

DISSERTATION

THE IMPACT OF NATURAL DUST AEROSOL ON
WARM AND COLD CLOUD FORMATION

Submitted by

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In partial fulfillment of the requirements

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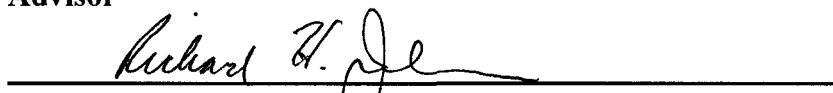
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ABSTRACT OF DISSERTATION
THE IMPACT OF NATURAL DUST AEROSOL ON WARM AND COLD
CLOUD FORMATION

Dust particles' ability to scatter and absorb radiation and their potential to interact with water vapor may lead to important direct and indirect radiative impacts on the climate. Due to differences in solubility, hygroscopicity, chemical and surface properties, dust particles from different regions may interact with cloud development in a variety of ways that are not fully understood. In this work four types of dust from the Southwestern U.S. and Northern Africa were studied. The characteristics of the samples used cover a range of soluble contents, geographic locations of origin, and collection methods. In most experiments, particles were resuspended from bulk samples by two different generation methods and size selected prior to sampling, yielding a quasi-monodisperse particle stream, generally with mean diameters between 100-400 nm. The two generation methods, suspension in water prior to reaerosolization and using a fluidized bed to aerosolize a dry sample, represent the most common ways that aerosols are generated for laboratory experiments. This study is one of very few that used more than one generation method for the same sample. Dust interactions with water vapor were found to vary dramatically by generation type. Further, the isolation of the effects of particle size that was achieved in these studies provided another level of information that is rarely available in ice nucleation experiments.

Hygroscopic growth of the particles was determined using a humidified tandem differential mobility analyzer (HTDMA) at relative humidities (RH) from 5-95% and

cloud condensation nuclei (CCN) activity was measured using a continuous flow CCN counter at supersaturations up to 2%, both at a temperature of $\sim 30^{\circ}\text{C}$. At cold temperatures ($-60 < T < -20^{\circ}\text{C}$), the ice nucleation behavior was examined using the Colorado State University continuous flow diffusion chamber (CFDC) for RH values from ice saturation to significantly above water saturation. Generating aerosol from a water suspension appeared to significantly alter the surface properties of the dust aerosol, increasing its hygroscopicity but decreasing its activity as an ice nucleus (IN), that is, shifting conditions required for ice initiation to colder temperatures and/or higher humidities as compared to the dry-generated aerosol. Dry generation is expected to produce aerosol most similar to particles in the atmosphere. While most dry-generated samples showed no hygroscopic growth at $\text{RH} < 95\%$, the particles did serve as CCN at lower supersaturations than are predicted for insoluble, wettable particles. Ice formation behavior of the dry-generated dust showed little dependence on temperature between -60 and -40°C , nucleating ice on 1% of particles at a similar relative humidity with respect to ice for any temperature, but with a strong dependence on particle size and sample type. Initiation of the ice phase by dry-generated particles occurred at RH values substantially lower than required for homogeneous freezing of aqueous solution particles; however, none of the samples supported ice formation at temperatures warmer than $\sim -30^{\circ}\text{C}$, for the sizes examined.

The particles which initiated the ice phase at the lowest RH conditions appear to be those with the smallest contents of soluble material. This interpretation of the data was substantiated by coating the most IN active dust sample with secondary organic compounds, which resulted in an increase in RH required for ice phase initiation.

Therefore, the impact of the dust on cold cloud formation may depend on the way freshly emitted dust ages in the atmosphere. Processes in which a dust plume mixes with hygroscopic material, such as from an anthropogenically polluted air mass or air masses over large forests which contain hygroscopic secondary organic aerosol, may lead to coagulation with dust thereby reducing its ice nucleation activity.

The collected ice nucleation data were used to develop a new parameterization of heterogeneous freezing for use in cloud-resolving models as a function of temperature, RH, and particle surface area. This study has shown that the temperature and RH conditions required for ice nucleation vary considerably with dust type; therefore, the types of measurements reported here are crucial for realistic simulations of mineral dust aerosol influences on clouds.

The data suggest that atmospheric dust particles have potential effects on both warm and cold cloud formation. Even the limited CCN activity determined for some samples could be relevant to cloud drop formation in the atmosphere, because dust aerosols generally have relatively large number concentrations of particles with diameters larger than 400 nm. Thus, the potential for dust particles to serve as large and giant CCN must be considered in determining the role of dust in warm cloud formation and microphysical properties. In cold clouds, even small number concentrations of heterogeneous IN can strongly impact the phase of the cloud above -30 °C, and below -30 °C, the presence of heterogeneous IN in sufficient number concentrations can influence formation and properties of cirrus in the upper troposphere. The parameterizations proposed in this work can be used to tie CCN and IN concentrations to measured

atmospheric dust number concentrations and size distributions, and thus to better-represent dust aerosol indirect effects on climate.

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Notation Index

A	Particle surface area
a_g	Radius of ice germ
$a_{o,i}$	Ice crystallographic lattice parameter
$a_{o,i}'$	Strained ice crystallographic lattice parameter
$a_{o,n}$	Substrate crystallographic lattice parameter
a_w	Water activity of solution
a_w^i	Water activity of solution in equilibrium with ice
C_c	Cunningham correction factor
$c_{i,s}$	Concentration of single water molecules adsorbed on the particle surface
$CCNfrac$	Fraction of particles activating as CCN
CVF	Core volume fraction
D_{dry}	Dry particle diameter
D_{wet}	Wet particle diameter
e	Water vapor pressure
$f_{het}(m,x)$	Function describing how a surface lowers the energy barrier for freezing.
F_i	Fraction of particles nucleating ice crystals
g	Number of water molecules in ice germ
GF	Hygroscopic growth factor
h	Plank's constant
J_{haze}	Homogeneous nucleation rate of haze droplets
J_{het}	Heterogeneous nucleation rate
J_{hom}	Homogeneous nucleation rate
J_{mix}	Nucleation rate of a mixed particle
J_w	Homogeneous nucleation rate of pure water droplets
k	Boltzmann's constant
K	Classical heterogeneous freezing theory kinetic factor
m	Compatibility factor ($\cos \alpha$)
$m_{i,v}$	Compatibility factor for deposition nucleation
m_{oi}	Ice crystal mass
$\dot{m}_w$	Mass of a water molecule
M_w	Molecular weight of water
N	Avogadro's Number
$N_{a,cont}/N_{a,imm}$	Contact/immersion ice nuclei number concentration from Lohmann and Diehl (2006)
N_{wc}	Number of water monomers in contact with an ice surface
N_c	Number concentration of cloud drops
N_i	Number concentration of ice crystals
N_{IN}	Number concentration of IN
N_u	Number concentration of unfrozen droplets
q_l	Cloud liquid water mass mixing ratio
R	Universal gas constant
RH_i	Relative humidity with respect to ice
RH_w	Relative humidity with respect to water
r_l	Mean volume droplet radius

r_m	Aerosol mode radius
r_N	Substrate radius
$S_{cr}^{hom} / S_{cr}^{het}$	Homogeneous/heterogeneous ice saturation freezing threshold
S_i	Ice saturation ratio
T	Temperature
T^*	Effective freezing temperature as described in Sassen and Dodd (1988)
T_m	Median freezing temperature from Diehl and Wurzler (2004)
T_o	273.15 K
T_{sup}	Supercooling temperature ($T_{sup}=273.15\text{ K}-T$)
V	Molar volume of water in the ice phase
V_d	Droplet volume
X_k	Factors controlling heterogeneous freezing in Kärcher and Lohmann (2003)
x	Fractional distance from cold wall in CFDC calculations
z	Height
Z_p	Particle electric mobility
Z_s	Zeldovich factor
α	Contact angle
δ	Misfit between ice and substrate surface
Δa_w	Water activity shift described by Koop et al. (2000)
ΔF_g	Work of ice germ formation
$\Delta F_{g,s}$	Work of ice germ formation on a surface
Δg	Gibb's free energy of activation for diffusion of water molecules across the water-ice boundary
ΔG_{des}	Energy of desorption per molecule
Δt	Time interval
ε	Elastic strain
η	Air viscosity
κ	Hygroscopicity parameter as in Petters and Kreidenweis (2007)
λ	Parameter relating freezing and melting point depressions
μ	Gas viscosity
ν_s	Frequency of vibration of an adsorbed molecule normal to the surface
ρ	Density of air
ρ_i	Density of ice
ρ_s	Density of solution
ρ_w	Density of water
$\sigma_{i,a}$	Surface tension of ice/air interface
$\sigma_{i,w}$	Surface tension of ice/water interface
$\sigma_{N,a}$	Surface tension of substrate/air interface
$\sigma_{N,i}$	Surface tension of substrate/ice interface
χ	Particle shape factor

1. Introduction

1.1. Motivation

Dust aerosols represent a dominant source of particulate matter (by mass) to the atmosphere, and emissions from some source regions have been shown to be transported on regional and hemispherical scales (Engelstaedter et al., 2006; Goudie and Middleton, 2001; Tegen and Fung, 1994). Dust particles may get lofted into the upper atmosphere after dust storms. Due to their ability to scatter and absorb solar and terrestrial radiation, and their potential to interact with water vapor in the atmosphere, these particles can have an important radiative impact on the climate system both directly and indirectly. The Intergovernmental Panel on Climate Change (IPCC) in their report from 2001 (IPCC, 2001, Figure 1.1) included dust as an important parameter in determining the future climate, but the confidence in the current knowledge was so low, only an error bar for expected dust forcing was given, with no indication of the sign of the forcing. The figure indicates dust forcing could be as large in magnitude as the sulfate aerosol forcing, but in either direction (warming or cooling) and is only due to the direct radiative effect, not accounting for possible influences on cloud development. Further, dust from various regions in the world can have very different solubilities, chemical and surface properties, and thus can interact with warm and cold clouds in a variety of ways that are not yet fully understood. This interaction can change the lifetimes of dust aerosols in the atmosphere,

which greatly impacts the direct radiative forcing. Modeling and satellite studies are divergent on the magnitude of this forcing (Balkanski et al., 2007). Additionally, the sizes of arid regions around the globe are increasing by millions of hectares per year due to changes in precipitation and anthropogenic disturbances (Sheehy, 1992), so the role of dust in atmospheric processes may amplify in the future.

