ICE NUCLEATING PROPERTIES OF SOOT, KAOLINITE, & GOETHITE AT CONDITIONS RELEVANT FOR THE LOWER TROPOSPHERE

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Abstract

Although soot and mineral dust are both ubiquitous in the Earth's atmosphere, their contribution to the formation of the ice phase in lower tropospheric clouds remains poorly understood. This thesis investigates the ice nucleating properties of a range of soot and mineral dust species in the deposition mode – below liquid water saturation – and at temperatures ranging from 239 to 258 K. It is found that under these experimental conditions soot exhibits no ice nucleating abilities whereas Kaolinite and Goethite are found to be effective ice nuclei. In experiments involving soot, ice nucleation was only observed at ~ 243 K on a few occasions. However, even at these temperatures the relative humidity with respect to ice (RH$_i$) was close to water saturation when ice nucleation was observed, suggesting water nucleation may have occurred first followed by ice nucleation during the condensation process. The ice nucleating abilities of soot exposed to atmospherically-relevant quantities of ozone were also investigated. Even after an exposure equivalent to 80 ppb O$_3$ at atmospheric pressure for 13.7 days, soot exhibited poor ice nucleating abilities. In the case of Kaolinite and Goethite, ice particles consistently formed below ~ 252 K and at RH$_i$ well below water supersaturation, suggesting deposition nucleation is the dominant mode of ice formation under these experimental conditions.

The ice nucleating abilities of soot and mineral dust were quantified by determining the heterogeneous nucleation rate coefficient, $J_{het}$; heterogeneous nucleation theory was employed to determine the contact angle for formation of an ice germ on the surface of soot, Kaolinite, and Goethite. The experimentally-determined $J_{het}$ was used to estimate the number density of ice particles that might form under given conditions of temperature, RH$_i$, and particle number density for soot and mineral dust in the atmosphere. Whereas soot alone cannot account for the number density of ice nuclei observed in field studies, these measurements show Kaolinite and Goethite may significantly contribute to the formation of the ice phase in lower tropospheric clouds. This is consistent with recent field measurements and some recent laboratory data.
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Chapter 1

Introduction

1.1 Global climate forcing

Scientific evidence strongly suggests that increased anthropogenic activity is influencing the Earth’s atmosphere and climate [IPCC, 2001]. Measurements in the Arctic and Antarctic regions, for example, imply that the Earth’s radiative budget is changing [Cavalieri, 1997]. Traditionally, radiative forcing is used to quantify the change in the Earth’s radiative budget, where radiative forcing is defined as “a change in the net vertical irradiance at the tropopause due to an internal change, or a change in the external forcing of the climate system” [IPCC glossary, 2001]. Figure 1.1 illustrates the best estimate and uncertainty of the radiative forcing for a number of components of the climate system for the period 1750 to 2000. Some forcings, such as that by the greenhouse gases, are well understood; while other components of the climate system, such as the indirect aerosol effect, are very poorly understood.

The indirect aerosol effect is driven by the ability of aerosols to act as cloud condensation nuclei (CCN, Type 1) or ice nuclei (IN, Type 2). By acting as CCN or IN, aerosols may impact microphysics, radiative properties, and the lifetime of clouds. In doing so, aerosols may change the ability of clouds to cool (Albedo Effect) and warm (Greenhouse effect) the atmosphere. Figure 1.1 only illustrates the estimated uncertainty in contribution of the indirect aerosol effect for Type 1 aerosols. The contribution of IN (Type 2) to radiative forcing is not included in the latest IPCC report because the confidence level in the quantitative estimates is very poor. However, the IPCC acknowledges that ice nuclei almost certainly play a critical role in the processes of mixed-phase and ice-phase clouds. Further research is clearly needed to understand the contribution of IN to climate change.

To accurately predict the impact of the indirect aerosol effect, it is important to quantify the ice nucleating properties of atmospheric aerosols. For solid particles in the atmosphere, this can be achieved by determining the heterogeneous nucleation rate coefficient (defined as the number of nucleation events per unit of surface area and per unit of time). By quantifying the ice nucleating properties of aerosols typically observed within the different regions of the atmosphere, the radiative forcing of IN may be better understood.
1.2 The Earth’s atmosphere

The Earth’s atmosphere consists of the troposphere, stratosphere, mesosphere, and thermosphere (Figure 1.2). Each of these regions possesses its own but interrelated chemistry and physics. The boundaries between these layers are referred to as the tropopause, stratopause, and mesopause. This thesis focuses on the ice nucleating abilities of aerosols at conditions relevant to the lower troposphere.
The troposphere extends up to 8 to 18 km in altitude with its altitude dependent on latitude and season [Wayne, 2000]. The troposphere is the densest part of the atmosphere (up to 80% of the total mass of the atmosphere), with temperature decreasing at higher altitudes up to the tropopause. The temperature of the tropopause can be as low as 180 K.

**Figure 1.2** Temperature profile of the Earth’s atmosphere as a function of altitude, z (km) (from Wayne [2000]). The curve represents the mean structure for latitude 40°N during the month of June.
1.3 Atmospheric nucleation processes

Clouds cover approximately 60% of the Earth’s atmosphere with only 10% of the total generating precipitation [Seinfeld and Pandis, 1998]. In the troposphere, they are created through two mechanisms of isobaric and adiabatic cooling [Seinfeld and Pandis, 1998]. Isobaric cooling refers to the cooling of an air parcel under constant pressure. This may involve radiative losses of energy or a horizontal movement of an air mass over a colder surface. Under adiabatic conditions an air parcel rises vertically and cools without releasing heat to the surroundings during its expansion. In the atmosphere, upward air flow may be caused by solar heating of the Earth’s surface, a cold front forcing a warm air mass aloft, or a mountain range at an angle to the wind.

The eventual formation of the liquid or the ice phase is a result of homogeneous or heterogeneous nucleation. Homogeneous ice nucleation occurs in a supersaturated water vapour phase and is defined as the formation of ice from the gas or the liquid phase, in the absence of foreign substances [Seinfeld and Pandis, 1998]. Homogeneous ice nucleation from the vapour phase is unlikely to occur under normal atmospheric conditions because atmospheric supersaturations are never large enough [Young, 1993]. Heterogeneous ice nucleation corresponds to the nucleation of an ice germ on a foreign substance, such as an ion or a solid particle [Seinfeld and Pandis, 1998].

Four modes of heterogeneous ice nucleation exist: deposition nucleation, condensation freezing, contact freezing, and immersion freezing [Pruppacher and Klett 1997; Vali 1985]. The various modes of ice phase formation are illustrated in Figure 1.3. Deposition nucleation occurs when vapour adsorbs onto a solid surface and is transformed into ice below water saturation. Condensation freezing refers to the sequence of events whereby cloud condensation initiates freezing of the condensate. Immersion freezing occurs when ice nucleates on a solid particle immersed in a liquid droplet, and contact freezing occurs when a solid particle collides with a liquid droplet, resulting in ice nucleation [Vali, 1985; Pruppacher and Klett, 1997]. Often condensation freezing and immersion freezing are grouped together due to the similarity in these modes. The theoretical treatments for the mechanisms relevant to this thesis will be discussed in Chapter 2.

At temperatures between 273 and ~235 K ice formation necessarily occurs through one of these heterogeneous mechanisms. This temperature range is most relevant to the lower
However, much disagreement on the dominant heterogeneous mode of formation of ice in the atmosphere exists particularly because very little is known about the ice nucleating properties of insoluble aerosols such as soot and mineral dust.

**Figure 1.3:** Homogeneous and heterogeneous IN modes of activation. Supersaturation with respect to ice is defined as $SS_{\text{ice}}$. 
1.4 Tropospheric aerosols

Aerosols in the Earth’s atmosphere are relatively stable suspensions of liquid or solid particles in the gas phase and range in size from 0.002 to 200 μm in diameter [Finleyson-Pitts and Pitts Jr., 2000]. Four distinct aerosol size classifications are recognized. Particles larger than 2.5 μm in diameter are termed course particles, whereas those smaller than 2.5 μm in diameter are fine particulates. The majority of aerosols found in the troposphere are grouped under the fine mode which can be further subdivided into three categories: accumulation mode (~0.08 – 2.5 μm), transient or Aitken mode (0.01 – 0.08 μm), and ultrafine mode (<0.01 μm).

Aerosols enter the troposphere by means of natural, anthropogenic, direct, and secondary sources. Direct sources include biomass burning (54 Tg/yr), sea spray loading (54 Tg/yr), and fossil fuel combustion (29 Tg/yr) [IPCC, 2001]. Aerosol composition varies strongly with season, location, and altitude. An average composition of urban fine particles, based on measurements at several different sites, is 31% organic carbon, 28% sulfate, 9% elemental carbon, 8% ammonium, 6% nitrate, and 18% other species [Heintzenberg, 1989]. Whereas the homogeneous ice nucleating properties of solution droplets composed of H⁺, NH₄⁺, SO₄²⁻, NO₃⁻ are fairly well understood [Martin, 2000; Koop et al., 2000], further research on the heterogeneous nucleating behaviour of insoluble soot and mineral dust aerosols under tropospheric conditions is still needed.

1.4.1 Soot

Soot is ubiquitous in the atmosphere. In fact, ice core measurements show that soot concentrations have increased from pre-industrialized to modern times [Lavanchy et al., 1999]. Globally, 13 Tg of soot is emitted into the troposphere annually, 54-57% of which is a result of fossil fuel combustion [Cooke and Wilson, 1996]. With an onion-like structure illustrated in Figure 1.4 (a,b), soot results from incomplete combustion processes and consists of an elemental carbon (EC) inner core coated with a layer of a polycyclic aromatic hydrocarbons (PAHs) and aliphatics under an amorphous outer shell of volatile compounds [Wal and Tomasek, 2003; Steiner et al., 1992; Haynes and Wagner, 1981; Finlayson-Pitts and Pitts Jr., 2001].
Figure 1.4: (a) A schematic model of the microstructure of the diesel soot particle [Ishiguro, 1997]. This turbostratic, onion-like structure consists of short graphite segments, also known as crystallites, often grouped together in short stacks which are randomly rotated with respect to each other along the c-axis. (b) HRTEM image of ethanol-derived soot aggregates exhibits the alignment of graphite segments [Wal and Tomasek, 2003].

If soot are effective IN, they have the potential to significantly impact the Earth’s climate indirectly by changing the properties and lifecycle of mixed-phase and ice clouds on a global scale [Demott, 2002; Demott et al., 1997; Gierens, 2003; Jensen and Toon, 1997; Lohmann, 2002; Lohmann and Feichter, 2005]. In the lower troposphere, an increase in soot particles may lead to more frequent glaciation of supercooled clouds. The presence of insoluble soot particles may increase the amount of precipitation by means of the ice phase. This may further reduce the cloud cover in the lower troposphere and result in increased absorption of solar radiation [Lohmann, 2002; Lohmann and Feichter, 2005]. However, this indirect aerosol effect on climate is highly uncertain, in part, because the conditions at which ice nucleates on soot particles in the atmosphere are poorly quantified [Penner et al., 2001].

At present there have only been three studies on the ice nucleating ability of soot particles at temperatures above 238 K [Demott, 1990; Diehl and Mitra, 1998; Gorbunov et al., 2001]. The soot particles investigated in the previous studies were produced from the combustion of acetylene [Demott, 1990], kerosene [Diehl and Mitra, 1998], benzene and toluene [Gorbunov et al., 2001], as well as soot produced by thermal decomposition of benzene [Gorbunov et al., 2001]. These measurements suggest that soot particles are potentially important IN in the atmosphere. However, more work is still needed to understand ice nucleation on soot at temperatures relevant for the lower troposphere. For example, the ice nucleating ability as a
function of relative humidity (RH) needs to be investigated, since the previous studies mainly focused on ice nucleation at or slightly above liquid water saturation. Further complications arise from the fact that soot is exposed to tropospheric oxidants such as hydroxyl and nitrate radicals, and ozone [Möhler et al., 2005a; Lelievre et al., 2004] which may change soot's nucleating abilities. Although previous authors [Gorbunov et al., 2001; Möhler et al., 2005a; Lelievre et al., 2004] speculate that soot's abilities to nucleate ice should improve following exposure to atmospheric oxidant, quantitative research is yet to be presented. In this thesis the ice nucleating properties of soot in the deposition mode and at conditions relevant for the lower troposphere are considered.

### 1.4.2 Mineral dust

Mineral dust is one of the most abundant aerosol species in the troposphere with global source strength estimates ranging from 1000 to 5000 Tg/yr, of which up to 50% may be anthropogenic in origin [IPCC, 2001; Raes, 2000]. 90% of global airborne mineral dust is generated in the northern hemisphere where it is deposited [Usher et al., 2003]. Typical volume median diameters of particles are of the order of 2 to 4 μm [IPCC 2001]. The two primary sources of dust are the deserts of the Mongolia and Saharan regions [Perry et al., 1997; Prospero 1996]. Additional sources include dry lake beds and regions dried as a result of anthropogenic activity [IPCC, 2001].

Multiple studies of the elemental component of windblown dust (originating from various locations around the world) report that mineral dust is approximately 60% SiO₂ and 10-15% Al₂O₃ [Usher et al., 2003]. The percentage of other oxides such as Fe₂O₃, MgO, and CaO, are slightly more varied and dependent on source location [Usher et al., 2003]. Some of the most common minerals found in atmospheric dust are listed in Table 1.1. Typically Saharan dust is dominated with mica-illite (55 to 65%), quartz (14 to 20%), kaolinite, hematite, chlorite, and calcite (all of which have concentrations less than 15% of the total) [Glaccum and Prospero, 1980; Usher et al., 2003]. The presence of Kaolinite in atmospheric dust has been noted in several studies [Goudie and Middleton, 2001; Shi et al., 2005]. Clay samples in Tamanrasset, Sessali, and In Guezzam, Africa, have been found to contain up to 25% Kaolinite dust [Goudie and Middleton, 2001]. Iron oxides have been observed in the atmosphere [Weber et al., 2000;
Chapter 1: Introduction

Table 1.1: A summary of commonly-observed mineral dust found in the troposphere along with their chemical formulas [Usher et al., 2003].

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>Chlorite</td>
<td>A₅₋₆Z₄O₁₀(OH)₈ᵃ</td>
</tr>
<tr>
<td>Corundum</td>
<td>α-Al₂O₃</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO₃)₂</td>
</tr>
<tr>
<td>Feldspars</td>
<td>WZ₄O₅ᵇ</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
</tr>
<tr>
<td>Halite</td>
<td>NaCl</td>
</tr>
<tr>
<td>Hematite</td>
<td>α-Fe₂O₃</td>
</tr>
<tr>
<td>Illite</td>
<td>(K,H₃O)(Al,Mg,Fe)₂(Si,Al)₄O₁₀[(OH)₂,H₂O]</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al₄Si₄O₁₀(OH)₈</td>
</tr>
<tr>
<td>Magnesite</td>
<td>MgCO₃</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>(Na,Ca)₀.₃₃(Al,Mg)₂Si₄O₁₀(OH)₂·nH₂O</td>
</tr>
<tr>
<td>Mica</td>
<td>W(X,Y)₂₋₃Z₄O₁₀(OH,F)₂ᶜ</td>
</tr>
<tr>
<td>Opal</td>
<td>SiO₂nH₂O</td>
</tr>
<tr>
<td>Palygorskite</td>
<td>(Mg,Al)₂Si₄O₁₀(OH)·4H₂O</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
</tr>
</tbody>
</table>

ᵃTypically A = Al, Fe, Li, Mg, Mn, and/or Ba; Z = Al,B, Si, and/or Fe. ᵇTypically W = Na, K, Ca, and/or Ba; Z = Si and/or Al. ᶜTypically W = K or Na; X and Y = Al, Mg, Fe²⁺, Fe³⁺, and Li; Z = Si and Al.

Hoffmann et al., 1996; Penn et al., 2001; Behra and Sigg, 1990. Hematite, α-Fe₂O₃, occurs in association with Goethite, α-FeOOH [Cornell and Schwertmann, 2003]. By mass, Hematite is typically present below 5% in mineral dust; it is often morphologically present as coatings on clay grains [Hung et al., 2003; Penn et al., 2001]. Goethite is the most common iron oxide in soils [Cornell and Schwertmann, 2003].

As is shown in Figure 1.5 (a), a typical atmospheric sample of mineral dust may contain a variety of sizes and morphological characteristics. In addition, during long-range transport the particles may undergo physical and chemical changes which may alter their ice nucleating abilities [Posfai et al 1994; Marin, 2000; Prospero, 1999; Usher et al., 2003]. Figure 1.5 (b) shows an SEM image of a pure Kaolinite sample and Figure 1.5 (c) illustrates Goethite microstructure.

