LABORATORY STUDIES OF DEPOSITION MODE HETEROGENEOUS ICE
NUCLEATION: EFFECTS OF ICE NUCLEI COMPOSITION, SIZE AND
SURFACE AREA

By

Zaminhussein Abdulali Kanji

A thesis submitted in conformity with the requirements
for the degree of Doctor of Philosophy

Graduate Department of Chemistry
University of Toronto

© Copyright Zaminhussein Abdulali Kanji (2009)
LABORATORY STUDIES OF DEPOSITION
MODE HETEROGENEOUS ICE NUCLEATION:
EFFECTS OF ICE NUCLEI COMPOSITION, SIZE
AND SURFACE AREA

Doctor of Philosophy 2009
Zaminhussein Abdulali Kanji
Department of Chemistry
University of Toronto

ABSTRACT

The indirect aerosol effect contributes to major uncertainties in determining the radiation budget of the earth. A large uncertainty is due to the formation of ice clouds onto natural or anthropogenic aerosols. Field studies have shown that mineral type particles are often associated with ice crystals in the mid-upper troposphere and given the long residence time in the atmosphere
of dust particles (~2 weeks in the absence of precipitation), their contribution to ice formation processes is not fully defined.

In order to probe ice formation onto natural mineral dust in a setting where it could be suspended as aerosol, a new continuous flow diffusion chamber (CFDC) was built. This allowed investigations of the effects of total aerosol surface area and particle size. The CFDC was also used in an international inter-comparison of ice nucleation instrumentation to compare efficiencies of soot, biological aerosol (bacteria) and samples of natural desert dusts from different regions of the world. The laboratory observations were parameterized using nucleation rates ($J_{\text{nuc}}$) and contact angles ($\theta$) as described by classical nucleation theory.

For both this experimental technique and a static one developed during the candidate’s Masters degree, mineral dust particulate proved to be the most efficient ice nuclei (IN) activating at RH with respect to ice (RH$_i$) as low as 105% at $T = 233$ K. The efficiency varied with particle size and aerosol surface area (SA). Large particles or higher SA activated at lower RH$_i$ than small particles or lower SA. The static chamber was sensitive to the first ice event out of a large SA and therefore gave true onset RH$_i$, which was lower than the onset defined by the CFDC studies, which was not sensitive to a single ice event. In addition the static chamber used a broader size range of particulate matter, including super micron particles while the CFDC particles sizes were restricted to below 0.5 µm. Soot and organic coated dust particles were inefficient IN compared to pure dust.
Soot aerosols showed some efficiency at $T < 233K$ where deposition ice formation was apparent. The hygroscopic organics had intermediate ice activity between dusts and alkyl-organics and soot. Bacteria aerosols were active in the deposition mode for $T$ as high as 247 K. Contact angles ($\theta$) computed for ice germs forming onto natural mineral dust were small, $7^\circ < \theta < 29^\circ$, at 223 K for RH ranging from ice to water saturation.

It was concluded that there is no single value for the onset of ice formation in the atmosphere via deposition freezing. The associated contact angles show that there is a distribution of active sites on IN and that not all active sites have the same affinity for initiation of ice formation even within the same aerosol type. This work provides evidence that deposition mode nucleation can be an alternate pathway to homogeneous nucleation when mineral aerosols are present in the troposphere since the high $T$ - low RH conditions required for deposition mode nucleation are more easily encountered in the atmosphere than the low $T$ - high RH required for homogeneous nucleation.
ACKNOWLEDGEMENTS

Compiling a thesis is a challenging yet fulfilling experience that is only possible after a few years of mentored research. During the last six years I realized that I could not have chosen a better man to learn from than Jonathan P. D. Abbatt, my supervisor. He encouraged me to think independently and allowed me the space to develop my own work style, consequently never imparting the notion of superiority, just his enthusiasm for research. I continue to remain stunned at his intelligence, well-rounded knowledge and foresight. He has taught me to evaluate my work with an objective perspective and a critical eye. His humility, understanding, patience, generosity and ability to perceive beyond what people need, have made my graduate school experience memorable and outstanding. Thank you, Jon. I can only aspire to become half the scientist you are.

I would like to thank my committee members Jamie Donaldson and Myrna Simpson for valuable encouragement at various stages of graduate school. Thanks also to Myrna for providing me with kaolinite samples. I would also like to thank Jennifer Murphy for agreeing to be my fourth examiner and Allan Bertram for being my external examiner and making the trip across the country.

The challenges faced in research never seemed insurmountable after seeking comfort from my colleagues. I would like to thank Dan Aubin, Rachel
Chang, Ingrid George, Nana Kwamena, Steve Sjostedt, Jay Slowik and Sasha Vlasenko. Nana always had a way of putting laboratory work into perspective for me. I am thankful for that. Albeit in my later years, I would like to express my thanks to Rob McWhinney, T Nathan Oldridge and Egda Escorcia for making part of a wonderful laboratory group. Daily life would not have been nearly as much fun if it weren’t for the Environmental Chemistry division 2005-2009. It has been a pleasure to get to know all of you. Thank you Daniel Aubin for being so accepting of my antics as an officemate, Craig Butt, Jessica Currie, Amila De Silva, Nana Kwamena, Jeff McCabe, Erin Marchington, Anne Meyers and Cora Young for being good listeners during my coffee breaks. The many serious and not-so-serious conversations had will be fondly remembered. I hope we all cross paths in the future. I would like to thank Amila De Silva for the many coffee breaks, lunch and dinner treats that made my research days at Lash Miller all the more fun and through which a wonderful friendship developed. In addition I would also like to thank Craig Butt and my friend Tamara Minnema for positively influencing my physical activity. I thoroughly enjoyed my runs, CN tower climbs and few attempts at rock climbing, not to mention the stimulating conversation! I hope we get the chance for more in the future!

No amount of gratitude expressed would do justice to my dear friend, Yusuf Kudrati. You have always been there, when it did or didn’t matter. The last 19 years are evidence of that. You have always believed in me (despite hating my English grammar skills) and encouraged me despite my shortcomings. I
appreciate the familiarity and laughter you bring to my life. I hope this experience carries into the next 19 years and more. The value of education and motivation to work hard sometimes dwindles through a long course of education. However, I found an unfailing determination for success in my good friend Brinda Bhattacharjee whose mere presence in my life motivated me to succeed in more way than one. I will always think fondly of our growth together and apart over the last 8 years and look forward to more. Thank you for the company!

Through the many sad and joyous times, I have come to hold very dear some friendships. Amila De Silva, Todd Koch and Kimberly Recoskie, in times of unrest and doubt I have always been able to gain peace of mind by leaning on you because you provided sound advice and challenged me. You celebrated my accomplishments no matter how minute they were. Amila, thank you for always being honest and sharing your experiences with me, I have developed a great deal of respect and admiration for you over the years. Todd, you have been an influence of stability in my life since I arrived in Toronto and still continue to be. In addition to being brilliant company, you have a balanced well-rounded approach to life that I have learnt so much from – thank you. Kim, the understanding, acceptance and tolerance that you have shown in our friendship is indicative of the beautiful person you are. I am lucky to have you as a close friend and I look forward to many more battery draining cell phone conversations!
The support I have received from my friends, Antony Chum, Eddie Farrell, Anjali Gopalani and Vivek Menon cannot go unmentioned. Antony, Eddie and Vivek have been present for most of the compilation of this thesis. They always accompanied me during my late night writing expeditions even during times when they had no work of their own – thank you – I appreciate it more than you know. Anjali has always been nurturing, soothing and thoughtful even during times when she is half-way across the world – thank you.

In the last year I got to know a few more people more closely who have become of regular presence in my life. I would like to thank Jeff Geddes and Corey McClary for a fun filled final school year and Ricky Varghese for his support and friendship. Ricky I look forward to more good food and brilliant conversation.

Last but most important, I would like to thank, my parents, Kush and Abduli, my aunt, Masooma, and my siblings Tahera, Saima and Mahmood. The unconditional support of my parents has been instrumental in getting me to where I am and who I am today. This is directly a result of the values and confidence they instilled in me. Thank you, Mom and Pappa. Tahera and Saima have always expressed their love and support for me by sheltering me from responsibilities in order to make life smooth sailing. I look up to them and I admire how they lead their lives. They always took an interest in what I pursued, encouraged me to work hard and believed in me. Thank you sisters, how could I have done it without you?!
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>v</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xiv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xv</td>
</tr>
<tr>
<td>PREFACE</td>
<td>xxi</td>
</tr>
<tr>
<td><strong>CHAPTER ONE</strong></td>
<td></td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1. Radiative Forcing and Clouds – The Aerosol Indirect Effect</td>
<td>2</td>
</tr>
<tr>
<td>1.1.1. Role of Cirrus in Radiative Forcing and Climate</td>
<td>3</td>
</tr>
<tr>
<td>1.1.2. Uncertainties of Cirrus Contributions</td>
<td>5</td>
</tr>
<tr>
<td>1.2. Ice Formation Processes in the Atmosphere</td>
<td>6</td>
</tr>
<tr>
<td>1.2.1. Homogeneous Ice Nucleation: Theory</td>
<td>6</td>
</tr>
<tr>
<td>1.2.2. Heterogeneous Ice Nucleation: Theory</td>
<td>9</td>
</tr>
<tr>
<td>1.2.2.1. Requirements for an efficient ice nucleus (IN)</td>
<td>10</td>
</tr>
<tr>
<td>1.3. Laboratory Techniques for Studying Ice Formation</td>
<td>11</td>
</tr>
<tr>
<td>1.3.1. Cold Stage Flow Cells</td>
<td>12</td>
</tr>
<tr>
<td>1.3.2. Continuous Flow Diffusion Chambers (CFDC)</td>
<td>13</td>
</tr>
<tr>
<td>1.3.3. Cloud Expansion Chambers</td>
<td>15</td>
</tr>
<tr>
<td>1.3.4. Other Techniques</td>
<td>16</td>
</tr>
<tr>
<td>1.4. Overview of Homogeneous Ice Nucleation Studies</td>
<td>17</td>
</tr>
<tr>
<td>1.5. Overview of Heterogeneous Ice Nucleation Studies</td>
<td>20</td>
</tr>
<tr>
<td>1.5.1. Early Laboratory Studies in Heterogeneous Ice Nucleation</td>
<td>21</td>
</tr>
<tr>
<td>1.5.2. Evidence of Mineral Dust Association with Glaciated Clouds in the Troposphere</td>
<td>24</td>
</tr>
<tr>
<td>1.5.2.1 Field Studies of Ice Nucleation and Detection</td>
<td>24</td>
</tr>
</tbody>
</table>
1.5.2.2 Mineral Dust Loading 27
1.5.3 Recent Studies of Mineral Dust Heterogeneous Ice Nucleation 28
1.5.4 Other Heterogeneous IN 33
1.5.4.1 Organic IN 33
1.5.4.2 Biogenic IN 34
1.5.4.3 Black Carbon/Soot as IN 35
1.6 Secondary Ice Formation Processes 36
1.7 Motivation 37
1.8 Thesis Objectives 38
1.9 References 41

CHAPTER TWO

ICE FORMATION VIA DEPOSITION NUCLEATION ONTO MINERAL DUST AND ORGANICS: DEPENDENCE OF ONSET RELATIVE HUMIDITY ON TOTAL PARTICULATE SURFACE AREA 58

2.1 Abstract 59
2.2 Introduction 60
2.3 Experimental Methods 64
2.3.1 Experimental Approach 64
2.3.2 Sample Preparation 65
2.3.3 Surface Area Determination 68
2.4 Results 68
2.5 Discussion 74
2.6 Acknowledgements 77
2.8 References 78

CHAPTER THREE

THE UNIVERSITY OF TORONTO CONTINUOUS FLOW DIFFUSION CHAMBER (UT-CFDC): A SIMPLE DESIGN FOR ICE NUCLEATION STUDIES 83
3.1. Abstract 84
3.2. Introduction 85
3.3. General Overview of Principle 88
3.4. Design of the UT-CFDC 90
  3.4.1. Aerosol Generation and Counting 91
  3.4.2. Ice Nucleation Chamber 92
  3.4.3. Ice Detection 96
3.5. Validation of Freezing Conditions 97
3.6. Attributes and Limitations of the IN Counter 106
3.7. Conclusions 109
3.8. Acknowledgements 110
3.9. References 111

CHAPTER FOUR

ICE NUCLEATION ONTO ARIZONA TEST DUST AT CIRRUS TEMPERATURES: EFFECT OF TEMPERATURE AND AEROSOL SIZE ON ONSET RELATIVE HUMIDITY

4.1. Abstract 118
4.2. Introduction 119
4.3. Experimental 120
4.4. Results and Discussion 123
  4.4.1. Effect of Temperature 123
  4.4.2. Effect of Particle Size 126
  4.4.3. Effect of Total Surface Area 130
  4.4.4. Classical Nucleation Theory Analysis 132
    4.4.4.1. Nucleation Rates, $J_{\text{het}}$ 132
    4.4.4.2. Contact Angles ($\theta$) Derived from Classical Nucleation Theory 135
4.5. Conclusions 141
4.6. Acknowledgements 142
CHAPTER FIVE

5.1. Abstract 150
5.2. Introduction 151
5.3. Experimental 155

5.3.1. Experimental Overview of UTOR at ICIS-2007 155
5.3.2. Overview of Expansion and CSU Experiments at ICIS-2007, adapted from Möhler et al. [2006] and Rogers et al. [2001] 158
5.3.3. Aerosol Preparation and Sampling 160
5.3.4. Activation of Aerosols: Ice Formation and Detection in UTOR 163

5.4. Results and Discussion 164

5.4.1. General comparison of Ice Nuclei (IN) Sampled 164
5.4.2. Arizona Test Dust 167
5.4.3. Saharan, Canary Island and Israeli Dusts 169
5.4.4. Graphite Spark Generator Soot 174

5.5. Inter-comparison of UTOR, CSU and Expansion Techniques 178
5.6. Conclusions 179
5.7. Acknowledgements 181
5.8. References 182

CHAPTER SIX

6.1. Conclusions 188

6.1.1. Relative Efficiencies of Atmospherically Relevant IN in the Cirrus Regime 190
6.1.2. For the Most Efficient IN, at What Temperature is
Deposition Mode Active?

6.1.3. Is There a Unique Onset Value That Can be Defined For Deposition Mode Nucleation? 193

6.2. Future Directions 194

6.2.1. Size Resolved Studies at Higher Temperatures 195

6.2.2. Chemical Processing Relevant to the Atmosphere 196

6.2.3. Urban/Industrial Aerosol – Tropospheric Relevance 196

6.2.3.1. Future Studies Deploying the UTOR System 197

6.3. References 201

APPENDICES 203

APPENDIX A 203

X-Ray Photoelectron Spectra (XPS) for Octyl-Coated Silica 204

APPENDIX B 209

Growth Calculations for The Continuous Flow Diffusion Chamber 210

APPENDIX C 214

Percentage composition of Dust Particles Using SEM-EDX Spectroscopy 215
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1.</td>
<td>List of Participating Ice Nucleation Instruments and Their Characteristics at ICIS 2007</td>
<td>156</td>
</tr>
<tr>
<td>5.2.</td>
<td>Size Distributions of Aerosol Size Samples</td>
<td>162</td>
</tr>
<tr>
<td>A1.</td>
<td>XPS results for processed silica</td>
<td>205</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

| Figure 1.1 | Modes of ice formation in the atmosphere. | 7 |
| Figure 1.2 | Adapted from Koop et al., [2000]. Experimental data used to derive water activity based parameterization. (a) melting temperatures (squares) and freezing temperatures (circles) of droplets ~ 1-10 μm of 18 different solutions as a function of solute molality. (b) same data as in (a) but as a function of water activity of water in solution. Dashed line: melting temperature and solid line: freezing curve shifted by Δaw = 0.305. | 20 |
| Figure 2.1 | Schematic of flow apparatus. Nitrogen is fed through a water bubbler from a mass flow controller and then to the vacuum chamber (~ 3.5 cm³) containing the cold stage. Pressures are measured in the cold stage and bubbler by capacitance manometers in order to calculate the partial pressure of water in the vacuum chamber [see Kanji and Abbatt, 2006]. | 65 |
| Figure 2.2 | Detailed schematic of cold stage where particles nucleate ice. | 66 |
| Figure 2.3 | Optical micrograph of oxalic acid dihydrate particles for a deposition time of 60 seconds from an aqueous solution of 0.4 mg/mL using a constant output atomiser (magnification × 50). | 69 |
| Figure 2.4 | Onset RH with respect to ice formation at 233 K as a function of surface area of particulates. Filled symbols: mineral dust particles, open symbols: hygroscopic particles, and crossed symbols: hydrophobic particles. Saharan Dust data taken from Kanji and Abbatt [2006]. Shaded region: maximum sustainable supersaturation in our system as determined with a blank Teflon substrate, i.e. ice nucleation at the indicated RH range occurred on the Teflon material. Note that each data point is the average of at least 9 measurements, for example consisting | 72 |

xv
of 3 repeat experiments on each of three different particulate samples. The error bars represent 1-σ standard deviation of the results.

Figure 2.5. Lower limit to heterogeneous nucleation rate as a function of onset RH at 233 K. Legend same as Figure 2.4. Star symbols: nucleation rates for 228 K from Archuleta et al. [2005] for Asian dust.

Figure 3.1. Supersaturation profile in a CFDC. This example illustrates a case where the cold wall is at 213 K and warm wall at 233 K (vertical dash-dotted lines), and sample temperature of 223 K in the centre. Red curve: equilibrium vapor pressure of water with respect to water. Green curve: the same but with respect to ice. Blue straight line: steady state partial pressure of water across the chamber. Dash dotted curve: saturation profile in chamber with respect to water. Dotted curve: same but with respect to ice. The coloured lines refer to the left axis and the black ones to the right. For most experiments the saturation ratio with respect to water did not exceed 1.

Figure 3.2. Schematic showing the setup of the entire system as an IN counter. Directions of arrows indicate direction of flow of aerosols. Refer to text for acronym definitions.

Figure 3.3. Lengthwise cross-section of chamber. Bold arrows indicate direction of particle-free sheath air that makes up about 90% of the total flow in the chamber. The remaining 10% is made up by the sample flow indicated by thinner arrow.

Figure 3.4. Top-view of the Teflon® spacer that is sandwiched between the warm and cold copper plates. The O-ring seal between the three pieces (on either side of the Teflon® spacer) ensures the chamber is air tight. The injector has 6 ports that allow sample into the chamber. The minimum residence time for the aerosol is achieved by pushing the injector in all the way so that aerosol is introduced into the chamber where the cone shape of the chamber begins. To ensure stability, the ends of the injector slide within a notch in the Teflon® spacer.

Figure 3.5. Activation curve for 230 K derived from a typical ice nucleation experiment. The RH of the chamber is
increased and concentration of ice crystals monitored. The activated fraction is the ratio of OPC counts to particle counts, derived from the CPC. The dashed line indicates for this temperature where we expect to see homogenous freezing of 100 nm H$_2$SO$_4$ taken from Koop et al. [2000]. Note that the large particle channel also increases indicating the presence of ice. The particles in the smaller size channel could also be water droplets after water saturation has been surpassed.

**Figure 3.6.** Fraction of ATD particles that activate as ice crystals as a function of residence time in the UT-CFDC. These data were collected at 223 K and RH$_w$ = 99%. The work presented in this paper was all carried out at a residence time of 12 seconds which corresponds to an injector position of 30 cm. The numbers next to the data points indicate the corresponding residence times.

**Figure 3.7.** Summary of the 100 nm H$_2$SO$_4$ homogeneous freezing experiments over a range of temperatures. Squares: Freezing fraction of at least 0.1% or more of the particles. Stars: freezing of 0.1% of 50 nm H$_2$SO$_4$ particles from Chen et al. [2000]. Also, refer to text for explanation of the circle shaped data points. The activated fraction was determined using the sum of the counts from the large and small particle channels. Error bars represent 1σ from at least 3 runs during an experiment.

**Figure 3.8.** Activation curve of H$_2$SO$_4$ aerosols at 240 K This temperature is above where we expect homogeneous freezing and therefore no ice formation should be observed. Note that once water saturation has been reached, the P > 0.5μm channel (squares) starts to increase indicating water droplet formation. However the P > 5μm channel (circles) remains at background level, indicating no ice formation.

**Figure 4.1.** Onset relative humidity with respect to ice for freezing of 0.1 and 1 % of 100 nm ATD particles as a function of temperature. Other data points are onset RH$_i$ for 100 nm Asian Dust particles from Archuleta et al. [2005], ATD particles from Möhler et al. [2006] and Köhler [2007], and RH$_i$ for one ice event taken by varying total surface area of
a poly-disperse ATD sample deposited on a hydrophobic support at 233 K (taken from Kanji et al. [2008], SA = 2.6 × 10^{-2} cm²). Dashed line: homogeneous freezing of sulfuric acid aerosol [Koop et al., 2000]. Solid line: water saturation [Murphy and Koop, 2005].

**Figure 4.2.** Onset relative humidity with respect to ice as a function of activated fractions for varying sizes of ATD aerosol at 223 K. Open symbols are for Asian Dust at 223 K taken from Archuleta et al. [2005]. Dashed Line: water saturation. Numbers in parenthesis: surface area of particles (cm² cm⁻³), assuming spherical geometry.

**Figure 4.3.** Onset relative humidity with respect to ice for one ice event as a function of activation surface area at 223 K. Surface areas were calculated assuming spherical geometry and correspond to activated fractions of 0.01, 0.1, 1 and 10% for each particle size. Diamonds: RHᵢ for one ice event for poly-disperse ATD particles on hydrophobic support taken at 233 K [Kanji et al., 2008]. Open star: Ice activation for 8% of poly-dispersed ATD aerosol in AIDA chamber [Möhler et al., 2006]. Dashed line: water saturation [Murphy and Koop, 2005].

**Figure 4.4.** Heterogeneous nucleation rates (Jₑₜₑ) as a function of onset RHᵢ. The data used to calculate Jₑₜₑ are from Figure 4.2. For 100 and 240 nm where two total surface areas are presented, we used the average of the two data sets for the Jₑₜₑ computation (see text). Dotted line: water saturation.

**Figure 4.5.** Contact angles (θ) as a function of onset RHᵢ. Data from Figure 4.4 were used to arrive at θ. The 0.5 – 5 μm points were derived from the data in Kanji et al [2008] and taken at 233 K while the work from this study was at 223 K. Dotted line: water saturation.

**Figure 5.1.** Schematic of instruments arranged relative to sampling chambers at ICIS 2007 at the AIDA facility at Karlsruhe, Germany. The height of the chamber spanned approximately 4 floors. The UTOR CFDC was one floor above the CSU CFDC which was on the ground floor. Arrows indicate the direction of aerosol flow. For details of analytic instruments coupled to the AIDA chamber see
Möhler et al [2006] and Möhler et al [2008].

**Figure 5.2.** Onset RH$_i$ for 0.1\% activated fraction as a function of temperature for all aerosols sampled with the UTOR CFDC. All data are based on the large particle channel (> 5 μm). Triangles: aerosol sampled from AIDA chamber. Squares: aerosol sampled from NAUA chamber. Stars: aerosol sampled after a cloud expansion experiment in AIDA. Black line: Water saturation [Murphy and Koop, 2005]. Uncertainty in all data points ±4\%.

**Figure 5.3.** Comparison of onset RH$_w$ for 0.1\% activated fraction as a function of temperature for Arizona Test Dust aerosols between UTOR, CSU and AIDA experiments. UTOR data based on 5 μm channel except for the size selected studies where backgrounds were low enough to use the 0.5 μm channel. Numbers next to the stars indicate the order of the cloud expansion experiment. Pre-exp and post-exp indicate sampling from the AIDA chamber before and after successive cloud expansion experiments. Error bars represent uncertainty in RH measurements. Dashed line: Water saturation [Murphy and Koop, 2005].

**Figure 5.4.** Comparison of onset RH$_w$ for 0.1\% activated fraction as a function of temperature for Saharan Dust aerosols between UTOR, CSU and AIDA experiments. UTOR data based on 5 μm channel. Error bars represent uncertainty in RH measurements (see text for details). Dashed line: Water saturation [Murphy and Koop, 2005].

**Figure 5.5.** Comparison of onset RH$_w$ for 0.1\% activated fraction as a function of temperature for Canary Island Dust aerosols between UTOR, CSU and AIDA experiments. UTOR data based on 5 μm channel. Error bars represent uncertainty in RH measurements (see text for details). Dashed line: Water saturation [Murphy and Koop, 2005].

**Figure 5.6.** Comparison of onset RH$_w$ for 0.1\% activated fraction as a function of temperature for Israeli Dust aerosols between UTOR, CSU and AIDA experiments. UTOR data based on 5 μm channel. Error bars represent uncertainty in RH measurements (see text for details). Dashed line: Water saturation [Murphy and Koop, 2005].
**Figure 5.7.** Onset RH\textsubscript{w} for 0.1\% activated fraction as a function of temperature for graphite spark generator soot. Numbers next to the stars indicate the order of the cloud expansion experiments. Pre-exp and post-exp indicate sampling from the AIDA chamber before and after a cloud expansion experiment respectively. Error bars represent uncertainty in RH measurements. Dashed line: Water saturation.

**Figure 5.8.** Comparison between soot results obtained at ICIS 2007 from the UTOR CFDC to previous results in the literature. Dashed line: water saturation. See text (section 5.4.4) for details on soot samples compared.

**Figure 6.1.** Ice activation spectra for ambient urban aerosol sampled in downtown Toronto at the University of Toronto at 223 K. Squares: particles activating to be larger than 0.5 \(\mu\text{m}.\) Circles: particles activation to be greater than 5 \(\mu\text{m}.\) Colours indicate the number of RH scans performed (see text). Dotted line: Homogeneous freezing of sulphuric acid droplets [Koop et al., 2000].
This thesis is based on manuscripts that have been published in or are in preparation for submission for publication in peer reviewed journals. Consequently there may be some overlap in material that is presented throughout the thesis. All manuscripts for which Zamin A. Kanji is listed as a first author were written by him with critical comments provided by Jonathan P. D. Abbatt. Contributions of any other authors are described below.

CHAPTER ONE:

Overview of ice formation pathways in the atmosphere.

Contributions: Written by Zamin A. Kanji with critical comments from Jonathan P. D. Abbatt

CHAPTER TWO:

Ice formation via deposition mode nucleation onto mineral dust and organics: dependence of onset relative humidity on total particulate surface area.

Published as: Kanji, Z. A., O. Florea and J. P. D. Abbatt (2008)


Contributions: Experimental approach was developed by Zamin A. Kanji. Experiments on Arizona Test Dust were performed and...
analysed by Zamin A. Kanji. Experiments on remainder of the samples were carried out by and analysed by Octavian Florea, a fourth year undergraduate student under the supervision of Zamin A. Kanji who interpreted the data. All optical micrographs collected and surface area determinations were conducted by Zamin A. Kanji. The manuscript was prepared by Zamin A. Kanji with critical comments from Jonathan P. D. Abbatt.

CHAPTER THREE:

The University of Toronto Continuous Flow Diffusion Chamber (UT-CFDC): A Simple Design for Ice Nucleation Studies.


Contributions: The CFDC was machined at the University of Toronto Machine Shop based on a design prepared by Zamin A. Kanji with assistance from Jonathan P. D. Abbatt. Assembly and empirical validation by homogeneous freezing of sulphuric acid were performed by Zamin A. Kanji. The manuscript was written by Zamin A. Kanji with critical comments from Jonathan P. D. Abbatt.

CHAPTER FOUR:
Ice Nucleation onto Arizona Test Dust at Cirrus Temperatures: Effect of Temperature and Aerosol Size on Onset Relative Humidity.

*Prepared for submission to Journal of Geophysical Research – Atmospheres*

Contributions: Experiments, data analysis, interpretation were performed by Zamin A. Kanji. The manuscript was written by Zamin A. Kanji with critical comments from Jonathan P. D. Abbatt.

**CHAPTER FIVE:**

Results From The University of Toronto Continuous Flow Diffusion Chamber (UTOR) at The Fourth International Workshop on Comparing Ice Nucleation Measuring Systems (ICIS-2007).

*Prepared for submission to Atmospheric Chemistry and Physics Discussions*

Contributions: Experiments, data analysis, interpretation were performed by Zamin A. Kanji. Data contributions in the manuscript for two other ice measurement techniques are from Paul J. DeMott and Ottmar Möhler for the CFDC and expansion experiments respectively. The manuscript was written by Zamin A. Kanji with critical comments from Jonathan P. D. Abbatt.