Dust particles have been suggested to play a role in warm and mixed phase clouds and in precipitation formation. Determining the ability of dust aerosols to serve as cloud condensation nuclei (CCN) is important in predicting the impact dust will have on clouds in a changing climate. The IPCC Fourth Assessment concluded that the level of scientific understanding of the indirect effects of aerosols on cloud processes is still very low (IPCC, 2007). Particles active as CCN at atmospherically-relevant supersaturations generally contain some hygroscopic, soluble material which grows by water absorption and activate as cloud droplets at relative humidity (RH) slightly above water saturation. Dust particles, containing primarily insoluble material, are generally expected to be poor CCN unless soluble material (e.g. sulfates, nitrates) has deposited on their surface creating mixed particles (Yin et al., 2002). Yet it is often overlooked that large particles, even if insoluble, have the ability to act as giant CCN (GCCN) even without a significant fraction of soluble material at atmospherically-relevant supersaturations (Seinfeld and Pandis, 1998). Laboratory studies have also found that dust and clay particles from arid regions are efficient at initiating ice formation by serving as heterogeneous ice nuclei (IN) at relatively warm and dry conditions (Archuleta et al., 2005; Möhler et al., 2006; Salam et al., 2006) as compared to homogeneous freezing of the background aerosol. The ability of these dust particles to serve as GCCN and IN in the atmosphere may

initiate precipitation formation by broadening the droplet spectrum and enhancing collision-coalescence processes earlier in a cloud cycle (Van den Heever et al., 2005). On the other hand, if dust particles increase CCN concentrations, this can produce a large number of small cloud droplets, diminishing the precipitation formation within a cloud and increasing the albedo of the cloud (Rosenfeld et al., 2001). Thus the impact of dust on a cloud droplet distribution may depend on the background aerosol population as well as the dynamic properties of the system.

Measuring the conditions for which dust initiates ice formation is especially important for global modeling. Accurate representations of cirrus onset conditions and ice cloud microphysical properties are crucial, since these clouds cover about 20% of the earth at any time (Liou, 1986). At temperatures colder than $\sim -38^{\circ}\text{C}$, particles that contain only hygroscopic material on their surface may absorb water as the relative humidity increases and subsequently freeze through the homogeneous freezing mechanism as the drop becomes dilute. In contrast, IN provide a surface for heterogeneous nucleation and contain active sites for nucleation and their activity depends on size, temperature, and relative humidity (Pruppacher and Klett, 1997). IN can induce glaciation in clouds at temperatures warmer than those required for homogeneous nucleation. These particles initiate the ice phase at temperatures below freezing via one or more mechanisms, for example, when vapor deposits as ice directly on their surface by deposition nucleation or as they take up water and activate to liquid droplets with the insoluble material subsequently initiating freezing through condensation or immersion freezing. Dust, uncoated or with various types of coatings, can contribute to each of these freezing types under certain circumstances.

1.2. Review of previous laboratory investigations

As early as 1959, it was suggested that mineral dust aerosol has the potential to heterogeneously nucleate the ice phase in the atmosphere (Isono et al., 1959). Roberts and Hallett (1968), using a microscope cold stage with controlled humidity environment, examined the ice nucleation ability of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), montmorillonite $[(\text{Na},\text{Ca})(\text{Al}, \text{Mg})_6(\text{Si}_4\text{O}_{10})_3(\text{OH})_6 \cdot n\text{H}_2\text{O}]$, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcite (CaCO_3), vaterite (CaCO_3 polymorph), albite ($\text{NaAlSi}_3\text{O}_8$), and biotite ($\text{K}(\text{Mg}, \text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{F}, \text{OH})_2$) particles with diameters between 0.5 and 3 μm . Threshold temperatures, the warmest temperature at which 1 in 10^4 particles could initiate the ice phase, were found to range from -10.5 to -26 °C. If the studies were repeated using the same particles, preactivation of the particles caused them to freeze more easily and the threshold temperatures then ranged from -4 to -12 °C. Work by Roberts and Hallett (1968) and Edwards and Evans (1971) suggested that after freezing, patches of ordered, ice-like layers of water molecules were retained on the IN and could serve as an active site upon refreezing. Schaller and Fukuta (1979) used a wedge-shaped ice thermal diffusion chamber to examine heterogeneous freezing of several smoke products as well as kaolinite and “local soil” taken from the campus of the University of Denver. Reasonable agreement with Roberts and Hallett (1968) was found for kaolinite and their “local soil” sample was found to require lower ice supersaturations for nucleation but had a colder threshold temperature than kaolinite. Beginning in the late 1970’s, ice nucleation studies focused predominantly on silver iodide and similar species for their potential in “weather modification” (e.g. Detwiler and Vonnegut, 1981). However, in the

last decade there has been a renewed interest in the potential for dust particles to serve as IN in the atmosphere.

The continuous flow diffusion chamber (CFDC, Rogers, 1988) is a unique way to examine mineral dust particles' ability to nucleate ice, as the temperature and RH can be precisely controlled and the particles are suspended in an air flow and thus are not subject to potential influence from substrates. This system has been used extensively to examine freezing of sulfates (Chen et al., 2000), organic species (Prenni et al., 2001) and natural aerosol during aircraft missions (e.g. DeMott et al., 2003b). Archuleta et al. (2005) examined the heterogeneous freezing of mineral dust surrogates (aluminum oxide, aluminosilicate and iron oxide) as well as a natural sample collected from the Tengger desert in China. In that work, particles were generated via atomization of aqueous solutions or suspensions, so changes to particle chemical and physical properties after suspension in water may have occurred. Archuleta et al. (2005) found for the mineral dust surrogates that there was a clear size dependence in the required onset relative humidity with respect to ice (RH_i) for ice nucleation at a fixed temperature, with the largest particles ($\sim 0.2 \mu\text{m}$) nucleating ice at RH_i as low as $\sim 135\%$ and smaller particles requiring higher RH_i . The onset RH_i was observed to vary with temperature depending on the mineral type, with aluminum oxide and aluminosilicate requiring higher RH_i with increasing temperature and iron oxide requiring lower RH_i with increasing temperature over the range $-60 \leq T \leq -45^\circ\text{C}$. When the particles were "coated" with H_2SO_4 , the onset RH_i increased, decreased or remained unchanged, depending on the mineral surrogate used. The natural dust sample from China was found to nucleate ice for larger sizes at the lowest RH_i values, with $0.2 \mu\text{m}$ particles acting as IN at $\sim 135\%$ RH_i ,

independent of temperature ($-60 \leq T \leq -45^\circ\text{C}$). However, $0.05\ \mu\text{m}$ particles required water saturation before freezing in this temperature range, while the mineral dust surrogates often froze at subsaturated conditions, particularly at the coldest temperatures.

Heterogeneous nucleation rates (J_{het}) for the metal oxide particles were calculated by Archuleta et al. (2005) using the assumption that heterogeneous nucleation is dependent on particle surface area using:

$$F_i = 1 - \exp(-J_{het} A \Delta t) \quad (1.1)$$

where F_i is the fraction of particles nucleating as ice crystals (0.01 in that study), A is the surface area of the particle, assuming the particles were spherical with diameter equivalent to the mobility diameter selected in a differential mobility analyzer (DMA) (see Section 2.2.1). For “coated” particles, an increased size was calculated assuming equilibrium water uptake of the H_2SO_4 coating, and Δt is the time the particles were exposed to saturated conditions in the CFDC chamber ($\sim 10\ \text{s}$). However, this is really a lower limit of the nucleation rate as the particles did not necessarily nucleate right before being detected, likely nucleating several seconds beforehand; unfortunately there is no way to determine the time at which nucleation occurred. Instantaneous nucleation rates for the “coated” mineral dust surrogates depended on size and were between 10^4 and $10^7\ \text{cm}^{-2}\ \text{s}^{-1}$, but assumed stochastic.

More recently, a large cloud chamber facility (Aerosol Interactions and Dynamics in the Atmosphere, AIDA) has been built in Karlsruhe, Germany and several publications have been devoted to examining heterogeneous nucleation of known particle types in this facility. Field et al. (2006) examined samples of Asian and Saharan dust over the temperature range $-53 \leq T \leq -21^\circ\text{C}$. Those authors used a distribution of particle sizes

between 0.1 and 2 μm with a number mode diameter between 0.3 and 0.5 μm . They found that Asian and Saharan dust could nucleate ice as low as 103% RH_i and typically between 110-130% RH_i . Mangold et al. (2005) used the same chamber to examine a distribution of commercially available Arizona Test dust (0.1-1.5 μm , count median diameter $\sim 0.5 \mu\text{m}$) and found that supersaturations with respect to ice of just several percent were sufficient to nucleate ice crystals. Möhler et al. (2006) extended the analysis of the Saharan, Asian and Arizona Test dust samples and found similarly low ice supersaturations required for ice nucleation. Those authors calculated nucleation rates from the ratio of the measured ice formation rate and the aerosol surface area concentration. The calculated nucleation rates were roughly consistent with the nucleation rates found by Archuleta et al. (2005), between $10^5 - 10^7 \text{ cm}^{-2} \text{ s}^{-1}$, but noted that nucleation rates appeared to depend only on ice saturation not on time.

Recently, a new CFDC was built at Dalhousie University, Canada and Salam et al. (2006) used it to examine kaolinite and montmorillonite mineral dust surrogate particles (diameter $< 5 \mu\text{m}$). Montmorillonite nucleated ice between 110-115% RH_i , while kaolinite required ice supersaturations between 115-125% RH_i , very similar to the required supersaturations found by Roberts and Hallett (1968) over the same temperature range. They also examined the threshold temperatures and found montmorillonite required $T = -15^\circ\text{C}$ and kaolinite required $T = -22^\circ\text{C}$ and that the fraction of particles nucleated increased with decreasing temperature at water saturated conditions.