The ice nucleating abilities of mineral dust in the atmosphere remain poorly understood. Previous research suggests that mineral dusts found in the Earth’s atmosphere exhibit strong ice nucleating abilities [Roberts and Hallett, 1968; Bailey and Hallett, 2002; Zuberi et al., 2002;
Hung et al., 2003; Archuleta et al., 2005; Mohler et al., 2005b; Knopf and Koop, submitted]. Consequently, these results suggest that dust is potentially a very important IN and may contribute strongly to the indirect aerosol effect [Lohmann and Feichter, 2005]. Several studies have attempted to quantify the nucleating properties of mineral dust in immersion mode [DeMott, 2002; Hung et al., 2003; Archuleta et al., 2005] and in the deposition mode [Roberts and Hallett, 1968; Bailey and Hallett, 2002; Archuleta et al., 2005]. However, further research is necessary to accurately predict the contribution of mineral dust to the formation of ice at lower tropospheric conditions. This thesis considers the ice nucleating properties of Kaolinite and Goethite in the deposition mode at conditions relevant to the lower troposphere.

Figure 1.5: (a) An electron micrograph showing large variability in mineral dust size and morphology [Falkovich et al., 2001]. (b) An electron micrograph of Kaolinite, shows its highly crystalline structure (http://www.ktgeo.com/tEX.html). (c) A high resolution electron micrograph of Goethite needles [Cornell and Schwertmann, 2003].
1.5 Thesis objectives

The primary goal of this thesis is to investigate the ice nucleating properties of soot, Kaolinite, and Goethite at conditions relevant for the lower troposphere. The thesis focuses on ice nucleating abilities of soot and mineral dust particles in the deposition nucleating mode - below water saturation - and at temperatures ranging from 239 to 258 K. Experiments were done as a function of both temperature and relative humidity. For these studies several different types of soot and black carbon particles with a range of physical and chemical properties were used. The ice nucleating abilities of Kaolinite and Goethite were investigated using similar experimental parameters as the experiments involving soot. Additionally, experiments were carried out to determine if the oxidization of soot particles increases their ability to act as ice nuclei. It has previously been speculated that oxidation of soot by ozone in the atmosphere will increase the ice nucleating ability of soot particles [Gorbunov et al., 2001]. As a test of this hypothesis, Lamp Black 101, a commercial black carbon, was exposed to ozone for extended periods of time, and then tested for its ice nucleating ability in the deposition mode.

1.6 Thesis overview

This thesis is organized into six chapters. Chapter 1 covered background information. This included an overview of the indirect aerosol effect, tropospheric nucleation modes, and the current state of knowledge of the contribution of soot and mineral dust to ice formation. The theoretical treatment of homogeneous and heterogeneous ice nucleation is discussed in Chapter 2. The apparatus and the methods used in this thesis are described in Chapter 3. Special attention is paid to sample preparation, flow cell design, and humidity control. Two separate experimental methods are discussed: ramp RHi experiments, constant RHi experiments. Experimental requirements for oxidation of soot with atmospherically-relevant quantities of ozone are also presented. The results for several different types of soot and black carbon particles with a range of physical and chemical properties (including soot exposed to ozone) are presented in Chapter 4. The ice nucleating ability of soot is quantified by determining the upper limit to the heterogeneous nucleation rate coefficient, \( J_{\text{het}}^{\text{up}} \), which is used to calculate the lower limit to the contact angle for the formation of a single ice germ on the surface of soot. Atmospheric implications of these results are considered by using \( J_{\text{het}}^{\text{up}} \) values to determine the
maximum number density of ice crystals that can be nucleated by soot at conditions relevant to the lower troposphere. By comparing this value against parameterizations of ice nuclei in the atmosphere [Meyers et al., 1992], soot is shown not to be an important IN in the lower troposphere. Results of the RH$_t$ ramp experiments for Kaolinite and Goethite are presented in Chapter 5. The ice nucleating properties of these mineral dust species are also quantified by determining the heterogeneous nucleation rate coefficient, $J_{het}$, which is used to calculate the contact angle of an ice embryo formed from supercooled water vapour. By utilizing the contact angle, the atmospheric implications of these mineral dust results are considered. Both Kaolinite and Goethite are found to exhibit strong ice nucleating properties which implies this type of mineral dust may significantly alter the formation of the ice-phase in lower tropospheric clouds. The thesis closes with Chapter 6 in which comparisons between the ice nucleating properties of soot and mineral dust are drawn.
Chapter 2
Nucleation theory

2.1 Introduction

Ice can form from supercooled water vapour and supercooled water droplets through various modes of \textit{homogeneous} or \textit{heterogeneous} nucleation. In order to place these theoretical concepts in an atmospherically-relevant context, variables relevant to formation of water and ice in the atmosphere are defined first. This includes the definition of the partial pressure of water and ice as well as saturation ratios. The theoretical approaches to homogeneous and heterogeneous ice-forming mechanisms are reviewed in sequence. While homogeneous nucleation is not directly related to the experimental study, the theory introduces concepts relevant to heterogeneous ice nucleation.

Homogeneous nucleation of a single ice crystal from a supercooled liquid droplet is discussed in terms of the Classical Nucleation Theory (CNT). The equations presented here are taken from Young [1993]. CNT is used to determine the activation energy for the formation of a critical-size cluster from the homogeneous nucleation rate coefficient, $J_{\text{hom}}$. These principles are applied to the formation of an ice germ on a foreign and insoluble particle. Through a simple approach, the heterogeneous nucleation rate coefficient, $J_{\text{het}}$, for the formation of a spherical-cap ice embryo on a flat and insoluble surface is determined. The relationship between $J_{\text{het}}$, temperature, saturation, and the contact angle is assessed.
2.2 Saturation

Formation of a liquid droplet or an ice crystal in the atmosphere depends on saturation and temperature. The saturation ratio with respect to liquid water \((S_w)\) and ice \((S_i)\) can be determined from the equilibrium vapour pressure:

\[
S_w = \frac{p_{H_2O}}{p_w(T)} \quad \text{Eq. 2.1}
\]

\[
S_i = \frac{p_{H_2O}}{p_i(T)} \quad \text{Eq. 2.2}
\]

where \(p_{H_2O}\) is the water vapour partial pressure, \(p_w(T)\) is the saturation vapour pressure over pure liquid water, and \(p_i(T)\) is the saturation vapour pressure over ice. A number of empirical formulas have been developed to describe \(p_i(T)\) and \(p_w(T)\) [Murphy and Koop, 2005]. The discrepancy between some of these models is illustrated in Figure 2.1 for \(p_i\). For the purpose of this study, inconsistencies in defining the partial pressure of water and ice between 253 and 239 K are very small and consequently will not alter the conclusions drawn from results presented in this thesis.

For the purpose of this study the partial pressure of ice and water is defined by the following equations:

\[
p_i(T) = \exp\left(28.868 - \frac{6132.9}{T}\right) \quad \text{Eq. 2.3}
\]

and

\[
p_w(T) = p_i(T) \exp\left[-\frac{210368 + 131.438T - \frac{3323730}{T} - 41729.1\ln(T)}{RT}\right] \quad \text{Eq. 2.4}
\]

where the units of pressure and temperature are Pa and Kelvin respectively. \(R\) is the molar gas constant \((8.31447 \text{ J mol}^{-1} \text{ K}^{-1})\). The equation for the partial pressure of ice was obtained by Marti and Mauersberger [1993] and is based on direct measurements. The equation for the partial pressure of liquid water was proposed by Koop et. al. [2000]. Consequently, since \(p(T)_i\) is lower than \(p_w(T)\) for a given temperature (Figure 2.2), \(S_i\) will always be higher than \(S_w\) for a given \(p_{H_2O}(T)\) below the freezing point.
Figure 2.1: Relative humidity with respect to ice ($\text{RH}_{\text{ice}} = S_i \cdot 100\%$) for supercooled liquid water in equilibrium with the surrounding water partial pressure using several different models (from Murphy and Koop [2005]).

Figure 2.2: Equilibrium vapour pressure of water (dashed curve) [Koop et. al., 2000] and ice (solid curve) [Marti and Mauersberger, 1993] as a function of temperature.
2.3 Homogeneous nucleation of ice from supercooled water

In Classical Nucleation Theory the change in Gibbs free energy associated with the formation of a single spherical solid cluster of \( i \) molecules formed in pure water is defined as

\[
\Delta G_i = i(\mu_{\text{solid}} - \mu_{\text{liq}}) + A \sigma_{LI}
\]

Eq. 2.5

where \( \mu_{\text{solid}} \) and \( \mu_{\text{liq}} \) are the chemical potentials of the solid and liquid phase, and \( \sigma_{LI} \) corresponds to the interfacial tension between the liquid water and the ice phase over the surface area, \( A \). The number of molecules, \( i \), within the cluster is defined as

\[
i = \frac{4\pi r_i^3 N_i}{3}
\]

Eq. 2.6

where \( r_i \) is the radius and \( N_i \) is the molecular concentration of a spherical crystalline cluster. The chemical potential term in Eq. 2.5 can be expressed in terms of the saturation ratio:

\[-(\mu_{\text{solid}} - \mu_{\text{liquid}}) = kT \ln S_i\]

Eq. 2.7

where \( k \) is the Boltzmann constant and \( T \) is absolute temperature. Using the above definitions and assuming that \( A = 4\pi r_i^2 \), Eq. 2.5 can be rewritten as

\[
\Delta G_i = -\frac{4\pi r_i^3 N_i}{3} kT \ln S_i + 4\pi r_i^2 \sigma_{LI}
\]

Eq. 2.8

The change in Gibbs free energy of formation consists of two terms. The first term in Eq. 2.8 describes the decrease in Gibbs free energy due to the transfer of molecules from the supercooled liquid to the solid phase (i.e. \( \mu_{\text{solid}} < \mu_{\text{liquid}} \)). The second term corresponds to the amount of work required to create an interface between the two phases.

The change in Gibbs free energy of formation of a solid cluster as a function of its radius and saturation is shown in Figure 2.3. When the conditions are under-saturated (\( S < 1 \)) embryos will never reach a critical size because they are energetically not favoured (both terms in Eq. 2.8 are positive). Since the particles do not reach their critical size they are energetically unstable and the liquid will not freeze. Under supersaturated conditions (\( S_i > 1 \)) embryos with radii smaller than the critical size (\( r^* \)) will also dissociate because they are energetically not favoured. However, if the cluster reaches its critical size, the first term in Eq. 2.8 will be larger than the surface energy term, allowing the cluster to grow continuously. This critical radius is determined by setting the derivative of the activation energy to zero and solving for \( r^* \) to give:

\[
r^* = \frac{2\sigma_{LI}}{N_i kT \ln S_i}
\]

Eq. 2.9
Consequently, the barrier for formation of a stable cluster of radius \( r^* \) is defined by the following parameters:

\[
\Delta G^* = \frac{16\pi \sigma_{ll}^3}{3(N/kT \ln S_i)^2} \quad \text{Eq. 2.10}
\]

\[
i^* = \frac{32\pi \sigma_{ll}^2}{3(N/kT \ln S_i)^2} \quad \text{Eq. 2.11}
\]

where \( \Delta G^* \) is the barrier to formation of a critical germ and \( i^* \) is the critical number of molecules needed to achieve a single ice nucleation event. An increase in the saturation ratio \( (S_2 > S_1) \) reduces \( r^*, \Delta G^*, \) and \( i^* \).

The experimental quantity of interest is the rate at which ice germs appear in the system as a function of the saturation ratio and temperature. This frequency of nucleation, termed the homogeneous nucleation rate coefficient \( (J_{\text{hom}}) \), is measured as the number of ice crystals appearing per unit volume and per unit time:

\[
J_{\text{hom}} = A_{\text{hom}} \exp \left( -\frac{\Delta G_{\text{act}}}{kT} \right) \quad \text{Eq. 2.12}
\]

where \( A_{\text{hom}} \) is the pre-exponential factor approximated to 1·10^{28} \text{ cm}^{-3} \text{ sec}^{-1} [Young, 1993] and \( \Delta G_{\text{act}} = \Delta G^* + \Delta G_{\text{diff}} \). In homogeneous freezing the activation energy for the formation of a critical size embryo in the liquid phase depends on \( \Delta G^* \) and the molar Gibbs free energy of activation for the diffusion of molecules across the liquid-solid boundary, \( \Delta G_{\text{diff}} \).
Figure 2.3: The Gibbs free energy, $\Delta G$, for the formation of an ice cluster as a function of its size, $r$, and the saturation ratio, $S$. The energy of formation of an ice embryo is defined by Eq. 2.8. When $S < 1$, ice nucleation is not favoured. Under supersaturated conditions (i.e. $S > 1$) the ice germ will grow spontaneously only if it reaches its critical size, $r^*_{1}$ (Eq. 2.9), and overcomes the energy barrier, $\Delta G^*_1$ (Eq. 2.10). An increase in the saturation ratio ($S_2 > S_1$) reduces the critical radius, $r^*_{2}$, and the activation energy, $\Delta G^*_2$. 
2.4 Heterogeneous nucleation

When the relative humidity is not high enough or the temperature is not low enough for homogeneous nucleation to occur, ice formation is attributed to the presence of solid insoluble particles which may promote ice formation. However, several requirements must be met before such a solid acts as an IN and can induce ice nucleation [Pruppacher and Klett, 1997].

First, a particulate acting as an IN must be partially-soluble or insoluble. If it is soluble, it will dissolve into the aqueous phase and will not provide a rigid substrate surface needed for ice germ formation. Second, since the ice crystal lattice is held by hydrogen bonds, IN nucleating properties will be enhanced if they contain hydrogen bonds at the particle surface. However, any difference in the geometric arrangement of these bonds between the substrate and the ice phase may lead to elastic strain, $\varepsilon$, within the ice lattice. Elastic strain increases the activation energy of formation of an ice germ. If the misfit between the substrate lattice and the ice lattice is small, the ice lattice will have coherent geometry and nucleate on the substrate surface; however, if the misfit is large, ice will not form on the substrate surface.

Heterogeneous nucleation may be considered either in terms of the stochastic or the singular hypothesis. The stochastic model follows the homogeneous classical point of view where the effects of IN depend on the probability of the random nucleating events. The singular model recognizes individual nucleating characteristics of active sites located on the surface of the IN. Presence of the so-called active sites may allow formation of crystalline germs at characteristic temperatures. Thus, the density of active sites available for ice formation at a specific temperature determines nucleation efficiency. In this work, the stochastic model will be employed to quantify the ice nucleating abilities of soot and mineral dust.

2.4.1 Deposition nucleation – the stochastic model

The stochastic model of deposition nucleation assumes that at a given temperature all equal-sized embryos have an equal probability of reaching their critical size. Consequently, the basic theory for deposition nucleation on a uniform and insoluble surface is an extension of the homogeneous nucleation approach. The equations presented here are taken from Young [1993] and describe heterogeneous nucleation of ice from the vapour phase on a flat insoluble surface.
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More complex treatments involve spherical aerosols which will not be discussed here (see Young [1993] for further discussion).