**CHAPTER SIX:**

Final Thoughts and Future Studies.

Contributions: Written by Zamin A. Kanji with critical comments from Jonathan P. D. Abbatt
CHAPTER ONE

INTRODUCTION
1.1. Radiative Forcing and Clouds – The Aerosol Indirect Effect

The climate of the Earth results from the energy balance between absorbed incoming shortwave radiation and radiative losses of heat from the Earth and its atmosphere to space. Clouds play an important role in this balance because they can reflect sunlight back into space which reduces the solar radiation available to the Earth (albedo effect). However, clouds also reduce radiative heat losses to space by trapping outgoing terrestrial radiation (greenhouse effect) \cite{Stephens90}. Which of these two opposing processes dominates will depend on a number of factors such as cloud particle composition, structure, location and cover \cite{Stephens81}. Changes to any of these variables will alter the radiation budget of the Earth and can therefore have significant implications for climate.

Cloud formation is a result of aerosols spontaneously growing as water droplets or freezing to form ice crystals under required temperature and supersaturation conditions \cite{Rogers89}. The resulting role that clouds play in affecting the radiation budget of the Earth is called the aerosol indirect effect. Clouds can be composed of either water droplets or ice crystals, or both. Low altitude clouds that form usually below 2000 m are composed mostly of water droplets and form at warm temperatures \cite{Aguado99}. Generally, a high density of water droplets will decrease the cloud droplet size and increase the albedo of a cloud if the liquid water path is held constant \cite{Han2000}.
3

The greenhouse effect for liquid clouds will be small due to their low altitude and their albedo effect will dominate, resulting in a net cooling.

High altitude clouds that generally form above 6000 m are almost always composed of ice crystals (cirrus clouds) because of the cold temperature regime [Aguado and Burt, 1999] that is described by the adiabatic lapse rate (6.5K/1000m). Cirrus cloud coverage is substantial according to satellite cloud climatology studies [Rossow and Schiffer, 1999 and references therein]. In contrast to liquid clouds, high altitude cirrus clouds have a strong greenhouse effect that may outweigh their albedo effect [Stephens et al., 1990]. The magnitude of these processes are somewhat known but with high levels of uncertainty [IPCC, 2007]. The relative importance of the aerosol indirect effect to radiative forcing is strongly affected by properties of cirrus clouds that remain poorly understood and form one of the outstanding issues in current climate science [Karcher et al., 2006].

1.1.1. Role of Cirrus in Radiative Forcing and Climate

The amount of sunlight that cirrus clouds reflect, absorb and transmit depends on their coverage, position, thickness, ice-crystal shape and size distributions. Cirrus clouds also reflect and transmit the thermal infrared emitted from the surface and the atmosphere and at the same time emit infrared radiation according to their temperature structure [Stephens and Webster, 1981]. These radiative effects are determined by the scattering and absorption
properties of the ice crystals, which require knowledge of the refractive index of bulk ice, particle size, crystal shape, and orientation relative to incident light. The latter two variables make the determination of radiative forcing by cirrus more complicated than that of warm clouds which are composed of spherical water droplets [Kärcher and Spichtinger, 2009]. The scattering process from cirrus can result in redirecting solar and thermal energy thus having a warming effect. In addition, previous modelling studies have shown that the type of freezing processes in the atmosphere may significantly affect the radiative properties of cirrus clouds both in the visible and infrared [Karcher and Lohmann, 2003; Karcher et al., 2007].

Water vapour is an especially active greenhouse gas in the upper troposphere and its budget will greatly influence the radiation balance at the top of the atmosphere [Lindzen, 1990]. Determining the frequency of cirrus occurrence and size of ice particles is important in predicting water vapour mixing ratios since they are a sink of gas phase water. Gas phase depletion of water can cause dehydrated air to enter the stratosphere affecting the ozone concentrations [Holton and Gettelman, 2001].

Cirrus particles trap or adsorb chemically active trace gases, such as nitric acid [Ullerstam and Abbatt, 2005; Ullerstam et al., 2005; Karcher and Voigt, 2006] and initiate heterogeneous halogen chemistry [Thornton et al., 2007]. In order to represent the above processes accurately in climate prediction models, modelling ice particle occurrence with reasonable accuracy in the atmosphere is required.
1.1.2. *Uncertainties of Cirrus Contributions*

Cirrus clouds are a highly uncertain component of models that predict the global climate, simulate atmospheric chemistry or forecast the weather [Lynch et al., 2002]. Some of the uncertainty surrounding climate change prediction using general circulation models arises from interactions between temporally evolving, microphysical and radiative processes affecting cirrus [Zhang et al., 2005]. Climate models are sensitive to small changes in cirrus cloud cover [Lohmann and Karcher, 2002] or ice microphysics [Lynch et al., 2002]. All models estimate a negative mean global radiative forcing associated with the cloud albedo effect in the range -0.22 to -1.85 W m\(^{-2}\) [IPCC, 2007]. The main uncertainty of cirrus contribution to the radiative budget stems from the assumptions used in calculating the scattering of incident solar radiation in cirrus due to the different sizes and irregular shapes of ice crystals [Macke and Mishchenko, 1996; Macke et al., 1998].

To fully understand the processes above, knowing the mechanisms of ice initiation and growth conditions in the atmosphere is important [Kärcher and Spichtinger, 2009]. Due to the significant presence of aerosol concentrations in the atmosphere, which on average are on the order of 10\(^4\) cm\(^{-3}\), studying the interactions of natural or anthropogenic aerosols with water vapour becomes necessary, given that they act as precursors to ice formation by either homogeneous or heterogeneous ice nucleation.
1.2. Ice Formation Processes in the Atmosphere

Liquid phase clouds in the troposphere exist at temperatures well below the melting point of ice because of an energy barrier associated with phase transitions. Many liquid droplets can supercool to as low as -30°C [Rauber and Tokay, 1991], especially those that are micron and submicron sized. Very small pure water droplets can supercool down to -38°C [Koop et al., 2000] while larger particles will freeze at higher temperatures. Supercooled aerosols are therefore quite common in the atmosphere [Martin, 2000 and references therein]. The two main pathways of ice formation in the atmosphere are homogeneous and heterogeneous nucleation (Figure 1). Homogeneous ice formation is the spontaneous freezing of supercooled aerosol while heterogeneous freezing is aided by a solid foreign substrate or suspended particle and can occur through three different pathways (Figure 1). The requirements for both these pathways are different and are discussed in more detail in the next section.

1.2.1. Homogeneous Ice Nucleation: Theory

Homogeneous freezing is the stochastic or spontaneous freezing of supercooled pure liquid or solution droplets that occurs when a given temperature (T) and relative humidity (RH) is attained at which the supercooled liquid aerosols overcome an energy barrier associated with freezing. This freezing is similar to that which occurs in pure water droplets i.e. without
catalysis from a foreign substance. Homogeneous freezing of nearly pure water droplets occurs in the atmosphere, for example in updrafts of cumulus clouds.

Homogeneous Nucleation

Spontaneous Freezing

Heterogeneous Nucleation

By Immersion

By Deposition

By Contact

Figure 1.1. Modes of ice formation in the atmosphere. Particle legend is as follows: ▲- Solid substrate (ice nucleus), ⊙- Ice crystal and ●- Solution droplet.

[Rosenfeld and Woodley, 2000; Heymsfield et al., 2005]. Ice formation of micron sized concentrated solution droplets (haze) may occur at ~233K via homogeneous nucleation at RH with respect to water (RH\textsubscript{w}) < 100%. The presence of solute depresses the freezing point compared to that of a pure water drop of comparable size.

The initiation of homogeneous freezing in a liquid drop occurs when statistical fluctuations of the molecular arrangement of water produce a stable, ice-like structure that can serve as an ice nucleus. Two factors determine the conditions for freezing in this manner: the probability of occurrence of an ice
embryo by random rearrangement of water molecules and the size of the stable ice nucleus [Rogers and Yau, 1989]. These quantities will depend on the surface free energy of the crystal/liquid interface which is analogous to the surface tension at a liquid/vapour interface [Pruppacher and Klett, 1997]. The numerical value of the surface free energy is not known accurately, but is accepted to be close to $2.0 \times 10^{-2}$ N m$^{-1}$. This value can be used to predict that droplets smaller than 5 μm will spontaneously freeze at 233K and larger droplets are predicted to freeze at slightly warmer temperatures, in agreement with most observations [Rogers and Yau, 1989]. The spontaneous freezing process is described by classical nucleation theory that defines a homogeneous nucleation rate, $J_{\text{hom}}$, as a function of the freezing temperature (T) and the activation energy barrier ($\Delta E$) given by [Pruppacher and Klett, 1997]:

$$J_{\text{hom}} = A \exp\left(\frac{-\Delta E}{kT}\right)$$

(1.1)

where $J_{\text{hom}}$ and $A$ have units of cm$^{-3}$ s$^{-1}$, $\Delta E$ is given in J, $k$ is the Boltzmann constant in J K$^{-1}$ and temperature in K. The activation energy barrier is given by [Pruppacher and Klett, 1997]:

$$\Delta E = \Delta E_{\text{act}} + \Delta E_g$$

(1.2)

where $\Delta E_{\text{act}}$ is the activation for movement of water molecules from the solvent to the ice phase and $\Delta E_g$ is the energy barrier of formation of the critical embryo. The activation energy barrier becomes smaller with increasing size of the ice embryo for water supersaturated conditions [Pruppacher and Klett, 1980]. The pre-
exponential factor $A$, is proportional to the interfacial energy of the ice/solution interface and the density of ice; Pruppacher and Klett [1980] suggest a value of $9.0 \times 10^{21}$ cm$^{-3}$s$^{-1}$. This expression is attractive because it provides a basis against which experimental data can be evaluated to explain measurements of ice formation by homogeneous freezing in pure water drops. Experimental data can be used to compute $J_{\text{hom}}$ by applying the following relationship [DeMott in Lynch et al., 2002]:

$$F_{\text{hom}} = 1 - \exp(-J_{\text{hom}} V_d \Delta t)$$

(1.3)

where $F_{\text{hom}}$ is the fraction of droplets with volume $V_d$ (cm$^3$) that freeze homogeneously in a small time interval $\Delta t$ (s). Equation 1.3 is also used in numerical modelling calculations of cirrus ice formation [Lynch et al., 2002 and references therein].

1.2.2. **Heterogeneous Ice Nucleation: Theory**

There are three broadly categorised pathways of heterogeneous freezing that can be described (Figure 1). In general, this pathway of ice formation involves a solid substrate, called an ice nucleus that can act as a ‘template’ for water molecules to adsorb to in a configuration close enough to that of ice germs, thus initiating ice growth. In Figure 1, the first mechanism is immersion nucleation. This may occur when freezing is initiated at the interface of the phase boundary of the ice nucleus that is immersed in a solution droplet. The freezing temperature can be a function of the type of inclusion and/or the solution
concentration [Zuberi et al., 2002]. The second mechanism, deposition nucleation, takes place when ice condenses on a solid aerosol particle directly from the vapour phase. For this to occur, RH with respect to ice (RH$_i$) should be greater than 100% and typically RH with respect to water (RH$_w$) should be less than 100%. When RH$_w$ > 100%, one can expect the liquid phase to condense onto the ice nucleus followed by rapid freezing. This is referred to as condensation freezing and usually falls under immersion nucleation. Lastly, contact nucleation occurs when supercooled droplets collide with solid particles and cause instantaneous freezing.

An extension to homogeneous classical nucleation theory is often used to describe heterogeneous ice formation. Equation (1) still applies but the magnitude of the activation barrier will be smaller because of the influence of the substrate. A further analysis of classical nucleation theory as applied to heterogeneous nucleation is presented in Chapter 4. Not all solid particles favour ice formation with only certain characteristics leading to good ice nuclei (IN).

1.2.2.1. Requirements for an efficient ice nucleus (IN)

There are certain properties of atmospheric particles that are thought to contribute to efficient ice nucleation, however their relative contributions to lowering the activation barrier of ice formation are still unknown and difficult to ascertain. These requirements are discussed in [Pruppacher and Klett, 1997] and are briefly summarised here.
The ability of an aerosol to form a chemical bond with an oncoming water molecule [Fukuta, 1966] could easily initiate the ice phase due to favourable interactions with water vapour. If the IN has a surface crystal structure that is similar to that of ice it would also favour the formation of ice by acting as a template for the ice crystals [Davis et al., 1975]. Some sites on a particle that have crystal deformities, cracks or cavities can act as pockets for deposition of water molecules. Where this happens, water molecules accumulate and an ice germ can nucleate at such localised ‘active-sites’ [Bryant et al., 1959; Hallett, 1961]. Furthermore the larger the particle size, the higher is the surface area available for the aforementioned requirements. Experimentally, smaller particles have been observed to be inefficient ice nuclei [Edwards et al., 1962; Gerber, 1972]. Lastly, Pruppacher and Klett [1997] also discuss the requirement for an IN to be an insoluble solid, however given recent evidence of ammonium sulphate acting as IN at low RH [Abbatt et al., 2006], it would suffice to say that heterogeneous IN ought to be a solid at the point of ice formation thus providing the structural integrity for ice to from and the sustained insolubility is not a necessary requirement.

1.3. Laboratory Techniques for Studying Ice Formation

Methods for studying homogeneous and heterogeneous ice nucleation in the laboratory can be placed into various categories. In this section experimental
approaches that are used for ice formation studies are discussed, with particular emphasis on techniques that are most widely used.

1.3.1. Cold Stage Flow Cells

Cold stage flow cells are used to study freezing via a few different pathways. Ice nucleation is typically observed optically using a microscope coupled with a camera looking down on particles that are deposited onto a chilled hydrophobic (Teflon® coated) surface. The flow cells have an inlet which introduces water vapour that can establish saturation conditions by controlling the temperature of the stage supporting the particles. Solution droplets, drops with IN as inclusions, or solid particulate matter are nebulized onto the hydrophobic surface. The particles are usually prepared as aqueous suspensions. Homogeneous, immersion and deposition nucleation can be observed. For freezing experiments, if liquid condensate is observed before ice formation, condensation freezing is inferred whereas if ice forms without appearance of the liquid phase, deposition freezing is inferred [Koop et al., 1998; Dymarska et al., 2006; Knopf and Koop, 2006]. In addition, as with most cold cell techniques, if the RH of the cell compartment can be controlled, phase transitions of soluble solutes can be studied as a function of T and RH [Kanji and Abbatt, 2006]. The RH in the cells is determined either by direct measurements of water partial pressure [Dymarska et al., 2006], pressure of water vapour (in the absence of a buffer gas) [Knopf and Koop, 2006] or by assuming equilibrium conditions when a carrier gas
1.3.2. Continuous Flow Diffusion Chambers (CFDC)

Flow cell techniques have some limitations. There is no easy way of ascertaining if there is an influence from the substrate that needs to be accounted for during ice formation, since the exact location of an ice germ is not visible. There are limitations on particle sizes that can be studied due to detection limits in place by the optical system. Also, it is impossible to increase RH$_w$ > 100% due to condensation onto the cold stage.

Ice thermal diffusion chambers on the other hand allow for smaller particles sizes that are suspended in air. With appropriate detection techniques, measurements for RH$_w$ > 100% are possible. Supersaturated conditions are achieved in the chambers by varying the temperature of two parallel ice coated surfaces [Rogers, 1988]. The chambers may be oriented horizontally or vertically and can be geometrically cylindrical or flat. In both cases a temperature and water vapour gradient develop in the gap between ice coated walls into which aerosol is drawn. Determining the exact conditions of T and RH that the aerosol flow is exposed to is possible by focussing the aerosol into a lamina by sandwiching the flow in between particle free sheath flows. A continuous flow ensures that water vapour is not depleted by ice particle growth. Flow rates can
be changed in order to vary residence times of aerosols in the chamber. In cases where flow rates are constant, variable aerosol injecting positions allow for manipulation of residence times (see Chapter 3). Using this technique, phase transitions, and homogeneous and heterogeneous nucleation can be studied, provided some composition information of sampled aerosol is available. For heterogeneous nucleation, however, it is hard to distinguish between deposition and immersion freezing at conditions close to and beyond water saturation.

Detection of ice crystals in CFDCs is achieved by directing the exit flow through optical particle counters where size discrimination is used to indicate ice formation given that under most conditions ice will grow rapidly to sizes that will be larger than haze particles. In some cases an evaporation region that is held at ice saturation but below water saturation is added before the optical particle counter to ensure water droplets that formed in the growth region evaporate [Rogers, 1988; Salam et al., 2006]. In more recent developments, by taking advantage of the fact that liquid droplets will not depolarize light whereas ice crystals would, a light scattering depolarization technique has been utilised to count particles therefore providing active phase discrimination [Nicolet et al., 2008].

Lastly, CFDCs can be coupled to various other instruments that allow aerosol preconditioning for phase determination, chemical aging, size selection, composition analysis and counting. Recently instruments such as counter flow
virtual impactors and single particle mass spectrometers have been used to
detect IN composition [Cziczo et al., 2004; Richardson et al., 2007].

1.3.3. Cloud Expansion Chambers

Ice nucleation studies can also be performed in large volume chambers
that can simulate cloud formation conditions. Such methods allow aerosol
observations over long time periods or during slow cooling at ice saturation
[Disselkamp et al., 1996]. Other chambers are capable of processing aerosols
through thermodynamic pathways that are more atmospherically relevant
[White et al., 1987; DeMott and Rogers, 1990; Möhler et al., 2006] where aerosols can
be subjected to repeated cloud formation events, thus mimicking the real
atmosphere and possible cloud scavenging processes. This technique usually
employs dispersion of aerosols into the chamber, and then adding water vapour
followed by cooling to allow for a supersaturation to develop. Cooling is
achieved by adiabatic expansion (pumping out gas) and in some cases cryogenic
cooling is used prior to expansion to achieve low temperatures [Möhler et al.,
2006]. Relative humidity is usually determined using instruments that can
directly take measurements of water vapour or liquid water content [Möhler et al.,
2006].

Cloud chambers can use a variety of techniques, most that are in situ, for
ice detection. FTIR spectroscopy, optical particle counters, cloud particle imagers
and depolarization of light are some that have been implemented. Homogeneous
freezing can be studied and depending on the suite of detection techniques,
distinguishing between the various heterogeneous freezing mechanisms may be possible. Cloud chambers also allow \textit{in situ} processing of aerosols such as exposure to trace gas species for studying the effect of chemical processing on ice formation.

1.3.4. Other Techniques

Ice formation has also been studied using differential scanning calorimetric techniques where the heat release during a phase change is monitored. This technique employs the creation of solution droplet emulsions in, for example, mineral oil [Zobrist \textit{et al.}, 2006] that may or may not have IN as inclusions [Marcolli \textit{et al.}, 2007]. This would then allow the observation of homogeneous and immersion freezing. Typically reported are freezing temperatures as a function of composition of a given solute/water system.

Most recently, in the area of single particle experiments, particles are suspended in isolation from surfaces by optical, acoustic or electrodynamic levitation [Davis, 1997 and references therein]. The latter method has been used most commonly for phase change and growth studies [Carleton \textit{et al.}, 1997; Bacon \textit{et al.}, 1998; Xu \textit{et al.}, 1998] and recently for homogeneous ice nucleation of supercooled drops [Treuel \textit{et al.}, 2007].
1.4. Overview of Homogeneous Ice Nucleation Studies

In this section the main findings of homogeneous nucleation studies in the literature are summarized. There is in general a good understanding of the freezing process and numerous studies in the literature are in good agreement with each other [see references in Pruppacher, 1995; Martin, 2000].

There have been numerous studies that measure the homogeneous freezing nucleation rate of pure water. Methods involving droplets cooled on surfaces, as emulsions, or suspensions in air have been used. About 40 years of work in the field has been summarized [Pruppacher, 1995; Martin, 2000]. The major findings from the studies were:

1) The homogeneous freezing rate, \( J_{\text{hom}} \), increases with decreasing temperature and is very large on an experimental time scale for \( T < 235 \text{ K} \).

2) Solution droplets freeze at progressively lower temperatures as solute concentrations increased (theoretically, an expected tendency).

3) The temperature depression of the freezing point of solution droplets compared to pure water drops of equal sizes exceeded the equilibrium melting point depression by up to a few degrees.

In addition, a field study from an aircraft measurement campaign in Colorado in 1983 found that droplet freezing via homogeneous nucleation was a function of temperature, time and droplet volume [Sassen and Dodd, 1988]. The authors expressed the probability that a droplet would freeze as a function of the effective freezing temperature (\( T^* \)) given by:
where, $T$ is the drop temperature, $\delta T_m$ is the melting point depression and $\lambda$ is the parameter that relates freezing and melting point depressions. Experimentally determined values of $\lambda$ are on average about 1.7 but a range of values between 1 and 2 have been reported in the literature [DeMott in Lynch et al., 2002].

Classical nucleation theory suggests that the homogeneous nucleation process is driven in part by the solute effect on the ice/solution interface energy, by the activation energy for a water molecule to freeze from the solution phase, and also by the water activity [Pruppacher and Klett, 1997]. A water activity parameterization was developed [Koop et al., 2000] where it was proposed that the homogeneous freezing rate of solution particles is only a function of temperature and water activity in solution and not the character of the solute.

The water activity of a solution is the ratio of the solution vapour pressure to the vapour pressure over pure water under the same conditions. The melting point depression is thought to vary as a function of solute concentration and not with the properties of the solute (colligative property). However, for very concentrated solutions, this is false. If the melting or freezing temperatures are expressed as a function of solute molality, considerable scatter is observed for molalities greater than 5 mol Kg\(^{-1}\) (Figure 1.2) [Koop et al., 2000]. However, if the freezing temperature is expressed as a function of water activity, the scatter collapses onto one line that is a constant offset from the activity of water in a solution in equilibrium with ice (Figure 1.2). This lent validity to the proposition
that homogeneous nucleation is only dependent on water activity and $J_{\text{hom}}$ (cm$^{-3}$ s$^{-1}$) could be computed from:

$$\log(J_{\text{hom}}) = -906.7 + 8502\Delta a_w - 26924(\Delta a_w)^2 + 29180(\Delta a_w)^3$$  \hspace{1cm} (1.5)

where $\Delta a_w$ represents the offset from the water activity in equilibrium with the ice line and is given by:

$$\Delta a_w = a_w(c,T) - a_w^i(T)$$  \hspace{1cm} (1.6)

where $a_w(c,T)$ is the composition and temperature dependent water activity of the solution and $a_w^i(T)$ is the activity of water in a solution in equilibrium with ice. For example, for micron sized solution droplets, $T < 235$ K and $\text{RH}_i \sim 140\%$ will be required for freezing to take place. In general for, $200 < T < 235$ K, sulphuric acid, one of the most hygroscopic species in the atmosphere, will freeze only at $\text{RH}_i \geq 140\%$. This parameterization has been compared to many empirical measurements (laboratory and field observations) of homogeneous freezing of sulphuric acid that are in good agreement with one another \cite{sassen1989, heymsfield1993, jensen1998, lin1998, chen2000, field2001, prenii2001, moehler2003, abbatt2006} and the Koop et al. \cite{koop2000} model.

Finally, while there has generally been good agreement of laboratory and field studies concerning the ice formation in sulphuric acid aerosol, a study by Heymsfield and Miloshevich \cite{heymsfield1995} that sampled continental cirrus found that homogeneous freezing conditions were not satisfied. The discrepancy has since
been explained by a suggestion of the possible presence of effloresced ammoniated sulphate particles that can act as heterogeneous ice nuclei (IN) that would initiate freezing at lower RHs than those required for homogeneous freezing [Abbatt et al., 2006].

![Figure 1.2](image)

**Figure 1.2.** Adapted from Koop et al. [2000]. Experimental data used to derive water activity based parameterization. (a) melting temperatures (squares) and freezing temperatures (circles) of droplets ~ 1-10 μm of 18 different solutions as a function of solute molality. (b) same data as in (a) but as a function of water activity of water in solution. Dashed line: melting temperature and solid line: freezing curve shifted by $\Delta a_w = 0.305$.

1.5. **Overview of Heterogeneous Ice Nucleation Studies**

Observations generally suggest that ice exists in the atmosphere under conditions where homogeneous nucleation is not known to occur. For example, the lower RH inferred from Heymsfield and Miloshevich [1995] implies that heterogeneous freezing supports an ice formation pathway in cirrus. This is also
supported by observations of mixed phase clouds in the atmosphere at temperatures as high as 268 K [Sassen et al., 2003] and 253 K [Twohy and Poellot, 2005]. Heterogeneous ice nucleation may reduce the energy barrier required to initiate ice formation in the atmosphere by facilitating the ice phase formation [Karcher and Lohmann, 2003]. It is therefore reasonable to consider other pathways of ice formation that have a smaller activation barrier than homogeneous nucleation.

1.5.1. Early Laboratory Studies in Heterogeneous Ice Nucleation

Heterogeneous ice nucleation has been studied since the 1940’s. For example, the freezing of silver iodide was studied in the immersion mode at water saturated conditions and found to nucleate ice at temperatures as warm as 269 K [Vonnegut, 1947]. This was followed by more ice nucleation studies on silver iodide [Bryant et al., 1959] and as interest grew in applying it as a cloud seeding species for potential weather modification [Detwiler and Vonnegut, 1981].

In order to determine IN concentrations in air, a laboratory based study in Tokyo, Japan sampled outdoor air for ice nucleation at water saturation. This was accomplished using an air-tight copper cage that contained a concentrated sugar solution to collect ice crystals. Two litres of air were trapped into the copper cage and then cooled to temperatures of 260, 258 and 253 K followed by a supply of water vapour. Ice crystals were collected on the sugar solution and IN concentrations inferred [Isono et al., 1959]. The authors reported that low IN
concentrations were observed on days when air came in from the Pacific, but “abnormally high” IN concentrations were observed when air reached Japan from the arid regions of Northern China and Mongolia where heavy dust storms occurred in front of cold fronts [Isono et al., 1959]. This was one of the first instances when mineral dust was implicated in heterogeneous ice formation.

Subsequently, studies proceeded to demonstrate the efficiency of mineral dusts in ice formation. For example a study on kaolinite found that ice nucleated at temperatures as warm as 264 K [Mason and Maybank, 1958; Mason, 1960]. This was observed by suspending kaolinite particles in a chilled Pyrex cage within a freezer that had a constant supply of water vapour from a heated source of water. Ice crystals were collected on a soap film where they grew large enough to be seen and counted. Another laboratory study of pre-selected mineral particles also inferred a variety of dusts to be good IN by studying ice formation on a microscope cold stage with a controlled humidity environment [Roberts and Hallett, 1968]. The particles studied were kaolinite, montmorillonite, gypsum, calcite, vaterite, albite, biotite with diameters between 0.5 and 3 μm. The warmest temperature at which these particles initiated ice formation (1 event out of $10^4$) was reported in the range 247 – 263 K at water saturation. If the experiments were repeated on the same particles, the threshold temperature (temperature at which ice is formed at water saturation) increased and was reported in the range 261 – 269 K. This behaviour was attributed to pre-activation and it was suggested that after an initial freezing cycle, ordered water molecules were retained on the
particles that could then act as favourable sites for ice formation in subsequent cycles [Roberts and Hallett, 1968]. The idea of pre-activation was later observed and confirmed in a separate study on kaolinite, calcite and gypsum using a similar cold stage technique [Edwards and Evans, 1971].

Finally an ice thermal diffusion chamber was used to examine ice nucleation on smoke particles and ground soil samples taken from the University of Denver campus, and kaolinite [Schaller and Fukuta, 1979]. For freezing of kaolinite, Schaller and Fukuta [1979] observed ice nucleation by condensation at 263.1 K and RH$_w$ = 103% which was in good agreement with Roberts and Hallett [1968] whose kaolinite samples also froze by condensation freezing forming ice at 262.5 K and RH$_w$ = 100%. Condensation freezing (at water saturation) for the local soil samples was observed at T = 260.5 K which was colder than that of kaolinite.

It is apparent that there was evidence from the early laboratory studies to indicate mineral dusts and clays are efficient IN. However, the efficiencies of different types of natural dust samples still remain unassessed. Investigations for ice formation in the deposition mode were also lacking. In addition, in part limited by the instrumentation capabilities, ice formation studies under conditions relevant to the cirrus regime were also sparse. There began to arise a need for systematic observations of ice formation onto dust over a range of T and RH in order to have clarity on the ice activation spectrum of dust aerosols.
1.5.2. Evidence of Mineral Dust Association with Glaciated Clouds in the Troposphere

This section will highlight field studies that have sampled ice crystals at various altitudes in a range of clouds using instrumentation mounted into aircraft. The goal is two fold: first to show the glaciation of clouds occur in warm and cold clouds and second, to provide empirical evidence that suggests mineral dust is in fact found in the centre of ice crystals that are sampled at altitudes of a few thousand meters. In addition, some modelling studies and ground observations are also presented that provide evidence for mineral dust loading, long range transport and lofting into the upper troposphere.