Other studies have focused on the ability of mineral dust surrogate aerosol with soluble coatings to nucleate ice. Hung et al. (2003) studied hematite and corundum cores surrounded by ammonium sulfate in an aerosol flow tube infrared spectrometer and found

that the freezing temperature increased, as compared to pure ammonium sulfate droplets, for droplets with inclusions and with increasing mole fraction of ammonium sulfate. The dependence of freezing on core size was not clear. Zuberi et al. (2002) similarly found that inclusions of the minerals kaolinite and montmorillonite increased the freezing temperature in large ammonium sulfate solution droplets (10-55 μm) and that this increase in freezing temperature in comparison to pure solution droplet homogeneous freezing was greater for more concentrated solution droplets. They found nucleation to occur between 135-150 % RH_i for $-78 \leq T \leq -33^\circ\text{C}$, with no significant difference between the two mineral types used, or if the solution droplet was composed of ammonium sulfate or sodium chloride.

Given the previous work presented above, clearly the low supersaturations with respect to ice and relatively warm temperatures required for heterogeneous ice nucleation by mineral dust aerosol, as well as the differences observed between mineral types, warrant further study of the ice nucleating behavior of pristine mineral dust as a function of temperature and size. These results will find application in constraining the ice nucleation behavior in the atmosphere. Kärcher and Lohmann (2003) postulated that condensation or immersion freezing was likely the dominant pathway for heterogeneous freezing in cirrus, as they believed that insoluble particles were unlikely to reach the upper troposphere without being coated by soluble material. DeMott et al. (2003a), however, determined the composition of residual ice nuclei particles that were measured in a CFDC from free troposphere air sampled at Storm Peak Laboratories, located on Mt. Werner (3200 m above mean sea level) in Colorado. They found that while mineral dust particles comprised only $\sim 1\%$ of the total submicron particles they represented 33% of

the heterogeneously nucleated ice crystals, and 25% of these IN-active mineral particles contained measurable sulfate or organic coatings. Laboratory studies which measured the heterogeneous reactions of gaseous SO₂ and NO_x with mineral dust have found that modestly soluble species were formed on the surface of the particles (Laskin et al., 2005; Usher et al., 2003). Secondary organic aerosol precursor gases are also present in the atmosphere which may form low volatility products which can deposit on the surface of dust aerosol. Dust particles may also become mixed with soluble material through collisions with soluble particles in the atmosphere or due to cloud cycles in which previously externally mixed aerosols will activate, then form larger cloud drops through collisional growth; upon evaporation, an internally mixed aerosol will be resuspended (Twohy and Poellot, 2005). Kelly et al. (2007) found that accounting for very small mass fractions of even modestly soluble species can increase the modeled ability of a particle to serve as a CCN. The impact of soluble coatings on the ability of dust particles to serve as IN is less clear given the results of Archuleta et al. (2005) for sulfate coated mineral surrogates. Thus it is also necessary to study mixed particle types in the laboratory, and in particular, to simulate the coatings that these particles may receive in the atmosphere, and to measure the interactions of these mixed particles with water vapor.

1.3. Challenges in modeling heterogeneous ice nucleation

At cirrus temperatures (-30 to -80°C), initiation of the ice phase is believed to occur either through the homogeneous freezing of haze particles, or through the action of IN which can promote heterogeneous nucleation by serving as catalysts to freezing. Koop et al. (2000) developed a parameterization for homogeneous freezing of aqueous solution droplets that depends only on the water activity of the solution:

$$\Delta a_w = a_w(c, T) - a_w^i(T), \quad (1.2)$$

where Δa_w represents an offset from the water activity in equilibrium with the ice line; $a_w(c, T)$ is the composition and temperature dependent solution water activity and $a_w^i(T, 0)$ is the water activity in a solution in equilibrium with ice, which has a temperature dependence given in Koop et al. (2000, details in Section 3.1.2). This parameterization has been implemented in many models (e.g. Kärcher and Lohmann, 2002) and provides a simple way to compute homogeneous nucleation rates, which are expressed by Koop et al. (2000) as solely a function of Δa_w . In contrast, parameterizing heterogeneous nucleation has faced many challenges in large scale models due to the lack of understanding of the factors controlling heterogeneous nucleation and lack of experimental data (Kärcher and Lohmann, 2003). The classical theory for heterogeneous nucleation will be presented in Chapter 3, along with problems in its use. For example, application of classical heterogeneous theory relies on the choice of values for many constants, such as the lattice parameter, which are unknown for most species in the atmosphere. The problem is complicated further for natural dusts which are a likely a mixture of mineralogy, each with different properties.

Many current models use a heterogeneous parameterization developed by Meyers et al. (1992). It was developed to correct the overestimation of ice crystal concentrations when the relationship proposed by Fletcher (1962), for which ice crystal concentrations depended only on temperature, was applied. Meyers et al. (1992) proposed:

$$N_i = \exp[a + (b * 100(S_i - 1))], \quad (1.3)$$

where N_i is the number of pristine ice crystals, S_i is the fractional ice saturation. The parameterization is based on data from -7 to -20°C and for ice supersaturations from 2-

25%, but has often been used outside this range. Proposed values of the constants a , and b were provided in the text. This formulation was intended to capture the effects of both deposition and condensation freezing; contact nucleation was treated separately. Later studies proposed different parameterizations (DeMott et al., 1998; Diehl and Wurzler, 2004; Lohmann and Diehl, 2006; Spice et al., 1999; Van den Heever et al., 2006) and will be discussed in Chapter 3.

None of the current parameterizations claim superiority over any other due fundamentally to a lack of information on freezing behavior and a limited set of experimental data against which to test the formulations. Further, the current parameterizations do not account for particle size when calculating the fraction of dust particles freezing, although some studies suggest that size is important (e.g. Archuleta et al., 2005). In some parameterizations the maximum number of IN is not even restricted by the concentration of available particles in the atmosphere; most are not linked to aerosol properties at all. Except in dust plumes, in which high concentrations of dust are expected, dust only has the potential to impact ice crystal concentrations and mean size if ice formation is initiated at significantly lower S_i or at temperatures significantly warmer than the conditions in which homogeneous nucleation occurs, as there are always large numbers of haze particles present. To accurately capture the impact of dust on freezing, it is necessary that parameterizations initiate ice formation at realistic temperature and supersaturation conditions, as a function of particle size. This work will provide more size-resolved experimental data, over a wide range of temperature conditions to help develop improved models for aerosol-cold cloud interactions.

1.4. Impact on atmospheric clouds and precipitation formation

There has been growing evidence that dust from arid regions around the world, particularly from the Sahel and the Asian desert regions, can have a significant influence on the microphysics of warm and cold cloud formation (DeMott et al., 2003b; Mahowald and Kiehl, 2003; Sassen, 2002). The concentrations of IN and CCN in the atmosphere will alter the concentrations and size distributions of hydrometeors and thus the radiative properties of the cloud, which are strongly dependent on these properties. Lohmann and Diehl (2006), using their parameterization of heterogeneous ice nucleation, found that dust can have a significant impact on the liquid water path, cloud lifetime, precipitation rate and top of the atmosphere radiation. Further, they found significant differences in these properties if the dust was assumed to be composed of kaolinite or montmorillonite, two common mineral types found in atmospheric dust. Kelly et al. (2007) examined how conversion of insoluble dust material to slightly soluble components through reaction on the mineral surface with SO_2 or HNO_3 gases, or the addition of highly soluble species such as sulfate, can influence cloud droplet formation. Their simulations found that even for small fractions of slightly soluble species, the critical saturation ratio could be considerably reduced and for conditions of slow or fast updraft velocity the total droplet number concentration would either decrease or increase, respectively. Kelly et al. (2007) therefore concluded that global aerosol models could be improved if dust composition, particularly the carbonate content which is particularly reactive, was included in aerosol descriptions.

Some studies have found that under some conditions dust can enhance precipitation formation (Levin et al., 1996; Yin et al., 2002), while others find that it

suppresses it (Rosenfeld et al., 2001). Therefore the hygroscopicity, cloud condensation nuclei (CCN) activity, and ice nucleation ability of different dust types must be determined experimentally to aid in predicting the role this aerosol has on cloud droplet growth. There are three main mechanisms by which dust can affect precipitation efficiency: dust may decrease the precipitation efficiency if it contributes to an increase in CCN or IN concentrations because more, smaller drops have reduced coalescence efficiency (Albrecht, 1989; Van den Heever et al., 2006); large dust particles may act as giant CCN (GCCN) which are generally predicted to increase precipitation formation due to an increased coalescence efficiency (Feingold et al., 1999; Johnson, 1982; Rudich et al., 2002); or if dust particles contribute to an increase in IN concentrations, the formation of ice particles in a warm cloud can enhance precipitation because crystals grow faster than raindrops and broaden the hydrometeor size distribution (Lohmann, 2002). The role of GCCN in the atmosphere is further confused by inconsistencies in size definitions between different studies (e.g. Feingold et al., 1999; Levin et al., 1996). Levin et al. (1996) note that the dust particles themselves are not expected to be efficient CCN, but found that sulfate was present on most atmospheric particles in the Mediterranean region. He proposed that the sulfate particles were activated as CCN and then collected dust particles via in-cloud scavenging processes creating mixed dust/salt particles, which were subsequently able to serve as GCCN. Yin et al. (2002) further stated that these dust particles may go through several cycles of cloud development and evaporation and that in each cloud cycle, more sulfate would be deposited on the dust particles until they grew to the size of GCCN. These GCCN accelerated the precipitation process in their model by initially broadening the droplet spectrum and increasing the coalescence efficiency.

Pristine dust particles were not permitted to serve as GCCN or IN in the Yin et al. (2002) model simulations.

Conversely, Rosenfeld et al. (2001) found from satellite measurements that dust decreased the precipitation efficiency over the same region (Eastern Mediterranean) by enhancing CCN concentrations and suppressing droplet coalescence. This is consistent with the findings of Mahowald and Kiehl (2003) who examined correlations between dust amount, measured by the Total Ozone Mapping Spectrometer (TOMS) aerosol index and in situ at a ground station in Barbados, and cloud fraction from the International Satellite Cloud Climatology Project (ISCCP) over 16 years. Positive correlations were found in the region off the coast of North Africa, suggesting that the dust particles are indeed serving as CCN, decreasing collision-coalescence processes and thus increasing cloud lifetimes and likely reducing precipitation formation. However, Rosenfeld et al. (2001) indicate that the decrease in precipitation efficiency they observed was in comparison to conditions of relatively clean maritime clouds, whereas Levin et al. (1996) compared to already polluted clouds which contained high concentrations of sulfate aerosol from Europe and thus found that dust enhanced precipitation efficiency.