The expression for the thermodynamic potential of an ice embryo (with the shape of a spherical cap) formed on a flat substrate resembles Eq. 2.8, but accounts for the elastic strain, \( \varepsilon \), in the bulk ice lattice as well as the ice-substrate interface energy,

\[
\Delta G_i = V_i \left( -N_i kT \ln S_i + C \varepsilon^2 \right) + \sigma_{i\nu} A_{i\nu} + (\sigma_{i\nu} - \sigma_{\nu\nu}) A_{i\nu}
\]  

Eq. 2.13

In the above expression \( C \) is the estimated strain coefficient of \( 1.7 \times 10^{11} \) dynes cm\(^{-2} \) at 273.15K [Turnbull and Vonnegut, 1952], \( \varepsilon \) is the elastic strain, \( N_i \) is the molecular concentration of the ice embryo, and \( \sigma_{\nu\nu}, \sigma_{i\nu}, \) and \( \sigma_{i\nu} \) correspond to the vapour-nucleus, ice-nucleus, and ice-vapour interfaces. \( A_{i\nu} \) and \( A_{i\nu} \) correspond to the areas of the ice-vapour and ice-nucleus interfaces, and \( V_i \) is the total volume of the spherical cap ice embryo. These variables are defined geometrically as

\[
A_{i\nu} = 2\pi r_i^2 (1 - \hat{m}) 
\]

Eq. 2.14

\[
A_{i\nu} = \pi r_i^2 (1 - \hat{m}^2) 
\]

Eq. 2.15

\[
V_i = \frac{\pi r_i^3}{3} (2 + \hat{m})(1 - \hat{m})^2 
\]

Eq. 2.16

where

\[
\hat{m} = \cos \theta = \frac{\sigma_{\nu\nu} - \sigma_{i\nu}}{\sigma_{i\nu}} 
\]

Eq. 2.17

Once these geometric terms are substituted into Eq. 2.13, the free energy of formation of a single ice germ over the flat insoluble surface simplifies to

\[
\Delta G_i = f(\hat{m}) \left[ \frac{4}{3} \pi r_i^3 \left( -N_i kT \ln S_i + C \varepsilon^2 \right) + 4\pi r_i^2 \sigma_{i\nu} \right]
\]

Eq. 2.18

where

\[
f(\hat{m}) = \frac{(2 + \hat{m})(1 - \hat{m})^2}{4}
\]

Eq. 2.19

The geometric term introduces the contact angle, \( \theta \), which controls the ice nucleating ability of the aerosol. If \( \theta < 180^\circ \), \( f(\hat{m}) < 1 \) and heterogeneous nucleation may take place. However, if \( \theta = 180^\circ \), homogeneous condensation will commence in the gas phase once a germ of a critical radius, \( r^* \), forms at a sufficiently high supersaturation.
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Assuming heterogeneous nucleation takes place, the critical radius for spontaneous growth of the ice germ formed from vapour phase is consequently defined as

$$r^* = \frac{2\sigma_{iv}}{N_i kT \ln S_i^* - C \varepsilon^2}$$  \hspace{1cm} \text{Eq. 2.20}

The heterogeneous nucleation rate coefficient for the formation of a critical-size ice embryo is

$$J_{hef} = A \exp \left[ -\frac{\Delta G^*_{act}}{kT} \right] = A \exp \left[ \frac{-16\pi \sigma_{iv}^3 f(\hat{m})}{3kT(N_i kT \ln S_i - C \varepsilon^2)^2} \right]$$  \hspace{1cm} \text{Eq. 2.21}

$A$ is often estimated to be equal to $\{10^{26}\}$ cm$^{-2}$ sec$^{-1}$ [Pruppacher and Klett, 1997]. The particulate radius is approximated to a flat surface on which the ice germ forms.

Assuming the ice embryo is independent of lattice strain, the above equation is often written in the following form [Vali, 1999]

$$J_{hef} = A \exp \left[ -B \frac{\sigma_{iv}^3}{T^3} \frac{1}{(\ln S_i)^2} \right]$$  \hspace{1cm} \text{Eq. 2.22}

where

$$B = \frac{-16\pi f(\hat{m})}{3N_i^2 k^3}$$  \hspace{1cm} \text{Eq. 2.23}

The equation above shows that $J_{hef}$ can change rapidly with saturation, temperature, and surface tension. By applying these theoretical equations to experimental observations the contact angle of soot, Kaolinite, and Goethite will be quantified in this thesis.
Chapter 3
Experimental technique

3.1 Introduction

The apparatus used in these studies consisted of an optical microscope coupled to a flow cell in which the relative humidity could be accurately controlled. In the current experiments soot or mineral dust particles were deposited on the bottom surface of the flow cell; the relative humidity with respect to ice (RH$_i$) inside the cell was increased, and the conditions under which water droplets or ice crystals formed were determined with a reflected-light microscope.

3.2 Sample preparation

3.2.1 Soot and clay specifics

3.2.1.1 Soot

The various soots and black carbon used in these studies are listed in Table 3.1. Three different samples of n-hexane soot were provided by Dwight M. Smith (University of Denver). The first sample was produced by burning n-hexane under ambient conditions in an open vessel, resulting in a diffusion flame. The second and third samples were generated using an apparatus designed for producing soot from flames with variable oxygen to fuel ratios. It has been shown that there is a linear relationship between the state of soot surface oxidation and the air to fuel ratio [Chughtai et al., 2002]. The International Steering Committee for Black Carbon Reference Materials has recommended using n-hexane soot as a model for soot in the atmosphere because a large amount of soot characteristics and reactivity data already exists in the scientific literature on this type of soot and because of the option to vary the n-hexane soot properties by varying the combustion conditions (http://www.du.edu/~dwismith/bcsteer.html). Properties of n-hexane soot have been documented by Smith and co-workers [Chughtai et al., 2002; Akhter et al., 1985]. A two-dimensional model of n-hexane soot as formed in a flame is shown in Figure 3.1.
### Table 3.1: Physical characteristics of the soot types investigated in this study. Data was obtained from the manufacturer.  

1. Volatiles were determined by heating a sample in a muffle furnace for 7 minutes at 950°C.  
2. BET (Brunauer, Emmett, and Teller)-Surface area was calculated from the N\textsubscript{2} absorption isotherms recorded at 77 K.

<table>
<thead>
<tr>
<th>Type of Soot</th>
<th>Volatiles (^{1}) (%)</th>
<th>BET Surface Area (^{2}) (m(^2) g(^{-1}))</th>
<th>C%</th>
<th>H%</th>
<th>O%</th>
<th>N%</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-hexane soot - diffusion flame</td>
<td>n/a</td>
<td>89±2</td>
<td>87 to 95</td>
<td>1.6 to 1.2</td>
<td>11 to 6</td>
<td>n/a</td>
</tr>
<tr>
<td>N-hexane soot - Air/Fuel=0.53</td>
<td>n/a</td>
<td>100±2</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>N-hexane soot - Air/Fuel=2.4</td>
<td>n/a</td>
<td>156±11</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Lamp Black 101</td>
<td>1</td>
<td>20</td>
<td>98.5</td>
<td>0.4</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Degussa FW2 (Channel Black)</td>
<td>17</td>
<td>460</td>
<td>88</td>
<td>1.1</td>
<td>9.9</td>
<td>0.7</td>
</tr>
<tr>
<td>Printex 40 (Furnace Black)</td>
<td>0.9</td>
<td>90</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

**Figure 3.1:** Two-dimensional model of n-hexane soot formed in a flame [Akhter et al., 1985].
Lamp Black 101, Degussa FW2 (which is a channel type black), and Printex 40 (which is a furnace type black) are commercially available black carbon. Degussa FW2 is post-treated with NO₂ and has been used in the past in laboratory heterogeneous chemistry studies (see for example [Choi and Leu, 1998; Disselkamp et al., 2000; Tabor et al., 1994]). Lamp Black 101 is essentially non-volatile at 1223 K and has been used in the past for ice nucleation studies [DeMott et al., 1999]. Neither Lamp Black 101 nor Printex 40 were post-treated. Relevant properties of these soot particles and carbon blacks are summarized in Table 3.1.

3.2.1.2 Mineral dust

Two different types of mineral dust were used in our experiments: Kaolinite and Goethite. Kaolinite particles were purchased from Fluka Chemika (purum; natural grade). Listed previously in Table 1.1, Chapter 1, the chemical formula for Kaolinite chemical is $\text{Al}_4\text{Si}_4\text{O}_{10}\text{(OH)}_8$. Goethite, $\alpha$-FeOOH, samples were obtained from Ward Scientific and originated in Minnesota. They were crushed and sieved prior to use.

3.2.1.3 $O_3$-oxidized soot

As mentioned earlier the ice nucleating properties of Lamp Black 101 after controlled exposed to $O_3$ were examined. Lamp Black 101 particles were deposited on a hydrophobic glass cover slide and exposed to $O_3$ within a flow tube in which $[O_3]$ was measured with a downstream chemical ionization mass spectrometer (CIMS). This setup is illustrated in Figure 3.2. The flow tube and CIMS instrument have been described by [Knopf et al., 2005].

In these experiments, the pressure of $N_2$ in the flow tube was 2 – 4 Torr and $O_3$ was generated by photolysis of $O_2$ at 254 nm (ultraviolet source Jelight, model #600). Ozone entered the flow-tube through a movable injector. The following ozone exposures ($\rho_{O_3}t$) were used: $1.6\cdot10^{-3}$, $7.6\cdot10^{-3}$, $13.0\cdot10^{-3}$, $25.1\cdot10^{-3}$, $35.6\cdot10^{-3}$, $94.8\cdot10^{-3}$ atm sec. This is equivalent to exposing the soot to 80 ppb of $O_3$ at atmospheric pressure for 0.2, 1.1, 1.9, 3.6, 5.1, and 13.7 days, respectively. An $O_3$ concentration of 80 ppb at atmospheric pressure corresponds to relatively pollute atmospheric conditions [Finlayson-Pitts and Pitts Jr., 2000].

$O_3$ was detected as $O_3^-$ in the mass spectrometer after its chemical ionization by $\text{SF}_6^-$. $\text{SF}_6^-$ was generated by passing a trace amount of $\text{SF}_6$ in about 1000 STP cm$^3$min$^{-1}$ $N_2$ through a
\[ ^{210}\text{Po} \alpha \text{-source (NRD, model Po-2031). This process can be summarized by the following equations:} \]

\[ \text{N}_2 \xrightarrow{\alpha \text{-particles}} \text{N}_2^+ + e^- \quad \text{Eq. 3.1} \]

\[ \text{SF}_6 + e^- \rightarrow \text{SF}_6^- \quad \text{Eq. 3.2} \]

\[ \text{SF}_6^- + \text{O}_3 \rightarrow \text{SF}_6 + \text{O}_3^- \quad \text{Eq. 3.3} \]

Reaction of ozone with \( \text{SF}_6^- \) is a pseudo-first order reaction in which the amount of \( \text{SF}_6^- \) remaining is defined by

\[ [\text{SF}_6^-]_t = [\text{SF}_6^-]_0 \exp (-kt[\text{O}_3,\text{lab}]) \quad \text{Eq. 3.4} \]

where \( k \) is the reaction rate constant of \( (1.7 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} \) [Catoire et al., 2001], \( t \) is the reaction residence time of 0.004 s, and \( [\text{O}_3,\text{lab}] \) is the quantity of ozone. Reaction residence time was determined from the CIMS chamber volume (8.16 cm\(^3\)) and the total flow rate.
Figure 3.2 Sketch of the flow-tube coupled to the Chemical Ionization Mass Spectrometer (not to scale).
3.2.2 Slide preparation

The bottom surface of the flow cell, which supported the particles, consisted of a glass cover slide treated with dichlorodimethylsilane (DCDMS) to make a hydrophobic layer, which reduced the probability of ice nucleation directly on the surface. Prior to the treatment with DCDMS the glass slide was cleaned with a dry ice cleaning system (Sno Gun-II™, Va-Tran Systems) to remove any coarse impurities from the slide surface. Each slide was immersed in a piranha solution (3:1 mixture by volume of sulphuric acid and hydrogen peroxide) for approximately 5 minutes, rinsed in high purity water (distilled water further purified with a Millipore system Simplicity 185, 18.2 MΩ) and methanol (HPLC grade), and dried with a flow of purified N₂ (Spiwestek, Static Prevention Inc., SF4700 HC). Each glass slide was treated with a dry ice cleaning system and rinsed with high purity water and methanol for a second time. Once it was dried with the N₂-ionized gas, the clean slide was placed in a glass chamber. The treatment with DCDMS involved placing the slides in an airtight chamber with 2-3 droplets of DCDMS solution (Fluka, 5% DCDMS in heptane). The slides were not in direct contact with the droplets, rather the DCDMS would coat the glass slides via vapour deposition. The resulting substrates had a contact angle of ~100°, significantly better than that of a droplet on a clean glass slide (~65°). This is illustrated in Figure 3.3. The images were obtained after a droplet of water was deposited on the substrate surface. The droplet was viewed with an optical microscope from the side.

![Figure 3.3](image)

**Figure 3.3** Image of a droplet positioned on top of a (a) clean glass slide and (b) a silanized glass slide.
3.2.3 Sample preparation

All samples were prepared and the flow cell constructed within a filtered air laminar flow hood. This greatly reduced the possibility of contamination of the samples by ambient atmospheric and laboratory particles. Soot or dust particles were deposited on a hydrophobic glass slide (the bottom surface of the flow cell) using the following technique. The dry soot or dust particulates were placed in a glass vessel immersed in an ultrasonic bath. A flow of N$_2$ (99.999 %) was passed through the glass vessel, and vibrations from the ultrasonic bath caused the dry particles to be suspended in the flow of N$_2$. This flow was then directed at the hydrophobic glass slide, and the soot or dust particles were deposited on the slide by impaction. Soot agglomerates or dust particles deposited on the substrate were always less than 40 μm in diameter (Figure 3.4). The optical resolution limit of the microscope was ~1 μm. A typical sample held between 200 to 800 individual particles, a majority of which were between 1 and 10 μm in diameter. Particle size is characterized in terms of the surface mean diameter and geometric mean diameter throughout the thesis as defined by Reist [1993].

Figure 3.4 Average size distribution of eight different samples of Degussa FW2 (Channel Type Black) deposited on hydrophobic glass slides.
3.3 Flow cell setup

The flow cell was similar in design to the one used previously to measure super-micron organic and mixed organic-inorganic particles [Pant et al., 2004; Parsons et al., 2004a; Parsons et al., 2004b] and is illustrated in Figure 3.5. The flow cell was positioned on a cooling stage. The temperature of the cooling stage and hence the flow cell was regulated with a refrigerating circulator (Thermo Neslab ULT-95). The hydrophobic slide was positioned inside the cell body which was constructed out of aluminium. An insulating spacer, made from polychlorotrifluoroethylene (PCTFE), was placed between the hydrophobic glass slide and the

![Figure 3.5](image)

Figure 3.5 (a) Three-dimensional cut away illustration of the flow cell. (b) Cross-section of the flow cell and location of microscope objective (Al=aluminium, PCTFE = polychlorotrifluoroethylene).
flow cell body. This ensured that the coldest portion of the flow cell was the glass substrate (by ∼10 K), thus preventing unwanted ice nucleation in other parts of the cell. All seals within the cell were made with Viton O-rings.

The upper portion of the cell body and the inlet and outlet were made from stainless steel. A sapphire window (1 mm thick), positioned at the top of the cell body, was used to monitor any changes on the bottom surface of the cell. A reflected-light microscope (Zeiss Axiotech100) equipped with a 10x magnifying lens was coupled to a high-resolution industrial monochrome digital video camera (Sony, XCD-X700) which captured images of the particles deposited on the hydrophobic slide during the course of a typical experiment.

3.4 Humidity control

A flow of humidified gas was introduced to one side of the cell and exited on the other where its frost point was measured with a frost point hygrometer (General Eastern). From the frost point measurements, the water vapour pressure ($p_{H_2O}$) was calculated using the parameterization of Marti and Mauersberger [1993], defined by Eq. 2.3. A flow of humidified gas was generated by passing a flow of He (99.999 %) over a reservoir of ultra-pure water (distilled water was further purified using a millipore system). The desired $p_{H_2O}$ was adjusted by altering the temperature of the water reservoir and diluting the humidified flow with a second flow of dry He. A continuous and constant flow of between 1900 to 2100 cm$^3$ min$^{-1}$ (at 273.15 K and 1 atm) was maintained throughout the course of the experiments. The He gas used in these experiments was first passed through a trap containing molecular sieve (1/16" pellets, Type T4A) at 77 K and then through a 0.02 μm filter (Anodisc 25).

The RH$_i$ within the cell was calculated with the following equation:

$$RH_i = \frac{p_{H_2O}}{p_{ice(T_{cell})}} \cdot 100\% \quad \text{Eq.3.5}$$

where $p_{ice(T_{cell})}$ is the saturation vapour pressure of ice at the temperature of the bottom surface of the flow cell. $p_{ice(T_{cell})}$ was calculated using the parameterization of Marti and Mauersberger [1993], and $p_{H_2O}$ was calculated as discussed above. The relative humidity with respect to ice corresponds to the saturation ratio such that

$$RH_i = S_i \cdot 100\% \quad \text{Eq.3.6}$$
3.4.1 RH$_i$ ramp experiments

In most nucleation experiments, the RH$_i$ was ramped from below 100% to water saturation by decreasing the temperature of the cell at 0.1 K min$^{-1}$, and maintaining a constant $p_{\text{H}_2\text{O}}$ inside the cell. Typical experimental RH$_i$ trajectories are illustrated in Figure 3.6 for four different initial temperatures of 258 K, 253 K, 248 K, and 243 K. For the remainder of the document these experiments will be referred to as RH$_i$ ramp experiments. Images of the soot or clay particles were recorded digitally every 10 seconds or $\sim$0.017 K, while simultaneously recording $p_{\text{H}_2\text{O}}$ and the cell temperature. From these images the RH$_i$ at which water droplets or ice particles first formed was determined (i.e. the onset of water or ice nucleation).