1.5.2.1. Field Studies of Ice Nucleation and Detection

There is growing and compelling evidence of the association of desert dust plumes with ice formation at both warm and cold temperatures. Some of the earliest evidence of ice crystals appearing at warm temperatures (269 K) in a cumulus cloud was presented when aircraft sampling was conducted in a long lived cumulus cloud off the southern coast of Australia [Mossop et al., 1968] where ice concentrations were found to be close to 100 l$^{-1}$. The authors stated that this was at least 3 orders of magnitude higher than expected concentrations based on cloud chamber experiments and suggested perhaps ice multiplication mechanisms were at work.

In a much later field study over southern Florida, ice crystals were also observed when sampling in an altocumulus cloud at relatively warm
temperatures of about 268 K to 265 \cite{Sassen2003}. Polarization lidar showed that mineral dust particles transported form Saharan Africa were present in the cloud during sampling.

In a field and modelling study of a thin wave cloud over south-central Great Plains, USA, it was found that heterogeneous processes initiated ice nucleation before homogeneous processes. This allowed ice crystals to grow to large sizes implying that ice formation via IN will precipitate from the cloud first because of early growth initiation \cite{DeMott1998}. During the same field study, single particle analysis using analytical electron microscopy was performed to gain information on the composition of the heterogeneous IN collected. The dominant components were carbonaceous, crustal and metallic material \cite{Chen1998}.

During a sampling field study, CRYSTAL - FACE, concentrations of IN were reported to be 1 cm$^{-3}$ at 236.5 K and RH$_i$ = 123\% through a 2km deep cloud layer during a time period when dust presence from North Africa was confirmed in the layer through lidar data, air mass backtrajectories and surface sampling \cite{DeMott2003b}. These concentrations were considered to be quite high and related to a dust storm. Under normal meteorological conditions, the median concentrations of IN are a factor of 100 less \cite{Rogers1998}.

A ground based study at Storm Peak, Colorado showed the relative importance of mineral dust particles in heterogeneous ice forming processes \cite{DeMott2003a}. The authors used single particle laser mass spectrometry to
compare ambient aerosol composition to the composition of particles that acted as heterogeneous IN by activation in a CFDC. The heterogeneous IN were mostly dominated by mineral dust and/or fly ash and metallic particles [DeMott et al., 2003a; Richardson et al., 2007]. The crustal and metallic material was generally unmixed with sulphate and/or organics which were only detected on 25% of the particles in the mineral particle category.

In a separate field study a counter virtual flow impactor was used to collect residual particles larger than 0.1 μm in diameter from anvil cirrus clouds in the temperature range 252 to 217 K [Twohy and Poellot, 2005]. For warm temperatures, insoluble crustal and metallic particles were found to outnumber soluble salts and sulphates which dominated the IN composition at temperatures below 238 to 233 K. This implied a shift in mechanism from heterogeneous to homogeneous nucleation at this temperature range.

Lastly, three gravity-wave-induced clouds and a glaciating altocumulus layer were monitored with lidar at Leipzig, Germany [Ansmann et al., 2005]. The authors report that midtropospheric clouds formed in Saharan dust at a height of 3.5 to 6.5 km (264 to 246 K) and distinct ice formation in the altocumulus was triggered by the gravity wave.

Results from field investigations such as these presented evidence that dust is vital in ice formation and injected a renewed curiosity into laboratory based studies to better define the formation conditions and mechanisms that result in freezing of mineral dust aerosol. For laboratory investigations to target
samples that are representative of mineral dust in the atmosphere, more
information regarding direct dust emission and atmospheric loadings is also
needed.

1.5.2.2. Mineral Dust Loading

The annual global mineral dust burden in the atmosphere is on the order
of 1600 Tg yr\(^{-1}\), second only to sea salt in terms of aerosol production \cite{Andreae,Rosenfeld,2008}. Quantifying the role of dust’s participation in ice formation
requires in part knowing regions of high atmospheric dust sources, particle size
distributions and residence times. There has been considerable progress made in
recent years to define the geographical areas that are dust emitting including the
mechanisms of emission. Dry lake beds in arid areas are considered to have
strong dust emitting potential \cite{Prospero et al.,2002; Tegen et al.,2002} due to the
lack of moisture. There is a strong variability of dust emission based on
geography suggesting that factors such as low vegetation cover, soil texture, low
soil moisture content resulting from low rainfall and high wind speeds are major
contributors to dust emitting sources \cite{Washington and Todd,2005}.

Direct anthropogenic disturbances are not thought to be a major
contributor to dust emission into the atmosphere \cite{Mahowald et al.,2005}. For
example, contributions of dust that result from agricultural activities are thought
to be less than 10% of total loading \cite{Tegen et al.,2004}. Increased dust transport
from the Sudano-Sahel region was initially thought to be due to human
disturbances of the soil cover but is now considered to be a result of reduced rainfall in the region [Prospero and Lamb, 2003] due to the global changes in the patterns of sea surface temperature [Giannini et al., 2003]. However, for regional influences on dust emission, poor land use or management such as overgrazing can have consequences on dust mobilization [Andreae and Rosenfeld, 2008].

There are still major discrepancies in dust size distributions in the atmosphere predicted by models and observations. Closer to emission sources, models and observations indicate mode sizes of 10 μm or greater based on mass distributions. More relevant to the atmosphere is what the size distributions are after atmospheric transport and/or processing has occurred. Considering long range transport, models have shown a mass mode in the range 1.5 – 3 μm while observations have shown mass modes of at least a factor of two higher [Reid et al., 2003; Andreae and Rosenfeld, 2008]. In contrast to the mass mode, the number mode always shows particle sizes of less than 1 μm [Zender et al., 2003].

1.5.3. Recent Laboratory Studies of Mineral Dust Heterogeneous Nucleation

Some of the field studies discussed earlier provide evidence for crustal particles to be relatively ‘fresh’ and unmixed with inorganic or organic constituents in the atmosphere. Pure unmixed mineral dusts, clays and metal oxides therefore garnered attention in more recent laboratory investigations. For example, size selected Asian Dust aerosols were studied in a continuous flow diffusion chamber (CFDC) by exposure to ice supersaturated conditions in the
temperature range 228 to 213K [Archuleta et al., 2005]. It was found that the largest natural dust particles were most efficient at nucleating ice by deposition mode irrespective of temperature. Using the same instrument from the same group, Owens dry lake dust (large source of particulate matter in Western hemisphere) also nucleated ice heterogeneously at temperatures below 233K under RH$_i$ lower than those required for homogeneous ice nucleation [Koehler et al., 2007]. Finally also using a CFDC, kaolinite particles were found to be less efficient than montmorillonite at ice formation in the deposition mode for the temperature range 258 to 233K. The RH with respect to water at which ice was first detected decreased with temperature [Salam et al., 2006].

Arizona Test Dust (ATD), a surrogate for mineral dust in the atmosphere is commercially available and has been used as a reference material for numerous studies. For example, in cloud expansion experiments at the AIDA facility in Karlsruhe, Germany, adiabatic expansions are used to mimic cloud forming conditions in a large 84m$^3$ vessel. Arizona Test Dust was found to form ice in the deposition mode at RH$_i$ as low as 105% at 224K [Mangold et al., 2005]. In the same facility but in separate investigations, Asian and Saharan dusts were also tested for ice nucleation. At temperatures above 233K, only condensation freezing was observed, but at colder temperatures ice formation was observed in the range 110% < RH$_i$ < 130% [Field et al., 2006]. In addition it was inferred that ATD was more efficient at ice nucleation in the deposition mode than the Saharan and Asian dust samples [Möhler et al., 2006].
Using a hydrophobic cold stage and a digital camera to observe the first ice formation event onto montmorillonite, silica, alumina and Saharan Dust in the temperature range $222 < T < 264\text{K}$, it was found that all particulate matter was efficient at forming ice in the deposition mode and that no significant differences in onset RH$_i$ were inferred for the different temperatures [Kanji and Abbatt, 2006]. In the same study it was found that at 233K exposing higher surface areas of Saharan Dust particulates gave lower onsets for ice formation. Arizona Test Dust has also been studied on a cold stage flow cell using optical microscopy in the temperature range 197 to 260K [Knopf and Koop, 2006]. In this study it was found that the ATD particles formed ice by the deposition mode and activated over a broad range of RH suggesting that different minerals in the ATD had different ice nucleation thresholds, some activating at lower RH than others. Using a similar technique but in a separate study, kaolinite and muscovite particles were found to nucleate ice at RH$_i < 112\%$ for the temperature range 233–246K while quartz and calcite particles were less efficient for the same temperature range and required close to water saturation conditions [Eastwood et al., 2008].

Differential scanning calorimetry has also been used to investigate immersion mode nucleation of ATD particles in pure water [Marcolli et al., 2007]. Ice was found to nucleate at temperatures as high as 256 K. Using experimental observations and classical nucleation theory Marcolli et al. [2007] concluded that efficiency of ice formation increased with increase in size of the IN. Furthermore
it was suggested that active sites of ice formation would only be present if the diameter of the ATD particles was greater than or equal to 100 nm.

Lastly, a recent study that used a CFDC to look at ice formation for $T > 233$K onto montmorillonite that was previously exposed to atmospherically relevant concentrations of ammonia gas showed that the particles’ efficiency to nucleate ice increased by a factor of two when compared to the unexposed montmorillonite particles [Salam et al., 2008]. This suggests that atmospheric processing of aerosols may significantly alter ice nucleation characteristics.

The recent laboratory studies presented provide strong evidence for dust being an efficient IN. However, other than knowing the general efficiency, properties of the particles that contribute to this efficiency such as particle size or surface area have only been investigated in a handful of studies [Archuleta et al., 2005; Koehler, 2007; Welti et al., 2009].

Interest in cirrus ice formation has also motivated laboratory studies to investigate the inclusion of dust particles into solution droplets that would usually freeze homogeneously without an inclusion. Two common constituents of atmospheric mineral dust, montmorillonite and kaolinite, were studied as immersion nuclei in ammonium sulphate solutions by depositing particles onto a cold stage and using optical microscopy to observe ice in the temperature range 239 to 203K [Zuberi et al., 2002]. For droplets in the size range 10 – 55 $\mu$m, solution droplets with dust inclusions froze 10K higher than those without the inclusions. Using a similar technique, sulphuric acid and ammonium sulphate coated
kaolinite particles showed that the onset RH, required was about 30% higher for cases where the coatings are believed to be aqueous. However, for ammonium sulphate at 236K where the coating could have remained effloresced, the coated particles were as efficient as the uncoated kaolinite [Eastwood et al., 2009].

Hematite and Corundum aerosol particles immersed in an ammonium sulphate solution in the temperature range 232.1 to 216.4K were studied using aerosol flowtube infrared spectroscopy. The mineral inclusions resulted in the freezing temperatures increasing by as much as 6K [Hung et al., 2003]. Inclusion of dust particles therefore can provide an explanation of early onset of freezing in aqueous sulphate solutions that would otherwise remain unfrozen until homogeneous conditions are encountered.

In order to compare the effect of the inclusion composition on ammonium sulphate crystallization in the atmosphere, optical microscopy was used to detect phase changes as a function of changing RH when soot and kaolinite particles were used as inclusions [Pant et al., 2006]. No difference in crystallization relative humidity (CRH) was found with soot, but there was up to a 10% increase in CRH when kaolinite was used. This has implications on the possible existence of solid phases at higher RHs than predicted from droplets free of inclusions.

There is evident influence of mineral dust on the freezing and crystallization conditions of salt solution droplets. Sulphate species were the obvious choice for coatings given their ubiquity. Knowing the contributions of other species found in the atmosphere that are sometimes externally mixed with
mineral dust, such as organics or carbonaceous material, to ice nucleation will also be relevant. Importance for investigation of mineral dust as heterogeneous IN arises from wanting both a fundamental and practical understanding of their effectiveness as IN. For deposition mode freezing this is particularly relevant since previous studies focussed on high T and only recently are low T studies beginning to investigate the mechanism.

1.5.4. Other Heterogeneous IN

This section highlights the roles of other species that can act as potential IN in the atmosphere. Their role as IN is relevant either due to their abundance in the atmosphere (bacteria) or in the case of organics their presence in the same field studies that implicated mineral dust as being efficient.

1.5.4.1. Organic IN

The efficiency of organic species as IN is thought to be varied due to the wide range of organic species present in atmospheric aerosol. To cloud physicists organic molecules appear promising for cloud seeding due to their wide variety and effectiveness [Szyrmer and Zawadzki, 1997]. The first organic ice nucleating substance reported was phloroglucinol, \( C_6H_3(OH)_32H_2O \) [Bashkirova and Krasikov, 1957]. This molecule was possibly studied because of its wide used in black ink making and its natural occurrence in the bark of trees (e.g. found in apple trees). A study that compared ice nucleation at water saturation of phloroglucinol to
kaolinite found that the organic substance froze at 268K which was higher than the threshold temperature of kaolinite at 260K [Edwards and Evans, 1971]. Organic compounds such as phenols and benzoic acids [Parungo and Lodge, 1965], oxalic acid [Zobrist et al., 2006], maleic acid [Shilling et al., 2006], long-chain alcohols in particular heptadecanol [Ochshorn and Cantrell, 2006], have also been found to act as efficient IN in the immersion and deposition mode. For a more detailed discussion on organics species as IN refer to the introduction in Chapter 2 (Section 2.2).

1.5.4.2. Biogenic IN

Under the category of organic substances, there is also biogenic material, living or dead, that has been reported to induce freezing well below temperatures required for homogeneous freezing. For example, pollen nucleated ice by condensation freezing at 265 K for RH slightly above water saturation [Diehl et al., 2001]. Other studies have demonstrated the efficiency of bacterial cells, in particular Pseudomonas Syringae, to be extremely high at forming ice. It can initiate the freezing process as temperatures as high as 271K in the immersion freezing mode [Maki et al., 1974; Vali et al., 1976]. These studies concluded that decaying plant matter can be sources of IN and cannot be ignored due to their ubiquitous nature. Deposition mode nucleation onto bacteria has been reported to take place at T < 265K at slight water subsaturated conditions [Szyrmer and Zawadzki, 1997]. In a more recent study, the same species of live and
dead bacteria was investigated in a cloud expansion chamber at the AIDA facility in Karlsruhe, Germany [Mohler et al., 2008]. The authors reported condensation freezing where 1 in $10^4$ particles froze for the live bacteria in the temperature range 266 to 262K, whereas the dead bacteria froze via immersion mode even at temperatures of 267.3K. Reasons as to why bacteria are efficient IN are still largely unknown, but suggestions are that their ice nucleating ability is a key adaptation that should shorten atmospheric residence time due to precipitation or gravitational settling. This would prevent rapid dessication and help the bacteria access the biodiversity on the earth’s surface due to precipitation and settling of ice crystals that form as a result of its IN activity [Szyrmer and Zawadzki, 1997].

1.5.4.3. Black Carbon/Soot as IN

One of the prime candidates for ice nucleation at cirrus relevant temperatures are soot particles due to direct emissions into the troposphere from aircraft emissions and biomass burning. Ice nucleation onto soot can be complex. For instance, relatively pure soot particles have been known to heterogeneously induce ice formation from the vapour phase [DeMott et al., 1999; Möhler et al., 2005a; Möhler et al., 2005b], typically at supersaturations higher than those required for mineral dust. However, this ability is reduced by the presence of organic coatings, sulphuric acid or if the soot has a high organic content [DeMott, 1999; Möhler et al., 2005a; Möhler et al., 2005b].
1.6. Secondary Ice Formation Processes

The concentration of ice crystals in the atmosphere, especially in cumulus and stratus where heterogeneous ice formation is common, can exceed the concentration of IN by orders of magnitude. Mechanisms other than heterogeneous nucleation are implied for production [Cantrell and Heymsfield, 2005]. A commonly proposed mechanism to reconcile this discrepancy is the Hallet-Mossop process [Hallett and Mossop, 1974; Mossop and Hallett, 1974; Mossop, 1976]. This process includes formation of ice by riming followed by splintering of the ice to produce particles. Riming is the formation of ice that occurs when an ice crystal comes into contact with liquid particles. The two variables that are thought to control this process are the temperature of the supercooled liquid cloud and the speed at which graupel (particles that result from the riming process) falls through the cloud. In the experiments of Hallet and Mossop they found that splinters were only formed if the air temperature was less than 270K but higher than 265K and that the number of ice crystals produced increased with speed of falling graupel. However, in a later study it was found that the maximum number of crystals produced is when graupel falls at a speed of 6 m$^{-1}$ [Saunders and Hosseini, 2000]. A number of studies found this process to be sufficient in explaining the discrepancies observed in the atmosphere between ice
crystal numbers and IN [Blyth and Latham, 1993; Blyth et al., 1997; Ovtchinnikov et al., 2000; Hogan et al., 2002; Phillips et al., 2003]. However, the Hallet-Mossop process could not explain the increase in ice crystal number outside the specified temperature range. Therefore at temperatures lower than 265K, the questions of ice particle multiplication still remained [Bower et al., 1996]. Further mechanisms of ice production were proposed after it was found that primary ice nucleation and the Hallet-Mossop process did not quantitatively account for ice crystal numbers [Hobbs and Rangno, 1985; Hobbs and Rangno, 1990; Rangno and Hobbs, 1991; Rangno and Hobbs, 1994]. Subsequently, mechanisms such as mechanical fracture of crystals were invoked in addition to the Hallet-Mossop process in order to reconcile ice crystal numbers with IN numbers. However, the time scale upon which fracturing would occur was still not sufficient to explain the observations from Rangno and Hobbs [1994]. Lastly, in addition to the existing discrepancy it was later discovered that the shattering of ice large ice crystals on the aircraft sampling probes and re-suspension of previously deposited ice particles on inlet shrouds could have led to false high counts for ice crystals [Gardiner and Hallet, 1985; Weber et al., 1998; Murphy et al., 2004].

1.7. Motivation

In the previous section, compelling evidence is presented from past work to show that mineral dust is an active IN in the atmosphere. There is also evidence to show some organic molecules are ice active as well. The current
work is motivated by the fact that deposition mode nucleation may be an important pathway to ice formation and that it has been poorly studied, since earlier works focussed on high temperature. This work examines whether the various IN (dust, hygroscopic and hydrophobic organic particulate) will be active in the deposition mode at cirrus relevant temperatures. For organic molecules, motivation comes from the studies that found varying degrees of IN effectiveness and from measurements of high organic content of free tropospheric particulates [DeMott et al., 2003a]. It is important to identify what types of functionalities result in good IN and if there is relevance to deposition mode nucleation. Also, in part motivated by my previous work [Kanji and Abbatt, 2006], that found that the efficiency of Saharan Dust as IN varied with particle number, the current work further examines the effect of particle number related variables on deposition mode nucleation.

1.8. Thesis Objectives

The specific goals of this work are two fold. First, this work seeks to identify the relative efficiencies of ice nuclei for atmospherically relevant particles in the cirrus regime (T~ 233 K). This includes identifying the temperature at which deposition mode freezing is applicable. The second goal is to gain a deeper understanding of how the variables associated with mineral dust loading in the atmosphere, such as particle and concentration, will influence the ice formation process. The questions that arise are:
• What are the relative ice nucleation efficiencies of atmospherically relevant IN for the cirrus regime?
  o Is there an observable difference for dusts sourced from different regions?
  o How do organics of varying degrees of oxidation compare in efficiency?
  o What is the contribution of atmospherically abundant particles like soot and bacteria?
  o Is there a suppression of the IN activity due to chemical processing of dusts?

• For the most efficient IN, what is the temperature at which deposition mode is active?

• As with homogeneous freezing, is there a unique onset of deposition freezing that can be defined?
  o How do particle size and surface area influence onset?

These questions are answered by quantifying relative humidity and temperature conditions at which various particles will form ice at 233 K in Chapter 2. This is done by using a cold stage flow cell design for RH and T monitoring and digital camera to detect ice formation. This experimental
apparatus was developed as part of my Masters degree at the University of Toronto.

To be able to probe further the efficiency of mineral dust aerosol and to perform preliminary kinetic growth experiments, a new continuous flow diffusion chamber was designed, built and validated as discussed in Chapter 3.

The chamber was then used to perform size and surface area selected studies on Arizona Test Dust particles at 223 K, as described in Chapter 4.

Finally, to identify the temperature range where deposition mode nucleation becomes applicable for dusts, and to compare the ice formation conditions for bacterial aerosol and soot, the CFDC was operated at an international ice nucleation workshop (ICIS 2007) to compare ice measurement instruments in Karlsruhe, Germany at the AIDA facility. Chapter 5 presents the results of this study as well as a comparison to CFDC results and those of the expansion chamber technique.


Szyrmer, W. and I. Zawadzki (1997). "Biogenic and anthropogenic sources of ice-
209-228.

Tegen, I., S. P. Harrison, K. Kohfeld, I. C. Prentice, M. Coe and M. Heimann
(2002). "Impact of vegetation and preferential source areas on global dust aerosol:
Results from a model study." *Journal of Geophysical Research-Atmospheres* 107(D21):

importance of climate and land use in determining present and future global soil

C. Richard, K. H. Rosenlof, T. L. Thompson, M. J. Mahoney and J. C. Wilson


Vali, G., M. Christensen, R. W. Fresh, E. L. Galyan, L. R. Maki and R. C. Schnell


CHAPTER TWO
Ice Formation via Deposition Nucleation onto Mineral Dust and Organics: Dependence of Onset Relative Humidity on Total Particulate Surface Area

2.1. Abstract

We present ice nucleation results for Arizona Test Dust, kaolinite, montmorillonite, silica, silica coated with a hydrophobic octyl chain, oxalic acid dihydrate, Gascoyne Leonardite (a humic material), and Aldrich humic acid (sodium salt). The focus was on deposition mode nucleation below water saturation at 233 K. Particles were deposited onto a hydrophobic cold stage by atomisation of a slurry/solution and exposed to a constant partial pressure of water vapour. By lowering the temperature of the stage, the relative humidity with respect to ice ($\text{RH}_i$) was gradually increased until ice nucleation was observed using digital photography. Different numbers of particles were deposited onto the cold stage by varying the atomization solution concentration and deposition time. For the same total particulate surface area, mineral dust particles nucleated ice at lower supersaturations than all other materials. The most hydrophobic materials, i.e. Gascoyne Leonardite and octyl-silica, were the least active. For our limit of detection of one ice crystal, the ice onset $\text{RH}_i$ values were dependent on the total surface area of the particulates, indicating that no unique threshold $\text{RH}_i$ for ice nucleation prevails.
2.2. Introduction

Cloud-aerosol interactions still provide some of the greatest uncertainties in predictions of climate change [IPCC, 2007]. In part, this results from an incomplete understanding of the processes of cloud formation, particularly those giving rise to mixed phase and ice clouds. The two basic mechanisms of ice formation in the atmosphere are homogenous and heterogeneous nucleation. The former usually occurs at high supersaturations and low temperatures, as are encountered at times in the upper troposphere. However, it has been known that heterogeneous mechanisms prevail as well, given the relatively high temperatures and low supersaturations at which ice can form [Pruppacher and Klett, 1997].

Recent field studies have confirmed the importance of heterogeneous nucleation emphasizing, for example, the role of mineral dust particles as ice nuclei (IN). Taking just one example, Prenni et al. [2007] examined ice formation processes in cumulus clouds in Florida during CRYSTAL-FACE and found that the highest concentrations of ice crystals occurred on the same date as the highest concentrations of heterogeneous IN when ice crystal residuals were tested for nucleation in a continuous flow diffusion chamber (CFDC) while flying through Saharan aerosol layers [DeMott et al., 2003b]. By taking CFDC measurements of anvil particle residuals they concluded that the high ice crystal numbers were due to intake of Saharan dust by the clouds.
Knowing that heterogeneous nucleation occurs in the field, the challenge to the laboratory community is to identify the materials that act as good IN and to express the rates of nucleation in a form that can be usefully employed in cloud-climate models. In that regard, early studies have identified both mineral dust materials and organics as possible candidates. For example, Higuchi and Fukuta [1966] and Roberts and Hallet [1968] showed that the montmorillonite and kaolinite clays are good IN at temperatures much higher than required for homogeneous nucleation. And Parungo and Lodge [1965] tested a series of organics, i.e. substituted phenols and benzoic acids, for ice formation abilities in the immersion and deposition mode. It was found that there was a free energy relationship between molecular structure and nucleating ability.

More recent studies take advantage of new experimental techniques and of our improved knowledge of particulate types that may be present in the atmosphere. For example, differential scanning calorimetry has been used to show that solutions containing immersed solid oxalic, adipic, succinic, phthalic and fumaric acids were found to be poor IN. By contrast, the dihydrate of oxalic acid was found to be a quite efficient [Zobrist et al., 2006]. This was in partial agreement with a study carried out by Parsons et al. [2004] which showed that some dicarboxylic acids are inefficient IN. It is also consistent with the findings that another soluble solid, ammonium sulphate (AS), can also act as a heterogeneous IN [Zuberi et al., 2002; Abbatt et al., 2006; Shilling et al., 2006]. Other organics are also active at warmer temperatures between -10 and -17 °C. In
particular, Ochshorn and Cantrell [2006] found that long-chain alcohols promote ice nucleation by stabilising ice-like clusters with their hydrophilic tails. In the case of mineral dusts, a number of studies have shown different dust types to be efficient IN in the deposition mode at temperatures below 240 K. For example, Asian dust studied by Archuleta et al. [2005] and Field et al. [2006], Arizona Test Dust (a reference dust material) studied by Knopf and Koop [2006] and Möhler et al. [2006], kaolinite studied by Dymarska et al. [2006], and Owens Lake dust (a significant dust source in the Western hemisphere) studied by Koehler et al. [2007] were all found to be good IN, forming ice at RHs well below those required for homogeneous freezing requirements.

With these past studies in mind, we focus in this work on the role of deposition nucleation under the largely unexplored cold conditions of the mid and upper troposphere, where cirrus clouds form. We are particularly interested in comparing the relative efficiencies of a range of mineral dust types and organics using the same experimental technique that is sensitive to the nucleation of a single ice crystal from a large total number of particles. This work extends earlier measurements of Kanji and Abbatt [2006] that showed efficient deposition nucleation onto a number of pure minerals as well as Saharan Dust. Particularly interesting was the dependence of the ice onset RH on the number of Saharan Dust particles being examined, i.e. demonstrating that there is no unique threshold at which nucleation occurs. In this work, we continue to address mineral dust samples by extending the work to the dependence of the ice onset
One question we seek to answer is whether the findings for Saharan Dust are general or not. As general motivation, dust and its components are prime candidates for study given that dust is often associated with ice particles and has been shown to be an active IN in the cirrus regime [e.g. DeMott et al., 2003a].

A second focus of the paper is on organics. In particular, the residence time of crustal material can be on the order of several weeks [Prospero, 1999]. And so, it is likely that physical and chemical processing will produce coatings of various types on the dust. Ice formation on dust that is immersed in AS has been investigated before [Zuberi et al., 2002; Hung et al., 2003], however the role of organic coatings has not. In this regard, we have also studied the effects of placing a highly hydrophobic material on a silica surface. In later work, we will study how oxidation of this coating may affect IN abilities. With the wide range of atmospheric organics, we have also focussed on humic materials given that they may be lofted as particulates and because they act in some way as a model of humic-like substances in the atmosphere [Graber and Rudich, 2006]. Lastly, we have studied oxalic dihydrate acid given the findings of Zobrist et al. [2006] described above.

The results of the study indicate that a wide range of materials can act as deposition mode IN with a consistent trend of increasing activity from mineral dusts to hygroscopic solids to hydrophobic materials. Also, we confirm the findings from Kanji and Abbatt [2006] that the ice onset RH, for a specific
particulate type is dependent on the number of particles being studied, i.e. their total surface area.