Van den Heever et al. (2005) investigated the effect of changing CCN, GCCN, and IN concentrations from relatively clean conditions to dusty conditions using measurements from the CRYSTAL-FACE field campaign. They independently and simultaneously increased the concentration of each type of aerosol to see the impact on the convective system observed on 28 July 2002, a day heavily influenced by Saharan dust over the Florida peninsula. The modeling allowed determination of the relative effect each aerosol type imparted on the convection. Important changes in updraft

velocity, cloud liquid water content, accumulated precipitation and hail were noted by those authors for changes in concentration of each aerosol type. Updrafts were increased due to the greater amounts of latent heat released when condensation (both liquid and ice) forms on an increased number of aerosol particles. Including all aerosol types, particles had a positive feedback on convection; increased updraft velocity yielded higher liquid water contents, which quickly transferred higher in the cloud and froze, releasing latent heat, which in turn further increased updraft velocity. Van den Heever and colleagues noted that in addition to increased updraft velocities, there was an increased area of convection. This was also seen by Stephens et al. (2004), who found an increased occurrence of deep convection when dust was added to their two-dimensional model, and also by Teller and Levin (2006) in another two-dimensional simulation. Thus, there is substantial evidence from modeling studies that microphysical processes affect the dynamics of convective clouds.

Although Van den Heever et al. (2005) found more liquid water was produced under the dusty conditions, precipitation processes were suppressed as compared to the “clean” case and there was a reduction in total precipitation reaching the ground. They found this to be true even if only the GCCN concentrations were increased. In contrast, Teller and Levin (2006) found that enhancement in GCCN decreased precipitation in clean clouds (CCN concentration $< 600 \text{ cm}^{-3}$) but increased the total precipitation for polluted clouds, and that enhancement of IN concentrations reduced total precipitation in all but the most polluted cases. The reduced precipitation efficiency due to increased IN concentrations resulted in transport of water vapor from lower levels to the mid troposphere. The enhancement in precipitation from increased GCCN concentrations

was found to be due to increased graupel production within the clouds, while the IN decreased the graupel content within the modeled clouds by creating small pristine ice crystals. Rosenfeld et al. (2002) noted that precipitation in polluted clouds could be initiated more easily in the presence of GCCN, but did not comment on the amount of precipitation produced compared to a cleaner cloud. A positive climate feedback may exist, in which larger dust concentrations reduce total precipitation, increasing the extent of desert source areas and further decreasing total precipitation.

In cirrus clouds forming *in situ* at high altitudes, a small concentration of IN that activate at modest ice supersaturations can have a large impact on cloud particle size distributions (DeMott et al., 1997a). If a small fraction of the dust particles can nucleate ice at RH_i below the homogeneous freezing threshold of the constituents that make up the majority of the particles (e.g. sulfates), then these few ice crystals will start to grow rapidly due to the supersaturation with respect to ice that exists in the upper troposphere. The liquid grown haze particles will start to lose water to these crystals and a distribution of very few but large ice crystals will result, particularly at low updraft conditions (Lin et al., 2002). In the absence of these active dust particles, the cloud distribution would be comprised of a large number of small crystals formed via homogeneous nucleation. These two cloud types have significantly different radiative properties and potentially different lifetimes, however, changes in cloud lifetime due to increases in IN concentrations are uncertain (DeMott et al., 2003a), so the total change in radiative forcing is not clear. Gierens (2003) found that including heterogeneous freezing of particles (not specifically from dust sources) had a stronger impact on northern hemisphere midlatitudes than anywhere else, leading to increased cirrus coverage over

the northern hemisphere. The IPCC (2001) indicated that the radiative forcing due to cirrus clouds is relatively small compared to direct and other indirect aerosol forcings, however, due to large uncertainties in freezing behaviors and in global IN concentrations, studies extrapolating the potential role of dust as a heterogeneous IN to the global scale were not found in the literature.

1.5. Objectives and Expected Significance

In this work the interaction of four different dust samples with water vapor was measured over a broad temperature range. A humidified tandem differential mobility analyzer (HTDMA) measures the water uptake of a size selected aerosol flow at 30°C and relative humidities below water saturation. The CCN counter measures the CCN activity of size selected particles, also around 30°C, at water supersaturations between 0.1-2.0%. The CFDC is utilized to investigate the freezing behavior of the particles in the temperature range $-60 < T < -15^{\circ}\text{C}$ and a broad range of controlled water and ice saturation ratios. Details on each of the instruments used in the work can be found in Chapter 2.

HTDMA data will provide information on particle soluble content and also can indicate the heterogeneity of particle hygroscopicities within a single size. CCNC measurements will provide activation information which can be used to predict warm cloud impacts of dust particles. Over this temperature range the ability of dust to initiate ice formation in cirrus and convective systems will be observed. By measuring ice formation as a function of particle size, one of the major sources of uncertainties in heterogeneous freezing modeling, according to Kärcher and Lohmann (2003), will be addressed.

Since mineral dust has been seen to represent a disproportionately large fraction of IN, even during times not affected by strong dust transport (DeMott et al., 2003a), dust samples have been obtained to provide information on freezing behavior representative of various regions around the globe. The dust samples used cover a range of solubility contents, geographic locations of origin, and collection methods. Arizona Test dust is a milled product, purchased commercially from Powder Technology, Inc. Its composition is expected to be representative of dust in the southwestern United States, but the effect of the milling process on surface properties is uncertain. Owens (dry) Lake dust was collected by the US Geological Survey at various locations around a dry lakebed (playa) in southeastern California. This dust is unlike the others in that it has a large mass fraction of soluble material, predominantly in the forms sodium carbonate and sodium sulfate. The Canary Island dust was collected near the small village of Mala on the Canary Island of Lanzarote, about a mile from the sea. Surface dust was collected on a sparsely vegetated hillside and likely contains deposited Saharan dust, beach sand, and coral. The final sample is Saharan dust, collected in Egypt, near Cairo. This sample has been processed through a wind tunnel and contains only particles smaller than $\sim 75 \mu\text{m}$. While the largest sources of dust aerosol in North Africa are the Bodélé depression in Chad and an area covering eastern Mauritania, western Mali and southern Algeria (Goudie and Middleton, 2001), samples from these locations were not available for study. It is unknown how the samples from Lanzarote and Egypt differ in composition from dust from these larger source areas. More details on each of the sample types can be found in their respective chapters.

Additionally, a limited set of data were collected examining the role of coatings on dust particles. The coatings serve to add hygroscopic material to the particles, increasing the particle size at relative humidities relevant to visibility studies and also increasing the CCN activity of the dust particles. The expected effect of the soluble coatings on freezing is harder to predict. The coatings may promote formation of a liquid layer on the surface of the dust particles which is expected to be a higher barrier to freezing (Bassett et al., 1970). This may prevent the particles from serving as deposition nuclei and force the dust to initiate freezing only in the condensation freezing, immersion freezing or homogeneous nucleation regimes.

Clearly, if general circulation models are going to be used to accurately assess the current and future climate, more work is needed to understand and simulate realistic behaviors of aerosol-cloud interactions. It is often assumed that dust is non-hygroscopic and not able to serve as a CCN at atmospherically relevant supersaturations unless soluble material is deposited on the dust surface (e.g. Yin et al., 2000), however, few experimental studies have been attempted to verify this assumption (e.g. Vlasenko et al., 2005). In cold and mixed phase clouds, freezing mechanisms are complicated, particularly for the case of heterogeneous freezing, as model descriptions must incorporate the uncertain physical and chemical processes on the surface of an IN (Kärcher and Lohmann, 2003). A goal of this work is to establish a broader set of size resolved experimental data for use in heterogeneous freezing parameterizations. Another goal of this work is to provide a set of CCN measurements which can constrain the role of dust in enhancing CCN concentrations in the atmosphere. Finally, using the data collected, a new parameterization of the heterogeneous nucleation will be developed.

This parameterization will be a function of particle diameter, temperature and relative humidity. It is hoped that this parameterization will provide a more realistic approach for modeling heterogeneous ice nucleation by dust in the atmosphere.

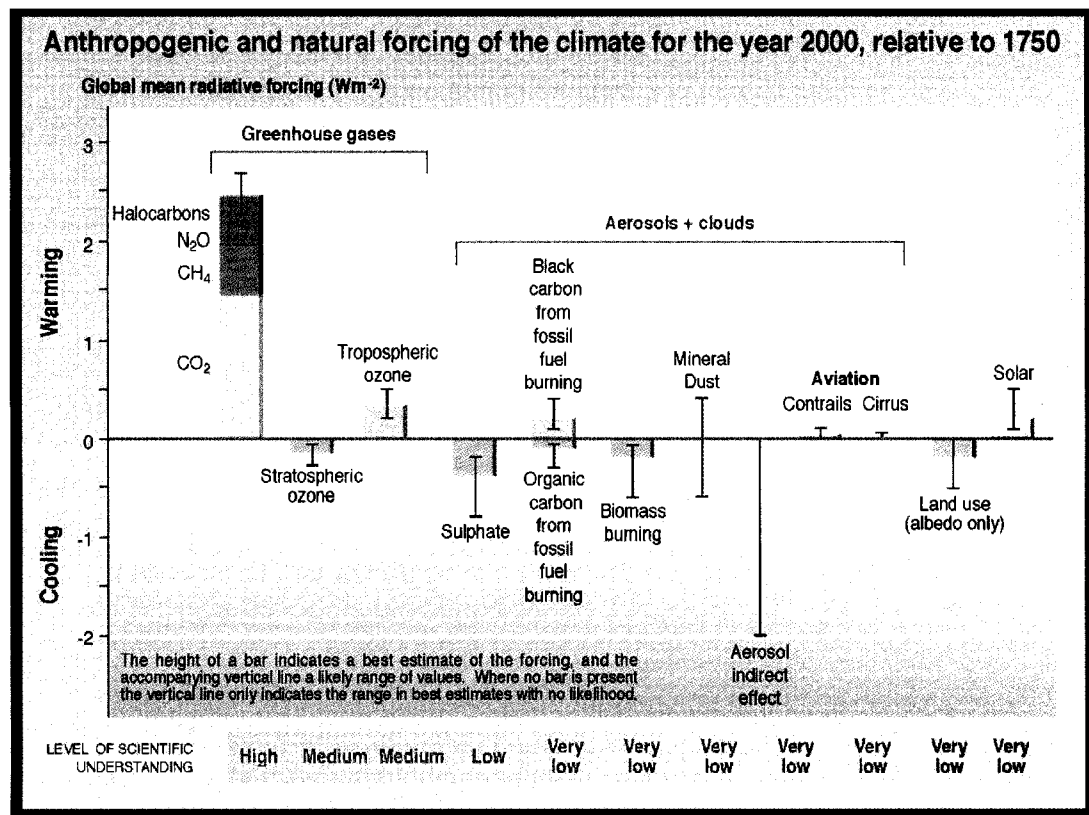


Figure 1.1: Mineral dust forcing in W m^{-2} compared to many other forcings expected to play an important role in the future climate. From the IPCC (2001).