![Figure 3.6](image-url)

**Figure 3.6** Typical experimental trajectories of RH$_i$, where temperature was reduced at a rate of 0.1 K min$^{-1}$, while the water partial pressure was constant. The trajectories were calculated using the saturation vapour pressure of water from Koop et al. [2000] and the saturation vapour pressure of ice from Marti and Mauersberger [1993]. The arrows show the experimental trajectory.
3.4.2 Constant RH<sub>i</sub> experiments

Nucleation experiments with long observation times and at constant RH<sub>i</sub> were carried out in order to constrain, as much as possible, the heterogeneous nucleation rate coefficient of ice on soot in the deposition mode (see Chapter 4.2.4 for a further discussion). For the remainder of the document these experiments will be referred to as *constant RH<sub>i</sub> experiments*. In these experiments n-hexane soot (air/fuel ratio = 2.4) was employed. This is the most oxidized soot and therefore will have the greatest ice nucleating potential. As mentioned above, the International Steering Committee for Black Carbon Reference Materials has recommended using n-hexane soot as a model for soot in the atmosphere. In the *constant RH<sub>i</sub> experiments*, the temperature of the particles was held at ~248 K, while the relative humidity was held at 124 ± 4 % RH<sub>i</sub>, which is just below water saturation. The particles were held at these conditions for an extended period of time (approximately 8 hours) and were monitored to determine if ice nucleated during this long observation time.

3.5 Cell temperature & temperature calibration

A Pt-100 resistance temperature detector (RTD) from Omega was embedded within the aluminium base to measure the temperature of the bottom surface of the cell. The RTD was calibrated against the dew point or ice frost point within the cell, as done previously [Middlebrook et al., 1993; Parsons et al., 2004b]. In order to determine the difference between the measured RTD reading and the temperature of the bottom surface of the cell, the temperature of water droplets or ice particles was varied while images of the particles were simultaneously recorded. From these images the temperature at which the size of the droplets or ice particles did not change was determined. While their size remained constant, the liquid droplets or ice particles were in equilibrium with the water vapour inside the cell, which was precisely known. Hence it was possible to determine the offset temperature between the measured RTD reading and the temperature of the liquid droplets or ice particles formed on the bottom surface of the cell.

As an example, Figure 3.7 illustrates the change in the surface area of liquid droplets as a function of RH<sub>i</sub>, frost point, RTD readings, and the time. First, the temperature of the cell was decreased (A) at a rate of 0.1 K min<sup>-1</sup> until water droplets were formed (B) and grew (C). Then
the cell temperature was slowly ramped up (rate = 0.1 K min$^{-1}$) until the water droplets were observed to shrink (D). Next the cell temperature was slowly decreased again until the water droplets started to grow. From these observations the temperature at which water droplets were in equilibrium with the gas-phase water vapour was determined.

In Figure 3.7 water droplets were observed to nucleate at $\sim$10:41 am, 254.59 ± 0.03 K (RTD), and a frost point of 256.3 ± 0.2 K. During the calibration process, the surface area of the liquid droplets remained constant a total of three times (shaded portions of the plots in Figure 3.7 between $\sim$10:53 to 10:58 am, 11:02 to 11:08 am, and 11:16 to 11:25 am). These regions were assigned by considering the scatter in the data for which the average RTD reading was determined. This approach was compared against a more quantitative technique in which a polynomial function was fitted over the surface area data. The derivative provided RTD values well within uncertainty. This indicates that the visual assignment of the point at which the liquid droplets are in equilibrium with water vapour pressure is valid.

At some point during each of these intervals the temperature of the bottom surface of the cell was equal to the dew point of the vapour, which was determined independently from the hygrometer measurements. Although the hygrometer measurements gave the ice frost point, this reading was converted into a dew point using the saturation vapour pressure of water from Koop et al. [2000] and the saturation vapour pressure of ice from Marti and Mauersberger [1993]. An average RTD offset of 0.29 K was determined from all three time intervals. By applying this offset correction to the RTD reading at the onset of liquid droplet formation, the temperature of the bottom surface of the cell was determined to be 254.3 ± 0.3 K. The uncertainty was determined by incorporating hygrometer error (± 0.2 K) with the spread in the calibration readings (based on the shaded portions of the plot). The relative humidity for the formation of the liquid droplets at water saturation was determined based on the correct temperature reading and the frost point. The uncertainty in onset RH$_i$ was determined by incorporating the hygrometer error and calibration error to give the RH$_i$ of 121.6 ± 4.7% at the onset of liquid droplet formation.

This calibration process over liquid water saturation is illustrated in Figure 3.8 through a sequence of images. Each image ties in with the above calibration description (i.e. image (B), taken at 10:40:49 am, illustrates the initial condensation of water droplets on a substrate coated with Degussa FW2).
The multi-step temperature calibration for experiments in which ice crystals were observed to form is very similar to the above technique. In the event of deposition nucleation of ice, the RTD was calibrated against the ice frost point within the cell rather than against liquid water saturation.
Figure 3.7 This figure illustrates the change in surface area of liquid droplets condensed on a hydrophobic slide in relation to RH$_i$, dew point, RTD, and cell temperature (corrected for offset). As the cell temperature was ramped down (A) at a constant rate of 0.1 K min$^{-1}$, the RH$_i$ over deposited particles increased. Liquid droplets were first condensed when RH$_w$ = 100% (B). They continued to grow in size (C) until RH$_w$ < 100% (D). Once again the cell temperature was decreased at a constant rate and the droplet surface area increased above 100% RH$_w$. 
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Figure 3.8 Images were recorded as the temperature of the cell was ramped down and up at constant $p_{H_2O}$. Labels (A) to (D) correspond to labels in Figure 3.7. The black deposits are Degussa FW2 soot on a hydrophobic surface. Each image is accompanied by experimental time, $T_{cell}$, and the RH$_i$. 
Chapter 4

Ice nucleating properties of soot

4.1 Introduction

Although soot is abundant in the atmosphere [Cooke and Wilson, 1996; IPCC, 2001], its contribution to the formation of ice under lower tropospheric conditions is yet to be quantified and remains uncertain. This section details the results obtained through RH_i ramp experiments for Lamp Black 101, Degussa FW2, Printex 20, and n-hexane soots in the temperature range of 243 to 258 K and the constant RH_i experiment with n-hexane soot. Data collected on nucleating properties of Lamp Black 101 following controlled oxidation with ozone is also presented. The contribution of soot to formation of ice in the lower troposphere is quantified by evaluating the upper limit to the nucleation rate coefficient, \( J_{\text{het}}^{\text{up}} \). The lower limit to the contact angle for formation of a critical-size ice germ on soot is then determined by applying heterogeneous nucleation theory (Chapter 2). \( J_{\text{het}}^{\text{up}} \) and the contact angle are used to determine the maximum number of ice particles that can nucleate on soot particles in the atmosphere at 248 K in the deposition mode. This value is compared against field data in order to determine whether the ice nucleating contribution of soot can account for the presence of the ice phase at lower tropospheric conditions.

4.2 Results

4.2.1 RH_i ramp experiments

In a typical experiment, \( p_{\text{H}_2\text{O}} \) was held constant while the temperature of the cell was reduced in order to increase the RH_i within the flow cell. The temperature was decreased until either water droplets or ice particles were observed. The RH_i at which either water droplets or ice particles were observed is illustrated in Figure 4.1 for the blank hydrophobic glass slide as well as the different soot samples. The dashed lines in the figure represent water saturation (i.e. relative humidity with respect to water is 100%). The open symbols indicate that water droplets
Figure 4.1  The RH$_i$ at which liquid water droplets or ice particles were first observed as the RH$_i$ inside the cell was slowly increased. The open symbols indicate that water droplets were first observed (sometimes ice was observed to form after water droplets condensed) and the solid symbols indicate that only ice particles were observed with no indication of the formation of water droplets prior to ice formation. Panel (A) illustrates the results from a control experiment, where no particles were deposited on the hydrophobic substrate. Panel (B) to (F) illustrates the results from the six soot types listed in Table 3.1.
were first observed and the solid symbols indicate that only ice particles were observed with no indication of the formation of water droplets prior to ice formation. From this information conclusions are made on the ice nucleating properties of various soots in the deposition mode below water saturation (see below).

In the experiments where water droplets were first observed (open symbols), ice nucleation would occasionally occur at a later time, presumably by immersion freezing. This occurred with both the blank as well as with soot particles. However, it is not possible to determine if the formation of ice after the formation of liquid droplets was due to the soot particles or the substrate. Hence this information is not included. The current experimental configuration is not well suited for investigations of immersion freezing. The results in Figure 4.1 show that at 248 K and above, water droplets, rather than ice, always appeared first in our experiments. This occurred at water saturation, as expected. From this observation it may be concluded that ice nucleation never occurred at temperatures above 248 K and below water saturation for the current experimental conditions (observation time and soot particle concentrations).

If ice nucleation did occur, ice particles would rapidly grow and prevent the formation of water droplets or new ice crystals at water saturation by depleting the water vapour. At ~ 243 K, occasionally only ice particles formed with no indication of the formation of water droplets prior to ice formation (a total of three times). However, in the few experiments where ice did form, the RH_i was close to water saturation when ice nucleation was observed, suggesting water nucleation may have occurred first, followed by ice nucleation during the condensation process. In other words, for the few experiments where ice did form condensation freezing cannot be ruled out. In fact, at temperatures between 243 and 258 K all the results (including when ice nucleated first) clustered around water saturation, suggesting water saturation is a prerequisite for both water and ice nucleation.

4.2.2 Ice nucleation of soot particles oxidized by O_3

Lamp Black 101 was exposed to various amounts of ozone and then RH_i ramp experiments were performed to test the ice nucleating properties of these soots. The results are shown in Figure 4.2. The open symbols indicate that water droplets were observed first in all experiments. The results for Lamp Black 101 exposed to ozone are the same as the results from
unexposed Lamp Black 101. In all cases, water droplets were first observed, indicating that ice did not nucleate below water saturation. Even after an $O_3$ exposure of $9.5 \times 10^2$ atm sec, which is equivalent to an exposure of 80 ppb at atmospheric pressure (polluted conditions) for 13.7 days, the results were not different from results of unexposed Lamp Black 101. Either $O_3$ did not oxidize Lamp Black 101 significantly or the oxidation process did not change the ice nucleating ability significantly. Further research is needed to determine the extent of oxidation of Lamp Black 101 by $O_3$. Also more research is needed to determine if exposure to atmospherically relevant concentrations of ozone, as well as other atmospheric oxidants such as OH and $NO_3$ radicals, can modify the IN properties of other types of soot in the deposition mode as well as other modes of ice nucleation. These initial experiments show that exposure to atmospherically-relevant concentrations of ozone did not modify the ice nucleating ability of Lamp Black 101 in the deposition mode below water saturation.

Figure 4.2 The RH$_i$ at which water droplets were observed for Lamp Black 101 soot samples treated with a range of $O_3$ exposures. In all experiments water droplets were observed first (i.e. ice particles did not form unless water droplets first condensed). The exposure times indicated in the plot are equivalent to an atmospheric mixing ration of 80 ppb (see text for details).
4.2.3 $J_{\text{het}}^{up}$ for RH$_i$ ramp experiments

For the experiments where water droplets first formed, an upper limit to the deposition nucleation rate coefficient of ice on soot particles was estimated. This rate coefficient provides a quantitative measure of the ice nucleating ability, which may be used in modeling studies of ice formation in the atmosphere. Based on Poisson statistics, if ice nucleation did not occur during the course of an experiment, an upper limit to the heterogeneous nucleation rate coefficient, $J_{\text{het}}^{up}$, can be calculated with the following equation [Biermann et al., 1996; Koop et al., 1995; Koop et al., 1997]:

$$J_{\text{het}}^{up} = \frac{1}{\tau A_s} \ln \left[ \frac{1}{x} \right]$$

Eq. 4.1

where $\tau$ is the observation time, $A_s$ is the total surface area available for heterogeneous nucleation, and $x$ is the confidence level (95% was used). During RH$_i$ ramp experiments $\tau$ was approximately 60 seconds (the cell temperature changed by 0.1 every 60 seconds) and $A_s$ ranged from $1 \times 10^5$ to $4 \times 10^5$ $\mu$m$^2$. $A_s$ was calculated by assuming a spherical geometry with surface area equal to $4\pi r_0^2$, where $r_0$ is the radius of the soot particles. This is a conservative estimate as the surface area exposed to the gas phase is in most cases larger than the geometric surface area. For instance, in the case of n-hexane (air/fuel = 2.4) the BET surface area was found to be 156 ± 11 m$^2$·g$^{-1}$, which corresponds to a scaling factor of 490% larger than the geometric surface area (assuming the particle was 10 $\mu$m in diameter and had a density of 1.86 g·cm$^{-3}$). However, this area measurement may not be equal to that available for ice nucleation and is not applied to the calculation of $J_{\text{het}}^{up}$. Based on a conservative surface area of $1 \times 10^5$ $\mu$m$^2$, $J_{\text{het}}^{up}$ was calculated to be 50 cm$^{-2}$·sec$^{-1}$. In the subsequent section the upper limit of ice nucleation will be further constrained in the constant RH$_i$ experiments.

4.2.4 Constant RH$_i$ experiments

During the constant RH$_i$ experiment, n-hexane soot particulates (air/fuel = 2.4) were held at ~247.5 K and close to liquid water saturation for approximately 8 hours. The surface distribution of soot particles is shown in Figure 4.3. The surface mean diameter of particles in this sample was 19 $\mu$m, whereas the geometric mean diameter was 7.1 $\mu$m. The experimental
conditions are plotted in Figure 4.4. The plot illustrates relative humidity fluctuations as a function of the cell temperature and the frost point drift during the eight-hour period. During this experiment soot particles were held at $124 \pm 4\% RH_i$, 1 to 8% below liquid water saturation.

Figure 4.3  (a) N-hexane (air/fuel = 2.4) soot particles on a hydrophobic slide. The surface area of the soot particles is $1.1 \times 10^5 \mu m^2$. (b) Sample size distribution during the constant $RH_i$ experiment. The geometric mean diameter is 7.1 $\mu m$, with standard deviation of 1.2 $\mu m$. 
Figure 4.4 Change in relative humidity with respect to ice (black) during the constant RH$_i$ experiment. The liquid water saturation in terms of RH$_i$ is also plotted (pink); it shows that water saturation was never reached. The drift in the frost point (green) and the cell temperature (blue) is also illustrated. For a period of approximately 8 hours cell temperature was held at 247.5 K and RH$_i = 124 \pm 4\%$, close to water saturation. Water droplets or ice crystals were not observed to form.
In this experiment the surface area of soot exposed to the vapour was $1.1 \times 10^5 \mu m^2$. Even during this long observation time at humidities close to water saturation, no ice was observed. From this an upper limit to the heterogeneous nucleation rate coefficient was calculated using Eq. 4.1. In this case the upper limit to $J_{\text{het}}^{\text{up}}$ was determined to be $0.1 \text{ cm}^{-2} \text{ sec}^{-1}$. The upper limit is much smaller than the upper limit calculated from the RH$_i$ ramp experiments, of $50 \text{ cm}^{-2} \text{ sec}^{-1}$, since the observation time was much longer (8 hours compared with 1 minute). This estimate provides a better constraint on the rate coefficient of ice nucleation on n-hexane soot in the deposition mode.

4.3 Comparison with other results

There have been several measurements of the ice nucleation ability of soot at temperatures above 238 K. In addition there have been a few studies at lower temperatures. DeMott et al. [1999] investigated ice nucleation on Lamp Black 101 at temperatures ranging from 233 K to 213 K using a continuous flow diffusion chamber. In Figure 4.5, these results are compared with the current data. At approximately 230 K, DeMott et al. [1999] observed ice nucleation only at water saturation. Hence, at warmer temperatures it is highly unlikely that they would observe ice nucleation below water saturation, which is consistent with findings presented in this thesis.

Mohler et al. [2005a] investigated ice nucleation on spark generated soot at temperatures less than 240 K using a low-temperature aerosol and cloud chamber (Aerosol Interactions and Dynamics in the Atmosphere, AIDA). At temperatures between 235 K and 240 K, ice nucleation only occurred on uncoated soot particles after approaching water saturation. The authors commented that ice seems to form immediately in this temperature range after liquid activation of the soot particles either by condensation freezing or homogeneous freezing of the growing liquid water layer. This finding is consistent with the current studies. More recently, Mohler et al. [2005b] used the AIDA chamber to investigate ice nucleation at low temperatures on soot produced from combustion of propane with various elemental carbon to organic carbon ratios. If these results are extrapolated to warmer temperatures they are also consistent with findings presented in this thesis.
Figure 4.5 A comparison of current results for Lamp Black 101 (open squares) with those of DeMott et al. [1999] (filled triangles). Our data points correspond to the conditions at which water droplets were observed using soot particles ranging in size from 1 to 40 um in diameter. In these experiments water droplets were always observed first. If ice did form it was only after the appearance of water droplets. The results from DeMott et al. correspond to the onset for which 1% of Lamp Black soot particles (a number mean diameter of 240 nm) nucleated ice.