2.3. Experimental Methods

2.3.1. Experimental Approach

Ice nucleation measurements were obtained using the flow system shown in Figure 2.1. The detailed instrument design and performance characteristics are described in Kanji and Abbatt [2006]. Briefly, aerosol particles are deposited onto a Teflon-coated, copper cold stage that is housed in a vacuum chamber and is in thermal contact with a re-circulating chiller to allow temperature control. The Teflon-coated stage is the coldest part of the system and is exposed to a constant partial pressure of water while its temperature is reduced, to increase RH$_i$. The entire Teflon surface of the cold stage is under observation by a digital camera (Figure 2.2) that captures ice formation as soon as an ice crystal forms (minimum detectable size 100µm) The system is sensitive to one ice crystal and the RH$_i$ at which ice is first observed is defined as the onset RH$_i$. The RH$_i$ changes by 1% every 6 seconds as the stage cools. Upon observation of an ice formation event, the experiment is concluded. In this study the measurements are conducted at 233 K to mimic the cirrus regime. The error associated with the reported RH$_i$ is ±2%, arising largely from the uncertainty in temperature [Kanji and Abbatt, 2006].

As described in detail previously [Kanji and Abbatt, 2006], the operating principle of this technique is that the first ice nucleation event over the entire
Figure 2.1. Schematic of flow apparatus. Nitrogen is fed through a water bubbler from a mass flow controller and then to the vacuum chamber (~ 3.5 cm$^3$) containing the cold stage. Pressures are measured in the cold stage and bubbler by capacitance manometers in order to calculate the partial pressure of water in the vacuum chamber [see Kanji and Abbatt, 2006].

cold stage occurs on a single particle and that it is observable with the digital camera. In particular, the rate of growth of the crystal to the minimum detectable size is essentially instantaneous within our observational timescale. Thus, by varying the numbers of particles on the stage, we can measure the dependence of the ice onset RH$_i$ on the total surface area present. This allows us to evaluate lower limits to nucleation rates, as described later. A unique feature is that our technique is sensitive to a very low fraction of particles on the cold stage participating in ice formation on the cold stage (down to 1 particle in $10^5$).

2.3.2. Sample Preparation

The particulates were prepared as aqueous suspensions/solutions with 18 MΩ water, except in the case of silica. For silica and octyl-coated silica, methanol
was used because it was shown [Kanji and Abbatt, 2006] that water leads to clumping of silica particles on the cold stage resulting in a non-uniform distribution. The particulates were atomized from a constant output atomizer (TSI model 3076) at specific concentrations and deposition times so as to vary the total surface area of aerosols on the stage. The particles were then exposed to low RH conditions at low pressure and room temperature (RH < 1 %) for 18 hours to remove water. Arizona Test Dust (Powdered Technology Inc., 0-5 µm), kaolinite (KGa-1b, Clay Mineral Society, Source Clays Repository), oxalic acid (Aldrich

**Figure 2.2.** Detailed schematic of cold stage where particles nucleate ice.
Chemicals), pure silica (Lancaster Synthesis Inc., 1.5 µm,) octyl-coated silica (see below for preparation), Aldrich humic acid (Aldrich Chemicals, sodium salt) and Gascoyne Leonardite (International Humic Substances Society, IHSS) were all prepared in water solutions/suspensions. We anticipate that the oxalic acid will be present as the dihydrate on the cold stage before ice nucleation because the RH at which the transition from anhydrous to dihydrate occurs has been shown to be as low as \( \text{RH}_w = 20\% \) at 258 K and has a very weak temperature dependence \([\text{Braban et al.}, 2003]\).

The octyl-coated silica was prepared using a synthesis from \textit{Usher et al.} [2003]. Briefly, the functionalisation was accomplished by reacting 1.5 g of SiO\(_2\) powder that was baked in an oven for 12 hours with 10 drops of n-octyltrichlorosilane and 5 drops of pyridine in a 100 mL dry toluene solution, all from Aldrich. The solution was refluxed for 3 hours at approximately 363 K and the product collected with vacuum filtration followed by thorough rinsing with dry toluene. Characterization of the octyl chain on the silica particles was performed with XPS (Leybold Specs MAX 200 XPS, Specs GmbH, Berlin, Germany) using a Mg K alpha source operating at 15 kV and 20 mA and TOF-SIMS (ION-TOF GmbH, Munster, Germany). A Ga liquid-metal gun was used. The XPS analysis showed that there was a significant increase in C-C bond intensity in the product as well as the C/Si and C/O ratios increased in the product when compared to the blanks. The SIMS results showed the presence of \( \text{C}_3\text{H}_7 \) (\( m/z = 43.1 \)) and \( \text{C}_4\text{H}_9 \) (\( m/z = 57.1 \)) peaks in the product but not in the pure
silica sample. The intensity of the C$_2$H$_5$ ($m/z = 29.1$) peak grew from 1.07 to 6.24 (normalized to hydrogen intensity). The C ($m/z = 12.0$) intensity increased from 0.1 to 4.3 and a small OH ($m/z = 17.0$) peak was present in the control but absent in the product. While these results can not indicate whether the surface was fully functionalised or not, we note that the same procedure used by Usher et al. [2003] led to a full monolayer coverage, as determined by solid state NMR data.

2.3.3. Surface Area Determination

The deposited samples were analyzed under an optical microscope for surface area measurements [Kanji and Abbatt, 2006]. Several optical images (e.g. Figure 2.3) were taken to ensure a uniform distribution across the stage. The images were used to obtain a size-resolved particle count per image area. This was then applied to the entire sample to determine a total surface area assuming the particles are spherical.

2.4. Results

Arizona Test Dust (ATD) nucleates ice at relatively low RH$_i$, with RH$_i$ decreasing with increasing surface area (Figure 2.4). This is consistent with there being more nucleation sites available when the surface area is higher, i.e. the probability of nucleating ice becomes higher. As mentioned earlier, the unique nature of our experiment that allows us to see this dependence is that the criterion for establishing the onset relative humidity is that a single ice crystal
forms. By increasing the total surface area on the cold stage, we increase the probability that a site that is active for the conditions of the experiment (i.e. temperature, relative humidity) will be present on the particulates. We assume that the distribution of active sites per unit surface area is uniform regardless of the size of the particulate, i.e. the same results would be seen whether a large number of small particulates or a small number of large particulates were used, provided that the total surface area were constant.
The same trend is also seen for data points for Saharan dust from Kanji and Abbatt [2006], which have been plotted against surface area for the first time, confirming the generality of this finding. However, the slopes of the two trends differ with ATD exhibiting a stronger dependence on surface area and lower overall activity. It is not clear whether this difference can be attributed to the difference in composition of the two dusts or the preparation methods before the sample is received. In both cases ice nucleation occurs well below water saturation, which is at RH$_i$ = 147\% at 233 K.

Knopf and Koop [2006] also showed that deposition mode nucleation is the favoured pathway for ice formation onto ATD below 240 K, whereas Archuleta et al. [2005] showed this to be true for Asian Dust. In the study by Knopf and Koop [2006] RH$_i$'s for ATD as low as 105\% were observed, but it should be noted that this was for pre-activated particles. Pre-activation is a term used to describe the effect of a previous ice formation event on a particle [Higuchi and Fukuta, 1966; Roberts and Hallett, 1968]. This effect was not observed in this work, when we performed ice nucleation on the same sample multiple times. The cause for the difference between this work and Knopf and Koop [2006] could be because between each run we warmed our sample up to room temperature and therefore dried it to a very low RH (< 3\%). Even though Archuleta et al. [2005] saw efficient deposition mode nucleation on Asian dust and also observed that as particle size increases the RH$_i$ decreases, their RH$_i$ values are higher than seen for ATD in this study. We offer two explanations for this. First, that in this work we use
polydisperse particles in the size range 0.5 – 5 µm whereas they used monodisperse particles and their largest size was 200 nm, which will present much lower surface areas than we have on our cold stage. Secondly, our technique is sensitive to the first ice nucleation event over the entire sample, whereas their reported values are for 1% of particles nucleating.

Silica, montmorillonite and kaolinite, components that partially make up the composition of the mineral dusts, were also studied (Figure 2.4) and were observed to nucleate ice within the range of the Saharan dust and ATD. Montmorillonite also showed the same surface area dependency as ATD and nucleated ice efficiently at 233 K, as recently observed by Dymarska et al. [2006]. It can be concluded that mineral dusts are very efficient at nucleating ice in upper tropospheric conditions, but with somewhat varying efficiencies.

To compare dust to hygroscopic aerosols in the atmosphere, we also studied ice nucleation onto oxalic acid dihydrate and Aldrich humic acid. These aerosols were found to be less efficient than mineral dusts. For example, oxalic acid dihydrate exhibited the same trend, where higher surface area gave lower RH. However, it is not as good an IN as mineral dust, with higher onset RH’s for the same total surface area. The work of Zobrist et al. [2006] indicates that this material can act as an immersion IN and our studies confirm it also acts as a deposition IN. Aldrich humic acid, which exists as a sodium salt, was found to be less efficient than mineral dusts as well, but with comparable efficiency to oxalic acid dihydrate (see Figure 2.4), i.e. the data point lies along the same trend.
Figure 2.4. Onset RH with respect to ice formation at 233 K as a function of surface area of particulates. Filled symbols: mineral dust particles, open symbols: hygroscopic particles, and crossed symbols: hydrophobic particles. Saharan Dust data taken from Kanji and Abbatt [2006]. Shaded region: maximum sustainable supersaturation in our system as determined with a blank Teflon substrate, i.e. ice nucleation at the indicated RH range occurred on the Teflon material. Note that each data point is the average of at least 9 measurements, for example consisting of 3 repeat experiments on each of three different particulate samples. The error bars represent 1-σ standard deviation of the results.

The line of particulate surface area versus onset RH$_i$ as does oxalic acid dihydrate. These results are in agreement with a data point for another hygroscopic solid, solid ammonium sulfate, published in Abbatt et al. [2006]. In particular, for a large total surface area of about 0.6 cm$^2$, ammonium sulfate also acted as an IN with an onset RH$_i$ of 107 % at 224 K.
The Gascoyne Leonardite, which was visually observed to be less soluble than the sodium humic salt, was less efficient at nucleating ice than the Aldrich salt and the mineral dusts. The composition of Leonardite may have a role to play given that it has a higher carbon content and lower oxygen content compared to the sodium salt, as specified by their respective suppliers. In addition the Leonardite sample is composed mostly of aromatic moieties (from $^{13}$C NMR data, as specified by IHSS).

Finally, we studied octyl-coated silica as an example of a hydrophobic material. By functionalising the silica surface with approximately a monolayer of an $n$-octyl hydrocarbon, we have shown that its ice nucleability can be suppressed greatly (see Figure 2.4). For both surface areas tested, ice was observed to form only in the range of the maximum sustainable supersaturation of the Teflon-coated stage. As such, these values for RH$_i$ represent lower limits to RH$_i$ for this material given that the nucleation may have occurred on the Teflon surface. It is clear that a hydrophobic surface exposed to an incoming water molecule will require much higher supersaturations for deposition mode nucleation to take place, given its surface properties. While we do not expect that octyl-silica will be present in the atmosphere, these results highlight how ice nucleation is a process that is highly surface-specific whereby a hydrophobic monolayer is sufficient to effectively shut down ice nucleation relative to the uncoated material. These high onset RH$_i$’s for such hydrophobic materials are consistent with our findings for large surface areas of n-hexane soot that also did
not nucleate ice below the maximum sustainable supersaturation \cite{Kanji and Abbatt, 2006}.

2.5. Discussion

With respect to specific findings, our experiments with the octyl-coated silica indicate that surface functional groups determine the conditions and efficacy of deposition mode nucleation. Currently, we are not able to precisely delineate the surface properties that give rise to the varying efficiencies observed within the different types of mineral dusts. This is an area that needs to be further investigated, however it is possible that the preparation or processing of the different dusts may lead to some of the differences observed. As an example, Koehler et al. \cite{Koehler et al., 2007} found that generating Owen Lake aerosol from an aqueous suspension led to no size dependency for onset of ice nucleation, whereas this was not the case when the aerosols were generated dry. We also note that the conclusions made in this paper pertain to temperatures of 233 K and deposition freezing. At higher temperatures, it may be that other nucleation mechanisms – such as condensation freezing – will prevail.

Given that we have the dependence of the onset RH, on total surface areas and to put our results in a form that can predict behavior in the atmosphere, we can calculate (see Figure 2.5) the lower limit to ice nucleation rates using the following relationship:
\[ J_{\text{lower}} \left( \frac{\text{events}}{\text{cm}^2 \text{s}} \right) = \frac{1}{(SA)(t)} \]  

(2.1)

where the numerator is set to unity because one ice crystal is the detection limit of our system and the criterion by which we define ice onset. SA is the total surface area of particles on the stage and t is the time that the particles are exposed to a given RH, i.e. 6 seconds for our experiments. We refer to this as a lower limit to the nucleation rate because it may take the particles less than 6 seconds to form ice. The uncertainty associated in the calculation of \( J_{\text{lower}} \) is ±30%, mostly resulting from the error in surface area of the particles (±20%). Note, however, that we assume the particles are spherical. Errors associated with areas at the microscopic level above those of assuming spherical particles are not considered here.

Higher RH\( \text{i} \)'s lead to higher nucleation rates, as would be expected given that the deviation from thermodynamic equilibrium is higher. Thus, our data are consistent with the nucleation rate being not only dependent on the chemical nature of the particles but also the supersaturation with respect to ice [Bryant et al., 1959; Mason, 1960; Huffman, 1973]. In Figure 2.5, nucleation rate data points from Archuleta et al. [2005] are included which show a similar trend for Asian dust, i.e. that nucleation rate is dependent on RH\( \text{i} \). Note that this dependence is sometimes expressed as a dependence of the onset RH\( \text{i} \) on the size of a particle. This is a valid approach if the threshold for determining ice onset is constant from one experiment to another. For example, for a specified threshold of 1 ice
crystal per a fixed number of particles, then it would be expected that the onset RH would be higher if smaller particles are used. This is indeed the case in the Archuleta et al. [2005] results. We note the value of comparing nucleation rates measured with different experimental approaches, as this allows for more confidence in prediction of rates appropriate for atmospheric conditions.

The particulates tested for ice nucleation were chosen to be surrogates for aerosol materials found in the atmosphere. Using the same experimental

**Figure 2.5.** Lower limit to heterogeneous nucleation rate as a function of onset RH at 233 K. Legend same as Figure 2.4. Star symbols: nucleation rates for 228 K from Archuleta et al. [2005] for Asian dust.
technique for each, we found that mineral dusts were most efficient at nucleating ice followed by hygroscopic solids and then non-hygroscopic solids. It is widely recognized that a variety of aerosol types are observed externally and internally mixed in any air mass. The range of aerosol types extends from internally mixed sulfate-organic particles, to soot, mineral dust, and biogenics. As pointed out in Abbatt et al. [2006], the degree to which ice nucleates upon this complex mixture will be dependent upon both the relative surface areas of each aerosol present and their intrinsic ice-forming capabilities. The results here indicate that it is likely that mineral dusts will be the first materials that ice will form upon under the cold conditions of the mid and upper troposphere. Once these dusts have been removed by either ice nucleation or CCN processing, nucleation will then proceed via heterogeneous nucleation onto hygroscopic, soluble solids, such as crystallized organics, ammoniated sulfates or humic-like substances. Although these materials appear to nucleate ice with similar efficiencies, the overall importance of each will be determined by their relative abundances in the atmosphere.

2.6. Acknowledgements

The authors acknowledge NSERC for the support of these studies. The authors also thank Dr. Dan Cziczo for helpful discussions on the importance of deposition nucleation of different aerosol types in the atmosphere.
2.7. References


CHAPTER THREE
The University of Toronto Continuous Flow Diffusion Chamber (UT-CFDC):
A Simple Design for Ice Nucleation Studies

3.1. Abstract

A new instrument, the University of Toronto Continuous Flow Diffusion Chamber (UT-CFDC), has been designed to study ice nucleation at low temperatures. Based on previous continuous flow instruments, it is a parallel plate model that minimizes convective instabilities by operating horizontally with the warmer plate on top. A variable position sample injector can account for effects arising from gravitational settling of ice particles that form. The residence time in the chamber can vary between 2.6 to 25 s and ice particle formation is monitored with a two-channel optical particle counter. Observation of homogeneous freezing of 100 nm sulfuric acid aerosols was used to verify the accuracy of the calculated relative humidities (RHs) in the chamber to be ±4 %, where we report onset RHs for 0.1% of the particles freezing in the temperature range of 218 to 243 K. We also show that the chamber accurately establishes conditions of water saturation by conducting water uptake studies onto sulfuric acid aerosol at 243 K. The two channel OPC allows for ice and water droplet formation to be distinguished under such conditions. The chamber is a simple, cheap and small design that can be readily assembled for laboratory studies.
3.2. Introduction

Aerosols and clouds in the upper troposphere and lower stratosphere play an important role in the Earth’s radiation budget. Cirrus ice clouds cover about 25% of the Earth and strongly affect the radiative properties of the Earth by scattering and absorption of incoming and outgoing radiation. Contributions of ice clouds to the Earth’s radiation budget still remain highly uncertain [IPCC, 2007], with one issue being the identification of ice crystal formation mechanisms. For example, a common observation is that the numbers of ice crystals in supercooled clouds are larger than those of ice nuclei (IN) measured under similar relative humidity (RH) and temperature (T) conditions [Hobbs and Radke, 1975; Cooper and Saunders, 1980], a measurement that is complicated by ice multiplication mechanisms and shattering of large ice crystals in airborne probes. There is thus a need to better quantify the number of IN in the atmosphere.

Heterogeneous ice nucleation can take place by contact, condensation or deposition freezing onto a solid aerosol particle at higher T’s and lower RHs than those required for homogeneous nucleation. In particular, deposition freezing has been observed to take place well below water saturation [Dymarska et al., 2006; Kanji and Abbatt, 2006; Knopf and Koop, 2006; Koehler et al., 2007]. This suggests that other mechanisms beyond homogeneous nucleation should be included when accounting for the ice crystals observed at conditions that do not fulfill the homogenous freezing criteria.
Instruments have been deployed in the past few years to bridge the gap between field observations of ice crystal concentrations and laboratory measurements of ice nuclei [Al-Naimi and Saunders, 1985; Mizuno and Fukuta, 1995; Chen et al., 1998; DeMott et al., 2003a; DeMott et al., 2003b; Prenni et al., 2007]. These field instruments use continuous flow diffusion chambers (CFDC) based on earlier designs [Hussain and Saunders, 1984; Al-Naimi and Saunders, 1985; Tomlinson and Fukuta, 1985; Rogers, 1988]. The CFDC’s have also been used in the laboratory as ice nucleation counters to investigate homogeneous freezing of sulfuric acid [Chen et al., 2000], and heterogeneous freezing onto mineral dust [Archuleta et al., 2005], silver iodide [Stetzer et al., 2008], montmorillonite and kaolinite [Salam et al., 2006], and soot and soot coated with sulfuric acid [DeMott et al., 1999]. While groundbreaking in their capabilities, some limitations from earlier chambers include the offline manner by which ice crystals are observed [Tomlinson and Fukuta, 1985] and concentric cylindrical geometry which makes their design complex for cooling the chamber and for introduction of the sample and sheath flows [Rogers, 1988; Salam et al., 2006]. The fixed position of sample introduction also means that the particle residence time can only be changed by altering the total flow in the chamber. Finally, the chambers have typically used special treatment of the inner chamber walls to minimize background signals. At present, there is no commercial IN counter.

Other methods of measuring ice formation in the laboratory include using static diffusion chambers [Dymarska et al., 2006; Kanji and Abbatt, 2006; Knopf and
Koop, 2006] and differential scanning calorimetry [Zobrist et al., 2006; Marcolli et al., 2007] to measure ice formation in the immersion, condensation-freezing and deposition mode onto various mineral aerosols and organics. While the above methods can be sensitive to a very small fraction of particles freezing there can be upper limits for the maximum attainable RH because particles are typically deposited onto a supporting substrate. In the case where microscopy is used to observe ice crystals, there are size limitations associated with detection of small particulates and ice crystals. By contrast a CFDC permits high RHs to be used, as well as smaller particles that are suspended as aerosol. The CFDC is also easy to couple to other detection devices to study physical, chemical and size effects on ice nucleation.

In the current study at the University of Toronto a new CFDC (UT-CFDC) is built based on the working principle of early continuous flow instruments [Hussain and Saunders, 1984; Al-Naimi and Saunders, 1985; Tomlinson and Fukuta, 1985; Rogers, 1988] and by modifying the design of the [Kumar et al., 2003] parallel-plate CCN chamber. In previous ice nucleation studies we have examined ice formation onto solid particulates in a static chamber and used microscopy and digital photography to detect ice formation [Abbatt et al., 2006; Kanji and Abbatt, 2006; Kanji et al., 2008]. The UT-CFDC was developed to further investigate deposition mode nucleation onto dust particles, including the effects of chemical processing and particulate size on nucleation.
The UT-CFDC was particularly designed for low temperature ice nucleation in the deposition mode and can also be used for homogeneous nucleation that is relevant to cirrus regimes. However, it also has the capability to work at warmer temperatures where condensation freezing at water saturation occurs. Recognizing that there are no commercial ice chambers on the market, the specific design goals were to develop a small, compact continuous flow chamber that is simple to build, easy to cool to low temperatures, has inner surfaces that are easily coated with ice, and yet is capable of measuring ice formation much like other continuous flow chambers. Unlike many chambers, it is a flat parallel plate design that is horizontally oriented to minimize convective effects. For the first time, a variable position sample injector is used that has the ability to account for both potential ice crystal losses by gravitational settling as well as to allow for ice particle nucleation and growth kinetic studies. Finally, background signals are required to be sufficiently low that this instrument could be used at future times in field studies for ground level ambient aerosol sampling.

3.3. General overview of principle

The principle used for detection of ice formation in the current study is similar to that described in detail by Rogers [1988], as well as by Al-Naimi and Saunders [1985]. Continuous flow thermal gradient diffusion IN counters operate with an aerosol sample flow sandwiched between two particle free sheath flows set to have flow rates at least 10 times that of the sample. The overall flow in the
chamber is in the laminar regime to ensure that the sample flow is maintained in the middle of the particle-free sheath flows. The upper and lower walls of the chamber are maintained at different temperatures and have their inner surfaces coated with ice. With a linear temperature gradient, the temperature and RH conditions in the centre of the chamber can be determined by knowing the temperature on both the cold and warm walls. A steady state partial pressure of water develops between the cold and warm walls and is linear as a function of distance between the two walls. However, the equilibrium vapour pressure as a function of T is not linear therefore establishing a supersaturated region close to the centre of the chamber.

Figure 3.1 illustrates this situation for a sample temperature of 223 K with the warm wall at 233 K and cold wall at 213 K, where the vapour pressures over ice and water were calculated from Murphy and Koop [2005]. In this case the temperature difference between the two walls is quite large and so there is not only a supersaturated region with respect to ice but also with respect to water; most work reported in this paper occurred with somewhat smaller temperature gradients where only ice supersaturations prevailed. Knowing this temperature profile then allows the determination of RH at any point between the two plates. By passing particles through the supersaturated region, some fraction of the added aerosol particles nucleate to form ice.
Figure 3.1. Supersaturation profile in a CFDC. This example illustrates a case where the cold wall is at 213 K and warm wall at 233 K (vertical dash-dotted lines), and sample temperature of 223 K in the centre. Red curve: equilibrium vapor pressure of water with respect to water. Green curve: the same but with respect to ice. Blue straight line: steady state partial pressure of water across the chamber. Dash dotted curve: saturation profile in chamber with respect to water. Dotted curve: same but with respect to ice. The coloured lines refer to the left axis and the black ones to the right. For most experiments the saturation ratio with respect to water did not exceed 1.

3.4. Design of the UT-CFDC

The apparatus used in this work consists of three components (Figure 3.2): 1) aerosol generation, conditioning, size selection, and counting, 2) ice nucleation in the UT-CFDC under controlled and defined temperature and supersaturation, and 3) ice detection using an optical particle counter (OPC).
Instruments Inc. data acquisition board logs to a computer the temperature from thermocouples, and the particle and ice crystal concentrations from a condensation particle counter (CPC) and the OPC, respectively.

3.4.1. Aerosol generation and counting.

For the validation of the IN counter, aerosols are formed by a TSI® constant output atomizer using a 70% w/w composition sulfuric acid prepared from 96% concentrated H$_2$SO$_4$ (Fisher Scientific, ACS grade). The sulfuric acid particles were passed through a silica-gel diffusion drier to remove excess moisture. In some cases a dilution flow of dry N$_2$ (Figure 3.2) was added to achieve the desired concentration of particles. The poly-disperse aerosol from the atomizer was then passed through a scanning mobility particle sizer (SMPS, TSI electrostatic classifier model 3080, DMA column 3081) to size select for 100 nm particles. The flow of mono-disperse particles (typically 0.6 lpm) was then split equally and fed into the CPC (TSI model 3010) and the main chamber. The CPC measures particles in the size range 10 nm-3\(\mu\)m and requires a sample input flow of 1 lpm. Since the aerosol flow was 0.3 lpm, the remaining make-up flow came from filtered room air and the concentrations recorded by the CPC were adjusted to reflect the dilution. Typical concentrations in the sample flow entering the CFDC were 350 – 1000 particles cm$^{-3}$. 
3.4.2. Ice nucleation chamber

Ice formation takes place in a rectangular-shaped chamber that has outer dimensions of $50.8 \times 25.4 \times 3.84$ cm. The chamber is made up of two horizontal flat copper plates (Figure 3.3) that sandwich a Teflon® spacer (Figure 3.4). The inner surfaces of the copper plates are lined with quartz-fibre filter paper (Pall Corporation, Michigan) that is wetted prior to any experiment. This ensures a uniform coating of ice along the inner walls of the chamber. After initial wetting, the filter paper adhered strongly to the copper surfaces and did not degrade with time as occurs with paper-fibre filter paper. The top copper plate has five sealable ports that can be used to wet the top and bottom plate. Three of the
ports are in contact with the filter paper that lines the top plate. The other two provide access to the bottom plate filter paper by creating holes in the filter paper that lines the top plate. While normally resting horizontally, the chamber can be easily tilted to a 45° angle. In this position, the chamber is wetted by introducing approximately 26-30 ml of de-ionized distilled water (Aldrich, 18.2 MΩ) through the five ports. The chamber is subsequently drained of any excess water through the exit at the downstream end while still in the slant position. The chamber is then raised back to the horizontal position and the OPC is connected to the exit of the chamber.

Figure 3.3. Lengthwise cross-section of chamber. Bold arrows indicate direction of particle-free sheath air that makes up about 90% of the total flow in the chamber. The remaining 10% is made up by the sample flow indicated by thinner arrow.

Cooling coils (0.95 cm o.d. and 172 cm length per plate) soldered to the copper plates (Figure 3.3) have a coolant (Syltherm XLT, Dow Corning Corporation) flowing through them from two re-circulating chillers, one for the...
warmer wall (Julabo USA Inc., Model FP88-MW) and the other for the colder wall (Neslab Instruments Inc. Model ULT-90). Holes (0.32 cm diameter) are drilled into the sides of the copper plate (Figure 3.3) for insertion of thermocouples to take temperature measurements. The holes are centered 3.2 mm below the inner surface of the copper plates and they are 12.7 cm in length, so that the thermocouples are measuring the temperature in the centre of the chamber. Temperature measurements at four collinear points along the length of each plate are possible.