2. Experimental

This chapter outlines the experimental apparatus used in this work. Later chapters will provide specific details of how each was used for an individual sample, but the purpose of this chapter is to demonstrate the operating principles for each system: the humidified tandem differential mobility analyzer (HTDMA), the cloud condensation nuclei counter (CCNC) and the continuous flow diffusion chamber (CFDC). Each allows measurements of the interaction of water vapor with a flowing particle stream over a specified temperature (T) range and set of relative humidity (RH) conditions, as described below.

2.1. Aerosol Generation

Due to the heterogeneous chemical composition and irregular shape of the particles studied in this work, two methods of aerosol generation were used. Typically an atomizer is used for generation of particles for single, soluble compound studies. A solution of the soluble compound is atomized, the spray is dried, and solid solute particles at large number concentrations are obtained. However, with the dust samples, there is the possibility for significant particle alteration during the suspension in water atomization processes. Therefore we also created particles by fluidized bed generation, when possible. Positive and negative aspects of each generation method are discussed below.

2.1.1. Constant Output Atomizer

A continuous, stable flow of suspended fine particulate matter, with relatively high concentrations of submicrometer particles, is generally needed for our laboratory studies of hygroscopicity, CCN activation and ice nucleation. To accomplish this, drops are usually generated from an aqueous solution. Aerosol is generated and subsequently dried to yield a submicrometer particle size distribution using a Constant Output Atomizer (TSI Model 3076, Figure 2.1). Material of interest is suspended in high purity water in an atomizer bottle at concentrations, generally, of one weight percent or less. Dry, filtered air is sent through a small orifice forming a high velocity jet. Liquid is supplied from the bottle to the atomizing area through the solution inlet by capillary action. The air jet impinging on the liquid produces a polydisperse droplet population. Large droplets will impact on the back wall of the atomizer and drip back into the solution bottle through the excess liquid outlet. Smaller droplets are carried out of the atomizer through the aerosol outlet with the dry air stream. The aerosol flow is then sent through diffusion dryers and diluted with dry air to remove any remaining water on the aerosol.

Atomization is straightforward to use and aerosol number concentrations can be easily controlled. The technique creates high number concentrations of sub-micron particles, with number concentrations generally dropping off sharply above ~200 nm. The potential to change the properties and mixing characteristics of insoluble particles is a significant concern in this work, as will be discussed further in subsequent chapters. Any soluble material present in the bulk sample from which the suspension is created will dissolve, then be redistributed among the insoluble cores during atomization. The final

dried particles may be unrepresentative of the particles present in the atmosphere. Bilde and Svenningsson (2004) found large differences in CCN activity using different levels of water purification in atomization systems. We determined the CCN activity of Arizona Test dust particles when the atomizer was run with pure nitrogen and with the laboratory air. Particles were observed to be significantly more CCN active if the particles were generated with lab air, which likely contains some soluble gases that may partition to the solution surrounding the particle and remain on the particle surface after drying. All experiments in this work were run with the laboratory air system. It is unclear how or if the water used in the atomizer solutions may have contributed soluble material to the atomized particles. Further, it is unclear if dispersing the insoluble particles in water affects their shape or surface characteristics.

2.1.2. Fluidized Bed

The fluidized bed used in this work was described by Prenni et al. (2000). A schematic is shown in Figure 2.2. Aerosol material of interest (typically 1-10g) is mixed with bronze beads ($D = 40 \mu\text{m}$) in the cylindrical bed, the bottom of which has a stack of filters. Air flows one way through a three way solenoid valve (Burkert 49Z8) and is supplied continuously through the bed, creating a pressure drop as it flows through the filters. At high enough flow rates (approximately greater than 4 lpm) the mixture fluidizes, allowing small dust particles to be suspended and carried out of the bed with the air flow. Higher flow rates increase the output number concentrations of particles and a flow rate of ~ 10 lpm is typically used. The bronze beads help deagglomerate the dust particles, but are too heavy to escape and fall back into the bed. Dry air pulses from the third direction providing a random pulse of new particles and bronze beads into the bed

from the reservoir. This helps keep particle concentrations more constant. Particles generated in the fluidized bed are often highly charged so the particles are charge-neutralized with Krypton and/or Polonium radiation sources before size selection imparting a Boltzmann charge distribution to the particles.

It is difficult to maintain constant number concentrations over a several-hour period from the fluidized bed, and even using a fairly large quantity of dry material (> 10 g) it is often difficult to get number concentrations over 300 cm^{-3} of size-selected, submicron particles. For most of the samples studied, it was also nearly impossible to generate particles smaller than ~ 200 nm in concentrations sufficient for any of the measurements. The fluidized bed is expected to keep particle composition intact and is less likely to disturb surface features. It is expected that the fluidized bed produces particles whose properties are more consistent with those of dust particles that reach the atmosphere during a dust storm. CCN measurements of Arizona Test dust using nitrogen and the laboratory air in the fluidized bed were completed and no differences were observed. All experiments were run using the laboratory air system.

2.2. *Humidified Tandem Differential Mobility Analyzer*

The HTDMA (Figure 2.3) measures water uptake by aerosol particles exposed to an elevated relative humidity with respect to water RH_w . It has been used previously in our laboratory for many studies (e.g. Brechtel and Kreidenweis, 2000; Koehler et al., 2006; Prenni et al., 2003). This section will describe the HTDMA, and subsequent sections will describe components of the HTDMA in greater detail. In HTDMA studies, aerosol generated as described in Section 2.1 is sent to a dilution chamber where it is mixed with dry air. The sample is allowed to circulate in this dilution chamber with an

average residence time of 40 seconds. This is a sufficient time for atomized aerosol particles to become dry before entering the HTDMA and the residence time helps damp out fluctuations in concentrations from the fluidized bed. The RH_w is less than 5% at the inlet to the HTDMA.

The HTDMA is housed within a ventilated and warmed Plexiglas chamber, used to maintain the system temperature close to 30°C. The dry polydisperse flow is first sent to a Differential Mobility Analyzer (DMA1), which size selects the particles and creates a quasi monodisperse stream. Part of the monodisperse sample flow is sent to a Condensation Particle Counter (CPC), which gives a real-time measurement of particle concentrations for particles larger than 0.01 μm . The remainder of the flow is sent to a humidified loop, which contains sheath air held at a controlled RH_w . In the loop, the aerosol is allowed to reach equilibrium with the water vapor with a residence time of 2-4 seconds. The humidified flow then enters a second DMA (DMA2), which scans through particle sizes, and then a second CPC counts the particles as a function of size to obtain the grown size distribution, which is inverted to find the peak and thus determined to be the wet size. The RH_w is increased in a stepwise manner yielding a series of grown distributions as a function of relative humidity. Results are expressed in terms of the hygroscopic growth factor (GF) where:

$$GF(RH_w) = \frac{D_{wet}(RH_w)}{D_{dry}} \quad 2.1$$

where D_{wet} is the diameter of the particle after exposure to the elevated RH_w and D_{dry} is the selected dry size from DMA1 and measured by DMA2 at $RH_w < 10\%$.

2.2.1. Differential Mobility Analyzer

The HTDMA requires two Differential Mobility Analyzers (TSI Model 3071A). The DMA makes use of particle electric mobility, which is related to particle size and charge, to size-select particles. The quasi-monodisperse output will generally have mostly a narrow size range of particles carrying a single charge, but some contamination by larger, multiply-charged particles is also present. A schematic of a DMA is shown in Figure 2.4. Since artificially generated aerosol tends to carry a high and unknown electrostatic charge, the polydisperse stream is first sent to a neutralizer, containing krypton-85 and/or polonium-210 sources. The particles are bombarded with bipolar ions, producing an equilibrium charge distribution on the aerosol and yielding a known percentage of particles in each size class with no charge, one charge, or multiple charges.

The neutralized aerosol is then sent to the main DMA chamber. The chamber consists of a central conductive rod surrounded by a grounded cylinder. The rod is connected to a negative DC voltage, which can be set between 1-10000 V, creating an electric field in the annular space. As the polydisperse aerosol enters the chamber, positively charged particles will be drawn toward the rod; their motion is opposed by the particles' drag force. Neutral and negatively charged particles will exit the DMA with the excess flow. The mobility, Z_p , may be calculated from the force balance between drag and electrical attraction and is related to spherical particle diameter by:

$$Z_p = \frac{neC \cdot 10^5}{3\pi\eta D_p \chi}, \quad 2.2$$

where C is the slip correction factor given by (Hinds, 1999):

$$C = 1 + 2.34 \frac{\lambda}{D_p} + 1.05 \frac{\lambda}{D_p} e^{-0.39 \frac{D_p}{\lambda}}, \quad 2.3$$

and e is the elementary unit of charge in Coulombs, n is the number of charges on the particle, D_p is the particle diameter in meters, η is the gas viscosity in poise, λ is the mean free path of gas molecules in meters, and χ is a correction for nonsphericity, since the drag force was computed for a spherical particle (see Section 2.2.1.2). $\chi = 1$ for spheres, and $\chi > 1$ for irregular particles. As particles encounter the electric field, only those particles with mobility within the selected range will be able to escape through the small opening at the bottom of the chamber. Smaller particles will impact on the rod and larger particles will be carried out with the excess flow.