DeMott [1990] investigated ice nucleation on soot produced by combustion of acetylene at temperatures between 233 K and 253 K using an expansion cloud chamber. Due to the experimental design and experimental conditions, mainly condensation and immersion freezing were investigated. DeMott [1990] commented that there was some evidence of ice formation by deposition, but ice certainly did not precede cloud droplet formation significantly. One of the conclusions from this study was that immersion freezing nucleation is an efficient ice nucleation process after water has condensed on soot particles.
Diehl and Mitra [1998] investigated ice nucleation on soot produced by the combustion of kerosene. Combined deposition and condensation freezing (deposition/condensation freezing) were studied in a single experiment using a soap film method. Ice nucleation occurred in these experiments at temperatures as high as 253 K. In these experiments, the relative humidity was not measured, so a direct comparison with present results is difficult. All the deposition/condensation experiments may have been carried out slightly above water saturation and condensation freezing may have dominated. The authors also studied immersion freezing and contact freezing, and they found that kerosene-burner exhaust particles are effective ice nuclei in these freezing modes.

Finally, Gorbunov et al. [2001] investigated soot produced by the combustion of benzene and toluene, as well as soot produced by thermal decomposition of benzene using a cloud chamber at temperatures ranging from 253 to 268 K. All experiments were carried out close to liquid water saturation: saturation with respect to liquid water was equal to $1.02 \pm 0.02$. It was found that the fraction of aerosol particles forming ice crystals was influenced by the concentration of surface chemical groups that can form hydrogen bonds with water molecules. A large difference in the ice-forming activity (3 orders of magnitude in the fraction of soot particles forming ice crystals) was observed for soot aerosols obtained with different generators. Soot particles produced by combustion of benzene and toluene were very potent ice nuclei, whereas soot particles produced by thermal decomposition of benzene were poor ice nuclei. They concluded that highly oxidized soot particles are extremely efficient ice nuclei. The difference between the present results and the results from Gorbunov et al. [2001] may be due to a difference in experimental conditions: current research focuses on ice nucleation below water saturation whereas the work presented by Gorbunov et al. [2001] was carried out at or slightly above water saturation. Alternatively, the soot particles studied by Gorbunov et al. [2001] were more effective IN than the soot investigated in this study.

Combining all the previous results and those presented in this thesis, it appears at temperatures above 243 K and below water saturation, ice nucleation on many types of soot particles is not efficient [DeMott, 1990; DeMott et al., 1999; Mohler et al., 2005a; Mohler et al., 2005b]. In contrast, once the RH is above liquid water saturation, water can condense on soot particles, and then most types of soot may be important ice nuclei in the condensation or immersion mode [DeMott, 1990; DeMott et al., 1999; Diehl and Mitra, 1998; Gorbunov et al., 2001; Mohler et al., 2005a; Mohler et al., 2005b].
4.4 Contact angle

Although other authors have utilized experimental data to determine the contact angle of an ice embryo in the immersion mode on various insoluble IN [Hung et al., 2000; Archuleta et al., 2005], values pertaining specifically to the formation of ice on soot particles in the deposition mode are yet to be published. The contact angle, $\theta$, is thought to be independent of RH, hence $\theta$ obtained from different insoluble species, that nucleate ice at different RH, may be compared. Here, heterogeneous nucleation theory (Chapter 2) is employed to determine the lower limit to the contact angle of the ice germ formed on soot under conditions defined by the constant and ramp RH experiments.

The experimentally-determined $J_{het}^{up}$ is used to constrain the contact angle of the critical-size ice embryo formed on the surface of soot. The lower limit to the contact angle is determined by first finding the limiting value to the activation energy, defined as

$$\Delta G_{act}^{*} = -kT \ln \left( \frac{J_{het}^{up}}{A} \right)$$

Eq. 4.2

where cell temperature, $T$, is 247.5K, $J_{het}^{up}$ is 0.1 cm$^2$sec$^{-1}$, and $A$ is the pre-exponential term ($10^{26}$) cm$^2$sec$^{-1}$ [Young, 1993]. These conditions correspond to the constant RH experiment (at which $S_i = 1.24$). Based on these definitions $\Delta G_{act}^{*}$ for formation of a single ice embryo is $2.1 \cdot 10^{-19}$ J. If a single critical-size spherical-cap ice germ forms on an insoluble soot surface, independent of lattice strain (i.e. $\epsilon = 0$), the size of the germ is calculated with Eq. 2.20. The lower limit radius of critical size is 9.4 nm.

The lower limit to the contact angle may be calculated by re-evaluating Eq. 2.22 for the geometric term, $f(\tilde{m})$, such that

$$f(\tilde{m}) = \frac{3}{16} \frac{[kTN_i \ln S_i]^2}{\pi \sigma_{iv}^3} \cdot \Delta G_{act}^{*}$$

Eq. 4.3

In the above equation $N_i$ is the molecular concentration of water molecules within the ice germ and equals to $3.1 \cdot 10^{28}$ molecules m$^{-3}$. This value is calculated based on ice density of 0.92 g cm$^{-3}$ and is a reasonable estimate, as the density of hexagonal ice varies only slightly with temperature [CRC, 2001-2002]. In order to estimate the lower limit to the contact angle, the interfacial tension between the ice and vapour phase of water was assumed to be 106.5 mJ m$^{-2}$ [Kay et al., 2000; Pruppacher and Klett, 1997]. It is of importance to note that $\sigma_{iv}$ is yet to be determined.
exponentially. For this reason, $\sigma_{iv}$ should be considered highly uncertain [Kay et al., 2000]. If the ice germ forms on a flat insoluble soot surface, the geometric term, $f(\hat{m})$, is defined by the following parameterization

$$f(\hat{m}) = \frac{\hat{m}^3 - 3\hat{m} + 2}{4}$$

Eq. 4.4

where $\hat{m} = \cos \theta$. With these assumptions, the lower limit to the contact angle for the formation of an ice germ on the flat soot surface is 24°. The inclusion of the lattice misfit parameter in the above calculation is expected to alter the contact angle. However, large variability in soot morphology makes the misfit parameter difficult to estimate – hence, it is neglected here.

This approach was also applied to several ramp $RH_i$ experiments for which the total soot surface area was determined. Table 4.1 summarizes parameters involved in the calculation of the lower limit to the contact angle (i.e. onset temperature, onset $RH_i$, and limiting values of $J_{het}$, $\Delta G^*_{act}$, and $r^*$). The calculated lower limit of the contact angle is plotted against temperature in Figure 4.6. The data reflects the dependence of the contact angle on the liquid saturation ratio. As the onset temperature decreases, the lower limit to the contact angle for formation of the ice embryo increases with liquid water saturation.
### Table 4.1

Onset parameters pertaining to formation of a single ice crystal in multiple ramp RH experiments for which $J_{het}^{up}$ was determined. The confidence level for $J_{het}^{up}$ is 95%. The limiting values of $\Delta G_{act}^*$, $r^*$, and the contact angle are also included. $\Delta G_{act}^*$ was evaluated under the assumption that the pre-exponential term, $A$, equals to $10^{26}$ cm$^2$ sec$^{-1}$. The size of the critical-size ice germ was evaluated based on Eq. 2.20 pertaining to the maximum Gibbs free energy of formation. Finally, a lower limit to the contact angle was determined using Eq. 4.4.

<table>
<thead>
<tr>
<th>Soot type</th>
<th>Onset Temperature (K)</th>
<th>Onset RH$_i$ (%)</th>
<th>$J_{het}^{up}$ (cm$^2$ sec$^{-1}$)</th>
<th>$\Delta G_{act}^*$ (J·10$^{-19}$)</th>
<th>$r^*$ (nm)</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Printex 40</strong></td>
<td>258.5±0.2</td>
<td>113±3</td>
<td>53</td>
<td>1.99</td>
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<td>18</td>
</tr>
<tr>
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<td>252.9±0.2</td>
<td>123±4</td>
<td>23</td>
<td>1.98</td>
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<td>23</td>
</tr>
<tr>
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<td>248.4±0.2</td>
<td>127±4</td>
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<td>1.95</td>
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<td>25</td>
</tr>
<tr>
<td></td>
<td>242.2±0.2</td>
<td>138±4</td>
<td>131</td>
<td>1.84</td>
<td>6</td>
<td>28</td>
</tr>
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<td>13</td>
<td>20</td>
</tr>
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<td>249.0±0.2</td>
<td>124±3</td>
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<td>1.92</td>
<td>10</td>
<td>23</td>
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<td>1.89</td>
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<tr>
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<td>1.90</td>
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<td>25</td>
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<tr>
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<td>1.43</td>
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<td>2.04</td>
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<tr>
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<td><strong>n-hexane (6,X)</strong></td>
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<td>119±3</td>
<td>13</td>
<td>2.04</td>
<td>11</td>
<td>22</td>
</tr>
<tr>
<td></td>
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<td>123±3</td>
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<td>2.00</td>
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<tr>
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<tr>
<td><strong>n-hexane (11,X)</strong></td>
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<td>119±3</td>
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<td>2.01</td>
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<tr>
<td></td>
<td>250.5±0.2</td>
<td>125±3</td>
<td>18</td>
<td>1.97</td>
<td>9</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>248.5±0.3</td>
<td>127±5</td>
<td>18</td>
<td>1.95</td>
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<td>25</td>
</tr>
<tr>
<td></td>
<td>243.8±0.2</td>
<td>132±3</td>
<td>140</td>
<td>1.85</td>
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<tr>
<td><strong>Degussa FW2</strong></td>
<td>257.6±0.2</td>
<td>114±3</td>
<td>100</td>
<td>1.97</td>
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<td></td>
<td>253.5±0.3</td>
<td>122±6</td>
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<td>1.98</td>
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<tr>
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<td>133±3</td>
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<td>1.91</td>
<td>7</td>
<td>27</td>
</tr>
</tbody>
</table>
Figure 4.6 Lower limit to the contact angle vs. temperature. Here a critical-size, spherical-cap ice germ was assumed to form on an insoluble soot surface approximated to be flat. The contact angle was determined for $N_i = 3.1 \times 10^{28} \text{ m}^{-3}$ and $\sigma_v = 106.5 \text{ mJ m}^{-2}$ using Eq. 4.3 and Eq. 4.4. Plotted data corresponds to the constant and ramp RH$_i$ experiments for which the soot surface area was known. Since the contact angle is a limiting value, it depends on liquid water saturation, and increases at lower temperatures.

4.5 Atmospheric implications

The maximum number of ice particles that can be produced in the atmosphere at 247.5 K and at RH$_i = 124\%$ can be estimated from the nucleation rate coefficient, $J_{\text{nuc}}^{\text{wet}}$. The purpose is to place the magnitude of $J_{\text{nuc}}^{\text{wet}}$ determined experimentally into an atmospherically-relevant context. Since soot quantities vary with season, source proximity, and altitude, the maximum possible
number of ice particles depends on carbon mass concentrations dictated by specific environmental conditions. The subsequent treatment focuses on conditions resembling a typical US urban-influenced rural area [Seinfeld and Pandis, 1998].

The following equation can be used to estimate the maximum number of ice particles that can be produced during a specified time period [Pruppacher and Klett, 1997],

\[
n_{\text{ice}} = n_{\text{soot}} \left[ 1 - \exp\left(-J_{\text{ice}} A_p \tau\right)\right]
\]

Eq. 4.5

where \(n_{\text{ice}}\) is the number density of ice particles produced (litre\(^{-1}\)), \(n_{\text{soot}}\) is the number density of soot (litre\(^{-1}\)), \(A_p\) is the surface area of a single soot particle (cm\(^2\)), and \(\tau\) is the total time (seconds). For ice nucleation in the atmosphere it was assumed \(\tau\) was approximately 60 minutes, \(n_{\text{soot}}\) was \(1.5 \times 10^5\) litre\(^{-1}\), and \(A_p\) was \(1.3 \times 10^{-9}\) cm\(^2\). A value of \(1.5 \times 10^5\) litre\(^{-1}\) for \(n_{\text{soot}}\) was calculated by assuming a soot radius of 0.1 \(\mu\)m, a soot density of 2 g cm\(^{-3}\), a geometric surface area for soot, and an elemental carbon mass concentration in the atmosphere of approximately \(1.3 \times 10^{-6}\) g m\(^{-3}\) (which corresponds to urban-influenced-rural areas [Seinfeld and Pandis, 1998; Shah et al., 1986]). A value of \(1.3 \times 10^{-9}\) cm\(^2\) for \(A_p\) was calculated based on a geometric surface area and a soot radius of 0.1 \(\mu\)m. Soot radius was obtained from Blake and Kato [1995]. This is in excellent agreement with more recent work [Berner et al., 1996; Longfellow and Ravishankara, 2000]. With these assumptions, a maximum number density of ice of 0.07 litre\(^{-1}\) was obtained from Equation 4.5. This approach can be applied to different carbon mass concentrations. Illustrated in Table 4.2, the scenarios include conditions characteristic of the upper troposphere, free troposphere, US remote areas, and polluted urban areas.

Based on field observations, Meyers et al. [1992] developed an empirical relationship between the number concentration of ice nuclei and ice supersaturation

\[
N_{\text{id}} = \exp\{a + b[100(S_t - 1)]\}
\]

Eq. 4.6

where \(N_{\text{id}}\) (litre\(^{-1}\)) is the number of ice crystals predicted as a result of deposition nucleation or condensation freezing, \(a = -0.639\), and \(b = 0.1296\). This parameterization predicts that at 124 % RH\(_t\), the number of ice nuclei in the atmosphere is \(\sim 12\) litre\(^{-1}\). Ice nucleation on soot particles below water saturation (with properties similar to the soot studied in our experiments and \(n_{\text{soot}} = 1.5 \times 10^5\) litre\(^{-1}\)) cannot account for this number density at 124 % RH\(_t\) and 247.5 K. This suggests atmospheric aerosols other than soot contribute to the number density of ice crystals observed in the field.
Table 4.2  A summary of the number density of predicted ice particles per litre nucleated by soot particles for five locations: upper troposphere, free troposphere, USA remote area, USA urban-influenced rural area, and USA polluted urban area. Elemental carbon mass concentrations vary with location and latitude. Soot radius was assumed to be 0.1 \( \mu m \) \cite{Blake and Kato, 1995}. The experimentally-determined upper limit to the heterogeneous ice nucleation rate coefficient was 0.1 cm\(^2\) sec\(^{-1}\) at 124\% RH, and 247.5 K. The maximum amount of ice particles that can be produced for each scenario increases with soot density. Under these conditions Meyers et al. \cite{1992} predicts that at 124\% RH, the number of ice particles in the atmosphere is approximately 12 litre\(^{-1}\).

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Elemental carbon mass concentration (g m(^{-3}))</th>
<th>Number density of soot per litre (litre(^{-1}))</th>
<th>Upper limit to the number density of ice per litre (litre(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Troposphere</td>
<td>1.8x10(^{-9})_a</td>
<td>215</td>
<td>8.9x10(^{-5})_</td>
<td>(^a)Blake and Kato [1995]</td>
</tr>
<tr>
<td>Free Troposphere</td>
<td>25x10(^{-9})_b</td>
<td>2.9x10(^3)</td>
<td>1.2x10(^{-3})_</td>
<td>(^b)Hauglustaine [1996]</td>
</tr>
<tr>
<td>USA remote area</td>
<td>0.5x10(^{-6})_c</td>
<td>5.97x10(^4)</td>
<td>0.025</td>
<td>(^c)Seinfeld and Pandis [1998]</td>
</tr>
<tr>
<td>USA urban-influenced rural area</td>
<td>1.3x10(^{-6})_d</td>
<td>1.55x10(^5)</td>
<td>0.065</td>
<td>(^d)Seinfeld and Pandis, [1998]; Shah [1986]</td>
</tr>
<tr>
<td>USA polluted urban area</td>
<td>3.8x10(^{-6})_e</td>
<td>4.54x10(^5)</td>
<td>0.19</td>
<td>(^e) Seinfeld and Pandis [1998]</td>
</tr>
</tbody>
</table>
4.6 Conclusions

The results presented in this section demonstrate that the soot types investigated here are poor deposition-mode ice nuclei between 243 to 258 K, below water saturation. In the present study soot particles were exposed to conditions resembling those of the lower troposphere. At 248 K and above, water droplets always nucleated first. Consequently, it was concluded that at these temperatures ice nucleation does not occur below water saturation for the defined experimental conditions. At ~ 243 K, ice formed first occasionally with no indication of the formation of water droplets prior to ice nucleation. However, even at these temperatures the RH$_i$ was close to water saturation when ice nucleation was observed.