As determined by the OPC internal pump, the total flow through the chamber is 2.83 lpm. The sample flow was set to be 10% of this and the
remainder of the flow, i.e. the sheath flow, was made up of dry particle-free N$_2$. The sample is injected through a 0.64 cm diameter stainless steel T-shaped movable injector that has 6 holes (1.6 mm diameter) across the width of the chamber as shown in Figure 3.4. The outermost holes on the injector are 6.2 cm from the walls of the Teflon® spacer so as to avoid inhomogeneous relative humidity and particle loss effects. The injector is movable so that the position at which the aerosol is introduced can be varied to change the residence time of the particles in the chamber. The sheath flow is injected at the upstream end (Figure 3.4) of the chamber through 4 ports (0.64 cm diameter) that are drilled into the Teflon® spacer. With the sheath and sample flows, the maximum residence time in the centre of the chamber is 25 seconds (calculated with the bulk flow) and can be achieved when the injector is pulled back all the way. The sheath flow is introduced above and below the stainless steel injector and ensures the particle flow is kept in the center. The Reynolds number for the given flows and dimensions at a temperature of 223 K is 20 which is well below the critical value where the transition from laminar to turbulent begins to occur in parallel plates. For reference, if air at room temperature is entering the chamber, it takes about 0.3 - 2 seconds to achieve steady state temperature and water vapor partial pressure conditions [Hussain and Saunders, 1984; Rogers, 1988]. The downstream end of the chamber is funnel shaped so as to direct the flow into the center as it exits into the OPC.
3.4.3. Ice detection

Ice is detected using an optical particle counter (OPC) that is directly coupled to a 0.64 cm tube exiting the chamber through a single 0.64 to 0.95 cm o-ring compression fitting. This ensures that the flow exiting the CFDC does not warm sufficiently that the ice particles evaporate before being analyzed by the OPC. The commercial OPC (Climet, Model CI-20) is capable of measuring particles in two size bins, particles greater than 5 µm and those between 0.5 and 5 µm. It samples at a flow rate of 2.83 lpm and encounters 10% coincidence errors when the particle concentration exceeds $3.5 \times 10^2$ particles cm$^{-3}$. Since the smallest particle size detectable by the OPC is 500 nm, the particle size for validation experiments introduced into the CFDC was chosen to be 100 nm so that when there is no ice formation, no background counts from the OPC are recorded arising from particle introduction. However, when ice forms, the particle always grows to sizes larger than 500 nm and usually to larger than 5 µm. The applicability of each OPC channel to ice detection under specific conditions is discussed later in the paper. The background count rate in the smaller size bin was typically quite low, around 0.02 particles cm$^{-3}$; in the larger size bin, the background count rate was typically 0.0005 particles cm$^{-3}$. The source of background counts come from frost particles that may dislodge themselves from the ice-covered walls, and also from particles that coagulate or coalesce during their transmission through the chamber.
A typical experiment starts with the cold and warm walls approximately 2 K apart in temperature (ΔT), providing a very small supersaturation with respect to ice and subsaturated with respect to water. The temperature difference between the warm and cold wall is then increased by changing the temperature set points on each re-circulating chiller while keeping the average temperature constant, thus increasing the supersaturation in the chamber. The point at which ice starts forming is readily apparent as the concentrations recorded by the OPC begin to increase from the low background level. An activation plot (e.g. Figure 3.5) of the fraction of aerosol that forms ice as a function of RH can then be produced and the RH for various activated fractions can be determined. See the next section for a full discussion of Figure 3.5.

### 3.5. Validation of Freezing Conditions

To validate the UT-CFDC we sought to determine whether the relative humidity conditions discussed in Section 2 are accurately achieved. For this we chose to study the homogeneous freezing of 100 nm sulfuric acid aerosols since these conditions have been the best characterized of any particle system, both in the laboratory [Martin, 2000] and via modeling work [Koop et al., 2000].

Homogeneous freezing of sulfuric acid is only observed at temperatures below 235 K [Koop et al., 2000]. Using sulfuric acid aerosols generated from a 70% w/w solution, freezing experiments were conducted for the range 217 K < T < 244 K. The RH of the chamber was increased by increasing ΔT in the chamber.
Figure 3.5. Activation curve for 230 K derived from a typical ice nucleation experiment. The RH of the chamber is increased and concentration of ice crystals monitored. The activated fraction is the ratio of OPC counts to particle counts, derived from the CPC. The dashed line indicates for this temperature where we expect to see homogenous freezing of 100 nm H₂SO₄ taken from Koop et al. [2000]. Note that the large particle channel also increases indicating the presence of ice. The particles in the smaller size channel could also be water droplets after water saturation has been surpassed.

The injector position, $d$, was chosen to be at an intermediate position (30 cm) from the edge of the chamber (see Figure 3.4) so as to give sufficient time (residence time of 12 s) for the ice crystals to grow to be detected by the larger
size bin, but also short enough to avoid potential gravitational settling losses (see below).

From a gravitational settling perspective, we note that Rogers [1988] has described in detail that for various typical CFDC supersaturation conditions ice particles consistently grow to a maximum of 5-10 µm. The corresponding settling velocities for this size range of ice crystals for our temperature and pressure conditions are 0.1 – 0.3 cm s⁻¹ [Finlayson-Pitts and Pitts, 2000]. For our chamber, the particle must fall 0.95 cm in order to settle out of the flow and hit the bottom plate. So, for an ice crystal 5 µm in size, it would require approximately 10 seconds to settle out of the flow. Using ice crystal and water droplet growth equations [Rogers and Yau, 1989], we conducted calculations to show that at 233K, RHₜₐₐₜₜ = 100% it would take the particle about 6 seconds to grow to this 5 µm criterion, which is roughly the size at which gravitational settling would become important. However, it would then take approximately 10 seconds more for the ice crystal to fully settle out of the flow, at which point it would have been sampled by the OPC.

Clearly, particle growth and gravitational settling are coupled processes, and so this simple analysis is only an approximation to the true behavior. And so, for validation that gravitational settling is not a major effect in our experiments we have conducted residence time experiments with Arizona Test Dust particles atomized from a suspension of ATD in water (approximately 0.015 g/ml), passed through a diffusion dryer, and then studied in the CFDC under conditions close
to water saturation. In Figure 3.6, we plot the activated fraction of particles measured with both the smaller and larger size bins, as a function of sample injector position. It is shown that for the residence time used in this work (12 seconds), the smaller size bin data are converging to a plateau value at about 30 cm injector position and higher, i.e. there is sufficient time for particles to grow to the detectable size. For the larger size bin, corresponding to particles larger than 5 μm, the effects of insufficient growth time are clearly observed for positions less than 30 cm. Also, since the activated fraction between the 14 and 25 second residence time is similar we believe that for these temperature conditions that having a much longer residence time is not leading to gravitational settling. This is also consistent with the observations in Tomlinson and Fukuta [1985] and Rogers [1988] that despite various T’s and RH’s ice crystals consistently grew to average sizes of 8μm. Note that the maximum activated fraction in these experiments was somewhat below unity, possibly because of water vapour depletion arising from ice formation. In particular, we have noted that this maximum value for the activated fraction increases as the supersaturation values in the chamber are increased. This effect is due to a change in ice forming mechanism to condensation freezing, where the less active IN will only form ice at water supersaturations and therefore not form ice in the deposition mode. This would be consistent with not having the activated fraction reaching unity at water saturation.
For the sulfuric acid experiments used to validate the supersaturation conditions in the chamber, the fraction of particles that nucleated ice is plotted as a function of RH in Figure 3.5 for an experiment conducted at 230 K. The freezing conditions for 0.1% of the particles are reported as a function of temperature in Figure 3.7 juxtaposed against the homogeneous freezing curve for 100 nm H$_2$SO$_4$ aerosols. Although the data are calculated from counts in both the
small and large size channels, it is the signal in the small size channel that dominates. Each data point in Figure 3.7 arises from a measurement where the RH is increased and decreased in cycles so as to observe the RH conditions where the activated fraction increases to values of 0.1% or greater. At all temperatures the values for at least 0.1% of particles activated have been plotted. Since these points are close to the homogeneous freezing line it shows that particles are observed to freeze at the expected values thus validating the RH measurements in the chamber. On the same plot, to compare our values with previous studies, we have data points for freezing of 50 nm sulfuric acid particles from Chen et al. [2000]. These match up quite well with our data and serve as an additional confirmation that the chamber operates as expected in the temperature range studied.

In addition, note that even though homogeneous freezing is only observed at $T < 235$ K, there are data for 240 and 243 K in Figure 3.7. Even though at this temperature the data indicate that 0.1% of the particles ‘activate’ at water saturation, we do not believe that freezing has occurred at this temperature. This is illustrated in Figure 3.8 which shows the activation curve for 100 nm H$_2$SO$_4$ aerosols at 240 K. Note that at water saturation the smaller size channel indicates activation while the larger channel remains at background levels. However, we know that ice formation is indicated by growth in both channels since ice grows at faster rates than do water drops. In particular, in data not shown here, we have observed that for experiments at 243 K that Arizona Test Dust (ATD) both
OPC channels activate when ice formation occurs, presumably via a condensation-immersion freezing mode. This shows that there is sufficient residence time in the chamber for ice particles to grow to at least 5 μm in size at 243 K. For the case of sulfuric acid at 240 K, since the growth is only in the smaller size channel it can be concluded that the observation is due to growth of the particle due to activation of water uptake to form water droplets, and that it is not due to ice formation. In addition, since the transition to 0.1% activation coincides with the water saturation line (see Figure 3.7), the experiments confirm the calculated RHs in the chamber under these warmer temperature conditions.

To further validate the behavior observed in the chamber, we have conducted a number of calculations. First, using the online Aerosol Inorganic Model (AIM) 1 (http://www.aim.env.uea.ac.uk/aim/aim.php) [Carslaw et al., 1995; Massucci et al., 1999; Clegg and Brimblecombe, 2005] we have confirmed that uptake of water by 100 nm sulfuric acid particles at 99% RH and from 243 > T > 223 will give rise at equilibrium to 410 nm particles i.e. without water droplet activation, the conditions would be insufficient to give rise to 500 nm particles and be detected in the small OPC channel. Since sulfuric acid is the most hygroscopic material encountered in the atmosphere, it is safe to say that if aerosol is size selected to 100 nm or smaller, growth in the 0.5 μm channel must be due to ice formation.
Figure 3.7. Summary of the 100 nm H$_2$SO$_4$ homogeneous freezing experiments over a range of temperatures. Squares: Freezing fraction of at least 0.1% or more of the particles. Stars: freezing of 0.1% of 50 nm H$_2$SO$_4$ particles from Chen et al. [2000]. Also, refer to text for explanation of the circle shaped data points. The activated fraction was determined using the sum of the counts from the large and small particle channels. Error bars represent 1σ from at least 3 runs during an experiment.

Second, to confirm that we indeed do not have water droplets that grow to 5 µm thus contaminating the large OPC channel, we calculated the droplet growth rates using equations from Rogers and Yau [1989] for 12 s residence time, the maximum saturation reached in Figure 3.8 (RH$_w$ = 103%) and 243 K. We find that a water droplet would grow to approximately 4.6 µm under such conditions, and that either a higher saturation ratio or residence time would be required for
Figure 3.8. Activation curve of $\text{H}_2\text{SO}_4$ aerosols at 240 K. This temperature is above where we expect homogeneous freezing and therefore no ice formation should be observed. Note that once water saturation has been reached, the $P > 0.5\mu\text{m}$ channel (squares) starts to increase indicating water droplet formation. However the $P > 5\mu\text{m}$ channel (circles) remains at background level, indicating no ice formation.

Water droplets to make it into the 5 $\mu\text{m}$ channel. For cooler temperatures, 233 and 223 K, the growth is even slower at this supersaturation. This shows that it would require high water saturations before the large particle channel would be contaminated by water droplets. For the current configuration we therefore describe our upper $\text{RH}_w$ limit as 103% for the highest temperatures.
Finally, again using the approach described in Rogers and Yau [1989], we calculated the conditions required for ice crystals to grow in size, for a range of temperatures. For 233 K and 243 K, there is no kinetic constraint for growth into the 5 µm channel down to an RH\textsubscript{i} value of 112 and 104 % respectively, for a residence time of 12 seconds. At the lowest temperature studies, 223 K, ice crystals just approach the 5 µm size for a RH\textsubscript{i} value of 145%. Indeed, Figure 3.6 confirms this behavior, where incomplete activation into the 5 µm channel is observed at 223 K and 12 second residence time. Figure 3.6 illustrates that longer residence times are required for more complete activation at this low temperature.

The uncertainty in calculated chamber RH values will come mostly from uncertainties in temperature measurements (±0.1 K) along the length of the copper plates. For two measurements from the upper and lower plates, the maximum uncertainty that could arise is ±0.2 K, which translates into an uncertainty in RH of approximately ± 4% in the centre of the chamber. This estimated uncertainty is roughly consistent with the agreement between the measured and expected values for ice/water formation in Figure 3.8, which is on the order of a few percent as well.

3.6. Attributes and Limitations of the IN counter

Designed for laboratory studies, the UT-CFDC design is based on a flat plate horizontal CCN chamber [Kumar et al., 2003]. One of the biggest advantages
is that the design requires minimal machining and is easily built in house. In addition, the introduction of sample and sheath flows is relatively straightforward compared to what is involved in a cylindrical geometry. The ice detector used is a commercially available optical particle counter that is inexpensive ($5000) and can nevertheless distinguish between water droplets from ice particles by virtue of having two different size channels. In particular, the large particle channel indicates ice formation exclusively because water drops do not grow to that large a size in the given residence times, for temperatures up to 243 K and RH\textsubscript{w} = 104%. The chamber also has one standard total flow rate that is determined by the total flow of the OPC, and no external vacuum pumps are required. For the first time to our knowledge, the design allows the residence time of particles in the chamber to be changed by adjusting the position of the movable sample injector. This allows for effects of gravitational settling or insufficient crystal growth time to be assessed. The icing process for both the cold and warm wall does not require pumping water in and out of the chamber under freezing conditions as is performed by other systems, nor does it require special mechanical treatment such as ebonizing \cite{Rogers, 1988} or sand blasting \cite{Stetzer et al., 2008} of the inner walls of the chamber. All that is required is that commercially available quartz filter paper lines the walls. Nevertheless, the background count rates, especially in the large particle size bin, are sufficiently low that measurements of IN numbers in the field may eventually be possible. Finally, the temperature of the plates is easily controlled by two separate re-
circulating chillers therefore allowing precise achievement of sample T and RH’s during a given experiment. If only one chiller is available, then automated, rapid switching of the flow between the two plates with variable durations of cold flow would provide a stable temperature gradient.

On the other hand, there are limitations to the chamber imposed by its simplicity and cost. For the coldest temperatures (roughly 220 K and below), the ice crystal growth rate is sufficiently slow that 5 µm particles may not be formed. In such a case, the 0.5 µm OPC channel can be used, so long as the diameters and composition of the incoming particles are known. In particular, for insoluble solids, no particles larger than 0.5 µm could be injected else the background counts will increase; for the most hygroscopic material, the particles would have to be no larger than about 0.1 µm due to water uptake which would also lead to higher background counts. Alternatively a more expensive OPC with more sizing channels could be utilized, in particular one with sizing capabilities between 0.5 and 5 µm.

A second potential limitation is that the current design of the chamber has no water droplet evaporation region (where RH<sub>w</sub> < 100% but RH<sub>i</sub> = 100% ) that has been incorporated into a number of chambers [Rogers, 1988; Salam et al., 2006; Stetzer et al., 2008]. The purpose of this evaporation region is to allow ice particles to transit but for water droplets to evaporate. In our case, for temperatures below 243 K and for RH<sub>w</sub>, 103%, we are confident that using the 5 µm channel allows us to distinguish cases where both ice and liquid water
droplets may be present. The configuration of the chamber is such that additional optical devices, such as those that distinguish between ice and water droplets by observing the degree of depolarization of a polarized laser beam could still be employed, if necessary.

In terms of potential future development into a field-based instrument, the current design would have to be re-engineered with regards to its refrigeration. Also, the present pumping capabilities may be insufficient for operation at low pressures, as from an aircraft. Nevertheless, the design of the chamber itself would probably not have to be substantially altered.

3.7. Conclusions

We report here the development of a new parallel plate ice nucleation chamber that is designed to study low temperature ice nucleation in the laboratory. The UT-CFDC follows the same general operating principles of other CFDC instruments, but it is constructed with a simple, small and cheap design that is nevertheless able to distinguish between ice and water particles up to temperatures of about 240 K. In addition, it has a novel capability of performing particle growth and settling studies, through the use of a movable sample injector that allows aerosol residence times to be varied. Mono-disperse sulfuric acid aerosol was used to validate the accuracy of calculated RH in the chamber. In particular, homogeneous freezing of the aerosols occurred within experimental uncertainties at the well-defined literature values described by the
Koop et al. [2000] parameterization. We also note that freezing of sulfuric acid was not observed at temperatures above the homogeneous freezing temperature, but rather water uptake was observed at RH$_w$ = 100% and 243 K, confirming that we also accurately establish water saturation conditions in the chamber.

3.8. Acknowledgements

This work was funded by NSERC. We acknowledge the valuable comments from the two anonymous reviewers.
3.9. References


Kumar, P. P., K. Broekhuizen and J. P. D. Abbatt (2003). "Organic acids as cloud condensation nuclei: Laboratory studies of highly soluble and insoluble species" *Atmospheric Chemistry and Physics* **3**: 509 - 520.


CHAPTER FOUR
Ice Nucleation onto Arizona Test Dust at Cirrus Temperatures:
Effect of Temperature and Aerosol Size on Onset Relative Humidity

Zamin A. Kanji and Jonathan P. D. Abbatt*

Department of Chemistry
University of Toronto
80 St. George St.
Toronto, ON
M5S 3H6

In preparation for submission to Journal of Physical Chemistry A
June, 2009
4.1. Abstract

The University of Toronto Continuous Flow Diffusion Chamber (UT-CFDC) was used to study ice formation onto mono-disperse Arizona Test Dust (ATD) particles. The onset relative humidity with respect to ice ($\text{RH}_i$) was measured as a function of temperature in the range 251 – 223 K for 100 nm ATD particles. It was found that for 0.1% of the particles to freeze, water saturation was required at all temperatures except 223 K where particles activated at $\text{RH}_i$ below water saturation. At this temperature, where we believe deposition mode freezing is occurring, we find that the larger the particle size, the lower the onset $\text{RH}_i$. We also demonstrate that the total number of particles present may influence the onset $\text{RH}_i$ observed. The surface area for ice activation, aerosol size and temperature must all be considered when reporting onset values of ice formation onto ATD mineral dust particles. In addition, we present nucleation rates and contact angles of ice germs with ATD aerosols which indicate that there exists a range of active sites on the surface with different efficiencies for activating ice formation.
4.2. Introduction

Cirrus clouds cover about 30% of the earth’s atmosphere and their principal component is ice [Rossow and Schiffer, 1999; Wylie and Menzel, 1999]. They contribute to the Earth’s radiation budget by reflecting solar radiation or trapping terrestrial radiation. Understanding the contribution of aerosol particles to ice formation processes is also relevant to understanding the aerosol indirect effect. Ice formation in the atmosphere can take place via homogeneous or heterogeneous nucleation. Heterogeneous nucleation typically occurs between a solid interface and water, and can take place via contact, immersion or deposition freezing. The first two require the presence of liquid phase water before freezing takes place and the latter mechanism involves ice condensing directly from the vapour phase. Deposition nucleation can take place under conditions that are substantially subsaturated with respect to liquid water and sometimes at relative humidities lower than those required for homogeneous freezing. The type of ice nuclei (IN) involved in heterogeneous ice nucleation will have a strong influence on the formation conditions of ice clouds in the atmosphere and could have an impact on climate change [IPCC, 2007].

Particles of crustal origin and high in mineral content have been found in ice crystals in many field investigations suggesting they are effective IN [Chen et al., 1998; DeMott et al., 2003; Cziczo et al., 2004; Ansmann et al., 2005; Twohy and Poellot, 2005]. They are also efficient IN in laboratory studies, forming ice at low RH\textsubscript{i} over a wide range of temperatures [Archuleta et al., 2005; Mangold et al., 2005;
Most of the aforementioned studies have used a wide range of particulate or aerosol sizes whereas there have been fewer studies that have looked specifically at the impact of dust particle size [Archuleta et al., 2005; Koehler et al., 2007] or total particulate surface area [Kanji et al., 2008] on ice formation properties, particularly the onset relative humidity with respect to ice, RH\textsubscript{i}.

Climate models, for example the ECHAM GCM [Lohmann et al., 2004], frequently use a single value for the onset of ice nucleation onto mineral dust particles whereas there is most likely a spectrum of values over which ice formation initiates heterogeneously. The spread of onset values will arise as a function of temperature, chemical composition [Hoose et al., 2008], particle size [Archuleta et al., 2005] and how the onset is defined. To reduce uncertainties in this area, we have studied the effect of temperature on ice nucleation onto monodisperse ATD particles, a surrogate for naturally occurring mineral dust in the atmosphere, and we also report the influence that aerosol size and total aerosol surface area (SA) have on ATD ice nucleation.

### 4.3. Experimental

The UT-CFDC has been described in detail in Kanji and Abbatt [2009]. Briefly, ATD particles (Powder Technology Inc.) are prepared as an aqueous (18.2 MΩ Millipore water) suspension (approximately 15 mg ml\textsuperscript{-1}) for
atomization followed by diffusion drying. The concentration of the suspension was adjusted to change the number concentration of the particles and thus the total aerosol surface area. The particles are size selected using a differential mobility analyzer (TSI electrostatic classifier model 3080, DMA column 3081) and counted using a condensation particle counter (CPC, TSI 3010). The particle flow (typically 500 – 1000 cm$^{-3}$) is also fed into the centre of the ice nucleation continuous flow diffusion chamber that operates on a similar principle to that of Rogers [1988], but has a few differences in design that are addressed in more detail in Kanji and Abbatt [2009]. The main difference is the parallel plate geometry of the chamber and the absence of a water droplet evaporation region. Ice coated walls held at different temperatures set the relative humidity and temperature profile inside the chamber between the warm and the cold walls [Kanji and Abbatt, 2009]. The particle flow is sandwiched between two particle-free nitrogen sheath flows that make up 90% of the total flow (2.8 L min$^{-1}$).

Ice is detected optically using a Climet (CI-20) optical particle counter (OPC) that can detect particles in two channels, between 0.5 and 5 μm and greater than 5 μm. By injecting particles that are below the detection limit of the OPC, low background counts are obtained. When particles are exposed to an elevated RH they form ice and grow to larger sizes that are detectable by the OPC. The activated fraction is the ratio of the counts from the OPC to the counts from the CPC. For conditions below water saturation, we believe that response in both the 0.5 and 5 μm channels is due to ice formation, because ATD dust
particles do not show significant hygroscopic growth prior to ice formation. For our experiments at water saturation at 233 K and above, we have shown in experiments involving sulfuric acid particles [Kanji and Abbatt, 2009] that water droplets have time to grow to 4.5 μm (at RH$_w$ = 103%), so contaminating the 0.5 μm channel, but they do not grow to sizes that impact the 5 μm channel. For these conditions, the signal in the 5 μm channel indicates ice formation.

For all results in this paper, the residence time of the particles in the chamber was 12 seconds. A typical experiment was conducted by starting with the warm and cold wall at similar temperatures so that RH$_i$ = 100%. This was followed by increasing the difference in temperature between the two walls simultaneously so that the average temperature in the centre remained constant and RH$_i$ increased. The relative humidity was raised to water saturation at which point the experimental run was concluded. Ice formation was apparent when the counts observed in the small particle channel on the OPC increased above background for RH$_w$ < 100%, and in cases where water saturation was reached (warmer temperatures) the large particle channel was used to indicate ice formation. Each run was repeated at least 3 times each on 3 different days. The uncertainty in temperature (± 0.1 K) contributes to most of the uncertainty in RH (± 4%). This uncertainty was empirically confirmed at various temperatures by observing homogeneous freezing of 100 nm H$_2$SO$_4$ aerosols and comparing to the freezing onsets to those from the Koop et al. [2000] model.
4.4. Results and Discussion

4.4.1. Effect of Temperature

Data for ice nucleation onto 100 nm ATD particles are presented in Figure 4.1 for the temperature range 251 - 223 K. The data points shown are for 0.1 and 1% of the particle number freezing. For this particle size it can be concluded that deposition mode freezing is only apparent at 223 K, with condensation freezing occurring at water saturation for all other temperatures. On the same plot are data from Koehler [2007] for 1% of ATD freezing, which are in excellent agreement with our results. Also, the 1% freezing fraction of 100 nm Asian Dust from Archuleta et al. [2005] exhibit freezing at 223 K with RH$_i$ freezing values slightly higher than those reported here. Note however, that the dust source is different between these two experiments, which may affect the ice nucleation efficiencies [Hoose et al., 2008]. Also, soluble coatings have been found to suppress ice nucleation efficiencies of dust particles [Hung et al., 2003; Archuleta et al., 2005; Mohler et al., 2008]. The ATD used in this study is ‘washed’ and baked and therefore would have less soluble material on it compared to the Asian dust used in Archuleta et al. [2005] which was not a ‘washed’ sample. Both deposition and condensation freezing onto ATD have been observed for 260 > T > 235 [Knopf and Koop, 2006], however the particle size range was 0.7 – 10 μm. It is likely that the larger, more efficient particles initiated ice formation below water saturation and the smaller particles activated at water saturation for the temperature range mentioned.
Figure 4.1. Onset relative humidity with respect to ice for freezing of 0.1 and 1 % of 100 nm ATD particles as a function of temperature. Other data points are onset RH$_i$ for 100 nm Asian Dust particles from Archuleta et al. [2005], ATD particles from Möhler et al. [2006] and Koehler [2007], and RH$_i$ for one ice event taken by varying total surface area of a poly-disperse ATD sample deposited on a hydrophobic support at 233 K (taken from Kanji et al. [2008], SA = 2.6 × 10$^{-2}$ cm$^2$). Dashed line: homogeneous freezing of sulfuric acid aerosol [Koop et al., 2000]. Solid line: water saturation [Murphy and Koop, 2005].

In further comparison to the literature, Möhler et al. [2006] show that when larger ATD particles are present, the activated fractions can be high for a lower onset RH$_i$. For example, whereas we report 0.1% of 100 nm ATD particles freezing at RH$_i$ = 149% at 223 K (for a surface area of 3 × 10$^{-8}$ cm$^2$ cm$^{-3}$), Möhler et al. [2006] observe 8% of the particles nucleating ice at RH$_i$ = 105% for the same
temperature (Figure 4.1). There could be two reasons for this apparent discrepancy. First, the Möhler et al. [2006] study used a lognormal distribution of ATD particles with a median size of 350 nm. It is likely that the most efficient IN were the large particles (as will be seen in the next section) that are absent in our 100 nm data shown in Figure 1. In fact, using the information provided in Mohler et al. [2006] we can calculate the surface area based particle-diameter mode and find that it is 650 nm. Second, the method of aerosol preparation was different in the two experiments. We atomized from an aqueous suspension whereas Möhler et al. [2006] dry dispersed their sample. It has been reported that the method of aerosol generation may change its ice nucleating properties. For example Koehler et al. [2007] found that wet generated Lake Owen’s dust and ATD required higher RH$_i$ than was required for dry generated aerosol, for temperatures where deposition freezing is important. Wet generated dust may require higher RH$_i$ because nebulization from an aqueous suspension may mobilize the soluble material in the dust to the bulk solution and eventually onto the surface of the dust particle upon being atomized. Prior to ice formation in the CFDC, the dust particles are passed through the diffusion drier to drive off moisture that likely occupies hydrophilic sites on the dust particle. The soluble matter is left behind on these hydrophilic sites that are also likely to be the ice active sites.

In Figure 4.1 a data point is also plotted for ice formation onto ATD from Kanji et al. [2008], which is significantly lower than the current study, and more comparable to the results from Möhler et al. [2006]. The onset RH$_i$ from Kanji et al.
[2008] is for a high surface area sample, deposited from poly-disperse, wet generated ATD aerosol with particulate size in the range 0.5 - 5 μm. Plotted is the first observed ice nucleation event for the entire sample, which corresponds to a much smaller activated fraction (about 1 in $10^5$) than those from the CFDC studies.

This comparison between different literature values illustrates factors to consider when reporting the RH for ice nucleation results. In particular, the fraction that activates as well as the size, surface area and preparation mode of the sample may affect the reported onset RH$_i$.

4.4.2. Effect of Particle Size.

To investigate the dependence of ice onset RH$_i$ on particle size and activated fraction we conducted experiments where the mono-disperse particle size was varied, but the total aerosol surface area in the chamber was kept constant at 3 to 4 × 10$^{-8}$ cm$^2$/cm$^3$. The results are shown in Figure 4.2 as the filled circle, square and star data points, for 40, 100 and 240 nm diameter particles, respectively. These data from Figure 4.2 have also been re-plotted in Figure 4.3, where the onsets for ice formation are expressed as a function of surface area per ice nucleation event, i.e. the surface area that gives rise to one ice event at a given RH$_i$.

In Figure 4.2 it is evident that for all fractions reported, in particular the lower fractions where smaller supersaturation with respect to ice is required for
ice formation, there is a strong size dependency for the onset RH$_i$ when comparing the 240 nm data to those for 40 and 100 nm. On the same figure are data from Archuleta et al. [2005] for the 1% freezing fraction of Asian dust samples. It is notable that the two studies both observe significantly lower RH$_i$ for 200-240 nm particles compared to results for the smaller particles. This effect could arise from the limited availability of active sites on the smaller particles.

![Diagram](image_url)

**Figure 4.2.** Onset relative humidity with respect to ice as a function of activated fractions for varying sizes of ATD aerosol at 223 K. Open symbols are for Asian Dust at 223 K taken from Archuleta et al. [2005]. Dashed Line: water saturation. Numbers in parenthesis: surface area of particles (cm$^2$ cm$^{-3}$), assuming spherical geometry.

