrared spectroscopy shows that nucleation experiments conducted on smectite clay would have
been conducted during the second slow uptake phase on clay that has taken up an appreciable amount of water but which remains unsaturated. Similar results, have been observed for adsorption at 222 K using Na-montmorillonite (SWy-2), a different clay than used in this study (SAz-1, section 2.3.3). As deposition of dust for our experiments is less controlled than for experiments specifically designed to measure the uptake of water into clays, it is difficult to compare quantities and rates of uptake.

When the source of water is closed off from the system, the pressure quickly drops; the temperature is quickly lowered to approximately 180 K. This reduction in temperature is necessary to prevent the saturation ratio from reaching exceedingly low values and to make the desorption temperature more applicable to Mars. As the system is equilibrating from the reduction in pressure and temperature, the first few minutes of the desorption phase are non-representative as they have low pressures with an equilibrating temperature.

At the temperature reached after equilibration dramatically low $S$ values of approximately 0.002, smectite clay gives water up slowly over 3 hours. It is remarkable that desorption of water does not occur quickly or completely, even under very dry conditions, implying that the water adsorbed is quite strongly bound. The water taken up at the after the rapid uptake looks approximately equal to that of the water desorbed. Without further data it is unknown if the desorption would have continued as would be projected by the few hours of data. Measuring adsorption and desorption through a full cycle could be used to calculate the binding energy at the given temperature for the cycle using the partial specific Gibbs energy equation with respect to relative water vapor.
pressure. The spectra shown in Figure 4.17 show that water ice is not detected during the adsorption of desorption phase.

Figure 4.16: Integrated peak area during an Adsorption/Desorption experiment on smectite clay. The sample was first exposed to water vapor at 2 min with the pressure set to $7.0 \times 10^{-4}$ Torr till 205 min. Cooling from room temperature was started at 30 min and stabilized at $196.9 \pm 0.5$ K by 50 min till 205 min, using this temperature with equation (5), $V P_{\text{ice}} = 7.5 \times 10^{-4}$ Torr, $S = 0.9$. Desorption was started at 205 min with the closing of the water line; pressure fell to $1.7 \times 10^{-6}$ Torr till 395 min, with temperatures reduced promptly to $179.9 \pm 1.5$ K, with temperature and pressure stable by 215 min till 395 min, at this temperature with equation (5), $V P_{\text{ice}} = 4.0 \times 10^{-6}$ Torr, $S = 0.04$. Uncertainty in pressure is estimated to be 5 % of the value for this experiment.
Figure 4.17: Infrared spectra for Adsorption/Desorption experiment on smectite clay. Each spectrum is labeled with the collection time, which relates to Figure 4.16. Spectra are labeled in gray scale with traces getting lighter going upward. Note that later spectra are not always above earlier spectra.

4.2.2 Water Adsorption/Desorption on JSC Mars-1 Regolith Simulant

Adsorption/Desorption experiments carried out on un-fractionated JSC Mars-1 regolith simulant (Figure 4.18) looked similar to those done on smectite clay (Figure 4.16). Rapid uptake of water is observed during cooling to and $S$ of 0.85, followed by slow steady uptake of water. Adsorption of water by JSC Mars-1 was dominated by uptake during the first half hour after cooling. Fractionated JSC Mars-1 was not tested in
an adsorption/desorption experiment. Further testing with more controlled applications of dust, and testing of each fraction would be of great interest.

With the fast uptake period lasting ~30 min, it is likely that all nucleation experiments done on JSC Mars-1 were conducted during the later slow adsorption phase. Although the full layered clay structure may not be present in the JSC Mars-1, the sample showed similar uptake behavior, which may affect the nucleation of crystalline ice.

Desorption from JSC Mars-1 is also observed to be slow, with the dust giving up little of the adsorbed water when conditions were shifted from adsorption conditions to $S = 0.04$ and held for 1.5 h. Adsorbed water observed in this experiment is likely bound strongly, similar to that of clay.
Figure 4.18: Integrated peak area for Adsorption/Desorption experiment on Whole JSC Mars-1 Regolith Simulant. The sample was first exposed to water vapor at 2 min with the pressure set to $6.9 \times 10^{-4}$ Torr till 133 min. Cooling from 228 K was started at 7 min and stabilized at $197.8 \pm 0.5$ K by 28 min till 133 min. Using equation (8) with the observed temperature a $VP_{\text{ice}} = 9.2 \times 10^{-4}$ Torr, and $S = 0.75$. Desorption was started at 133 min with the closing of the water line. Pressure fell to $1.6 \times 10^{-6}$ Torr till 225 min, with temperature reduced promptly to $181.2 \pm 1.5$ K, with temperature and pressure stable by 137 min till 225 min, $VP_{\text{ice}} = 5.1 \times 10^{-6}$ Torr, and $S = 0.03$. Uncertainty in pressure is estimated to be 10% of the value for this experiment.
Figure 4.19: Spectra for Adsorption/Desorption experiment on Whole JSC Mars-1, each spectrum is labeled with the collection time, which relates to Figure 4.17. Spectra are labeled in gray scale with traces getting lighter going upward. Note that later spectra are not always above earlier spectra.
5. Conclusions

Laboratory measurements of critical saturation show significant temperature dependence of water ice nucleation conditions on a variety of dust analogs under martian conditions. Critical saturations were observed to vary from $1.1 \pm 0.2$ at $185.0 \text{ K}$ to $3.3 \pm 0.8$ at $155.1 \text{ K}$ on martian dust analogs. Variations in the temperature dependence of $S_{\text{crit}}$ among different substrates were also observed. From these experiments it is clear that extrapolation of terrestrial values to martian temperatures does not take into account the temperature behavior observed in these experiments.