The results of ice nucleation on Lamp Black 101 exposed to ozone were similar to the results from unexposed Lamp Black 101. Even after an O$_3$ exposure of $9.5 \cdot 10^2$ atm sec, which is equivalent to an exposure of 80 ppb at atmospheric pressure for 13.7 days, the results were not significantly different from results of unexposed Lamp Black 101.

An experiment was carried out at a constant RH$_i$ and over a long observation time (8 hours) on n-hexane soot (air/fuel = 2.4). Even after a long observation time at 248 K and close to water saturation (RH$_i$ = 124 ± 4%), no ice was observed. From this measurement an upper limit to the heterogeneous nucleation rate coefficient of 0.1 cm$^2$ sec$^{-1}$ was calculated.

Combining all the previous results and the current data, it appears that below water saturation at temperatures above 243 K, ice nucleation on many types of soot particles is not efficient [DeMott, 1990; DeMott et al., 1999; Mohler et al., 2005a; Mohler et al., 2005b]. In contrast, once the RH$_i$ is above liquid water saturation, water can condense on soot particles, and then most types of soot may be important ice nuclei in the condensation or immersion mode [DeMott, 1990; DeMott et al., 1999; Diehl and Mitra, 1998; Gorbunov et al., 2001; Mohler et al., 2005a; Mohler et al., 2005b].

In order to further quantify the ice nucleating abilities, heterogeneous nucleation theory was employed to determine the contact angle of an ice germ formed under conditions defined by constant and ramp RH$_i$ experiments. In the constant RH$_i$ experiment, the upper limit to heterogeneous nucleation rate was employed to determine the lower limit to the contact angle of 24°. The lower limit to the contact angle for RH$_i$ ramp experiments was also determined. Since the $J^\infty_{het}$ is limited to liquid water saturation, the contact angle increased at lower temperatures.
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The consequences of the ice nucleating abilities of soot in the lower troposphere were considered. Based on results obtained from the constant RH, experiment, $J_{\text{het}}^i$ was used to determine the upper limit number density of ice particles under typical atmospheric conditions. For conditions resembling the USA urban-influenced rural areas, the number of ice particles produced by the characteristic number density of soot of $1.5 \cdot 10^5$ litre$^{-1}$ was at most 0.07 particles litre$^{-1}$. This result corresponds to the number of ice particles formed as a result of deposition nucleation below liquid water saturation. The value was found to be significantly smaller than the number of ice particles predicted at RH$_i = 124\%$ by Meyers et al. [1992], and implied that soot will not significantly alter the formation of clouds in the lower troposphere at temperatures above 243K, below water saturation.
Chapter 5
Ice nucleating properties of mineral dust:
Kaolinite and Goethite

5.1 Introduction

The deposition-mode ice nucleating properties of Kaolinite and Goethite particles were investigated between 239 to 258 K, below liquid water saturation. Kaolinite particles are believed to be a significant component of dust particles in the atmosphere [Glaccum and Prospero, 1980; Pye, 1987], consisting of up to 25% of the total clay concentration in Tamanrassett, Sessali, and In Guezzam, Africa [Goudie and Middleton, 2001]. Goethite is one of the most stable iron oxides found in soils at ambient temperature [Cornell and Schwertmann, 2003]. The iron content of soil dust varies globally, but on average makes up 3% [Jickells et al., 2005; Usher et al., 2003].

This section details the results obtained from RH$_i$ ramp experiments for Kaolinite and Goethite in the temperature range of 239 to 258 K. The onset of ice formation is quantified with $J_{het}$. The contact angle for the formation of a single ice embryo on Kaolinite and Goethite is also determined for each experiment. By utilizing the contact angle, the atmospheric implications of these mineral dust results are considered.
5.2 Results

5.2.1 Ice nucleation on Kaolinite

During a typical $RH_t$ ramp experiment, $p_{H_2O}$ was held constant while the temperature of the cell was reduced in order to increase the RH$_t$ within the flow cell. The temperature was decreased until either water droplets or ice particles were observed. The RH$_t$ at which either water droplets or ice particles were observed is illustrated in Figure 5.1 for the blank hydrophobic glass slide as well as for Kaolinite. The dashed line in the figure represents water saturation (i.e. relative humidity with respect to water is 100 %). The open symbols indicate that water droplets were first observed and the solid symbols indicate that only ice particles were observed with no indication of the formation of water droplets prior to ice formation. From this information conclusions are drawn on the ice nucleating ability of Kaolinite in the deposition mode (only) below water saturation.

In the experiments involving Kaolinite particles at temperatures above ~ 252 K, water droplets were first observed (open symbols), with ice nucleation occurring at a later time, presumably by immersion freezing. However, whether or not the formation of ice following the formation of liquid droplets was due to the Kaolinite particles or the substrate cannot be determined. Consequently, this information is not included. However, the results in Figure 5.1 show that at temperatures above ~ 252 K, water droplets, rather than ice, always appeared first in $RH_t$ ramp experiments involving Kaolinite. This occurred at water saturation, as expected. This result implies that for the present experimental conditions ice nucleation never occurred at temperatures above ~ 252K and below water saturation.

At temperatures below ~ 252 K ice nucleation was consistently observed. Ice particles grew rapidly and prevented the formation of water droplets and new ice particles by depleting the water vapour. Images illustrating formation of ice on Kaolinite are shown in Figure 5.2. These ice particles nucleated with no indication of the formation of water droplets prior to ice formation. As is shown in Figure 5.1, ice formed at RH$_t$ below water saturation. Additionally, the ice nucleating abilities of Kaolinite particles appeared to improve with decreasing temperature. The saturation at which ice was observed to form decreased at lower temperatures. Also, as the temperature decreased, the number of particles able to nucleate ice increased.
Figure 5.1  The RH$_i$ at which liquid water droplets or ice particles were first observed to form on Kaolinite as the RH$_i$ inside the cell was slowly increased. The open symbols indicate that water droplets were first observed and the solid symbols indicate that only ice particles were observed with no indication of the formation of water droplets prior to ice formation.

Figure 5.2  Images of ice crystals and Kaolinite particles from two different experiments at 245.2 and 243.2 K. Cell temperature was decreased at a constant rate of 0.1 K min$^{-1}$ until ice crystals were observed to form.
5.2.2 Ice nucleation on Goethite

The ice nucleating abilities of Goethite were determined by applying the RH$_{t}$ ramp experiment conditions. The RH$_{t}$ at which either water droplets or ice particles were observed are illustrated in Figure 5.3 for the blank hydrophobic glass slide as well as Goethite. The open symbols indicate that water droplets were first observed and the solid symbols indicate that only ice particles were observed with no indication of the formation of water droplets prior to ice formation.

In the experiments involving Goethite particles at temperatures above ~ 252 K, water droplets were observed first (open symbols). Ice nucleation was not observed to occur at a later time. The results in Figure 5.3 show that at temperatures above ~ 252 K, water droplets condensed at water saturation, as expected. This observation leads to the conclusion that ice nucleation never occurred at temperatures above ~ 252 K and below water saturation for the current experimental conditions (observation time and Goethite particle concentrations).

At temperatures below ~ 252 K ice nucleation was always observed. Images illustrating formation of ice on Goethite are shown in Figure 5.4. The formation of the liquid phase did not precede ice nucleation. As is shown in Figure 5.3, ice formed at RH$_{t}$ well below water saturation. Comparable to Kaolinite, the ice nucleating abilities of Goethite particles appeared to improve with decreasing temperature. At temperatures below 252 K ice was observed to form close to ice saturation, and well below water saturation.
Figure 5.3  The RH at which liquid water droplets or ice particles were first observed on Goethite as the RH inside the cell was slowly increased. The open symbols indicate that water droplets were first observed and the solid symbols indicate that only ice particles were observed with no indication of the formation of water droplets prior to ice formation.

Figure 5.4  Images of ice crystals and Goethite particles obtained from two different experiments at 241.3 and 239.2 K. Here cell temperature was decreased at a constant rate of 0.1 K min\(^{-1}\) until ice crystals were observed to form.
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5.3 Comparison with other results

5.3.1 Kaolinite

Ice nucleating properties of Kaolinite were first investigated by Roberts and Hallett [1968]. Dust samples, consisting of up to $\sim 10^4$ particles, were placed on a microscope cold stage under controlled RH$_i$ conditions. The authors noted that at temperatures of 254 K and above, it was always necessary to reach water saturation before the appearance of ice crystals. Below $\sim 254$ K deposition nucleation was observed on particles between 0.5 to 3 $\mu$m in diameter. This observation is generally consistent with the results presented in this thesis. During RH$_i$ ramp experiments involving Kaolinite, deposition nucleation was observed below $\sim 252$ K. In Figure 5.5, the current onset RH$_i$ for Kaolinite is compared with results obtained by Roberts and Hallett [1968]. Whereas Roberts and Hallett [1968] observed an approximately constant onset RH$_i$ at $\sim 120\%$ below 254 K, in the current data the onset RH$_i$ at which ice nucleates decreases with temperature. The discrepancy may be explained by the fact that Roberts and Hallett [1968] decreased the total number of Kaolinite particles used to nucleate ice at lower temperatures. Also, the Kaolinite sample employed by Roberts and Hallett [1968] may have different characteristics to that employed in the current study.

During their investigation of ice habits, Bailey and Hallett [2002] considered the onset of ice formation on Kaolinite dust between 213 to 261 K. The corresponding data is plotted in Figure 5.5 and represents the nucleation onset at which less than 0.1% of the dust particles acted as IN. The data was obtained by adhering Kaolinite particles, 5 to 10 $\mu$m in diameter, to a glass filament which was positioned inside a thermal diffusion chamber. The authors noted their data converged smoothly with earlier nucleation results of Bailey and Hallett [2002]. However, there appears to be an offset of $\sim 5\%$ RH$_i$. The reason for the difference in results obtained in the current study and those presented by Bailey and Hallett [1968] is unclear. However, the number of particles used to coat the bare glass filament was not quantified by Bailey and Hallett [1968], suggesting a different Kaolinite surface area may have been used.
Figure 5.5 A comparison of current onset RH\textsubscript{i} results for Kaolinite with those of Roberts and Hallett [1968] and Bailey and Hallett [2002]. Current data corresponds to the conditions at which water droplets (open squares) or ice crystals (solid squares) were observed. Roberts and Hallett [1968] observed immersion freezing above 254 K and deposition nucleation at lower temperature on particles between 0.5 to 3 μm in diameter. The threshold of nucleation activity was taken as the appearance of one ice crystal in ~10\textsuperscript{4} particles. The results from Bailey and Hallett [2002] correspond to the onset of several ice crystals on Kaolinite particles (between 5 to 10 μm in diameter) adhered to a glass filament.
5.3.2 **Comparison of current data with previous mineral dust studies other than Kaolinite**

Several different studies have shown that mineral dust can efficiently nucleate ice below water saturation and in the deposition mode. Here, current Kaolinite and Goethite results are compared with previous mineral dust studies [Mohler et al., 2005b; Archuleta et al., 2005; Knopf and Koop, submitted]. Mohler et al. [2005b] investigated ice nucleation on Arizona test dust (ATD) particles between 194 and 241K. ATD is composed of a mixture of different minerals, but mainly consist of silicates, calcite, and clay minerals. Dry particles, ~0.1 to 1.5 μm in diameter, were injected directly into a large AIDA aerosol chamber. As is shown in Figure 5.6, ATD particles were observed to nucleate ice at low supersaturations in the deposition mode.

The ice nucleating abilities of commercially available aluminium oxide (Al₂O₃), alumina-silicate (3Al₂O₃:2SiO₂), and iron oxide (Fe₂O₃) were investigated by Archuleta et al. [2005]. The authors considered particles that were 50, 100, and 200 nm in diameter. Only the ice nucleation results for alumina-silicate and iron oxide particles are plotted in Figure 5.6. Archuleta et al. [2005] noted that all particle types were as effective or better at initiating ice formation as compared with homogeneous freezing conditions. Second, the ice nucleating properties of mineral dust were observed to improve at lower temperatures and for larger particle sizes.

In the study by Knopf and Koop [submitted] the ice nucleating properties of ATD were investigated between 197 to 293 K and below liquid water saturation. ATD particles, 0.7 to 10 μm in diameter, were deposited on a hydrophobic Herasil quartz plate positioned inside a chamber which operated in the Knudsen regime. Below 240 K ice nucleated on ATD particles via deposition nucleation at RH below water saturation. This onset RH data for ATD is plotted in Figure 5.6.

The results from the previous studies corresponding to the ice nucleating abilities of various types of mineral dust in the deposition mode are plotted in Figure 5.6. The data illustrates that the ability of mineral dust to nucleate ice is controlled by its composition, size, and morphology. Several conclusions can be drawn from these observations. First, all studies have found that, in general, mineral dust is clearly an active IN below water saturation in the deposition mode. Second, the ice nucleating properties of mineral dust are size dependent. This was conclusively shown by Archuleta et al. [2005]. Finally, the variety of different types of mineral dust in the atmosphere makes the task of quantifying the overall ice nucleating ability of
mineral dust difficult. Hence, more systematic studies are required to quantify the ice nucleating properties of these particles. A logical start would be to determine the \( J_{het} \) and the contact angle for each type of mineral dust component. This could set the basis for modelling or predicting IN of authentic atmospheric samples. In the subsequent section of this thesis the ice nucleating properties of Kaolinite and Goethite are quantified in this manner.

**Figure 5.6** A comparison of the current measurements of the onsets of ice nucleation of Kaolinite and Goethite particles with data for other mineral dust measured in previous work.
5.4 Determination of onset $J_{het}$ for mineral dust

The above results are used to determine the heterogeneous nucleation rate coefficient, $J_{het}$, for mineral dust in the deposition mode. In the deposition mode, $J_{het}$ depends on the number of ice nucleation events, available surface area, and time. During the RH$_i$ ramp experiments involving Kaolinite and Goethite either water droplets or ice crystals were observed to form first, depending on temperature. Hence, two different approaches for calculating $J_{het}$ were applied, depending on whether ice or water was observed first.

In the experiments involving Kaolinite and Goethite at temperatures above $\sim 252$ K, water droplets condensed at liquid water supersaturation on four separate occasions. When ice did not nucleate first, the ice nucleating properties of mineral dust were quantified by determining the upper limit to heterogeneous nucleation rate coefficient, $J_{up}^{het}$, in an approach similar to that involving soot. The upper limit to the heterogeneous nucleation coefficient for Kaolinite and Goethite was determined with Eq. 4.1 by taking $\tau = 60$ seconds, $x = 0.95$, and $A_s =$ geometric surface area of the dust particles. The $J_{up}^{het}$ corresponding to the specific experimental conditions is summarized in Table 5.1 and Table 5.2.