The mean mobility of particles, Z_p , extracted through the opening, as defined by Knutson and Whitby (1975), is:

$$Z_p = \frac{q_s \ln(r_2 / r_1)}{2\pi V L} \quad 2.4$$

where q_s is the sample flow and q_a is the aerosol flow in $\text{cm}^3 \text{s}^{-1}$, r_1 and r_2 are the inner and outer radii of the annular gap space in centimeters, V is the applied voltage in volts and L is the length of the collector rod in centimeters. The width of the mobility, ΔZ_p , which represents the spread in mobility that will be allowed to exit the DMA, is described by:

$$\Delta Z_p = \frac{q_a \ln(r_2 / r_1)}{2\pi V L} \quad 2.5$$

In this way the resolution of the DMA depends on the flow rates and the dimensions of the instrument. For example, for a 5:1 sheath to aerosol flow ratio the selected voltage to produce a peak diameter of 100 nm yields a distribution of particles with diameters from 90-113 nm. Since the spread is equal in mobility space, but mobility is inversely proportional to diameter, the spread in diameters is not centered about the selected size.

Table 2.1 shows the width of distributions for several flow ratios at nominal sizes used most frequently in this work. Flow ratios between 10:1 to 5:1 were most common in this work.

2.2.1.1. *Effects of Multiple Charging*

Under ideal bipolar charging, the equilibrium charge level that a distribution of particles reaches is given by Boltzmann's Law, in which the number of particles carrying 1, 2, 3... n_p charges is described by:

$$\frac{N_{np}}{N_o} = \exp\left(\frac{-n_p^2}{2\sigma^2}\right); \quad 2.6$$

where:

$$\sigma = \left(\frac{D_p kT}{e^2}\right)^{1/2}. \quad 2.7$$

T is the absolute temperature, k is Boltzmann's constant and D_p is the particle radius. The fraction of particles carrying zero, one or two charges is given by Wiedensohler (1988):

$$f(N) = 10^{\left[\sum_{i=0}^s a_i(N) \left(\log \frac{D_p}{nm}\right)^i\right]}, \quad 2.8$$

which is valid for particles between $1 \text{ nm} \leq D_p \leq 1000 \text{ nm}$ for $N = -1, 0, 1$; and for $20 \text{ nm} \leq D_p \leq 1000 \text{ nm}$ for $N = -2, 2$. The coefficients $a_i(N)$ are found in Wiedensohler (1988). Larger particles will have a higher fraction of multiply charged particles. Particles with two or more charges will seem smaller than their true size due to their enhanced mobility (particles with higher charge will be drawn faster through an electric field). Therefore there will be some small percentage of particles that are larger than the selected size in the nearly monodisperse size selected flow. For $D_p < 20 \text{ nm}$, particles carry at most one

charge. For a 100 nm dry size, 21.3% of the particles will have one charge and will be correctly sized, whereas 5.5% of the 149 nm particles will carry two charges and will be sized like the 100 nm singly-charged particles. Therefore the number of doubly- or triply- charged particles passed by the DMA in the quasi-monodisperse stream depends on the size distribution of the polydisperse aerosol, specifically the number concentrations of larger particles present. Assuming the small percentage of larger, doubly-charged particles retain their charge during humidification, there may be a small bias in the growth factors as larger particles have a smaller Kelvin effect; however, this is likely to appear as little more than noise in the distributions. Because the fluidized bed often creates higher concentrations of larger particles the potential for sizing error from multiple charging is larger than in samples generated by atomization. For example, for a nominal 400 nm selected particle size, 15.7% of the 400 nm particles will be correctly sized, and 8.7% and 2.8% of doubly charged 684 nm and triply charged 957 nm particles will also be selected. Concentrations of particles larger than 400 nm generated in the fluidized bed can be equal to the concentration of 400 nm particles, and thus these multiply charged particles represent significant contamination of the monodisperse sample.

2.2.1.2. Sizing Errors in the DMA

For dry dust particles, the assumption of sphericity ($\chi=1$ in Equation 2.2) is certainly not accurate, as can be observed from scanning electron microscope images of 300 nm nominal size selected Arizona test dust particles shown in Figure 2.5. This non-spherical shape generally leads to a larger drag and thus a larger electrical mobility diameter, therefore the particle appears larger than its geometrical size in the DMA.

When a particle with a crystalline structure, takes up water in the HTDMA it will preferentially adsorb water at corners and steps and may transform to a nearly spherical shape (Mikhailov et al., 2004). This can actually make the particles appear smaller than the selected dry size when they first take up a small amount of water and a spherical shape is obtained (i.e. $GF < 1$). Shape factors (χ) can correct for the DMA's overestimate of the dry size:

$$GF(RH) = \frac{D_{wet}(RH)}{D_{dry}} * \frac{\chi_{dry}}{\chi_{wet}}, \quad 2.9$$

where χ_{dry} and χ_{wet} are the shape factors of the wet and dry particles and $\chi_{wet} \sim 1$.

A cubic structure, for example, has a shape factor of 1.08. Shape factors for complicated shapes are uncertain, but can be as large as 6 (Colbeck, 1990). We report DMA-measured dust diameters assuming $\chi=1$ since the appropriate correction factor is unknown.

Some species, such as ammonium nitrate (not studied), are also known to exist in several solid and liquid-like states with various chemical structures depending on the temperature, pressure, humidity, and purity (Mikhailov et al., 2004). Also some salts, such as sodium carbonate and sodium sulfate, can convert to hydrated crystalline structures with increasing RH (Tang et al., 1995). Further, particles with highly irregular shapes or of high porosity, as is the case for soot particles, can have extensive microstructural rearrangement as the humidity is increased yielding substantial compaction of the particles. This effect however is most common with mixed particles where net electric charges between the substances creates an enhanced electrostatic repulsion and reduced packing density of dry particles (Mikhailov et al., 2004). Another problem in the HTDMA system is evaporation of semivolatile species when exposed to

clean, dry sheath air, but this is not expected to occur for any of the particles studied in this work. Potential problems with sizing due to these uncertainties are noted in the individual chapters for each particle type.

2.2.2. Condensation Particle Counter

The condensation particle counter (CPC, TSI Model 3010) is essentially an optical particle counter, except particles are first exposed to a supersaturation of n-butyl alcohol, allowing for rapid growth of small particles to a size where they may be easily optically detected. The higher the supersaturation, the smaller the particle that can be optically detected. However, it is necessary to keep the supersaturation below the level where homogeneous nucleation of n-butyl alcohol will occur, giving unreliable counts. A schematic of the CPC is shown in Figure 2.6.

An aerosol stream is pulled into the instrument at 1 lpm. The flow then passes through a heated, alcohol soaked, porous plastic block. The alcohol evaporates, saturating the sheath flow with vapor. The flow then enters the condenser, which is an area cooled by a thermoelectric device. In this area the vapor becomes supersaturated and condenses on particles in the chamber. Finally, the flow encounters the optical detector with a laser diode light source, which measures light scattering as electrical pulses. These pulses are counted in real time and displayed on the front of the instrument, as well as being interfaced to the computer. The CPC is able to detect particles from 0.01 μm to greater than 3 mm at concentrations between 1-10,000 particles/ cm^3 , with a coincidence error <10% at 10,000 particles/ cm^3 (TSI Model 3010 CNC Manual, 2002). Coincidence occurs when two particles are in the optical laser at the same instant and thus the detector only registers the existence of one particle.

Experiments are always performed at much lower concentrations, to ensure that coincidence does not occur.

2.2.3. Humidification System

Humidity is supplied to the system by heating water and drawing vapor through an immersed Perma Pure tube (model MD-110-48S), which is permeable to water vapor but not liquid water. By controlling the temperature of the water, more or less vapor can be produced. The saturated air is then drawn into the instrument and mass flow controllers are used to control the fraction of moist air and dry air to produce the desired relative humidity of the sheath air in the humidified loop. The humidity may be controlled between 5-95% RH_w . Six relative humidity sensors (Rotronics Hygropalm) measure the relative humidity of the sheath, excess and aerosol flows in each DMA. The relative humidity is nominally held within $\pm 2\%$ of the desired value, the published accuracy of the sensor. The precision of the sensors is $\pm 1.5\%$ (Carrico et al., 2005).

2.2.4. Data Acquisition and Processing

Data are logged using National Instruments LabVIEW graphical programming software. The program reads in temperature and relative humidity from the six sensors in the DMAs. The temperature is monitored to ensure it is held at 30°C and the relative humidity of each sensor in DMA1 is less than 10%. The program waits until the sensors in DMA2 are steady at the set point, within $\pm 2\%$. The relative humidity of the sheath and aerosol flows in DMA2 are averaged over the scan interval at each set point. The program reads in the counts for each size and automatically inverts for $dN/d\log D_p$. Size distributions were fit to a theoretical model accounting for instrument transfer functions using the inversion algorithm of Zhou et al. (2002). Typically the curves are monomodal,

however for some species like Owens (dry) Lake dust the curves are bimodal, due to the complex chemical composition of the particles. In this case a bimodal fit is applied to obtain two peak diameters.

2.3. *Cloud Condensation Nuclei Counter*

The Droplet Measurement Technology cloud condensation nuclei counter (CCNC, Model CCN-2) employs the condition that water vapor diffuses faster than heat in air to expose an aerosol flow to supersaturated conditions. A linear temperature gradient is established along the wetted walls of a cylinder oriented vertically. Water is supplied to a porous ceramic material along the inner wall at a rate of 4 mL hr⁻¹. Aerosol flows between sheath flows in the center of the chamber, where the aerosol will experience a vapor pressure associated with saturation for an upstream wall temperature. Due to the increased time it takes the heat to diffuse in the moving flow, the temperature at that aerosol location will be lower than the temperature corresponding to that saturation value. Thus the partial pressure of vapor is greater than the saturation vapor pressure for the aerosol location temperature and a supersaturation is established (see Figure 2.7). By increasing the temperature gradient, the supersaturation can be varied between 0.1-2.0%. Flow rates are maintained sufficiently high to prevent convection from occurring in the chamber. Particles large enough to be counted by the OPC ($D_p > 0.75 \mu\text{m}$) are counted as CCN. In our studies, aerosol was generated as described in Section 2.1 and size selected with a DMA, with a portion of the flow counted by a CPC, and the remaining flow sent to the CCNC. Comparing the concentration of CCN measured in the CCNC with the concentration of aerosol measured by the CPC, the fraction of aerosol activated was calculated. By increasing the supersaturation or dry

particle size, a condition is found for which 50% of the particles activate as cloud droplets. This point was determined to be the critical supersaturation for the dry particle size. This 50% point is determined by fitting measured CCN fractions ($CCNfrac$) at dry diameter (D_p) to the form:

$$CCNfrac = a * \exp(-\exp(-b * (D_p - D_c))), \quad 2.10$$

where a and b are constants related to the width of the sigmoidal curve and D_c is the diameter for which 50% of the particles activate as CCN.