Since the mineralogical composition may vary with particle diameter [Vlasenko et al., 2005], it is possible that larger particles have a more favorable surface
structure for ice formation. We also note that the limited availability of active sites could arise from the surface area being considered for activation (i.e. the total surface area per ice nucleation event) is larger for the 240 nm particles than for the 100 and 40 nm particles. However, Figure 4.3 illustrates that this effect does not fully account for the observations. For similar surface areas per ice nucleation event, the 240 nm particles form ice at significantly lower RH$_i$’s than the 100 and 40 nm particles.

Given that the surface area mode diameter is 650 nm in the work of Möhler et al. [2006] the particle size effect may also explain why the Möhler et al. [2006] data for a poly-disperse sample of ATD at 223 K are at low RH$_i$ (see Figure 4.3). Figure 4.3 also includes data from Kanji et al. [2008] where polydisperse ATD samples mounted on a hydrophobic support, with particle sizes between 0.5 and 5 μm, were studied by a technique sensitive to the formation of one ice formation event. When comparing these data to the current study, the high sensitivity of ice detection and the large particulate size are apparent reasons as to why low onset RH$_i$’s are observed in Kanji et al. [2008].

Previous literature indicate that for deposition mode nucleation, spherical particles need to have a diameter of at least 100 to 200 nm to readily form ice germs [Pruppacher and Klett, 1997]. Below this size, the temperature necessary for ice formation decreases with decreasing particle size in order to readily form an ice germ. It is therefore possible that a particle diameter of roughly 100 to 200 nm is the threshold size beyond which there would be at least one active site per
particle that would initiate ice formation at low saturations. Recently, in a study by Marcolli et al. [2007], the efficiency of immersion mode freezing onto ATD particles was modeled as a function of particle size and active site occurrence probability on the particles. The efficiency of an active site was related to its contact angle with an ice germ, with smaller contact angles indicating more efficient active sites. A highly non-linear dependence of active site occurrence probability on contact angle best fit the experimental data. For example, they found that ATD particles had to be at least 160 nm in order to have on average at least one active site (with a contact angle of 110°) whereas a 620 nm particle would contain on average one (much more efficient) active site with a contact angle of 70°. The conclusions were that larger particles are more active because of both higher surface area but also because they contain more efficient ice nucleation sites. Although the nucleation mode in the Marcolli et al. [2007] study was immersion freezing, it is likely that similar active site distributions prevail for deposition mode freezing as well.

Since the 40 and 100 nm data fall onto a straight line in Figure 4.3, the increase in surface area per ice nucleation event explains the decrease in RH\textsubscript{i}. Thus, for particles less than 200 nm diameter, the probability occurrence of equally efficient active sites does not appear to depend substantially on size.
4.4.3. Effect of Total Surface Area

Finally, we varied the total surface area by using both high and low aerosol number concentrations for each of the 100 and 240 nm diameter experiments, to see if this would have an effect on RH$_i$. To show this behavior, we plot a second set of data in Figure 4.2 for 100 (filled diamonds) and 240 nm (filled triangles) particles. In both cases the total surface area per unit volume is close to an order of magnitude higher than in the earlier data points discussed. For the 100 nm particles we show only the smaller activated fractions because this is where we observed a significant lowering in the onset RH$_i$. At the higher activated fractions the RH$_i$ values fall within errors of the lower surface area data points. The observed onset RH$_i$’s for 100 nm high surface area experiments were significantly, i.e. 12 – 20%, lower than for the lower surface area runs. On the other hand, for the 240 nm data, we observed almost identical values between the two different total surface area experiments.

For experiments where ice nucleation onsets are reporting the first nucleation event, one expects to see a strong dependence on total particulate surface area, e.g. [Eastwood et al., 2008; Kanji et al., 2008; Wheeler et al., 2008]. However, such is not the case here, where an activated fraction is the criterion for defining onset. The 240 nm results are expected, whereas the 100 nm results are not. One possibility is that a small fraction of 100 nm dust particles were coagulating due to high number concentrations in the high surface area experiments, thus forming larger particles that would more easily activate. This
would explain why only the onset RH$_i$'s for lower fractions of activation ($10^{-4}$ and $10^{-3}$) are affected by total surface area. Presumably the 240 nm data are unaffected because lower particle concentrations are used.

![Graph showing onset relative humidity with respect to ice for one ice event as a function of activation surface area at 223 K.](image)

**Figure 4.3.** Onset relative humidity with respect to ice for one ice event as a function of activation surface area at 223 K. Surface areas were calculated assuming spherical geometry and correspond to activated fractions of 0.01, 0.1, 1 and 10% for each particle size. Diamonds: RH$_i$ for one ice event for poly-disperse ATD particles on hydrophobic support taken at 233 K [Kanji et al., 2008]. Open star: Ice activation for 8% of poly-dispersed ATD aerosol in AIDA chamber [Möhler et al., 2006]. Dashed line: water saturation [Murphy and Koop, 2005].

A second hypothesis is that the 240 nm data show no dependence on total surface area because these particles are sufficiently large that every particle contains at least one active site [Pruppacher and Klett, 1997; Marcolli et al., 2007],
i.e. the total number of particles present in the chamber should not affect the onset values for a fraction of these particles to form ice. However, for the 100 nm results, where not all the particles contain a highly efficient active site, then in the low surface area runs with smaller particle numbers there may not be any particles present that can activate at a low RH$_i$.

4.4.4. Classical Nucleation Theory Analysis

In the preceding section onset RH conditions for ice formation onto ATD particles are reported and we have shown that there is a dependency on a number of factors such as aerosol size and surface area available for nucleation. This makes the comparison between different studies difficult. For atmospheric relevance and applicability to climate models, the heterogeneous ice nucleation rate ($J_{het}$) is a more useful quantity for direct comparison between laboratory studies. It is evident that ice formation is dependent on supersaturation and thus using $J_{het}$, we can extract contact angles of ice germs with IN for deposition mode nucleation, and therefore define the contact angle as a function of onset RH$_i$. In the next sections the above parameterisations for ice formation are discussed.

4.4.4.1. Nucleation Rates, $J_{het}$

The heterogeneous nucleation rate is defined as the number of ice formation events per unit surface area of solid material (in this case ATD), per unit time. The $J_{het}$ can be related to the data obtained according to the following:
\[ J_{het} = \frac{1}{(SA)t} \]  

(4.1)

where \( J_{het} \) has units of ice events cm\(^{-2}\) s\(^{-1}\), \( SA \) = aerosol surface area being considered for activation of 1 ice event in cm\(^2\) and \( t \) is the residence time of particles in the CFDC in seconds. The nucleation rates can therefore be calculated for the data in Figure 4.2 for the mono-disperse particles at each fraction of activation by assuming spherical particles for the ATD and by using a residence time of 12 seconds at 223 K. For this calculation, we used the RH\(_i\) values that were an average of the low and high surface areas because for the higher activated fractions, no significant difference in onset RH\(_i\) was observed between the low and high surface area runs. For example, for an activated fraction of 0.1\%, (1 out of 1000) \( SA \) would be given by \( \pi D^2 \times 1000 \), where \( D \) is the diameter of the aerosol particles in cm. This can be done for various fractions of activation and expressed as a function of RH\(_i\) at a given fraction as shown in Figure 4.4.

Data in Figure 4.4 allows the prediction of the number of ice nucleation events to occur at a given supersaturation. It is evident that \( J_{het} \) increases with an increase in ice supersaturation conditions. Therefore, at low RH\(_i\) only the very efficient IN will form ice where the nucleation rate is low and the number of ice crystals to form will be small. The \( J_{het} \) is higher for larger particles than for smaller ones. However there seems to be a convergence of nucleation rates as water saturation is approached regardless of particle size. For the 40 nm particles
there is a steeper increase in $J_{\text{het}}$ as $\text{RH}_i$ increases indicating that their nucleation rates are more sensitive to RH and that nucleation onto small particles will only take place at large values of $\text{RH}_i$. Also plotted in Figure 4.4 are nucleation rates that were derived from data in Kanji et al. [2008] (see Figure 4.3). These data enforce the idea that indeed, at lower $\text{RH}_i$ nucleation rates will be much lower than those observed with the CFDC methods at higher $\text{RH}_i$. There is a spread in $J_{\text{het}}$ values

**Figure 4.4.** Heterogeneous nucleation rates ($J_{\text{het}}$) as a function of onset $\text{RH}_i$. The data used to calculate $J_{\text{het}}$ are from Figure 4.2. For 100 and 240 nm where two total surface areas are presented, we used the average of the two data sets for the $J_{\text{het}}$ computation (see text). Dotted line: water saturation.
observed for similar RH\textsubscript{i} with the polydisperse sample giving much lower J\textsubscript{het} values than the 240 nm data. In addition to the size of the particles, another difference between the two data sets is the temperature. The Kanji et al. [2008] data are for 233 K while those of the current study are for 223 K. In Figure 4.4 there is considerable amount of variation observed between all the data shown, implying that J\textsubscript{het} is dependent on RH\textsubscript{i} and in addition also varies with aerosol size and temperature. We therefore invoke classical nucleation theory [Pruppacher and Klett, 1997] and extend it to heterogeneous nucleation in order to parameterize our laboratory data using contact angles.

4.4.4.2. Contact angles (θ) derived from Classical Nucleation Theory

Classical nucleation theory has been used in previous studies to describe heterogeneous ice nucleation in atmospheric cloud models [Karcher, 1996; Jensen and Toon, 1997; Jensen et al., 1998; Karcher, 1998; Karcher et al., 1998; Karcher and Lohmann, 2003; Morrison et al., 2005] and also to analyze nucleation rates obtained from laboratory data [Fletcher, 1958; Marcolli et al., 2007; Chen et al., 2008; Eastwood et al., 2008]. The theory is based on the rate of heterogeneous nucleation per particle being proportional to the particle’s total surface area and rate of surface nucleation of an ice germ. The nucleation of an ice germ is dependent on the rate at which it can gain one molecule through interaction with the parent phase, in this case water vapour, to overcome the nucleation energy barrier [Pruppacher and Klett, 1997]. For this work we consider heterogeneous nucleation of solids
from a gaseous parent phase (deposition freezing) but could also be used for an aqueous parent phase (immersion/condensation freezing).

In the previous section \( J_{het} \) values were calculated using the activated fraction and surface areas of the particles. The heterogeneous nucleation rate theory is a function of the activation energy of ice formation and temperature. The activation energy is a function of a contact angle. The contact angle describes the wettability of the surface of IN (substrate). The wettability factor \( m \) scales from 0 to 1, and \( m = \cos \theta \), where \( \theta \) is the contact angle of the ice germ with the substrate. A value of \( m = 1 \), implies a very wettable surface and thus a \( \theta \) value of zero. Good IN are therefore expected to have small values of \( \theta \) implying very wettable surfaces and therefore favourable for ice formation. Contact angles can be calculated since the empirically determined nucleation rates have been computed. To determine \( \theta \), we follow an analysis method similar to that described in Eastwood et al. [2008] and to a lesser extent also in Chen et al. [2008]. The analysis in the latter is in greater detail and more complex than that presented here. From standard classical nucleation theory, the heterogeneous nucleation rate described above can be expressed as:

\[
J_{het} = A e^{-\frac{\Delta F_{g, het}}{kT}}
\]

where \( A \) is a pre-exponential factor in \( \text{cm}^{-2} \text{s}^{-1} \), \( \Delta F_{g, het} \) is the free energy of formation of the ice germ (critical embryo) in joules (J), \( k \) is the Boltzmann constant in \( \text{J K}^{-1} \) and \( T \) is the temperature in K. The pre-exponential factor is
dependent on the formation rate of the critical embryo, in particular the addition of gas phase molecules to the growing embryo. The value of $A$ is somewhat uncertain, however it is sufficient to know it to within a couple orders of magnitude since the end result that entails deriving free energies of formation is quite insensitive to this value [Fletcher, 1958]. The free energy of formation of an ice germ onto a substrate can be expressed as follows [Pruppacher and Klett, 1997]:

$$\Delta F_{g,\text{het}} = \frac{16\pi M_w^2}{3[RTP\ln S_i]} \cdot f(m,x)$$  

(4.3)

where $M_w$ is the molecular weight of water in g mol$^{-1}$, $\sigma_{i/v}$ is the surface tension at the interface between ice and vapour in J m$^{-2}$, $R$ is the universal gas constant in J mol$^{-1}$ K$^{-1}$, $\rho$ is the density of ice in g m$^{-3}$, $S_i$ the saturation ratio with respect to ice and $f(m,x)$ is a geometric factor associated with the solid substrate. The geometric factor $f(m,x)$ is a function of the wettability factor ($m$) and the ice germ size, $x$. If the substrate is flat then $f(m,x)$ reduces to being a function of $m$ alone. If we assume that the size of the ice germ is much smaller than that of the IN, the geometric factor, $f(m,x)$ reduces to Equation 4.4 and the simplified geometric factor is given by [Pruppacher and Klett, 1997]:

$$f(m) = \frac{(2 + m)(1 - m)^2}{4}$$  

(4.4)

The above description is one of the most fundamental approaches for extending classical nucleation theory to heterogeneous nucleation. For an insoluble substrate the ice germ of the new phase is assumed to be a spherical cap with $\theta$
related to the energies between the three interfaces (substrate, germ and air) involved. Thus Equation 4.3 can be re-written in light of Equation 4.4 to yield the following:

$$\Delta F_{g,het} = \frac{16\pi M_v^2 \sigma_{i/v}^3 \theta}{3[RT\rho \ln S_i]} \left(2 + \cos \theta \right) \left(1 - \cos \theta \right)^2 \frac{1}{4} \quad (4.5)$$

In order to arrive at $\theta$, we first use Equation 4.2 and the experimentally determined $J_{het}$ values to compute $\Delta F_{g,het}$. A value of $10^{25}$ cm$^{-2}$ s$^{-1}$ is used for $A$ in Equation 4.2 [Fletcher, 1958]. Equation 4.5 is then used to derive $\theta$ using $M_w = 18.015$ g mol$^{-1}$, $\rho = 9.2 \times 10^5$ g m$^{-3}$, $\sigma_{i/v} = 0.106$ J m$^{-2}$ [Pruppacher and Klett, 1997] and $T = 223$ K which is the temperature at which the data shown in Figure 4.4 were collected.

Figure 4.5 shows the contact angles associated with ice formation onto ATD particles as a function of supersaturation for data obtained at 223 K. It is evident that $\theta$ increases with supersaturation regardless of the size of the particles within the broad size range particles studied. In addition we have plotted data taken at 233 K using RH$_i$ from Kanji et al. [2008] which fit into the same trend quite well. The contact angles approach a plateau as water saturation is approached at 223 K (RH$_i = 161\%$) indicating that for deposition mode nucleation to occur on to ATD, $\theta < 30^\circ$ or else the mode of nucleation may change.

The values for all $\theta$ obtained are quite small indicating that ATD is a good ice nucleus. This is good agreement with values obtained for efficient IN such as
kaolinite and muscovite which were reported values of $\theta$ of 8.9° and 8.8° respectively \cite{Eastwood2008}. For inefficient IN, \textit{Eastwood et al.} \citeyear{Eastwood2008} quote average $\theta$ of 26° and 27° for calcite and quartz respectively. Given that the values of ATD span the range 8° to 30°, we can infer that there will be some particles in the sample, or active sites that are efficient while others will be less efficient at forming ice. In a study by \textit{Chen et al.} \citeyear{Chen2008}, $\theta$ for different types of IN were presented based on a fixed average aerosol size. For ATD they assigned a size of 0.35 $\mu$m while the actual size range used in the experiments was 0.1 – 2 $\mu$m. Using this approach they found for ATD $\theta = 5.9^\circ$ or 6.23° (when they accounted for curvature). This lends validity to the current work in two ways. First, the assumption we made regarding the IN surface being planar relative to the size of the nucleating ice germ does not result in changing the outcome of $\theta$ significantly. Second, for a 240 nm most efficient ATD particle, $\theta = 8.6^\circ$ while \textit{Chen et al.} \citeyear{Chen2008} quote a value of $\theta = 5.9^\circ$ for a 350 nm. The smaller $\theta$ is expected given it is for a larger sized ice nucleus.

For a given type of IN, one might have expected that the contact angle of the ice germ is constant since it is a function of the surface wettability and therefore not expected to change with size or surface area of the aerosol. However, since there is a range of $\theta$ observed it implies that $\theta$ represents the contact angles of all the sites that will activate at a critical supersaturation, i.e. not all sites are equal. The heterogeneity in composition from particle to particle therefore results in a range of surface sites and contact angles.
In Figure 4.4, there is a large variation of $J_{het}$ values for the different particles sizes and temperatures at a given supersaturation. However, this is not the case with $\theta$ implying that there is an insensitivity of the $\theta$ values to the $J_{het}$ values. Contact angles are useful for interpretation of results but may not be so important for prediction of ice formation rates in the atmosphere.

**Figure 4.5.** Contact angles ($\theta$) as a function of onset RH$_i$. Data from Figure 4.4 were used to arrive at $\theta$. The 0.5 – 5 $\mu$m points were derived from the data in Kanji et al [2008] and taken at 233 K while the work from this study was at 223 K. Dotted line: water saturation.
Finally, classical nucleation theory is a general approach that has uncertainties associated with it. Some studies have shown that for better description of laboratory data, active site theory is required [Hung et al., 2003; Archuleta et al., 2005; Marcolli et al., 2007], since ice formation will occur at preferential active sites for a given IN [Pruppacher and Klett, 1997].

4.5. Conclusions

We present results of ice formation conditions onto ATD, a reference dust material used as one proxy for naturally occurring mineral aerosol in the atmosphere. It was observed that deposition mode nucleation was active at 223 K for 100 nm particles, in agreement with past studies. Water saturation conditions were necessary for warmer temperatures up to 251 K. At 223 K, we investigated the influence of particle size on the onset RH\textsubscript{i} and found that larger particles require lower saturations with respect to ice to initiate ice activation. The effect is quite pronounced so that, for similar surface areas per ice event of $\sim 10^{-7} \text{cm}^2$, 100 nm particles require a higher onset RH\textsubscript{i} of 150% compared to 240 nm particles that require RH\textsubscript{i} of 127%. This demonstrates that the size of the particle plays an important role in providing active sites for ice formation, with larger particles containing more efficient ice nucleation sites than smaller ones. These results are in good agreement with those of Archuleta et al. [2005] for Asian Dust. In addition, increasing the total particulate surface area present did not influence the onset RH\textsubscript{i}’s for 240 nm particles, although a significant effect was observed.
for 100 nm particles, for small \(10^{-4}\) and \(10^{-3}\) activated fractions. Finally, the heterogeneous nucleation rates and contact angles were determined using the classical nucleation theory. A range of active site efficiencies are inferred given that it was shown that the contact angle increased as a function of increasing critical supersaturation required for activation.

This paper highlights that care must be given in reporting ice formation conditions with values depending on the activated fraction and particle size, as well as composition. Our results are in agreement with previous work in the literature that has shown mineral dusts to be efficient ice nuclei. For ATD, the mechanism of nucleation appears to be deposition nucleation at cold temperatures \((\approx 223 \, \text{K})\) whereas water saturation conditions are required for higher temperatures.

### 4.6. Acknowledgements

The authors would like to acknowledge NSERC for funding
4.7. References


CHAPTER FIVE
Results from the University of Toronto Continuous Flow Diffusion Chamber (UTOR) at The Fourth International Workshop on Comparing Ice Nucleation Measuring Systems (ICIS 2007)

Zamin A. Kanji$^1$ and Jonathan P. D. Abbatt$^1$

with data contributions from Ottmar Möhler$^2$ and Paul DeMott$^3$

In preparation for submission to Atmospheric Chemistry and Physics Discussions
June 2009

$^1$University of Toronto, Department of Chemistry, Toronto, ON, Canada
$^2$Institute of Meteorology and Climate Research (IMK-AAF), Karlsruhe, Germany
$^3$Colorado State University, Department of Atmospheric Science, Fort Collins, CO, USA.
5.1. Abstract

The University of Toronto continuous flow diffusion chamber (UTOR) was used to study heterogeneous ice nucleation at the Fourth International Workshop on Comparing Ice Nucleation Measuring Systems (ICIS 2007) in September 14-28, 2007. The goal of the workshop was to inter-compare different ice nucleation measurement techniques using the same aerosol sample source and preparation method. The aerosol samples included four types of desert mineral dust, graphite soot particles, and live and dead bacterial cells. Good agreement was found between the different instruments with a few specific differences attributed mostly to the variation in how onset of ice formation is defined or the size to which a particle grows, to be considered an ice crystal. It was found that when efficiency of ice formation is based on the lowest onset relative humidity, dead bacteria were most efficient followed by the desert dusts and then soot. For all aerosols, deposition mode freezing was only observed for $T < 235$ K except for the dead bacteria where freezing at $247$ K occurred below water saturation.
5.2. Introduction

The role of ice clouds in determining the global radiation budget is not fully understood [IPCC, 2007]. Part of the gap in knowledge comes from the lack of understanding or quantification of ice formation processes in the atmosphere, including those associated with heterogeneous ice formation where solid substrates called ice nuclei (IN) are involved in the ice forming process [Cantrel and Heymsfield, 2005]. Difficulties arise in quantifying conditions of heterogeneous ice formation because of the varied composition and size distributions of IN found in the atmosphere. For example IN can span compositions that are close to those of elemental carbon (soot), biological aerosols (bacteria and pollen) and crustal aerosol (mineral dusts) [Andreae and Rosenfeld, 2008 and references therein]. Within each classification there are further variations based on aerosol size, source or production method. For example, with desert dust from Arizona it has been observed that the mineralogical composition varies with size of the particle [Vlasenko et al., 2005]. Ice formation is dependent on the composition of IN, temperature and size of IN [Dymarska et al., 2006; Kanji and Abbatt, 2006; Kanji et al., 2008; Kanji and Abbatt, 2009a; Welti et al., 2009]. In addition when investigated in the laboratory more factors such as aerosol preparation and preconditioning as well as ice particle detection methods become important factors to consider when reporting ice formation requisites. Finally, exposure to trace species (organics, NH$_3$, NO$_x$, SO$_x$, ...
O$_3$) in the atmosphere will further modify the surface of IN [Salam et al., 2007; Kanji et al., 2008; Salam et al., 2008].

Prompted in part by the outstanding questions/issues in the field [Laaksonen et al., 1995; Szyrmer and Zawadzki, 1997; Cantrell and Heymsfield, 2005], a suite of laboratory studies have recently emerged on the study of heterogeneous ice nucleation. These include studies of immersion freezing [Zobrist et al., 2006; Marcolli et al., 2007] and condensation and deposition freezing [DeMott et al., 1999; Möhler et al., 2005; Abbatt et al., 2006; Dymarska et al., 2006; Knopf and Koop, 2006; Möhler et al., 2006; Salam et al., 2006; Eastwood et al., 2008; Stetzer et al., 2008; Eastwood et al., 2009]. In addition, field studies [Chen et al., 1998; DeMott et al., 2003; Cziczo et al., 2004; Ansmann et al., 2005; Twohy and Poellot, 2005] have also played a vital role in identifying aerosols that are good IN or most frequently associated with ice crystals in the atmosphere. These studies serve to direct the type of systematic investigations of heterogeneous ice nucleators in the laboratory setting. The general conclusions from laboratory and field investigations are that mineral dusts are more efficient ice nucleators than soot type aerosols and for studies that have included organics, oxidised organics are better at ice nucleation than reduced (alkyl type) species. However, there are a number of differences between results reported that arise from different techniques used. These could benefit from a more detailed comparison between the techniques used to investigate ice formation in order to better define the representation of ice nucleation results [Vali, 1975]. Given the wide variety of ice
nucleation instruments used currently (see Table 5.1 for examples), differences in ice nucleation observations will in part arise instrumentally from the different techniques used. To isolate these effects, it is important to eliminate variability that might arise from aerosol source, preparation and sampling methods.

Renewed interest in ice nucleation research and the development of new instruments prompted The Fourth International Ice Nucleation workshop, ICIS 2007. The goal of the workshop was to perform an inter-comparison of ice nucleation measurement systems while sampling aerosols of the same size distribution and source at similar temperatures. The workshop took place at the AIDA (Aerosol Interactions and Dynamics in the Atmosphere) facility at Forschungszentrum (Institute for Meteorology and Climate Research) in Karlsruhe, Germany, between September 10-28, 2007. The third such workshop took place in Laramie, Wyoming in 1975 [Vali, 1975]. Some of the major conclusions from the third workshop were that:

1) Supersaturation played an important role in determining the activation of IN and so investigations should be carried out for a given aerosol type at two supersaturation values.

2) Further ice nucleation measurements must completely document aerosol properties since the performance of instruments varies with aerosol type.
3) New instruments should undergo extensive testing, controls and validation by comparison to pre-existing instruments before being used for atmospheric sampling.

In response to these suggestions, new instruments are being validated before implementation in laboratory or field studies, for example see Stetzer et al. [2008] and Kanji and Abbatt [2009b]. This in part responds to some of the suggestions highlighted in the conclusions of the third workshop while ICIS 2007 takes into account the other suggestions, such as sampling at different supersaturations and temperatures for a given aerosol type and maintaining a complete database on aerosol properties.

In the current study we present a detailed comparison between results obtained from three different ice nucleation instruments that make use of two techniques. The first is a cloud chamber referred to as ‘expansion experiments’ from here on. The second and third are the Colorado State University and University of Toronto continuous flow diffusion chambers, referred to as CSU and UTOR respectively. Details about the operation of these chambers can be found in Möhler et al. [2006], Rogers et al. [2001], and Kanji and Abbatt [2009]. In addition, details of the experimental schedule and configuration of all instruments in the workshop can be found in Möhler et al. [2008a]. The differences between the CSU and UTOR instruments are primarily the orientation and geometry of the instrument and different detection criteria for ice crystals. Comparison between the expansion, CSU and UTOR experiments covers the
majority of the techniques used at the workshop since most instruments were vertically oriented CFDCs (see Table 5.1). Results from other participants in the workshop are also to be presented under a special issue entitled ICIS-2007 in Atmospheric Chemistry and Physics Discussions, 2008.

5.3. Experimental

For detailed descriptions of all the methods and operational limits in Table 5.1, readers are referred to corresponding articles in the special issue ICIS-2007 mentioned above. This study will focus primarily on comparing results between the cloud expansion chamber [Möhler et al., 2006], and the CSU [Rogers et al., 2001] and UTOR chambers. Figure 5.1 is a schematic of the set up of the relevant instruments.