Below $\sim 252$ K ice nucleated first on Kaolinite and Goethite. The heterogeneous nucleation rate coefficient for experiments in which ice was observed to form first may be calculated in the following manner [Salcedo et al., 2001; Salcedo et al., 2000],

$$J_{het} = \frac{\omega}{\tau A_s}$$  \hspace{1cm} \text{Eq. 5.1}

where $\omega$ is the number of ice crystals nucleated, $\tau$ is the observation time, and $A_s$ is the total surface area available for heterogeneous nucleation. At the onset of ice nucleation $\omega$ is equal to unity. The observation time for this single nucleation event was $20 \pm 10$ seconds. The total surface area, $A_{ss}$, ranged from $3.3 \cdot 10^4$ to $2.5 \cdot 10^5$ $\mu$m$^2$. These values are listed in Table 5.1 and Table 5.2. To calculate $A_s$ a geometric surface area for the clay particles was assumed. An example of a single Kaolinite dust sample is shown in Figure 5.7. The figure also includes an average size distribution of eleven Kaolinite samples used in RH$_i$ ramp experiments. Correspondingly, an example of a single Goethite dust sample is shown in Figure 5.8. The resulting values of $J_{het}$, with estimated upper and lower limits, are listed in Table 5.1 and Table
5.2 for Kaolinite and Goethite, respectively. The uncertainty in $J_{\text{het}}$ was determined by considering the error in $A_s$ and $\tau$. 
Figure 5.7  (a) An image of the bottom of the cell showing the deposition of ~ 300 particles of Kaolinite on a hydrophobic slide. The surface area of the particles is \((6.5\pm0.8)\times10^4\ \text{\(\mu\text{m}^2\)}

(b) Average size distribution of eleven different Kaolinite samples. Geometric mean diameter is 8.0 \(\mu\text{m}\); geometric standard deviation is 1.2; surface area mean diameter is 19.7 \(\mu\text{m}\) (parameters defined by Reist [1993]).
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Table 5.1 The heterogeneous nucleation rate coefficient for eleven separate Kaolinite experiments. Parameters describing experimental conditions include onset temperature and onset RH$_i$ at which either water droplets or ice crystals were observed to form first. The geometric surface area of each Kaolinite sample is also included. The uncertainty in $J_{het}$ was evaluated by considering error in the observation time (20±10 sec) and the surface area of particles. Here the lower and upper limits to $J_{het}$ are $J_{het}^{low}$ and $J_{het}^{up}$, respectively. The table also lists the total number of ice particles observed to form during the course of the experiment.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature (K)</th>
<th>RH$_i$ (%)</th>
<th>Surface area ($\times 10^4 \mu m^2$)</th>
<th>$J_{het}^{low}$</th>
<th>$J_{het} &lt; J_{het}^{up}$</th>
<th>Total number of ice particles formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>254.8±0.2</td>
<td>120±3</td>
<td>5±1</td>
<td>$98^a$</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>252.6±0.2</td>
<td>122±4</td>
<td>6.5±0.8</td>
<td>$77^a$</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>252.5±0.2</td>
<td>124±3</td>
<td>5±1</td>
<td>$98^a$</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>250.2±0.2</td>
<td>114±5</td>
<td>7±2</td>
<td>$38 &lt; 71 &lt; 175^b$</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>249.1±0.2</td>
<td>114±3</td>
<td>8±1</td>
<td>$37 &lt; 62 &lt; 142^b$</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>247.0±0.2</td>
<td>109±3</td>
<td>3.4±0.5</td>
<td>$87 &lt; 149 &lt; 352^b$</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>245.2±0.2</td>
<td>109±3</td>
<td>12±3</td>
<td>$23 &lt; 43 &lt; 114^b$</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>243.2±0.2</td>
<td>103±3</td>
<td>4.4±0.1</td>
<td>$69 &lt; 113 &lt; 255^b$</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>9</td>
<td>240.7±0.3</td>
<td>103±3</td>
<td>16±3</td>
<td>$18 &lt; 32 &lt; 73^b$</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>10</td>
<td>240.4±0.2</td>
<td>103±3</td>
<td>24±4</td>
<td>$12 &lt; 20 &lt; 48^b$</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>11</td>
<td>239.1±0.3</td>
<td>104±3</td>
<td>4±1</td>
<td>$64 &lt; 114 &lt; 276^b$</td>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>

`a` In Experiments no. 1, 2, and 3 ice nucleation was not observed; water droplets nucleated first, hence $J_{het}^{up}$ was determined by employing Eq. 4.1. The confidence level in $J_{het}^{up}$ is 95%.

`b` In Experiments no. 4 – 11 ice nucleated first, hence $J_{het}$ was determined by using Eq. 5.1.
Figure 5.8  (a) An image of the bottom of the cell showing the deposition of ~ 1000 particles of Goethite on a hydrophobic slide. The surface area of the particles is $(19\pm4) \cdot 10^4 \mu m^2$.
(b) Average size distribution of six different samples of Goethite. Geometric mean diameter is 6.1 $\mu m$; geometric standard deviation is 1.2; surface mean diameter is 17.8 $\mu m$ (parameters defined by Reist [1993]).
Table 5.2 The heterogeneous nucleation rate coefficient for six separate Goethite experiments. Parameters describing experimental conditions include onset temperature and onset RH$_i$ at which either water droplets or ice crystals were observed to form first. The geometric surface area of each Goethite sample is also included, noting that experiments no. 1, 5, and 6 were performed on the same sample. The uncertainty in $J_{het}$ was estimated by considering the error in the observation time (20±10 sec) and the surface area of the particles. Here the lower and upper limits to $J_{het}$ are $J_{het}^{low}$ and $J_{het}^{up}$, respectively. The table also includes the total number of ice particles formed during the course of the experiment.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature (K)</th>
<th>RH$_i$ (%)</th>
<th>Surface area ($10^4$ μm$^2$)</th>
<th>$J_{het}^{low}$ &lt; $J_{het}$ &lt; $J_{het}^{up}$ (cm$^{-2}$ sec$^{-1}$)</th>
<th>Total number of ice particles formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>256.9±0.3</td>
<td>119±5</td>
<td>19±4</td>
<td>27$^a$</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>250.1±0.3</td>
<td>118±5</td>
<td>10±2</td>
<td>28 &lt; 50 &lt; 118$^b$</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>247.0±0.4</td>
<td>108±6</td>
<td>18±3</td>
<td>15 &lt; 27 &lt; 66$^b$</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>244.6±0.5</td>
<td>110±7</td>
<td>5.0±0.7</td>
<td>57 &lt; 99 &lt; 227$^b$</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>241.3±0.2</td>
<td>102±3</td>
<td>19±4</td>
<td>15 &lt; 27 &lt; 65$^b$</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>239.2±0.3</td>
<td>102±2</td>
<td>19±4</td>
<td>15 &lt; 27 &lt; 65$^b$</td>
<td>10</td>
</tr>
</tbody>
</table>

$^a$ In Experiment no. 1 ice nucleation was not observed; water droplets nucleated first, hence $J_{het}^{up}$ was determined by employing Eq. 4.1.

$^b$ In Experiments no. 2 – 6 ice nucleated first, hence $J_{het}$ was determined by using Eq. 5.1.
5.5 Contact Angle

In order to determine the impact of the measured ice nucleating properties of Kaolinite and Goethite on the formation of the ice phase in lower tropospheric clouds, the ice nucleating behaviour of these mineral dusts must be characterized in terms of the contact angle. This step is necessary because it allows $J_{het}$ to be extrapolated to higher and lower saturations. The following discussion focuses on the calculation of the contact angle of an ice embryo formed on the surface of Kaolinite and Goethite between 239 and 258 K. Following the steps outlined in Chapter 4.4, experimentally-determined $J_{het}$ values (Chapter 5.4) have been used to determine $\Delta G_{ac}^*, r^*$, and $\theta$ for each Kaolinite and Goethite experiment and are listed in Table 5.3.

The uncertainty in the contact angle was determined by considering the uncertainty in the temperature ($\sim \pm 0.2$ K, depending on the experiment), RH$_i$ (arising from uncertainty in the temperature and the frost point), surface area (depending on the experiment), interfacial tension (102 to 111 mJ m$^{-2}$), and observation time (20±10 sec).

The contact angle pertaining to each of the experiments is plotted as a function of temperature in Figure 5.9. In the figure, solid symbols correspond to experiments in which ice particles nucleated first, with no indication of the liquid phase prior to ice formation; open symbols correspond to the limiting value of the contact angle for experiments in which water droplets were observed to form first. In the latter experiments in which water droplets were observed to form first at liquid water saturation, only the lower limit to the contact angle was determined. For the experiments in which ice was observed to nucleate first, a line of best fit is included. The linear regression between ~240 to 250 K for the contact angle of Kaolinite and Goethite is:

$$\theta_{\text{Kaolinite}} = -230.9 + 1.0 \, T$$  \hspace{1cm} \text{Eq. 5.2}

$$\theta_{\text{Goethite}} = -276.7 + 1.2 \, T$$  \hspace{1cm} \text{Eq. 5.3}

where $T$ is the temperature in Kelvin. The standard deviation, determined from the linear regression, is 1.4° and 1.9° for Kaolinite and Goethite data, respectively.
Table 5.3  Onset parameters pertaining to the formation of a single spherical-cap ice crystal in the Kaolinite and Goethite ramp RH$_i$ experiments for which $J_{het}$ was determined. $\Delta G_{act}^*$ was evaluated by using the pre-exponential term, $A$, equal to $\{10^{26}\}$ cm$^2$ sec$^{-1}$. The radius of the critical-size ice germ was evaluated by assuming no lattice strain in Eq. 2.20. Finally, the contact angle was determined by using Eq. 4.4. The uncertainty in $J_{het}$, $\Delta G_{act}^*$, $r^*$, and $\theta$ was evaluated by considering uncertainty in the temperature, onset RH$_i$, surface area, interfacial tension, and observation time.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Onset Temp (K)</th>
<th>Onset RH$_i$ (%)</th>
<th>$J_{het}^{low} &lt; J_{het} &lt; J_{het}^{up}$ (cm$^2$ sec$^{-1}$)</th>
<th>$\Delta G_{act}^*$ (10$^{-19}$ J)</th>
<th>$r^<em>_{low} &lt; r^</em> &lt; r^*_{up}$ (nm)</th>
<th>$\theta_{low} &lt; \theta &lt; \theta_{up}$ (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
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<td>120±3</td>
<td>98</td>
<td>1.94±0.03</td>
<td>11</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>252.6±0.2</td>
<td>122±4</td>
<td>77</td>
<td>1.94±0.03</td>
<td>10</td>
<td>23</td>
</tr>
<tr>
<td>3</td>
<td>252.5±0.2</td>
<td>124±3</td>
<td>98</td>
<td>1.93±0.03</td>
<td>9</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>250.2±0.2</td>
<td>114±5</td>
<td>38 $&lt; 71 &lt; 175$</td>
<td>1.92±0.03</td>
<td>12 $&lt; 15 &lt; 34$</td>
<td>12 $&lt; 18 &lt; 21$</td>
</tr>
<tr>
<td>5</td>
<td>249.1±0.2</td>
<td>114±3</td>
<td>37 $&lt; 62 &lt; 142$</td>
<td>1.92±0.03</td>
<td>12 $&lt; 15 &lt; 19$</td>
<td>16 $&lt; 19 &lt; 21$</td>
</tr>
<tr>
<td>6</td>
<td>247.0±0.2</td>
<td>109±3</td>
<td>87 $&lt; 149 &lt; 352$</td>
<td>1.87±0.03</td>
<td>17 $&lt; 23 &lt; 34$</td>
<td>12 $&lt; 15 &lt; 17$</td>
</tr>
<tr>
<td>7</td>
<td>245.2±0.2</td>
<td>109±3</td>
<td>23 $&lt; 43 &lt; 118$</td>
<td>1.90±0.03</td>
<td>17 $&lt; 23 &lt; 34$</td>
<td>12 $&lt; 15 &lt; 17$</td>
</tr>
<tr>
<td>8</td>
<td>243.2±0.2</td>
<td>103±3</td>
<td>69 $&lt; 113 &lt; 255$</td>
<td>1.85±0.03</td>
<td>30 $&lt; 62 &lt; 300$</td>
<td>4 $&lt; 9 &lt; 12$</td>
</tr>
<tr>
<td>9</td>
<td>240.7±0.3</td>
<td>103±3</td>
<td>18 $&lt; 32 &lt; 73$</td>
<td>1.88±0.03</td>
<td>34 $&lt; 78 &lt; 220$</td>
<td>0 $&lt; 8 &lt; 12$</td>
</tr>
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<td>240.4±0.2</td>
<td>103±3</td>
<td>12 $&lt; 20 &lt; 48$</td>
<td>1.89±0.03</td>
<td>32 $&lt; 68 &lt; 220$</td>
<td>0 $&lt; 8 &lt; 13$</td>
</tr>
<tr>
<td>11</td>
<td>239.1±0.3</td>
<td>104±3</td>
<td>64 $&lt; 114 &lt; 276$</td>
<td>1.82±0.03</td>
<td>30 $&lt; 52 &lt; 170$</td>
<td>5 $&lt; 9 &lt; 13$</td>
</tr>
<tr>
<td>Goethite</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>256.9±0.3</td>
<td>119±5</td>
<td>27 $^a$</td>
<td>2.01±0.03</td>
<td>11</td>
<td>22 $^b$</td>
</tr>
<tr>
<td>2</td>
<td>250.1±0.3</td>
<td>118±5</td>
<td>28 $&lt; 50 &lt; 118$</td>
<td>1.93±0.03</td>
<td>9 $&lt; 12 &lt; 17$</td>
<td>17 $&lt; 20 &lt; 24$</td>
</tr>
<tr>
<td>3</td>
<td>247.0±0.4</td>
<td>108±6</td>
<td>15 $&lt; 27 &lt; 66$</td>
<td>1.93±0.03</td>
<td>16 $&lt; 28 &lt; 110$</td>
<td>8 $&lt; 15 &lt; 18$</td>
</tr>
<tr>
<td>4</td>
<td>244.6±0.5</td>
<td>110±7</td>
<td>57 $&lt; 99 &lt; 227$</td>
<td>1.87±0.03</td>
<td>12 $&lt; 21 &lt; 70$</td>
<td>8 $&lt; 15 &lt; 20$</td>
</tr>
<tr>
<td>5</td>
<td>241.3±0.2</td>
<td>102±3</td>
<td>15 $&lt; 27 &lt; 65$</td>
<td>1.88±0.03</td>
<td>39 $&lt; 92 &lt; 220$</td>
<td>0 $&lt; 7 &lt; 12$</td>
</tr>
<tr>
<td>6</td>
<td>239.2±0.3</td>
<td>102±4</td>
<td>15 $&lt; 27 &lt; 65$</td>
<td>1.87±0.03</td>
<td>28 $&lt; 88 &lt; 220$</td>
<td>0 $&lt; 8 &lt; 14$</td>
</tr>
</tbody>
</table>

$^a$ If water droplets were observed first, $J_{het}^{up}$ was calculated with Eq. 4.1.

$^b$ The lower limit to the contact angle was determined from $J_{het}^{up}$.

$^c$ If ice nucleated first, $J_{het}$ was determined based on Eq. 5.1.
Figure 5.9  Contact angle of an ice crystal formed under heterogeneous nucleation conditions vs. temperature. Here a spherical-cap ice germ was assumed to form on a flat insoluble Kaolinite or Goethite surface (geometric mean diameter equal to 8 µm and 6.1 µm) respectively. Neglecting lattice strain, the contact angle was determined for $N_i = 3.1 \cdot 10^{28} \text{ m}^{-3}$ and $\sigma_v = 106.5 \text{ mJ m}^{-2}$ by using Eq. 4.3 and Eq. 4.4. Solid symbols correspond to experiments in which ice particles nucleated first, with no indication of the liquid phase prior to ice formation. Open symbols correspond to the limiting contact angles for experiments in which water droplets were observed to form first. For experiments in which ice was observed to nucleate first, the data is fitted to reflect the dependence of the contact angle on temperature. For Kaolinite and Goethite at temperatures between ~240 to 250 K, $\theta_{\text{Kaolinite}} = -230.9 + 1.0 T$ and $\theta_{\text{Goethite}} = -276.7 + 1.2 T$, respectively.
5.6 Atmospheric implications

In order to determine the impact of the measured ice nucleating properties of Kaolinite and Goethite on the formation of the ice-phase in lower tropospheric clouds, one must determine the maximum number of ice particles that can be produced under atmospheric conditions as a function of temperature and saturation. In order to do this \( J_{het} \) as a function of temperature and saturation is required. However, the present experiment setup is only sensitive to a narrow range of \( J_{het} \) values. In each of the \( RH_i \) ramp experiments, the temperature and saturation were ramped until either the liquid phase or the ice phase was observed to form. As soon as the saturation and temperature were such that \( J_{het} \) was equivalent to this narrow range, nucleation was observed. For atmospheric purposes \( J_{het} \) must be extrapolated to higher and lower supersaturations by using classical nucleation theory.

Figure 5.9 illustrates that the contact angle, \( \theta \), decreases with temperature for both Kaolinite and Goethite. Between ~240 to 250 K, the relationship between the contact angle and temperature is described by Eq. 5.2 and Eq. 5.3 for \( \theta_{Kaolinite} \) and \( \theta_{Goethite} \), respectively. Assuming \( \theta \) is independent of saturation, the contact angle is used in Eq. 2.22 to extrapolate \( J_{het} \) to higher and lower saturations (below \( RH_w = 100\% \)) for temperatures 240, 245, and 250 K.