The temperature of the walls was controlled by three sets of thermoelectric coolers (TEC) along the outside of the walls. The heat must travel through the wetted material on the inner wall and heat is continuously removed from the inner wall by the forced evaporation and convection, therefore the imposed temperature gradient from the TECs will overestimate the temperature gradient along the wetted inner wall. The instrument must be calibrated to account for this thermal efficiency through the wall (Lance et al., 2006). The thermal efficiency, $\eta = \Delta T_{inner} / \Delta T_{outer}$, is a function of the flow rate through the chamber, the magnitude of the temperature gradient, the chamber pressure and the thermal resistance where the TECs control temperature, through the aluminum outer wall, the ceramic inner wall, and the liquid layer. Neglecting this thermal efficiency creates a considerable overestimation of the supersaturation. Calibrations with size-selected ammonium sulfate particles were performed regularly; these data were used to calculate instrument supersaturation and the repeatability in the resulting critical supersaturations: $2\sigma = 0.042\%$ (Petters et al., 2006). Descriptions of the calibration procedure may be found in Appendix II.

2.3.1. Predicting CCN Activity from Hygroscopicity data

Following the method in Kreidenweis et al. (2005), data obtained by the HTDMA may be used to predict hygroscopic growth beyond the upper limit of RH_w ($RH_w = 92\%$) in the instrument from the measured hygroscopicity. The GF values were fit to the following functional form,

$$GF^3 - 1 = (a + b \cdot a_w + c \cdot a_w^2) \frac{a_w}{1 - a_w}, \quad (2.11)$$

where the water activity, a_w , was determined from the RH_w and wet size measured in the HTDMA using:

$$a_w = \frac{RH_w / 100}{\exp\left(\frac{4\sigma_{s/a} M_w}{RT\rho_w D_{wet}(RH_w)}\right)}. \quad (2.12)$$

The exponential term is the so-called Kelvin term, where $\sigma_{s/a}$ is the surface tension of the solution air interface, assumed throughout this work to be equal to that for pure water (72 dyn cm⁻¹), M_w is the molecular weight of water (18.015 g mol⁻¹), R is the universal gas constant, T is the temperature of the drop, assumed to be in equilibrium with the temperature in the HTDMA (30°C), and ρ_w is the density of water (1 g cm⁻³). Kreidenweis et al. (2005) and Koehler et al. (2006) used this method to predict critical supersaturations for a variety of inorganic and organic species with good agreement to measurements from a CCN counter.

Instead of using a polynomial to capture the variation of GF with RH_w , GF values can also be fit, using the HTDMA measurement at a single humidity, with the parameter, κ , (Petters and Kreidenweis, 2007). We use GF data at 90% RH_w to determine κ as follows:

$$GF(RH_w = 90\%)^3 - 1 = \kappa \left(\frac{a_w}{1 - a_w} \right). \quad (2.13)$$

The parameter, κ , then may be extrapolated to predict GF values at any water activity.

Observed critical supersaturations are compared to predictions for the particle types studied here using the fits to the HTDMA data from Equations (2.11) or (2.13) and the following calculation procedure. The equilibrium RH_w over an aqueous solution drop formed on a particle having dry diameter, D_{dry} , was computed for values of a_w from ~ 0 to 1, by determining GF (and hence D_{wet}) at that a_w from either equation, and then computing the ambient RH_w in equilibrium with the drop having this a_w via Equation (2.12). The supersaturation, expressed in percent is $s = RH_w - 100$ and the critical supersaturation, s_c , for the selected D_{dry} is the maximum in the s - D_{wet} curve defined by this calculation procedure. On the other hand, CCNC measurements can be used to find a best-fit κ value for the data and compared to κ values estimated from HTDMA measurements. In this case it is assumed that D_{dry} is well known, and the κ value is determined which gives the lowest error for the s_c - D_{dry} pairs. Figure 2.8 shows lines of constant κ in s_c - D_{dry} space with some CCNC data for common atmospheric species for comparison. Notice that CCNC data tends to have some scatter and therefore best-fit κ values must be found.

2.4. *Continuous Flow Diffusion Chamber*

2.4.1. **Basic Operation**

The CFDC is an instrument which allows real time measurement of ice nuclei (IN) concentrations from an aerosol flow. Two models of the instrument were used in this work, a laboratory unit and an aircraft unit, both of which are modified versions of

the original chamber design described by Rogers (1988). The laboratory unit is larger (chamber length $\sim 150\text{cm}$) with an aerosol residence time of $\sim 10\text{ s}$ and is generally operated between $-60 \leq T \leq -35^\circ\text{C}$. The aircraft unit (Rogers et al., 2001) was optimized for use in an aircraft missions, thus has lower power requirements and weight. The residence time in the growth region for this unit is $\sim 4\text{ s}$ and generally operates between $-40 \leq T \leq -10^\circ\text{C}$.

Figure 2.9 shows the system, which consists of two concentric copper cylinders with a $\sim 1.2\text{ cm}$ gap between the surfaces. In the laboratory unit, two low temperature circulating baths (Neslab ULT-80) circulate refrigerant oil (Sylterm XLT, Dow Chemical) independently controlling the temperature of the two walls. In the aircraft unit, two refrigeration compressors are used to cool the walls. Initially both walls are cooled to -25°C then water is pumped through the chamber and allowed to drain yielding an ice coating on both surfaces of $\sim 200\text{ micron}$ thickness. Both walls are then further cooled to the operating conditions, with one wall warmer (generally the outer wall) than the other wall. Aerosol generated as described in Section 2.1 is size selected by a DMA then a portion of the flow is sent to a CPC while the remaining flow is introduced to the chamber via a pre-cooler (laboratory unit only). This section consists of a $1/2''$ copper tube surrounding a $3/8''$ copper tube. The aerosol stream flows through the center tube and cooled Freon flows in the annular region, cooling the aerosol flow to $\sim -30^\circ\text{C}$, as measured at the entrance of the chamber. This ensures excess water vapor is removed from the flow and does not clog the inlet when the previously room temperature air enters the cold chamber. It also ensures that unresolved transient supersaturations are not established as the aerosol flow enters the chamber. The aerosol enters the chamber

between two particle-free sheath flows and is generally 10% of the total flow (~12 lpm). Since the air close to the cold wall is denser than the air closer to the warm wall, the aerosol position is shifted from the middle of the chamber toward the cold wall. The data system computes this location based on the temperatures measured along the walls and the flow rates through the instrument. The flow is maintained at sufficiently high rates to ensure that reverse, buoyancy-driven flow along the warm wall surface does not occur.

By holding the inner and outer walls at different temperatures, the temperature gradient between the walls of the chamber induces a supersaturation with respect to ice. Four type-T thermocouples (copper constantan) measure the temperature along each wall. The aerosol location between the two ice-coated plates, expressed as the fractional distance from the inner wall, x , is used to calculate the aerosol location temperature and supersaturation. The aerosol location temperature (T_x) is simply a linear interpolation:

$$T_x = T_c + x(T_w - T_c), \quad 2.14$$

where T_c is the average temperature of the cold wall and T_w is the average temperature of the warm wall. The saturation vapor pressure with respect to ice at each ice surface ($e_i(T)$) is calculated according to Buck (1981):

$$e_i(T) = 6.1115 * \exp \left[\frac{(23.036 - T)}{333.7} \frac{T}{(T + 279.82)} \right]. \quad 2.15$$

Then the vapor pressure at the aerosol location is interpolated between the ice saturated conditions at each ice wall:

$$e_x = e_i(T_c) - x[e_i(T_c) - e_i(T_w)] \quad 2.16$$

and the ice relative humidity (RH_i) is:

$$RH_i = 100 * \frac{e_x}{e_i(T_x)}. \quad 2.17$$

By increasing the temperature gradient, the RH_i is increased slowly until a condition is achieved in which a threshold fraction of the aerosol particles nucleate as ice. Figure 2.9 shows a steady-state temperature, saturation and velocity profile in the chamber for the given wall temperatures, based on the mathematical models presented in Rogers (1988).

The presence of ice crystals is determined using an optical particle counter (OPC, Climet Model 7350A). Particles that pass through the laser beam and are large enough to interfere with it produce voltage pulses in the OPC. These pulses are binned into 256 channels,, which roughly correspond to particle size, by a multichannel analyzer (MCA) PC card. The OPC is typically run in the high gain setting which detects particles in the size range of roughly $0.4 \leq D_p \leq 5 \mu m$. All larger particles are binned into the largest bin size. A cutoff size is determined which is too large for the particles to have grown by liquid water diffusional growth below water saturation and all particles larger than this cutoff size are counted as ice crystals. The relationship between OPC channel and particle size is determined by calibrating the OPC with polystyrene latex particles of known size. By comparing the aerosol concentration measured in the CPC with the concentration of ice crystals measured in the OPC above the cutoff size, the fraction of aerosol activating as IN is determined.

In the aircraft unit, where operating conditions are typically much warmer than in the laboratory unit, it is often necessary to approach or exceed water saturated conditions to observe ice crystal nucleation. To ensure that large particles counted in the OPC are indeed ice crystals and not large activated drops, it is necessary to have an evaporation region at the bottom of the chamber where ice saturation is maintained but the RH_w is sufficiently below water saturation such that any water droplets will evaporate to sizes

smaller than the detection limit of the OPC. The original aircraft unit (ACFDC-1), used for some of these data, had a lower section consisting of Delrin, a hydrophobic material. In this region, the outer wall was not coated with ice removing the vapor source in this region. While it was expected that ice saturation is maintained, water saturation was not. The second generation aircraft unit (ACFDC-2) has the lower section made of copper walls, that do get coated with ice, but both walls are held to the same temperature at the bottom section of the chamber prior to the OPC entrance. In this way, it is certain that ice saturation is maintained and the water relative humidity can be calculated, based on the wall temperature. In the laboratory unit, if water saturation is exceeded, it cannot be determined if the grown particles are liquid or ice phase.