5.3.1. Experimental Overview of UTOR at ICIS-2007

Ice nucleation was carried out in a continuous flow thermal gradient diffusion chamber whose operation has been described in detail [Kanji and Abbatt, 2009b]. Briefly, the chamber, whose inner walls are coated with ice and temperature controlled by external re-circulating chillers, is fed with aerosols through a movable stainless steel injector. The aerosol constitutes 10% of the total
Table 5.1. List of participating ice nucleation instruments and their characteristics at ICIS 2007

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Orientation</th>
<th>Flow</th>
<th>Inlet Impactor</th>
<th>Inlet dryer</th>
<th>Temperature Range (K)</th>
<th>Applicable maximum value of RH\textsubscript{w}</th>
<th>Detection Method</th>
<th>Ice Size (μm)</th>
<th>Phase Distinction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSU CFDC-1H</td>
<td>Vertical</td>
<td>Recirculated</td>
<td>Yes (1.2 μm)</td>
<td>Yes</td>
<td>265 – 231</td>
<td>105</td>
<td>OPC/active evaporation</td>
<td>2</td>
<td>No</td>
</tr>
<tr>
<td>ZINC (CFDC)</td>
<td>Vertical</td>
<td>One way</td>
<td>No</td>
<td>No</td>
<td>265 – 231</td>
<td>110</td>
<td>OPC/active evaporation</td>
<td>2</td>
<td>Yes</td>
</tr>
<tr>
<td>FINCH</td>
<td>Vertical</td>
<td>Recirculated</td>
<td>No</td>
<td>No</td>
<td>273 – 250</td>
<td>120</td>
<td>depolarization</td>
<td>4</td>
<td>Yes</td>
</tr>
<tr>
<td>MRI CFDC</td>
<td>Vertical</td>
<td>One way</td>
<td>Yes (2 μm)</td>
<td>No</td>
<td>263 – 238</td>
<td>110</td>
<td>OPC/passive evaporation</td>
<td>3</td>
<td>No</td>
</tr>
<tr>
<td>MINC (CFDC)</td>
<td>Vertical</td>
<td>Recirculated</td>
<td>Yes (1 μm)</td>
<td>Yes</td>
<td>263 – 238</td>
<td>110</td>
<td>OPC/passive evaporation</td>
<td>3</td>
<td>No</td>
</tr>
<tr>
<td>UKMO CFDC</td>
<td>Horizontal</td>
<td>One way</td>
<td>No</td>
<td>No</td>
<td>263 – 213</td>
<td>110*</td>
<td>OPC</td>
<td>5</td>
<td>No</td>
</tr>
<tr>
<td>FRIDGE</td>
<td>Horizontal</td>
<td>Static</td>
<td>N/A</td>
<td>N/A</td>
<td>263 – 243</td>
<td>100</td>
<td>CCD Microscope</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>AIDA</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>263 – 193</td>
<td>110</td>
<td>OPC/FTIR/CPI</td>
<td>N/A</td>
<td>Yes</td>
</tr>
<tr>
<td>IMK EDB</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>263 – 213</td>
<td>N/A</td>
<td>Drop Freezing</td>
<td>N/A</td>
<td>Yes</td>
</tr>
</tbody>
</table>

1 Colorado State University Continuous Flow Diffusion Chamber HIAPER version 1. 2 Zurich Ice Nucleation Chamber. 3 Frankfurt Ice Nucleation Chamber. 4 Meteorological Institute of Japan CFDC. 5 University of Manchester Ice Nucleation Chamber. 6 United Kingdom Meteorological Office CFDC. 7 University of Toronto CFDC. * at 223K 8 University of Frankfurt Freezing Ice Deposition Growth Experiment 9 Aerosol Interactions and Dynamics in the Atmosphere. 10 Forschungszentrum Karlsruhe Electro-dynamic Balance.
flow of 2.83 lpm and the remainder is made up of dry particle-free synthetic air. The temperature of both walls is varied at similar rates such that the temperature in the centre of the chamber, where the aerosols are injected, remains constant. Upon increasing the difference in temperature between the two walls, a supersaturation with respect to ice develops in the chamber. When ice forms, the particles grow to sizes beyond those of the background and are detected by a Climet optical particle counter (CI-20). The counter can measure particles in two size bins, greater than 0.5 and 5 μm. However, due to the size distribution of
sampled aerosols sometimes extending beyond 0.5 μm, the smaller channel often displayed a high background count and was not used to determine the onset of ice formation. All experiments were RH scans where the average temperature at the centre of the chamber was kept constant and the RH was increased. The temperature range of the experiments was 265 – 230 K. The number concentration of the aerosols was recorded with a condensation particle counter (CPC, TSI – 3010) that sampled at a flow rate of 1 lpm.

5.3.2. Experimental Overview of Expansion and CSU experiments at ICIS-2007, adapted from Möhler et al. [2006] and Rogers et al. [2001].

The cloud expansion experiments operate on the principle of adiabatic expansions that result in rapid cooling and thus increasing RH inside a 84 m³ cylindrical chamber. The ice chamber is located within a larger chamber that acts as a thermal buffer, and is cooled with liquid nitrogen to control initial temperature conditions before a cloud expansion is initiated. A mixing fan inside the chamber ensures well homogenised temperature conditions within the volume of ± 0.2 K. Before the start of an experiment the chamber is evacuated to 0.01 hPa and flushed twice with dry synthetic air. At the start of an experimental series, water vapour and synthetic air are added to bring the chamber to atmospheric pressure. This is followed by cooling the chamber to bring it to the starting temperature of the experiment which also results in ice condensing on the inner walls of the chamber. To simulate adiabatic cooling of rising air parcels,
the pressure within the chamber is reduced with a mechanical pump from 1000 to 800 hPa which resulted in typical mean cooling rates of 1-2 K min\(^{-1}\). Ice nucleation experiments started just below ice saturation and typically 2-3 expansion experiments were carried out on the same sample of aerosol. Aerosol concentrations were measured using a CPC (TSI, 3010) that was modified to sample at low pressures. Ice onset was observed when an increase in ice crystal numbers were observed using the Small Ice Detector (SID, University of Hertfordshire, UK) that can measure non spherical particles in the range 1 – 35 μm as well as a Cloud Particle Imager (CPI: Stratton Park Engineering Company, SPEC Inc.) that can samples particles in the size range of approximately 10 – 2000 μm. Temperature of the chamber wall and gas are measured at multiple locations with platinum resistance thermometers and thermocouples. The pressure is measured with high precision Baratron sensors (MKS, Munich). An in-situ multi-reflection path tunable diode laser absorption spectrometer directly measures the water vapour concentration in the chamber volume. Uncertainty estimates in computed RH, arising mostly from the water vapour and temperature measurements, are ± 3 – 4\% \cite{Field et al., 2006; Möhler et al., 2006}.

The CSU chamber operates on the same principle as the UTOR, however there are a few differences between the two instruments that are discussed in more detail. As previously stated, the main difference between the CSU and UTOR chambers is the orientation, the detection limit for what constitutes an ice crystal and the absence of an evaporation region in the UTOR CFDC. The CSU
chamber has a circular geometry with two vertically oriented concentric cylinders. Sample and sheath flows are injected into the annular gap between the outer and inner cylinders. Ice coatings on the inner walls of the chamber are achieved by flooding the chamber volume with water followed by prompt evacuation. A temperature gradient between the walls of the annular gap established a supersaturation profile in the gap. The warm wall is the outer cylinder and cooling is achieved by two refrigeration compressors and expansion valves. The chamber length is 100 cm and the lower third was actively controlled so that both walls were at the same temperature (ice saturation) so that water droplets would evaporate before passing into the detector [DeMott et al., 2008]. At the inlet of the chamber an inertial impactor removes particles larger than 1.2 μm. The detector was an optical particle counter (Climet 7350 A) that detected particles larger than 2 μm as ice crystals. The CN counts from the CPCs used for the expansion experiments were also used to provide CN counts for the CSU chamber. Six thermocouples at various locations along the chamber walls are used for temperature measurement to within ± 0.3 K for the outer and ± 0.2 K for the inner cylinder. This resulted in a RH uncertainty of ± 3%.

5.3.3. Aerosol preparation and sampling

The aerosols were all contained in and mostly sampled from the NAUA chamber, a 3.7 m³ evacuable vessel that is made of stainless steel and operated at room temperature with a stability of ± 2K. Except for the bacteria, the aerosols
were dry dispersed into the chamber using a rotating brush disperser (RGB 1000, Palas) in dry synthetic air. Size distributions were measured (SMPS) and have been tabulated in Table 5.2. For both the bacteria samples, aqueous solutions were made in de-ionised distilled water ($5 \times 10^9$ Cit7 cells/ml) and dispersed into the chamber using a dispersion nozzle. The aerosol samples used were:

1) Arizona Test Dust (ATD) (Powdered Technology Inc., Minnesota, USA).

2) Saharan Dust (SD) a surface sample collected 50 km north of Cairo City Egypt.

3) Canary Island Dust (CID) a surface sample collected from the town of Mala on the Canary Island of Lanzarote.

4) Israeli Dust (ID) collected from Ramat Hashron, Israel.

5) Graphite spark generated soot (GSG).

6) Live bacteria (LB) and Snomax® (dead bacteria) [Mohler et al., 2008b].

The soot particles were produced by a commercial graphite spark generator (GfG 1000, Palas) at maximum spark capacity between two pure graphite electrodes and with 99.999% purity Ar flowing at 5.0 lpm. Soot particles used were a surrogate for low organic carbon content (~10%) aerosol and contained mostly elemental carbon. More details on the soot aerosol can be found elsewhere [Mohler et al., 2005]. The bacteria come from cultures of Pseudomonas Syringae, in particular the Cit7 strain. The bacteria were grown in a microbiology laboratory, washed in a centrifuge before making an aqueous suspension. Snomax® is the
same species but freeze dried and killed by gamma radiation. It is used in artificial snow making.

Table 5.2. Size distributions of aerosol samples

<table>
<thead>
<tr>
<th>Aerosol Type</th>
<th>Approximate Size Range (μm)</th>
<th>Number Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATD</td>
<td>0.02 – 1.10</td>
<td>0.15</td>
</tr>
<tr>
<td>GSG</td>
<td>0.02 – 0.45</td>
<td>0.10</td>
</tr>
<tr>
<td>ID</td>
<td>0.02 – 1.30</td>
<td>0.30</td>
</tr>
<tr>
<td>SD</td>
<td>0.03 – 1.10</td>
<td>0.20</td>
</tr>
<tr>
<td>CID</td>
<td>0.02 – 1.00</td>
<td>0.30</td>
</tr>
<tr>
<td>Snomax®</td>
<td>0.03 – 0.90</td>
<td>0.05 and 0.15</td>
</tr>
<tr>
<td>LB</td>
<td>0.02 – 1.10</td>
<td>0.09 and 0.60</td>
</tr>
</tbody>
</table>

The aerosols were typically sampled from the NAUA chamber at ambient pressure, however there were also chances during the workshop to sample from the AIDA cloud expansion chamber directly where the aerosols were at lower temperatures than the NAUA chamber. Since the aerosol lines from the AIDA chamber to the respective instruments were at room temperature (except for the CSU-CFDC), it is likely that the aerosols warmed up to room temperature and thus the only difference in sampling between the two chambers is that the concentration of aerosols derived from the AIDA chamber was typically an order of magnitude lower. In addition there was also a chance to sample aerosols from the AIDA chamber after a cloud expansion (i.e. ice activation) experiment. This allowed the comparison of ice formation onto aerosols that had been previously activated as ice in an expansion experiment therefore enabling the study of effect of cloud processing on ice activation. Figure 5.1 shows the relative positions of the CSU and UTOR CFDC chambers. Note that during sampling from the AIDA
chamber there could be some variation in the size of particles sampled by the 
CSU and UTOR chambers since the larger particles will be found closer to the 
bottom of the AIDA chamber.

5.3.4. Activation of aerosols: Ice formation and detection in UTOR

Since the temperature range investigated ranged from 230 – 265 K, 
activation of aerosols could have occurred to form either water drops or ice 
crystals. The former would be of relevance here especially if activation is 
observed at or above water saturation since the particles would be able to grow 
into the 5 μm channel at T > 250 K and to be miscounted as ice. For more 
hygroscopic aerosols, water uptake can take place at conditions that are 
subsaturated with respect to water. However, these particles would not grow in 
to the 5 μm channel and are of no concern during this study.

To distinguish between the liquid and ice phases we depend on the size of 
the activated particles and therefore used the large channel of the optical particle 
counter (OPC) only to indicate ice formation. The residence time for the particles 
in the chamber was between 9 – 11 seconds, for the temperature range 273 to 230 
K respectively. For the residence times used we have determined that there is 
more than enough time for the ice particles to grow to 5 μm with any water 
drops remaining well below 5 μm in diameter for up to T = 250 K due to the 
different growth rates of the particles [Kanji and Abbatt, 2009b]. In particular, for 
the residence times used at ICIS 2007, water drops would grow to 5 μm at T =
233 K, \( \text{RH}_{\text{w}} > 110\% \) and at 250 K, \( \text{RH}_{\text{w}} > 103\% \). Therefore, for all experiments that are carried out at \( T > 250 \text{ K} \) we do not have the ability to attribute activation above water saturation specifically to ice or water. Finally, the activated fraction was calculated as the ratio of ice counts from the 5 \( \mu \text{m} \) channel to CN counts. The errors in all RH’s reported amount to \( \pm 4\% \) and mostly arise from the uncertainty of temperature (\( \pm 0.1 \text{ K} \)) measurements along the walls of the chamber.

5.4. Results and Discussion

In Figure 5.2, we first plot all the results from UTOR. This is followed by an inter-comparison between the different instruments while sampling from either the NAUA or AIDA chamber (Figures 5.3 – 5.7). For the bacteria samples we do not present an inter-comparison because of the small number of experiments performed and because most were are at \( T \sim 263 \text{ K} \) and \( \text{RH}_{\text{w}} \sim 100\% \) where we believe UTOR cannot distinguish between ice particles and water droplets. For all figures, onset RH’s are given for 0.1\% of particles activating.

5.4.1. General comparison of ice nuclei (IN) sampled

To infer mechanisms of ice formation we assume that activation below water saturation proceeded by deposition freezing and activation at or above water saturation proceeded by condensation freezing. In Figure 5.2, for the warmer temperatures the dust aerosols are only active at water saturation
indicating that deposition mode freezing is not the preferred pathway of ice formation. ATD begins to show some ice activation below water saturation at $T < 245\ K$ while SD and CID only become active in the deposition mode at $T < 240\ K$. When the temperature is approximately $230\ K$ both ATD and CID show efficient ice formation activating as ice crystals well below water saturation. There is some difference in observed ice onset RH’s when comparing particles sampled from the NAUA and AIDA chambers. For ATD, the AIDA onsets are higher than those for NAUA particles (see Figure 5.2). This could be due to reasons pertaining to the size of the aerosol sampled. The concentration of aerosols coming from the NAUA chamber was typically an order of magnitude higher than the concentration in the AIDA chamber. Since UTOR sampled from a higher portion of the AIDA chamber, it is possible that particle diameters were smaller than those being sampled from the NAUA chamber because gravitational settling occurs on the time scale of the experiments. As observed in chapter 4, larger particles lead to lower onset RHs of ice formation. Lower onsets would then be expected while sampling from NAUA.

The bacteria samples are mostly activating around water saturation, however even at warm temperatures ($265\ K$) Snomax® is showing some deposition mode freezing. It activates well below water saturation at $T = 247\ K$, which is more efficient than all of the dust particles sampled, forming ice at $RH_i$ that is 10% lower than that required for SD, ID and CID. The dead bacteria are clearly the most efficient IN of all the samples.
At the colder temperatures GSG is also found to be active in the deposition mode. However, it is a less efficient IN than ATD or CID. Activation below water saturation for GSG is apparent at $T < 235$ K. At warmer temperatures soot only activates as ice crystals via condensation freezing at or above water saturation. Warm temperature data points are not shown for soot since not enough growth was observed in the 5 \( \mu \text{m} \) channel to deduce 0.1%.

**Figure 5.2.** Onset RH$_i$ for 0.1% activated fraction as a function of temperature for all aerosols sampled with the UTOR CFDC. All data are based on the large particle channel (> 5 \( \mu \text{m} \)). Triangles: aerosol sampled from AIDA chamber. Squares: aerosol sampled from NAUA chamber. Stars: aerosol sampled after a cloud expansion experiment in AIDA. Black line: Water saturation [Murphy and Koop, 2005]. Uncertainty in all data points ±4%.
activated fractions. Background levels for soot in the 0.5 μm channel were lower than for dusts. However, for $T > 237$ K, activation occurred in water supersaturated conditions and therefore water droplets cannot be ruled out in the 0.5 μm channel. These data have been omitted from the comparison.

5.4.2. Arizona Test Dust

In Figure 5.3 we plot experiments carried out with ATD from 255 – 223 K. Also shown are results from the CSU chamber and the cloud expansion experiments. It is apparent that for most of the warmer temperature experiments ice formation is only observed at water saturation implying condensation freezing of ATD. Deposition mode freezing begins to become apparent at about 240 K. Below this temperature the ice onset is well below water saturation. For the warmer temperature work there is in general good agreement between the UTOR, CSU and expansion experiments.

For the UTOR experiments it is generally observed that the onsets of ice formation when sampling from NAUA are lower than when sampling from AIDA, as addressed in the previous section. For the CSU experiments this difference between NAUA and AIDA is not observed. It is possible that because the CSU instrument sampled from the bottom of the AIDA chamber, it still studied larger particles than UTOR. As verification, we also plot in Figure 5.3 data collected at The University of Toronto using the UTOR instrument from an aqueous suspension of ATD [Chapter 4, Kanji and Abbatt, 2009a]. For 100 nm
particles deposition freezing is only apparent below 233 K. At 223 K larger ATD particles are much more efficient at forming ice. Therefore, if sampling a polydisperse sample as was done in ICIS 2007, it is likely that lower onset RHs will be observed in the presence of larger particles.

**Figure 5.3.** Comparison of onset RH$_w$ for 0.1% activated fraction as a function of temperature for Arizona Test Dust aerosols between UTOR, CSU and AIDA experiments. UTOR data based on 5 μm channel except for the size selected studies where backgrounds were low enough to use the 0.5 μm channel. Numbers next to the stars indicate the order of the cloud expansion experiment. Pre-exp and post-exp indicate sampling from the AIDA chamber before and after successive cloud expansion experiments. Error bars excluded for clarity (see Figure 5.4). Dashed line: Water saturation [Murphy and Koop, 2005].

The data points between 233 – 231 K in Figure 5.3 show a significant spread in RH given that they are all collected at similar temperatures. For the
expansion data points there is a systematic increase in onset RH for each successive expansion experiment. Here, we believe that the loss of larger particles to gravitational settling upon ice formation leaves behind smaller, less efficient particles for the 2\textsuperscript{nd} and 3\textsuperscript{rd} activations, thus requiring higher RH to initiate ice formation. This is the reason for the systematic increase in onset from experiment to experiment. In addition to loss via ice activation, gravitational settling of unactivated particles during the full sequence of experiments may also be important.

In some cases when sampling from NAUA, the CSU instrument observes lower onsets than the UTOR chamber and this could be attributed to the detection abilities of the instruments. The OPC used with the CSU detects ice particles that are larger than 2 μm while UTOR detects ice particles that are larger than 5 μm, thus requiring slightly higher RHs for particles to grow to a larger size. This effect would be more pronounced if activations occurred at low RHs or at very cold temperatures where ice growth rates were lowest.

5.4.3. Saharan, Canary Island and Israeli Dusts

To assess the relative efficiencies of different dusts, three other mineral dust samples were studied. In Figure 5.4 we plot the data for ice formation onto SD aerosol. Deposition mode freezing is likely occurring at T < 246 K above which freezing is only observed at or above water saturation for all expansion, UTOR and CSU instruments. As with ATD there is a decrease in onset RH as
temperature decreases, indicating a change in freezing mechanisms from condensation to deposition freezing.

For the UTOR data points above water saturation, it is not clear whether ice or water activation occurs because they are at the limit for when water droplets can grow large enough to be detected in the 5 μm channel. For the data points observed below water saturation, while we can speculate the onset of deposition

**Figure 5.4.** Comparison of onset RH\(_w\) for 0.1% activated fraction as a function of temperature for Saharan Dust aerosols between UTOR, CSU and AIDA experiments. UTOR data based on 5 μm channel. Error bars represent uncertainty in RH measurements (see text for details). Dashed line: Water saturation [Murphy and Koop, 2005].
freezing, the onset RH is still close enough to water saturation such that it is within experimental uncertainty. In fact, deposition mode freezing onto SD particulates that were deposited on a hydrophobic support at $T = 233 \text{ K}$ have been reported well below water saturation at $RH_w = 73\%$ [Chapter 2, Kanji and Abbatt, 2006].

In Figure 5.5 data are plotted for CID ice formation onsets as a function of temperature. It is evident that at approximately $T = 242 - 240 \text{ K}$ there is a distinct shift from ice formation above water saturation to below water saturation. At $T > 242$ water saturation is required for ice formation and this is observed for the expansion, UTOR and CSU chambers. For NAUA sampling, at $242 \text{ K}$, CSU observes the onsets for both CID and SD at $RH_w = 99\%$ and at $240 \text{ K}$ the onset for both dusts by UTOR is observed at similar RH ($RH_w = 97\%$). However for CSU, at $T \approx 237.5 \text{ K}$, CID has an onset RH that is 10\% lower than SD implying that efficiencies at warmer temperatures appear to be similar for the two dusts, but at colder temperatures CID is more active than SD, at forming ice. At approximately $232 \text{ K}$, UTOR observes ATD onsets to be slightly lower (by $\sim 3\%$) than those of CID for NAUA sampling where as CSU finds the onsets to be similar at about $RH_w = 76\%$. Also at $T = 232 \text{ K}$, UTOR observes an onset RH for CID to be about 7 \% higher than that observed by CSU and this can be attributed to the delay that results in detection of 5 $\mu$m particles compared to 2 $\mu$m respectively. This delay is not observed in the UTOR results for the SD (Figure 5.4) perhaps because the UTOR and CSU experiments are about 8 – 11 K warmer
implying faster ice crystal growth rates which may help to eliminate the delay effects.

Figure 5.5. Comparison of onset RH\textsubscript{w} for 0.1\% activated fraction as a function of temperature for Canary Island Dust aerosols between UTOR, CSU and AIDA experiments. UTOR data based on 5 \textmu m channel. Error bars represent uncertainty in RH measurements (see text for details). Dashed line: Water saturation [Murphy and Koop, 2005]. Figure 5.6 shows a similar plot as the other dusts, but for ID. The same trend is observed as for SD and CID. Ice formation at or above water saturation for T > 244 K and below water saturation when T < 242 K. There is good agreement between UTOR, CSU and AIDA expansion chambers for the
measured onsets with only scatter of a few percent RH between observed onsets of ice formation. Based on the CSU data, at $T = 238 \text{ K}$, ID has the lowest onset $\text{RH}_w = 85\%$ followed by CID at $\text{RH}_w = 88\%$, ATD at $\text{RH}_w = 92\%$ and finally SD at $\text{RH}_w = 98\%$. It is evident that all the mineral dust samples show a consistent change in ice formation mechanism (from condensation to deposition freezing) in the temperature region of $240 \text{ K}$.

**Figure 5.6.** Comparison of onset $\text{RH}_w$ for 0.1% activated fraction as a function of temperature for Israeli Dust aerosols between UTOR, CSU and AIDA experiments. UTOR data based on 5 $\mu$m channel. Error bars represent uncertainty in RH measurements (see text for details). Dashed line: Water saturation [Murphy and Koop, 2005].
5.4.4. Graphite Spark Generator Soot.

In Figure 5.7 we plot the onset RH for 0.1% of GSG particles freezing as a function of temperature. Data from UTOR at warmer temperatures, $T > 235$ K, are not shown because no significant growth in the 5$\mu$m channel was observed for $\text{RH}_w < 110\%$, above which we cannot distinguish between water and ice. However, from the CSU data it is apparent that GSG is much less efficient than mineral dust at forming ice. It requires conditions well above water saturation in the warm temperature regime for ice to form. If CSU data are extrapolated to colder temperatures, we can conclude that the transition to deposition mode freezing for soot would occur at $T \sim 231$ K. In particular for UTOR the transition to deposition mode freezing is apparent at 234 K. When GSG was sampled from the AIDA chamber, the onset for the pre-expansion sampling is observed to be higher than post-expansion results. This is reverse of what is observed for ATD. From the expansion experiments, at $T < 234$ K soot is observed to be an efficient IN requiring lower onset RHs with decrease in temperature. At $T \sim 234$ K, the lowest RH is observed in the expansion experiments (deposition freezing) while CSU required water saturation.

It is also noteworthy that for the cloud expansion experiments RH onsets are lower for the 2$\text{nd}$ and 3$\text{rd}$ expansions compared to the 1$\text{st}$ expansions. This is similar to the observation from the pre and post expansion results from the UTOR technique.
Figure 5.7. Onset RH$_w$ for 0.1% activated fraction as a function of temperature for graphite spark generator soot. Numbers next to the stars indicate the order of the cloud expansion experiments. Pre-exp and post-exp indicate sampling from the AIDA chamber before and after a cloud expansion experiment respectively. Error bars represent uncertainty in RH measurements. Dashed line: Water saturation.

In this case it is possible that the initial ice formation process may alter the soot surface therefore making it more favourable to ice formation once the soot particles have been through an ice forming cycle. Mechanistically, the most variation between the results obtained from the three instruments being compared is observed for GSG. While the spread in RH values for the dust
experiments still exists, there is good overlap when instrument uncertainties are taken into account.

In Figure 5.8 our data are compared to literature reports for different types of soot particles. The data from Möhler et al. [2005] are for the same type of soot (GSG) as studied at ICIS 2007 and obtained using the same method as the expansion chamber. The DeMott et al. [1999] are for lamp black soot particles obtained using a laboratory version of the CSU instrument, while the Dymarska et al. [2006] data are also for lamp black particles that are deposited on a hydrophobic support where ice nucleation is observed through a microscope. Despite the different techniques and soot particles used, there appears to be a progression to deposition mode nucleation when temperatures of ice formation are below 235 K. The Dymarska et al. [2006] data points are all for condensation freezing since water drops were observed first, followed by subsequent freezing. All the other data points are for ice formation and for observations of ice onsets close to or at water saturation, so condensation freezing cannot be ruled out. However, at colder temperatures when ice onsets are occurring at significantly water subsaturated conditions, deposition nucleation is likely the pathway. At $T = 233$ K the spread observed between the Dymarska et al. [2006] and UTOR data could be due to use of different type of soot particles. However, Möhler et al. [2005] use the same type of soot particles as the current work and yet observe lower onset RH. There are two possible explanations for the observed differences.
Figure 5.8. Comparison between soot results obtained at ICIS 2007 from the UTOR CFDC to previous results in the literature. Dashed line: water saturation. See text (section 5.4.4) for details on soot samples compared.

First, the Möhler et al. [2005] values are quoted for an activated fraction < 0.3% and UTOR for 0.1%. This does not rule out the possibility that the Möhler et al. [2005] values could be for a very low fraction (first few ice events) and therefore a much lower onset reported. Second, ice particles need to grow to 1μm in diameter before being detected for Möhler et al. [2005] whereas the UTOR study this requirement is 5μm thus requiring a higher RH for detection of onset. Related to growth of the ice crystals is the time scale for the Möhler et al. [2005]
experiments, which were longer than UTOR residence times allowing only a short time for crystal to grow before it reaches the OPC for detection.

5.5. Inter-comparison of UTOR, CSU and Expansion techniques.

The results indicate that for all aerosol types sampled at ICIS 2007, the expansion chamber gave lower onset RHs of ice formation for 0.1% of particles freezing. This could be explained by the ‘residence time’ of particles in each of the chambers. For the CFDC techniques, particles pass through the chamber within seconds whereas in the expansion chamber, particles remain in the chamber throughout the experimental run that can last for a few minutes. This is evident from an observation of delayed growth of ice crystals in some of the expansion experiments (not shown here). For example, for the soot experiments, once the supersaturation had reached its maximum value in the expansion, the RH typically started to decrease thereafter. However, the ice fraction still continued to increase.

For the CSU and UTOR chambers, there are some differences to be addressed. For the UTOR chamber no inlet impactor was used and therefore some large particles could have been present in the samples that were absent in the CSU experiments. If this indeed was the case, it would offer an explanation for lower onset RHs observed with UTOR compared to CSU in some cases (see Figure 5.4 and 5.7). However, there are examples when CSU measures lower onsets than UTOR and in many cases significant overlap or good agreement is
observed. When CSU observed lower onset RH than those of UTOR, it could be due to the ice crystal size detection criteria being higher for UTOR (5 μm compared to 2 μm for CSU), therefore requiring higher RHs especially at colder temperatures. Given the different approach used to measure ice formation in the expansion and UTOR techniques, good consistency is observed when comparing results from pre-expansion to post-expansion experiments. However, the absolute RHs for these experiments overlap only in some cases. And so, different ice nucleus measurement techniques make it hard to quote an absolute value of onset RH due to the various experimental factors under consideration. Therefore it is easier to make relative claims when describing the results from the different techniques used.

5.6. Conclusions

Ice nucleation results for four types of naturally occurring mineral dust samples, graphite spark generated soot and bacterial aerosols (P. Syringae) in a horizontally oriented parallel plate CFDC have been presented as a function of temperature. Ice onsets have been defined at 0.1% of aerosols activating as ice particles. It was found that dusts are more effective at forming ice than soot in the range 253 K > T > 230 K. At warmer temperatures, circa 247 K, bacterial aerosols are found to form ice well below water saturation, thus being more efficient than the mineral samples studied. The onset of deposition freezing, where ice formation was observed below water saturation, for the mineral dust
samples takes place for $T < 240$ K. At higher temperatures, water saturation is required. Also presented are comparisons for the mineral dust and soot samples to two other instruments, the expansion chamber and a vertically oriented cylindrical CFDC. Generally good agreement between the three techniques was achieved when uncertainties for each of the techniques are taken into account. For prediction of the onset for deposition mode freezing, the three experimental methods agree on the approximate temperature range where this occurs. Significant differences in absolute values were observed in some cases (Figure 5.7).

This comparison has highlighted the advances made in ice nucleation studies. Some of the goals for future work that were set out at the conclusion of the previous workshop in Laramie, Wyoming in 1975 have been met. These include being able to conduct experiments for at least two supersaturations and validating instruments before field and/or laboratory implementation. However, absolute statements about definitive onset values are still challenging to make, since experimental techniques operate in different modes.