Arizona Test Dust (ATD) proved to be the poorest nucleator tested in this study with temperature dependent $S_{\text{crit}} = -0.0720T + 14.4$, $R^2 = 0.8$; values found approached those observed with silicon. These results, although not in conflict with current studies\textsuperscript{10, 13} for $T > 185 \text{ K}$, were not predicted by theory. A slight temperature dependence has been observed in previous studies\textsuperscript{13} for onset conditions of water ice on ATD at higher temperatures $> 200 \text{ K}$, but the trend is not as strong as observed in this study.

For the collected clay sample, critical saturation values were found to be described by $S_{\text{crit}} = -0.105T + 19.3$, $R^2 = 0.7$, showing clay to be the second-best nucleator tested. Infrared spectroscopy was used to clearly distinguish between absorbed water and water ice. With significant uptake of water observed; low values of $S_{\text{crit}}$ were expected with little to no temperature dependence. Observations of $S_{\text{crit}}$ values as high as 3.0 at 158 K show this to be not the case. While clay may not be a significant component of the lofted dust\textsuperscript{20, 22} in the atmosphere of Mars, a small fraction of efficient ice condensation nuclei can dominate cloud formation\textsuperscript{44}. Smectite clay was expected to be
the best nucleator, however lower results were observed for light fraction of JSC Mars-1 Regolith Simulant.

Nucleation experiments conducted on un-fractionated JSC Mars-1 Regolith Simulant (JSC Mars-1) showed results intermediate between those of ATD and smectite clay. Significant temperature dependence is observed with results ranging from over 3.3 at 155 K to 1.4 at 180 K, with a temperature dependence for nucleation parameterized by $S_{\text{crit}} = -0.0920 * T + 17.6$, $R^2 = 0.9$. As JSC Mars-1 is the currently available dust analog for Mars, simulations of the martian atmosphere that wish to include the effects of water ice nucleation will likely need values for critical saturations on this material. This is the first study to report critical saturation ratios for water ice nucleation on JSC Mars-1 Regolith Simulant.

After being ground and suspended in water, JSC Mars-1 < 1 mm size fraction was found to separate by gravitational settling. The light fraction showed temperature dependence in nucleation experiments. With the dark fraction showing strong scattering in the infrared spectra, the developed technique for measuring ice nucleation became inapplicable. The unexpected result of the light fraction showing lower critical saturations, $S_{\text{crit}} = -0.0469 * T + 9.38$, $R^2 = 0.8$, than the Whole JSC Mars-1 led to retesting of the un-fractionated control sample. Results from retesting the Whole JSC Mars-1 showed similar behavior to the light fraction. Because of these results we believe that observed nucleation properties may be dependent on sample preparation techniques.

Water adsorption/desorption experiments for both smectite clay and un-fractionated JSC Mars-1 showed two types of uptake, fast initial uptake followed by slow
gradual uptake, similar to results observed by Frinak et al.\textsuperscript{31} Striking results were observed during desorption, with little water leaving the clay after 3 h of exposure to extremely low water saturations. Similar behavior was observed for JSC Mars-1 after 1.5 h of desorption; at temperatures near 180 K water appears to be strongly adsorbed, taking considerable time to be removed.

These studies show the successful development of a new chamber and experimental protocol for conducting studies of water ice nucleation via vapor deposition. Temperature dependence for nucleation of water ice on four different substrates has been characterized. Fit values for $S_{\text{crit}}$ reported in this study should not be used beyond the range of experimental temperatures tested, as values are likely to asymptotically approach unity at higher temperatures. This laboratory work is the first to test martian dust analogs for water ice nucleation under a wide range of temperatures relevant to Mars, and is the first study to examine critical saturations for nucleation on JSC Mars-1 Regolith Simulant under any conditions.
References


7. Clancy, R. T.; Wolff, M. J.; Christensen, P. R., Mars aerosol studies with the MGS TES emission phase function observations: Optical depths, particle sizes, and ice cloud types versus latitude and solar longitude. *J. Geophys. Res.* 2003, 108(E9), 5098.