For example, at 240 K the contact angle for a nucleation of a single ice crystal on Kaolinite is 8.3\(^\circ\) (Eq. 5.2). Assuming \( \theta_{Kaolinite} \) is constant with saturation, \( J_{het} \) at water saturation (i.e. \( RH_i = 138\% \)) is equal to 7\cdot10^{25} \text{ cm}^{-2} \text{ sec}^{-1} \) according to Eq. 2.23. This value is determined by assuming \( \sigma_{lv} \) is 106.5 mJ m\(^{-2}\) and the density of ice is 0.92 g cm\(^{-3}\). Predicted \( J_{het} \) is plotted as a function of saturation in Figure 5.10 (Kaolinite) and 5.11 (Goethite). The uncertainty in \( J_{het} \) was determined by considering the standard deviation in \( \theta_{Kaolinite} \) and \( \theta_{Goethite} \) from the fit to the data in Figure 5.9.
Figure 5.10  The heterogeneous nucleation rate coefficient vs. supersaturation for Kaolinite. Each curve corresponds to a different temperature: 240, 245, and 250 K. The contact angle at each temperature was determined by applying the parameterization Eq. 5.2. Assuming that the contact angle is independent of saturation, the nucleation rate coefficient (Eq 2.22) at each temperature is plotted as a function of supersaturation. Each $J_{het}$ is extrapolated up to $RH_w = 100\%$. Dotted curves indicate the upper and lower bounds for $J_{het}$ as a result of the uncertainty in $\theta_{Kaolinite}$. 
Figure 5.11  The heterogeneous nucleation rate coefficient vs. supersaturation for Goethite. Each curve corresponds to a different temperature: 240, 245, and 250 K. The contact angle at each temperature was determined by applying the parameterization Eq. 5.3. Assuming that the contact angle is independent of saturation, the nucleation rate coefficient (Eq 2.22) at each temperature is plotted as a function of supersaturation. Each $J_{het}$ is extrapolated up to RH$_w$ = 100%. Dotted curves indicate the upper and lower bounds for $J_{het}$ as a result of the uncertainty in $\theta_{Goethite}$. 
The number of ice particles that can be produced under atmospheric conditions can be determined by modifying Eq. 4.5 to consider the number density of mineral dust instead of soot, such that

$$n_{\text{ice}} = n_{\text{dust}} [1 - \exp(-J_{\text{het}} A_p \tau)]$$

Eq. 5.4

where $n_{\text{ice}}$ is the number density of ice particles produced (litre$^{-1}$), $n_{\text{dust}}$ is the number density of mineral dust (litre$^{-1}$), $A_p$ is the surface area of a single dust particle (cm$^2$), and $\tau$ is the total time required to form a cloud (60 minutes). The number of ice particles produced by Kaolinite and Goethite will vary with $J_{\text{het}}$ and bulk surface area of dust in the atmosphere. A large quantity of data has been published on mass density of mineral dust in the atmosphere [Husar et al., 1997; Perry et al., 1997; Prospero, 1999; Falkovich et al., 2001; VanCuren and Cahill, 2002; Sassen et al., 2003; Clarke et al., 2004] and it ranges from 0.2 to 2000 $\mu$g m$^{-3}$. It has been found that the density of mineral dust varies with location, altitude, and season. Goudie and Middleton [1992] analyzed long-term meteorological records for a large number of regions and concluded that there is no single global pattern of dust-storm frequency trends. For this reason, the dust mass densities pertaining to specific topographical locations are not considered in this thesis. Instead, a mass density of $\sim 1 \cdot 10^{-6}$ g m$^{-3}$ (close to the lower limit of mass density of mineral dust in the atmosphere) is employed to estimate the number density of ice particles as a function of saturation and temperature.

An example calculation pertaining to Kaolinite is considered here. For ice nucleation in the atmosphere $n_{\text{dust}}$ and $A_p$ are assumed to be 91.8 litre$^{-1}$ and 1.3 $\cdot 10^{-7}$ cm$^2$. A value of 91.8 litre$^{-1}$ for $n_{\text{dust}}$ was calculated by assuming a dust radius of 1 $\mu$m, Kaolinite bulk density of 2.6 g cm$^{-3}$, a geometric surface area, and a dust mass concentration (consisting of Kaolinite particles only) in the atmosphere of $\sim 1 \cdot 10^{-6}$ g m$^{-3}$. A value of 1.3 $\cdot 10^{-7}$ cm$^2$ for $A_p$ was calculated based on a geometric surface area of spherical dust particles of 1 $\mu$m mean radius – a typical radius of atmospheric dust particles [Ginoux et al., 2001; Prospero 1999; Falkovich et al., 2001; Blanco et al., 2003; Perry et al., 1997; Petit et al., 2005; Jickells et al., 2005]. With these assumptions, $n_{\text{ice}}$ for temperatures between $\sim 240$ to 250 K could be determined in combination with the $J_{\text{het}}$ values plotted in Figure 5.10 and Figure 5.11. For example, at 240 K and an extrapolated relative humidity of 138% (equivalent to water saturation) $n_{\text{ice}}$ is 91.8 litre$^{-1}$ for Kaolinite. In the case of Goethite, $n_{\text{ice}}$ was determined by taking Goethite bulk density of 4.27 g cm$^{-3}$. 
The number density of ice produced as a function of saturation for Kaolinite and Goethite is plotted in Figures 5.12 and 5.13, respectively for temperatures of 240, 245, and 250 K. The uncertainty in $n_{\text{ice}}$ accounts for the standard deviation in the contact angle. In both cases, the number density of ice particles increased with a decrease in temperature and increasing saturation. For each experiment $n_{\text{ice}}$ is extrapolated up to RH$_w$ = 100%. Both figures include the Meyers et al. [1992] parameterization (Eq. 4.6) which predicts the total number of active ice nuclei in the atmosphere at a function of supersaturation, in the deposition mode and condensation freezing mode. If dust mass density is $\sim 1 \cdot 10^6$ g m$^{-3}$, at lower temperatures both Kaolinite and Goethite particles initiate the nucleation of enough ice crystals to account for the number of ice nuclei typically found in the atmosphere. This suggests that the contribution of mineral dust to formation of ice at conditions relevant to the lower troposphere is significant.

It is interesting to note that the curve describing typical atmospheric number densities of ice nuclei [Meyers et al., 1992] is significantly different from the trend predicted by classical nucleation theory. The current results consider the ice nucleating properties of Kaolinite and Goethite exclusively, whereas Meyers et al. [1992] considers the ice nucleating properties of atmospheric aerosols which are composed of a mixture of species. Each mineral type or other solid insoluble particle will have its own nucleating onset RH$_i$. Hence the continuous curve of Meyers et al. [1992] may reflect this non-homogeneity of atmospheric particles.
Figure 5.12  Number density of ice vs. saturation for Kaolinite assuming mass density of dust in the atmosphere is 1 μg m\(^{-3}\). The number density of ice is a function of the nucleation rate coefficient determined in Figure 5.10. The solid curves correspond to different temperatures of 240, 245, and 250 K for which the contact angle was 8.3°, 13.3°, and 18.3° respectively. Corresponding dotted curves reflect the standard deviation of θ\(_{\text{Kaolinite}}\). The Meyers et al. [1992] parameterization predicts the total number of active IN in the atmosphere at a function of supersaturation, in the deposition mode and condensation freezing mode.
Figure 5.13  Number density of ice vs. saturation for Goethite assuming mass density of dust in the atmosphere is 1 μg m$^{-3}$. The number density of ice is a function of the nucleation rate coefficient determined in Figure 5.11. The curves correspond to different temperatures of 240, 245, and 250 K for which the contact angle was 7.6°, 13.5°, and 19.4° respectively. Corresponding dotted curves reflect the standard deviation of $\theta_{Goethite}$. The Meyers et al. [1992] parameterization predicts the total number of active IN in the atmosphere at a function of supersaturation, in the deposition mode and condensation freezing mode.
5.7 Conclusions

The results presented in this section establish that Kaolinite and Goethite nucleate ice between 239 and 258 K, below water saturation, and in the deposition mode. In this study mineral dust particles were exposed to conditions resembling those of the lower troposphere. At temperatures above ~ 252 K, water droplets were observed to form first. This shows that at these temperatures ice nucleation does not occur below water saturation under the current experimental conditions. However, below ~ 252 K ice particles were consistently observed to form well below liquid water saturation. This suggests deposition nucleation on Kaolinite and Goethite particles occurs in this temperature range. Further, the ice nucleating abilities of Kaolinite and Goethite improved with decreasing temperature. As the temperature decreased, ice nucleated at relative humidities well below water saturation.

Combining all the previous results and the current study, it appears that below water saturation at temperatures below ~ 252 K, ice nucleation on many types of dust particles is efficient [Bailey and Hallett, 2002; Roberts and Hallett, 1968; Archuleta et al., 2005; Mohler et al., 2005b; Knopf and Koop, submitted].

In order to quantify the ice nucleating abilities of Kaolinite and Goethite, the heterogeneous nucleation rate for each of the experiments was determined. Also, classical nucleation theory was employed to determine the contact angle of an ice embryo formed under conditions defined by the specific RH_ramp experiments. The contact angle was determined by assuming a single spherical-cap ice germ formed from supercooled water vapour on a flat and insoluble Kaolinite or Goethite surface. In both cases, the contact angle was observed to decrease with temperature.

In the current study, at lower temperatures ice particles were observed to form well below water saturation. For this reason the determined \( J_{het} \) quantified the ice nucleating ability of Kaolinite and Goethite at the onset of nucleation defined by specific temperature and RH_r. In order to determine the atmospheric implications of this data, \( J_{het} \) was extrapolated to higher relative humidities by assuming that the contact angle does not vary with saturation. This allowed for the extrapolation of \( J_{het} \) as a function of saturation and temperature between ~ 240 and 250 K. This relationship was used to evaluate the implication of dust as IN in the lower
troposphere under typical atmospheric conditions. For mineral dust densities of 1 μg m\(^{-3}\) the \(n_{\text{ice}}\) values were often significantly higher than those predicted by Meyers et al. [1992], suggesting this type of mineral dust may significantly alter the formation of the ice-phase in lower tropospheric clouds at temperatures below ~252 K, and below water saturation.
Chapter 6

Summary and conclusions

6.1 Ice nucleating properties of soot and dust

In the previous chapters, the ice nucleating properties of several types of soot and mineral dust were investigated between 239 to 258 K, below water saturation, and in the deposition mode. For comparison, this data is plotted in Figure 6.1. In RH ramp experiments soot or dust particles were deposited on the bottom surface of the flow cell; RH inside the cell was increased, and the conditions under which water droplets or ice crystals formed were determined with a reflected-light microscope. In the case of soot (N-hexane soot, Lamp Black 101, Degussa FW2, and Printex 40) water droplets always nucleated first at temperatures above 248 K. This observation lead to the conclusion that ice nucleation does not occur below water saturation and in the deposition mode at these experimental conditions. Below ~ 243 K ice particles were occasionally observed first. However, since ice formed close to liquid water saturation, ice may have formed through condensation freezing.

This thesis also considered whether the ice nucleating abilities of soot would change following exposure to atmospherically-relevant quantities of ozone. However, even after an exposure equivalent to 80 ppb O₃ at atmospheric pressure for 13.7 days, the ice nucleating abilities of Lamp Black 101 were not different from results obtained for the unexposed samples.

RH ramp experiments were performed on Kaolinite and Goethite dust between 239 and 258 K. Below ~ 252 K, ice particles consistently formed first, demonstrating deposition nucleation is the dominant mode of ice formation for these experimental conditions. This data also showed that the ice nucleating ability of Kaolinite and Goethite improves with a decrease in temperature. This conclusion was drawn from the observation that, as the temperature decreased, ice formed at lower supersaturations.

The above observations may be explained by considering the composition and morphology of soot and mineral dust particles. Soot has an onion-like structure which consists of a graphite-like core coated with an amorphous organic layer (Figure 1.4). This amorphous coating may lack the ordered structure necessary to be a good IN.
Figure 6.1  A comparison of the RH$_i$ at which water droplets or ice crystals were observed to form first for RH$_i$ ramp experiments involving soot, Kaolinite, and Goethite. Solid symbols correspond to experiments in which ice crystals were observed to nucleate first; open symbols correspond to experiments in which water droplets condensed first.

In comparison, the nanostructure of Kaolinite and Goethite is crystalline. Kaolinite is built of alternate layers of Si$_2$O$_5$ and Al$_2$(OH)$_4$ in such a way that hydroxyl groups are exposed on one surface and silica on the other [Mason, 1960; Buol et al., 2003]; Goethite consists of Fe(III) that is surrounded by three O and three OH groups to give FeOOH an octahedral structure. Ice nucleating abilities of Kaolinite may be credited to the presence of the hydroxyl groups which allow water molecules to bind to the surface. Since the arrangement of OH groups
on basal plane of Kaolinite complements the hexagonal ice lattice, the ice lattice will have
cohherent geometry (Chapter 2.4) and form on the substrate surface by means of H-bonding. In a
similar manner, the arrangement of the OH groups in Goethite also favours ice nucleation.

6.2 The heterogeneous nucleation rate coefficient

The ice nucleating abilities of soot and mineral dust were quantified by determining the
heterogeneous nucleation coefficient at specific experimental conditions. For \( RH_i \) ramp
experiments involving soot the average \( J_{\text{het}}^{\text{up}} \) was determined to be 50 cm\(^2\)sec\(^{-1}\). This value was
calculated by assuming ice nucleation did not occur during an observation time of 60 seconds, at
a confidence level of 95%, and over a known surface area of soot. Since soot expressed poor ice
nucleating abilities between 243 and 258 K, the constant \( RH_i \) experiment was invoked to provide
a better constraint on \( J_{\text{het}}^{\text{up}} \) in the deposition mode. During this experiment n-hexane soot
(air/fuel = 2.4) was held at 247.5 K and below liquid water saturation. Since water or ice did not
nucleate during the 8 hour experiment, determined \( J_{\text{het}}^{\text{up}} \) was 0.1 cm\(^2\)sec\(^{-1}\), much smaller than the
previous result of 50 cm\(^2\)sec\(^{-1}\).

In order to quantify the ice nucleating abilities of Kaolinite and Goethite, the
heterogeneous nucleation rate for each of the experiments was also determined. If water droplets
were observed first, \( J_{\text{het}}^{\text{up}} \) ranged from 77 to 98 cm\(^2\)sec\(^{-1}\) at temperatures above \( \sim 252 \) K, at liquid
water saturation. For experiments in which ice nucleated first \( J_{\text{het}}^{\text{up}} \) was calculated by assuming a
single nucleation event took place over 20 seconds at a specific \( RH_i \) and temperature. For
Kaolinite, \( J_{\text{het}} \) values ranged from 20 to 149 cm\(^2\)sec\(^{-1}\) between 103 to 114% \( RH_i \), whereas for
Goethite \( J_{\text{het}} \) ranged from 27 to 99 cm\(^2\)sec\(^{-1}\) between 102 to 118% \( RH_i \), respectively.

6.3 Contact angle comparisons

In order to further quantify the ice nucleating abilities of soot and mineral dust,
heterogeneous nucleation theory was employed to determine the contact angle of the ice embryo
formed on the insoluble particle. The contact angle obtained for soot, Kaolinite, and Goethite is compared in Figure 6.2. The lower limit to the contact angle was determined for several RH\textsubscript{i} ramp experiments involving soot particles. Since water droplets or ice crystals were always observed to nucleate at liquid water saturation, the contact angle reflects this dependence on saturation. As the temperature decreased, water droplets or ice crystals were observed at higher supersaturations. Hence the lower limit to the contact angle increased at lower temperatures because it was constrained by liquid water saturation.

The contact angle for the deposition nucleation of an ice germ on Kaolinite and Goethite was also determined. The ice nucleating properties of Kaolinite and Goethite improved below ~252 K (i.e. ice was observed to form at lower relative humidities). Consequently, the contact angle decreased with temperature and saturation. This relationship was fitted with two equations: 

\[ \begin{align*}
\theta_{\text{Kaolinite}} &= -230.9 + 1.0T \\
\theta_{\text{Goethite}} &= -276.7 + 1.2T
\end{align*} \]

for temperatures between ~240 to 250 K.

### 6.4 Atmospheric implications

For soot, the upper limit of 0.1cm\textsuperscript{-2} sec\textsuperscript{-1} was used to determine the number density of ice formed at 124% RH\textsubscript{i}. By applying elemental carbon mass densities representative of specific scenarios, it was determined that the number density of ice particles formed as a result of \( J_{\text{het}}^{\text{sp}} \) was significantly less than the number of IN observed in field studies [Meyers et al., 1992]. This lead to the conclusion that soot alone cannot account for the presence of the ice-phase in lower tropospheric clouds, below water saturation, and above ~243 K.

Kaolinite and Goethite exhibited strong ice nucleating properties at temperatures below ~252 K. Since the current experimental setup was only sensitive to a narrow range of \( J_{\text{het}} \) values, heterogeneous nucleation theory was used to predict \( J_{\text{het}} \) at higher or lower supersaturations by assuming the contact angle is independent of saturation. The relationship between \( J_{\text{het}} \) and saturation was used to determine the number density of ice particles formed at conditions typical to the lower troposphere. If the mineral dust mass density is 1 µg m\textsuperscript{-3}, the number density of ice particles formed as a result of \( J_{\text{het}} \) is significantly larger than the number of IN observed in field studies [Meyers et al., 1992]. This lead to the following conclusion: Kaolinite and Goethite may
play an important role in formation of the ice-phase in lower tropospheric clouds, below water saturation, and below \( \sim 252 \) K.

Figure 6.2  Contact angle as a function of temperature for \( RH_i \) ramp experiments with soot, Kaolinite, Goethite, and constant \( RH_i \) experiment with soot. Solid symbols correspond to experiments in which ice crystals were observed to nucleate first; open symbols correspond to experiments in which water droplets condensed first.


References, 88


References, 89