For example, kinetic growth studies would be useful to determine if residence times in chambers influence the onset RH of ice formation. CFDC experiments could shorten or lengthen residence times and expansions can change their rates of cooling so that ice activation can be achieved within seconds.
In light of the studies discussed in chapter 4, using a range of aerosol sizes also introduces further heterogeneity in samples studied during ICIS 2007. This is because larger aerosol particles will activate as ice crystals at lower RHs than the smaller ones. Future ice nucleation workshops and studies may benefit from using size selected aerosols of pure substances such as oxides (e.g. silica and alumina) or pure clays (e.g. montmorillonite and kaolinite) that form a large proportion of mineral aerosol.

5.7. Acknowledgements

The authors would like to acknowledge the Centre of Global Climate Change Science (CGCS) scholarship and the Natural Sciences and Engineering Research Council (NSERC) for funding. In addition Zamin Kanji would like to thank Ottmar Möhler and Paul DeMott for useful discourse during the ice nucleation workshop and post-experiment analysis. The authors are also thankful for the skillful support from the AIDA team for organization issues and instrument set up. We also thank Thomas Schwartz from the Institut für Technische Chemie of Forschungszentrum, Karlsruhe for support in preparing the bacterial cultures. Forschungszentrum Karlsruhe provided funding for the facility infrastructure within the Helmholtz Research Programme “Atmosphere and Climate”. The U.S. National Science Foundation (Grant ATM-0611936) supported P. DeMott’s group for this project. The European Science Foundation’s INTROP program supported the data workshop in Pontresina, Switzerland.
5.8. References


activity of bacteria: new laboratory experiments at simulated cloud conditions."


CHAPTER SIX

FINAL THOUGHTS
AND FUTURE STUDIES
6.1. Conclusions

Recent work in heterogeneous ice nucleation studies has focussed on improving the understanding of the mechanisms responsible for ice nucleation for a range of tropospherically relevant temperatures [Cantrell and Heymsfield, 2005; Andreae and Rosenfeld, 2008]. To study heterogeneous ice nucleation, the interaction of a wide variety of atmospherically relevant aerosol with water vapour was investigated using two techniques to observe ice formation. First, a cold stage flow cell technique coupled to a digital camera was used to detect a single ice event out of up to $10^5$ particles. Second, a continuous flow diffusion chamber coupled to an optical particle counter was built, and validated using homogeneous freezing of sulphuric acid. Particulate matter studied using the cold stage technique included commercially available samples of Arizona Test Dust (ATD), montmorillonite, kaolinite, silica, alumina (mineral dusts), oxalic acid dihydrate, sodium salt of humic acid (hygroscopic particulate), octyl-coated silica and Gascoyne Leornardite (hydrophobic particulate). Particles studied with the continuous flow diffusion chamber included naturally sourced desert dusts from Saharan Africa (SD), Canary Island (CID) and Israel (ID), graphite spark generated soot and bacteria. In addition, parameterisations of the results using ice nucleation rates and contact angles are presented.

This thesis is a summary of laboratory measurements that were undertaken to study the effects of ice nuclei composition, size and surface area
on deposition mode ice nucleation. To reduce uncertainties in the area, we targeted the following broad research questions:

- What are the relative ice nucleation efficiencies of atmospherically relevant ice nuclei (IN) for the cirrus regime?
  - Is there an observable difference for dusts sourced from different regions?
  - How do organics of varying degrees of oxidation compare in efficiency?
  - What is the contribution of atmospherically abundant particles like soot and bacteria?
  - Is there a suppression of the IN activity due to chemical processing of dusts?
- For the most efficient IN, what is the temperature at which the deposition mode is active?
- Like homogeneous freezing, is there a unique onset of deposition freezing that can be defined?
  - How do particle size and surface area influence the onset?

In the following sections the major conclusions drawn from the studies presented in this thesis are described with regard to answering the research questions above.
6.1.1. Relative efficiencies of atmospherically relevant IN in the cirrus regime

To determine the relative efficiencies of the particulate matter, the cold stage flow cell technique was used. Particles studied were classified into three categories: mineral dusts, hygroscopic and hydrophobic solids. This study was presented in chapter 2. Additionally, naturally sourced desert dusts and graphite soot were also studied using the CFDC as presented in chapter 5. At 233K the onset relative humidity with respect to ice (RH$_i$) was lowest for the mineral dust samples followed by the hygroscopic particulates. The hydrophobic particulate was least efficient showing a significant increase in onset RH$_i$ for deposition mode ice nucleation in comparison to mineral dusts. At 233K Saharan dust was found to be more effective requiring lower RH$_i$ than Arizona Test Dust, using the flow cell technique. This could be due to the more clay like (calcium-silicates) composition of the Saharan Dust whereas Arizona Test Dust is composed mostly of mineral oxides with minor clay components, and higher carbon content. The CFDC studies at T~ 233K showed Arizona Test Dust and Canary Island Dust had similar efficiencies. This is consistent with the carbon content in Canary Island Dust being higher than that of Saharan Dust. For T = 238K Canary Island Dust required RH$_i$ = 13% less than that of Saharan Dust which required water saturation to form ice. Even though the carbon content is higher in Canary Island Dust than the Saharan Dust, the oxygen content is lower in the Saharan Dust. At warmer temperatures than 238K both dusts required water saturation for ice
formation. Soot displayed an efficiency that was similar to that of the hydrophobic particulates.

As a surrogate for oxidised organic particulate, oxalic acid was more efficient than Gascoyne Leonardite, a proxy for organics with a smaller degree of oxidation. In addition, chemical processing of silica particles to give a hydrophobic octyl surface coating demonstrated a suppressed efficiency of ice nucleation compared pure silica particles. Octyl-coated particles required at minimum a RH\textsubscript{i} that is 18\% higher than for pure silica particles. This is an expected tendency given that water must bind to the surface of IN to help ice formation and a surface layer composed of an alkyl functionality will not favour such an interaction.

Lastly, albeit not at typical cirrus temperatures, bacteria samples demonstrated a much higher efficiency than the desert dust samples at 248K requiring RH\textsubscript{i} to be 13\% less than that required for dust particles. At these warmer temperatures (T > 235K), no observable difference within experimental error in ice formation was observed for the desert dust samples studied. We note that a direct comparison of results from the two techniques is challenging given the detection criteria for the two techniques are different.

The composition of the IN is therefore instrumental in predicting the ice activity of particles. In addition, chemical processing of particles that might give rise to varying degrees of oxidation showed that surface chemical structure is crucial to ice formation efficiencies. The relative efficiencies of ice formation
imply that for the classes of compounds studied, in the cirrus regime mineral aerosols will initiate deposition mode nucleation. After these particles have been removed (e.g. due to precipitation, coagulation or cloud scavenging), ice nucleation will proceed onto crystallised organic or hygroscopic material. Although there exists a variation in efficiency within the mineral dust category, the overall importance of each type of particle will depend on its atmospheric abundance.

6.1.2. For the most efficient IN, at what temperature is deposition mode active?

In order to answer this question, ice formation experiments had to be performed over a range of temperatures that were relevant to the troposphere, so as to observe the transition in ice activation from at or above water saturation (condensation freezing) to below water saturation (deposition freezing). Deposition mode was apparent for Saharan Dust at $T \sim 248$ K, Arizona Test Dust at $T \sim 245$ K, Canary Island Dust at $T \sim 240$ K and for Israeli Dust at $T < 245$ K. For the latter, the coldest measurements obtained are at $245$ K at which ice activation was observed above water saturation, implying formation via condensation freezing. This also implies that deposition freezing will require a shift to a temperature below $245$K.

If the relative effectiveness of these dusts is based on the warmest temperature at which they can act as deposition IN, it would follow that SD is the most effective followed by ATD. In particular it is worth to note that in the
flow cell studies (chapter 2), we also concluded that SD was more effective than ATD, with the former exhibiting a lower onset RH$_i$ at 233K.

6.1.3. *Is there a unique onset value that can be defined for deposition mode nucleation?*

The results from chapter 2 and 5 illustrate that the composition of IN strongly influences the onset RH$_i$. Furthermore, there was an anti-correlation observed between the surface area of particles and onset RH$_i$, for low activated fractions using both the cold stage flow cell and for 100 nm ATD particles in the CFDC studies. ATD showed a stronger dependence on surface area than did SD. To this end we can say that a single onset value cannot be defined for deposition mode nucleation as is the case for freezing of micron-sized solution droplets with homogeneous nucleation.

To de-convolve the surface area relationship observed, size resolved studies on ATD were undertaken as presented in chapter 4. The results showed a significant increase in efficiency for 240 nm compared to the 100 nm ATD particles. It was also shown that even for the same total surface area of ice nucleation, the 240 nm particles were still more effective at ice formation than the 100 nm particles. Keeping the size constant at 240 nm and changing the total surface area had no influence on the RH$_i$ implying that particle size matters. In addition, size and surface area differences all converge when ice activation begins to approach water saturation. This suggests that the effects discussed will be relevant at lower RH$_i$ that typically corresponds to low activated fractions,
which are most atmospherically relevant given the low IN concentrations found in the troposphere.

Finally, using the approach outlined by the classical nucleation theory, heterogeneous ice nucleation rates ($J_{het}$) were calculated for the various particle types studied and presented in chapter 2 and 4. There was a positive correlation of $J_{het}$ with RH$_i$. However, significant scatter was observed as a function of IN composition and size. A further extension to the classical approach was applied in order to parameterise freezing conditions using the contact angle of an ice germ with ATD particles. The contact angles for ATD were found to be in the 8 – 30° range and increased with RH$_i$, the higher angles representing particles requiring higher RH to activate as ice crystals. A range of observed contact angles suggest that active sites on ATD have non-equal tendencies to nucleate ice with some being more efficient than others. This further exemplifies that a single RH value cannot be reported at which deposition mode nucleation will activate. Lastly, the contact angles were insensitive to $J_{het}$ values regardless of particle size and temperature (233 and 223K).

6.2. Future Directions

The work presented in this thesis was focussed at reducing uncertainties associated with deposition mode nucleation. The strongest influences of IN on deposition mode nucleation was found to be composition and particle size. Other issues include:
• Modifications of the chemical surface composition due to atmospheric aging.

• Aerosol size effects at warmer temperatures

While a suite of particles were investigated, the contributions of many types of atmospheric aerosol are still largely unknown. An area of high uncertainty with regard to the effectiveness of atmospheric particles as IN are emissions from industrial or urban areas [Szyrmer and Zawadzki, 1997], i.e. anthropogenically formed or modified particles. This section provides motivation and questions that still remain with regard to ice nucleation onto atmospheric aerosol.

6.2.1. Size resolved studies at higher temperatures

For the size resolved studies, larger particles were more efficient at ice formation. For $T > 250$K, deposition mode freezing was not observed even in cases when dust particle sizes had a high cut-off at ~800 nm, as indicated in Chapter 5. If dust particle sizes were to be increased to supermicron sizes, would there be initiation of deposition mode freezing at $T > 250$K? There has been evidence from previous work to show that when particles with sizes up to 5 μm are used, deposition freezing can be observed at $T$ as warm as 263K [Kanji and Abbatt, 2006]. The relevance of large particles at warm temperatures comes from two reasons. First, mass modes for mineral dusts in the atmosphere have been reported to be on the order of 10 μm [Andreae and Rosenfeld, 2008]. Second, it is likely that the large particles will not be lofted to cirrus altitudes due to shorter
atmospheric residence times. Thus, deposition freezing on supermicron sized
dust particles could have potential impact on warm cloud ice growth.

6.2.2. Chemical processing relevant to the atmosphere

The results from the work presented in chapter 2 demonstrated that
surface chemical composition can reduce the effectiveness of efficient IN (silica
vs. octyl-silica particles). Motivated by this observation, more work is needed on
how atmospheric aging, in particular, of most relevance to the troposphere is the
influence of oxidation on surface properties of dust particles and the resulting
effect on ice formation. There is evidence to show that ozone will change the
surface chemistry of alumina [Roscoe and Abbatt, 2005]. Is such an oxidative change
enough to observe a significant difference in ice nucleation ability? Furthermore,
processing of mineral dust by gases such as ammonia and sulphur dioxide have
been shown to significantly affect ice nucleation ability [Salam et al., 2007; Salam et
al., 2008].

6.2.3. Urban/industrial aerosol – Tropospheric relevance

A number of early studies have reported contradictory findings with
regards to the effectiveness of ice formation on urban aerosols. For example, a
study in the city of Seattle, USA, found that the number of IN active at 252 K
were an order of magnitude higher than those in an unpolluted region [Hobbs and
Locatell, 1970]. Higher IN counts were also observed in Manchester, England than
in rural sites [Al-Naimi and Saunders, 1985]. In contrast, observations in the St. Louis, Missouri area showed that on average IN concentrations were smaller downwind of the city than upwind [Braham and Spyersduran, 1974]. In agreement with this observation, an overall decrease in IN concentration over St. Louis was also reported in a later study [Czys, 1977]. Furthermore, in Valladolid, a typical urban site in Spain, IN concentrations were reported to be smaller by a factor of three in comparison to a nearby rural site [Perez et al., 1985b; Perez et al., 1985a]. To add to these contradictory findings, observations in Providence, Rhode Island suggested no effect of urban aerosols on the IN concentration when using ambient lead and iodine as tracers for urban aerosol [Borys and Duce, 1979].

Motivated in part by these early reports, as well as by the possibility of the impacts of urban aerosol on cloud formation regionally and globally, a project to measure IN in ambient particles in Downtown Toronto has been initiated. Preliminary information is presented in the following section which highlights the need to use composition analysis instruments to get accurate and useful information about IN in urban air.

6.2.3.1. Future Studies deploying the current UTOR system

The CFDC built was used to conduct ice formation measurements at 223K. Ambient aerosol was drawn in to the CFDC and RH scans as outlined in Chapter 3 were performed. Sampling was performed as relative humidity scans such that RH < RH for homogeneous freezing followed by at RH > RH for homogeneous
freezing. Ice activation spectra are presented in Figure 6.1. These were obtained from sampling outdoor air in downtown Toronto on the University of Toronto Campus. The sampling took place during a 150 minute period on March 5th 2009. Aerosols were drawn in to the chamber via an impactor with a 510 nm cut-off. Three RH scans were conducted where the temperature at the centre of the chamber was kept at a constant 223K, but the RH was raised from ice saturation to ~10% above water saturation. Note in Figure 6.1 that beyond water saturation the activated fraction plateaus to a maximum value that is below 1. This implies the possibility of there being inactivated aerosol given that at 223 K no significant ice crystal gravitational losses in the chamber are expected unless RH$_w > 110\%$.

Finally, note also the change in slope of the activation curves at water saturation, implying that a change in freezing mechanism may have occurred. These results indicate that for the first two scans ice activation in both the small and large particle channels took place at RHs below those required for homogeneous freezing. However, for the third scan at the end of the sampling period, activation shifted to a RH value that is above that of homogeneous freezing - closer to water saturation. This implies some change in aerosol properties, likely the composition.

In order to identify the active components of the aerosol and assess how the ice formation conditions change with temporal evolution of the active particles, experiments need to be run with a suite of analytic instruments. This would involve coupling aerosol analysis instruments to the CFDC. The
instrument coupling will afford information that is important in understanding onset RH<sub>i</sub>, such as background aerosol composition and particle size distributions. For this purpose an aerosol mass spectrometer (AMS) and a scanning mobility particle sizer (SMPS) can be used in parallel to the current system being employed.

**Figure 6.1.** Ice activation spectra for ambient urban aerosol sampled in downtown Toronto at the University of Toronto at 223 K. Squares: particles activating to be larger than 0.5 µm. Circles: particles activation to be greater than 5 µm. Three repetitions of RH scans (see text) were performed, each represented by a different colour. Dotted line: Homogeneous freezing of sulphuric acid droplets [Koop et al., 2000].
Furthermore, to identify the composition of the particles that act as IN, compared to the ambient composition, a counter flow virtual impactor (CVI) and other composition spectrometers (e.g. aerosol time of flight mass spectrometer or a single particle soot photometer) can be coupled in series to the exit of the CFDC. A CVI inertially selects ice crystals, which evaporate in a dry airflow thus isolating the IN that can subsequently be directed to the composition instruments for identification. The potential research described above will hopefully lead to complimentary information on the conditions needed for ice nucleation of a wide variety of aerosols.
6.3. References


APPENDIX A
X-ray Photoelectron Spectra (XPS) for Octyl-coated Silica

The spectra in this section provide evidence for there being a change in the surface chemical composition of pure silica particles and the processed particles. Refer to Chapter 2 for chemical procedures. Note that the spectra are presented as controls (pure silica particles) and product (silica with octyl-coating). XPS is a low vacuum technique that uses sticky carbon tape for sample mounting. This results in a noticeable carbon ‘impurity’ even in the control. We therefore rely on the relative increase in carbon signals when comparing controls to product characterisations.

The table below summarises the results from the spectroscopy:

<table>
<thead>
<tr>
<th>Peak Ratio</th>
<th>Control (Silica)</th>
<th>Product (OctylSilica)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon/Silicone</td>
<td>0.50</td>
<td>0.71</td>
</tr>
<tr>
<td>Carbon/Oxygen</td>
<td>0.28</td>
<td>0.41</td>
</tr>
<tr>
<td>C-C (285 eV) peak intensity</td>
<td>39 % of carbon signal</td>
<td>85% of carbon signal</td>
</tr>
</tbody>
</table>
control toluene 3h reflux

![Graph showing binding energy vs. intensity with peaks at specific binding energies.]

spec: abbot/zamin/zk control2
Control: Carbon, silicon and oxygen peak ratios

![Graph showing binding energy vs. intensity with peaks at approximately 500 eV, 300 eV, and 200 eV labeled as C, O, and S respectively.]

<table>
<thead>
<tr>
<th>Element</th>
<th>Atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>15.4</td>
</tr>
<tr>
<td>O</td>
<td>55.1</td>
</tr>
<tr>
<td>S</td>
<td>29.4</td>
</tr>
</tbody>
</table>
new product

Element | Atom %
--- | ---
C | 20.6
O | 50.4
Si | 29.0

Product: Carbon, silicon and oxygen peak ratios
APPENDIX B
Growth Calculations for the Continuous Flow Diffusion Chamber

This section describes the calculations used in order to arrive at the temperature and relative humidity limits at which the CFDC can be operated. These limits have been outlined in Chapter 3.

The need for the calculations arises from the nature of the ice detection system. The optical particle counter used detects ice crystals or water droplets in two channels, greater than 0.5 and 5 \( \mu \text{m} \). Since the detection of ice crystals is dependent on their growth rates being higher than those of water droplets, care must be taken to ensure that the latter are not being miscounted as ice crystals.

The growth calculations are based on the method described in Rogers and Yau [1989] and can be performed for ice and water supersaturated conditions at different temperatures, as a function of time for the growth of liquid droplets or ice crystals. In this case the time relates to the residence time of aerosol particles in the chamber. The residence time is calculated from the bulk flow, 2.83 lpm, in the chamber and the volume of the chamber the aerosols pass through. In the calculation we use a residence time of 12 seconds since this was used for majority of the CFDC studies. The radius of a droplet is given by [Rogers and Yau, 1989]:

\[
r(t) = \sqrt{r_0^2 + 2\xi t}
\]

where \( r_0 \) is the initial size of the particle (size of the ice nucleus) and \( t \) is the growth time of the particles (residence time). \( \xi \) is given by:
\[ \xi = \frac{(S - 1)}{F_k + F_d} = \left[ \frac{L}{R_v T} \right] \frac{S - 1}{KT} + \frac{L \rho_l}{KT} + \frac{\rho_l R_v T}{De_s(T)} \]  

(B2)

The variables in B2 and their corresponding units and values at 233 K are as follows:

\textbf{S: } \frac{e}{e_s(T)}, \text{ the ambient saturation ratio with respect to liquid water (RH}_w/100) \text{)}

\textbf{L: } \text{Latent heat of vapourisation of water (2603 J g}^{-1} \text{ at 233 K)}

\textbf{R}_v: \text{Gas constant for water vapour (461.5 J Kg}^{-1} \text{ K}^{-1})

\textbf{T: } \text{Temperature (233 K)}

\textbf{\rho}_l: \text{Density of water } (1000 Kg m}^{-3} \text{)}

\textbf{K: } \text{Thermal conductivity of air (2.07 \times 10}^{-2} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1} \text{ at 233 K)}

\textbf{D: } \text{Coefficient of diffusion of water vapour in air (1.62 \times 10}^{-5} \text{ m}^{2} \text{ s}^{-1} \text{ at 233 K)}

\textbf{e}_s(T): \text{Equilibrium vapour pressure over liquid water (19.05 Pa at 233 K)}

In order to calculate the size of an ice crystal the same equation (B2) applies so long as we assume spherical ice crystals and replace \textbf{L} with \textbf{L}_s, \textbf{e}_s with \textbf{e}_i and \textbf{\rho}_l with \textbf{\rho}_i. Where,

\textbf{L}_s: \text{Latent heat of sublimation of ice (2839 J g}^{-1} \text{ at 233 K)}

\textbf{e}_s(T): \text{Equilibrium vapour pressure over ice (12.85 Pa at 233 K)}

\textbf{\rho}_i: \text{Density of ice } (920 Kg m}^{-3} \text{ at 233 K)}

These calculations are presented for 243, 233 and 223 K. Note also that growth calculations can only be performed for supersaturated conditions. Any growth taking place prior to supersaturated conditions such as water uptake by aqueous
particles at RH\textsubscript{w} < 100\% needs to be ascertained by a different approach (see below). The initial radius (r\textsubscript{0}) in all cases is 100 nm. The end result in any case is insensitive to the initial radius up to a factor of 10 -15 times 100 nm. Given that all sampling done with the CFDC occurred for particles sizes below \~ 800 nm, using 100 nm initial radius does not skew the results presented.

In ensure 100 nm sulphuric acid particles did not grow to sizes larger than 0.5 $\mu$m prior to water saturation and/or freezing, calculations were performed using the online Aerosol Inorganic Model (AIM) 1 found at: http://www.aim.env.uea.ac.uk/aim/aim.php [Carslaw et al., 1995; Massucci et al., 1999; Clegg and Brimblecombe, 2005]. Presented below are all relevant conditions and corresponding particle diameters.

\textit{At 223 K}
- For RH\textsubscript{i} = 145\%, RH\textsubscript{w} = 90\%, an ice crystal will grow to a diameter of 5 $\mu$m
- For RH\textsubscript{w} = 110\%, a water droplet will grow to a diameter of 3 $\mu$m
- For RH\textsubscript{w} = 99\%, a 100 nm pure sulphuric acid particle will grow to 410 nm (assuming equilibrium)

\textit{At 233K}
- For RH\textsubscript{i} = 112\%, RH\textsubscript{w} = 76\%, an ice crystal will grow to a diameter of 5$\mu$m
- For RH\textsubscript{w} = 110\%, a water droplet will grow to a diameter of 5 $\mu$m
- For RH\textsubscript{w} = 99\%, a 100 nm pure sulphuric acid particle will grow to 410 nm (assuming equilibrium).

\textit{At 243 K}
- For RH\textsubscript{i} = 104\%, RH\textsubscript{w} = 78\%, an ice crystal will grow to a diameter of 5$\mu$m
- For RH\textsubscript{w} = 104\%, a water droplet will grow to a diameter of 5 $\mu$m
- For RH\textsubscript{w} = 99\%, a 100 nm pure sulphuric acid particle will grow to 410 nm (assuming equilibrium).

For RH\textsubscript{w} = 103\%
- Residence time = 12 s, T = 246 K, a water droplet will grow to 5 $\mu$m
- Residence time = 7 s, T = 253 K, water droplet will grow to 5 $\mu$m
The calculations above give the maximum RH$_w$ at which the CFDC in its current set up can sample so that the large particle channel is counting ice crystals exclusively. In addition the AIM calculations indicate that when a hygroscopic particle is being sampled, its diameter should be restricted to 100 nm or less. This is because water uptake prior to water saturation predicts the particle size to grow to be 410 nm. This is below the 500 nm threshold for the small channel, thus ensuring a low background signal in the small particle channel where particles larger than 0.5 μm are detected. In cases where the size of the aerosol is restricted to below 500 nm with no known water uptake, counts in the smaller particle channel can be regarded as ice crystals.

References


Composition of various dust samples used in this study are presented as clusters of dust samples. The composition of each cluster observed within a given dust type is presented. The analysis was performed using SEM-EDX (scanning electron microscopy energy-dispersive X-ray) spectroscopy and was carried out by Dr. Admir Taragino at The University of Manchester’s Centre for Atmospheric Science in Manchester, UK.

*Composition of Arizona Test Dust*

![Pie chart of Cluster 1](image1)

- **Si**: 40.2%
- **C**: 27.5%
- **K**: 1.3%
- **Fe**: 0.5%

![Pie chart of Cluster 2](image2)

- **Si**: 17.5%
- **C**: 51.8%
- **Al**: 3.8%
- **Mg**: 1.1%
- **Na**: 1.0%
- **K**: 1.4%
- **Ca**: 3.8%
- **O**: 16.5%
- **Fe**: 1.6%
Composition of Arizona Test Dust

Cluster 3
- C: 15.1%
- O: 1.4%
- Cl: 4.9%
- K: 3.4%
- Ca: 3.8%
- Si: 1.2%
- S: 3.4%
- Al: 65.7%

Cluster 4
- C: 89.2%
- Si: 1.8%
- Cl: 0.8%
- Ca: 0.6%
- O: 4.4%
Composition of Saharan Dust

Cluster 1
- C: 14.9%
- O: 8.7%
- Na: 17.8%
- Cl: 37.9%
- S: 1.1%
- Si: 3.9%
- Al: 1.4%
- Ca: 10.0%
- Mg: 0.9%
- Fe: 1.1%
- Cl: 6.1%

Cluster 2
- C: 18.5%
- O: 26.8%
- Na: 0.5%
- Al: 5.8%
- Mg: 2.8%
- Si: 23.4%
- Ca: 12.1%
- K: 1.2%
- Ti: 0.8%
- Fe: 3.0%
- Cl: 2.3%
- S: 1.1%
- S: 23.4%

16.6 %
Composition of Saharan Dust

Cluster 3
- C: 19.6%
- Si: 7.1%
- S: 3.8%
- Ca: 39.2%
- O: 17.4%
- Al: 2.3%
- Cu: 0.8%
- Fe: 2.3%
- Mg: 2.4%
- K: 0.8%
- Cl: 2.1%

Cluster 4
- C: 53.9%
- Si: 1.7%
- Al: 1.3%
- Cl: 1.4%
- Mg: 1.3%
- O: 13.5%
- Fe: 1.2%
- Cu: 0.5%

46.6% and 30.7%
Composition of Israeli Dust

Cluster 1
- C: 31.1%
- O: 19.2%
- Mg: 2.8%
- Al: 3.1%
- Si: 8.2%
- Ca: 28.6%
- Fe: 2.4%
- K: 0.9%

Composition: 10.2%

Cluster 2
- C: 38.1%
- O: 23.4%
- Si: 17.6%
- Al: 7.5%
- Mg: 1.3%
- Fe: 4.5%
- Ti: 1.0%
- Mg: 2.6%
- K: 1.4%

Composition: 16.8%
Composition of Israeli Dust

Cluster 3
- C: 13.1%
- O: 28.1%
- Si: 37.8%
- Al: 8.7%
- Mg: 1.4%
- Fe: 3.2%
- Ca: 2.0%
- K: 2.4%

Cluster 4
- C: 74.4%
- Si: 6.2%
- Al: 2.3%
- Ca: 2.5%
- Fe: 1.1%
- O: 10.9%

220
Composition of Canary Island Dust

Cluster 1

- C: 19.2%
- O: 18.4%
- Si: 9.6%
- Ca: 39.4%
- Al: 3.5%
- Mg: 2.7%
- Fe: 2.1%
- K: 1.5%

Cluster 2

- C: 34.5%
- O: 19.2%
- Si: 8.9%
- Ca: 26.6%
- Al: 3.1%
- Mg: 2.2%
- Fe: 1.7%
- K: 1.2%
Composition of Canary Island Dust

**Cluster 3**
- C: 64.4%
- Ca: 11.1%
- O: 12.4%
- Al: 2.1%
- Mg: 1.1%
- Si: 5.4%
- Fe: 1.0%
- K: 0.7%

**Cluster 4**
- C: 18.2%
- O: 25.2%
- Si: 34.0%
- Al: 5.8%
- Ti: 0.7%
- Mg: 2.0%
- Na: 0.5%
- Fe: 3.4%
- Ca: 6.5%
- K: 1.8%
- Ti: 0.7%