Appendix A: List of Calculated and Observed Variables:

Variables with associated equation in this text

<table>
<thead>
<tr>
<th>Equation#</th>
<th>Page</th>
<th>Subject</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>6</td>
<td>$S$, Saturation ratio</td>
</tr>
<tr>
<td>(2)</td>
<td>6</td>
<td>$\Delta G$, Gibbs free energy of forming a new phase</td>
</tr>
<tr>
<td>(3)</td>
<td>12</td>
<td>Voltage output by ion gauge</td>
</tr>
<tr>
<td>(4)</td>
<td>31&amp;33</td>
<td>$S_{\text{crit}}$, Critical saturation ratio</td>
</tr>
<tr>
<td>(5)</td>
<td>33</td>
<td>$T_{\text{eq}}$, Equilibrium temperature</td>
</tr>
<tr>
<td>(6)</td>
<td>34</td>
<td>$a$, Temperature offset</td>
</tr>
<tr>
<td>(7)</td>
<td>34</td>
<td>$T_{\text{n}}$, Nucleation temperature</td>
</tr>
<tr>
<td>(8)</td>
<td>34</td>
<td>$V_{\text{P,ice}}$, Vapor pressure ice</td>
</tr>
<tr>
<td>(9)</td>
<td>35</td>
<td>Voltage equation used for look up table</td>
</tr>
<tr>
<td>(10)</td>
<td>36</td>
<td>$P_{\text{bw}}$, Base pressure water</td>
</tr>
<tr>
<td>(11)</td>
<td>36</td>
<td>$P_{\text{bobs}}$, Base pressure observed</td>
</tr>
<tr>
<td>(12)</td>
<td>37</td>
<td>$\delta P_{\text{n}}$, Partial derivative of $S_{\text{crit}}$ with respect to nucleation pressure</td>
</tr>
<tr>
<td>(13)</td>
<td>37</td>
<td>$\delta V_{\text{P,ice}}$, Partial derivative of $S_{\text{crit}}$ with respect to vapor pressure ice</td>
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<tr>
<td>(14)</td>
<td>38</td>
<td>$\delta a$, Uncertainty in offset</td>
</tr>
<tr>
<td>(15)</td>
<td>38</td>
<td>$\delta T_{\text{ave}}$, Uncertainty in temperature average</td>
</tr>
<tr>
<td>(16)</td>
<td>38</td>
<td>$\delta P_{\text{n}}$, Uncertainty in nucleation pressure</td>
</tr>
<tr>
<td>(17)</td>
<td>39</td>
<td>$P_{\text{bair}}$, Equation for base pressure air</td>
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</tbody>
</table>
**Appendix A: List of Calculated and Observed Variables:**

Variables without associated equation in this text

<table>
<thead>
<tr>
<th>Page(s)</th>
<th>Subject</th>
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<tbody>
<tr>
<td>10</td>
<td>Wafer, wafer was used for the given experiment</td>
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<tr>
<td>13</td>
<td>Gain, gain used with detector for the given measurement</td>
</tr>
<tr>
<td>16</td>
<td>$\text{ppV}$, peak-to-peak voltage at the detector</td>
</tr>
<tr>
<td>25-26</td>
<td>Pre-step, minutes in the penultimate step prior to nucleation</td>
</tr>
<tr>
<td>33</td>
<td>$P_n$, nucleation pressure</td>
</tr>
<tr>
<td>33</td>
<td>$P_{eq}$, equilibrium pressure</td>
</tr>
<tr>
<td>34</td>
<td>$T_{pre}$, temperature of the step just prior to nucleation</td>
</tr>
<tr>
<td>34</td>
<td>$T_{post}$, temperature of the step that caused nucleation</td>
</tr>
<tr>
<td>36</td>
<td>$P_{\text{bair}}$, base pressure due to air</td>
</tr>
<tr>
<td>39</td>
<td>$\delta P_{\text{air}}$, uncertainty in equilibrium pressure</td>
</tr>
<tr>
<td>40</td>
<td>$\delta T_n$, uncertainty in nucleation temperature</td>
</tr>
<tr>
<td>40</td>
<td>$\delta P_{\text{eqobs}}$, uncertainty in equilibrium pressure</td>
</tr>
</tbody>
</table>
Appendix B: Appended Partial Derivatives

\[
\frac{\delta P_{\text{bair}}}{\delta P_{\text{bobs}}} = GF_{\text{air}} \left[ 1 + \frac{GF_{\text{air}}}{GF_{\text{w}}} \left( \frac{\omega}{1 - \omega} \right) \right]^{-1}
\]

\[
\frac{\delta P_{\text{bair}}}{\delta \omega} = \frac{-P_{\text{bobs}} GF_{\text{w}}}{\omega^2 \left[ 1 + GF_{\text{w}} \left( \frac{1 - \omega}{\omega GF_{\text{air}}} \right) \right]^2}
\]

\[
\frac{\delta P_{\text{bair}}}{\delta GF_{\text{air}}} = \frac{P_{\text{bobs}} \left[ GF_{\text{w}} (1 - \omega) \right]^2}{\left[ \omega GF_{\text{air}} + GF_{\text{w}} (1 - \omega) \right]^2}
\]

\[
\frac{\delta P_{\text{bair}}}{\delta GF_{\text{w}}} = \frac{P_{\text{bobs}} \left( \frac{\omega}{1 - \omega} \right)}{\left( \frac{GF_{\text{w}}}{GF_{\text{air}}} + \frac{\omega}{1 - \omega} \right)^2}
\]