Because vapor flows continuously across the chamber from the warm to the cold wall, the ice surface will eventually deplete and needs to be refreshed. This limits the duration of a single experiment to less than 3 hours in the aircraft units and 5 hours in the laboratory unit.

2.4.2. Data Acquisition and Processing

The data system records thermocouple temperature measurements, air flow measurements, chamber pressure, total aerosol concentration, and OPC detected particles binned into 256 MCA channels once every second. The data system uses these inputs to compute the lamina position and the corresponding temperature, RH_i and RH_w at the aerosol location, according to the equations in Rogers (1988). The RH_w is calculated according to the water saturation vapor pressure, $e_{sat,w}$ representation from Buck (1981):

$$e_{sat,w} = 6.1121 * \exp((18.729 - T/227.3) * T / (T + 257.87)); , \quad 2.18$$

where T is in degrees Celsius. Typically measurements are averaged over some period, ten seconds to one minute in this work, and the ice crystal fraction (F_i) is fit to the functional form:

$$F_i = a * RH_w^b + c, \quad 2.19$$

where a , b , and c are constants. In this way a threshold value of F is computed and compared for all temperatures. The threshold values used in this work are usually 1%, and in some cases 5%, of the total particles nucleated to ice crystals.

For data collected with the laboratory unit, the relative humidity specified for a given threshold condition at each temperature is shown as an average of at least three points. Error bars indicate the 95% confidence interval using the Student's t -statistic. The standard deviation is pooled for the data is:

$$s_{pooled} = \sqrt{\frac{\sum_{i=1}^{N1} (RH_{i,i} - \overline{RH_{i,1}})^2 + \sum_{j=1}^{N2} (RH_{i,j} - \overline{RH_{i,2}})^2 + \sum_{k=1}^{N3} (RH_{i,k} - \overline{RH_{i,3}})^2 + \dots}{N1 + N2 + N3 + \dots - N_s}}, \quad 2.20$$

where i, j , and k are for different temperatures, $N1, N2, N3$ are the number of repetitions of RH_i at each temperature, N_s is the total number of temperatures examined, $RH_{i,i}, RH_{i,j}, RH_{i,k}$ are the RH_i values and $\overline{RH_{i,1}}, \overline{RH_{i,2}}, \overline{RH_{i,3}}$ are the RH_i averages for each temperature. The denominator is the degrees of freedom used to determine the t -value. The confidence interval at each temperature is then:

$$95\%CL = \overline{RH_i} \pm \frac{ts_{pooled}}{\sqrt{N}}, \quad 2.21$$

where N is the number of samples for the average RH_i at the given temperature. For the aircraft units, difficulty in exactly reproducing temperature conditions for repetitions prohibited the use of this analysis. Therefore individual data points are shown.

2.4.3. Current configuration of the laboratory CFDC

Appendix I outlines a series of experiments which led to modifications to the laboratory CFDC during the course of this work. Any experiments run prior to these modifications were repeated. All experiments in this work were performed with the outer wall as the cold surface and the inner wall as the warm surface. A temperature gradient existed along the outer wall and the refrigerant was circulated such that the coldest temperatures (and thus the highest saturation values) existed at the bottom of the chamber. Only the two thermocouples along the lower half of the outer wall were used in the calculation of the aerosol location and associated temperature and saturation values. Details on the configuration may be found in the Appendix.

	Nominal Particle Size (nm)			
Flow Ratio (sheath:aerosol)	100 nm	200 nm	300 nm	400 nm
10:1	99-103 nm	187-216 nm	281-323 nm	370-432 nm
5:1	90-113 nm	179-230 nm	263-351 nm	352-473 nm
3:1	81-124 nm	166-260 nm	246-399 nm	324-543 nm
doublet size	149 nm	317 nm	496 nm	684 nm

Table 2.1: Mobility widths, expressed as diameter range, for commonly used nominal sizes and flow ratios in the DMA. Bottom row: size of doubly-charged particles which will be sized as the nominal size.

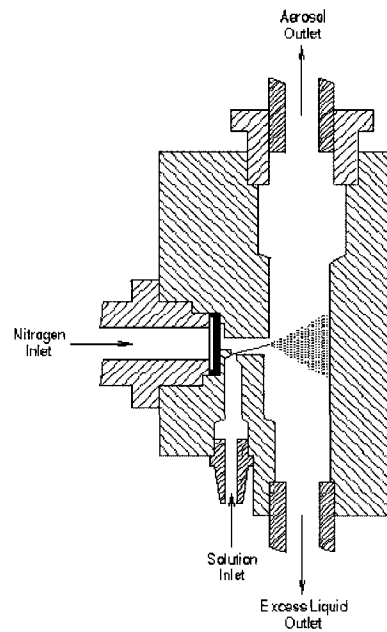


Figure 2.1: Schematic of atomizer (from TSI Model 3076 Constant Output Atomizer manual, 2003).

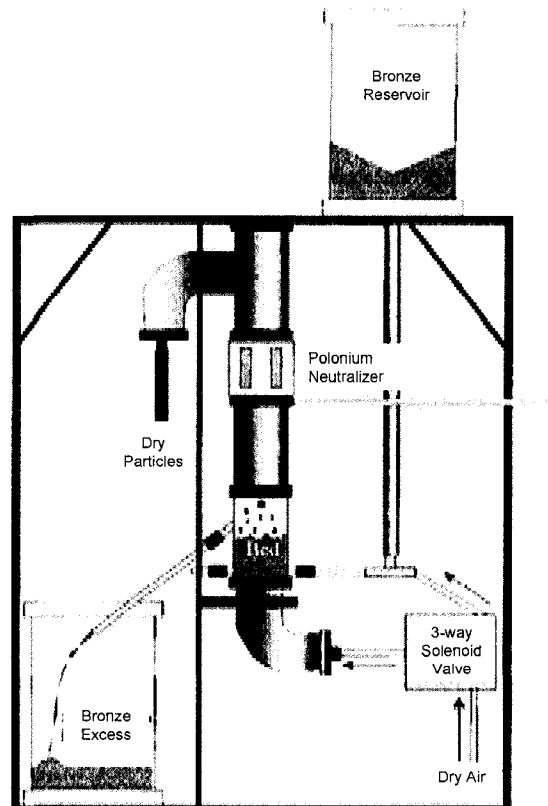


Figure 2.2: The fluidized bed, adapted from Prenni et al. (2000).

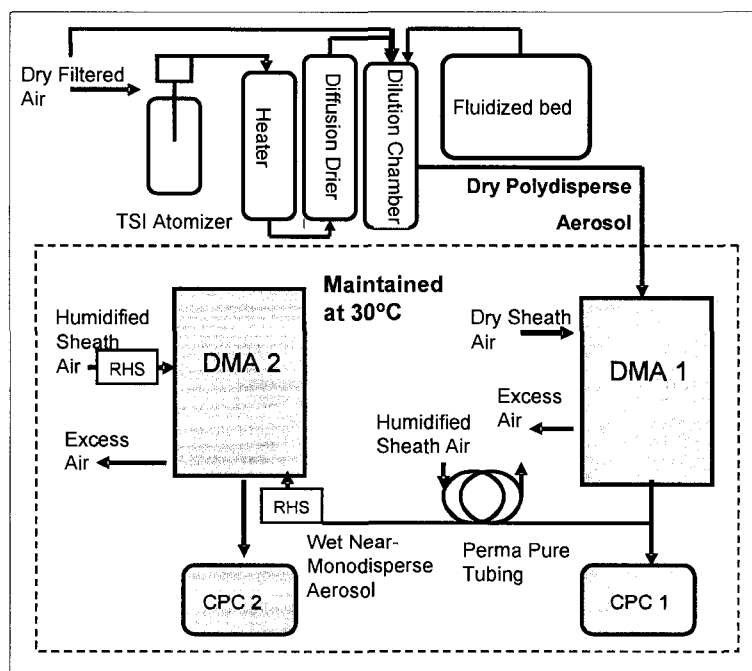


Figure 2.3: Schematic of the humidified tandem differential mobility analyzer.

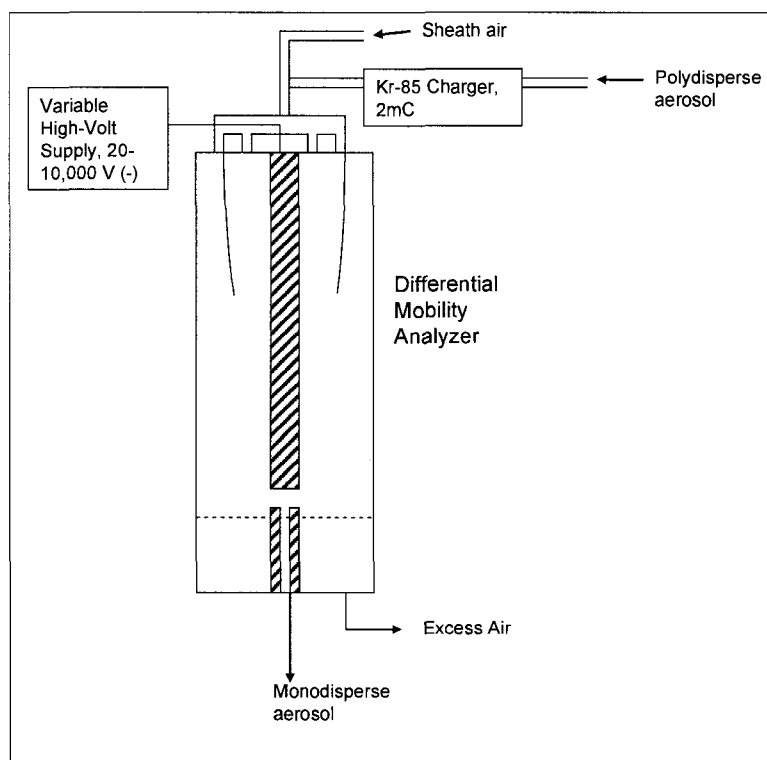


Figure 2.4: Schematic of Differential Mobility Analyzer (adapted from TSI Model 3071A Electrostatic Classifier manual, 2002).

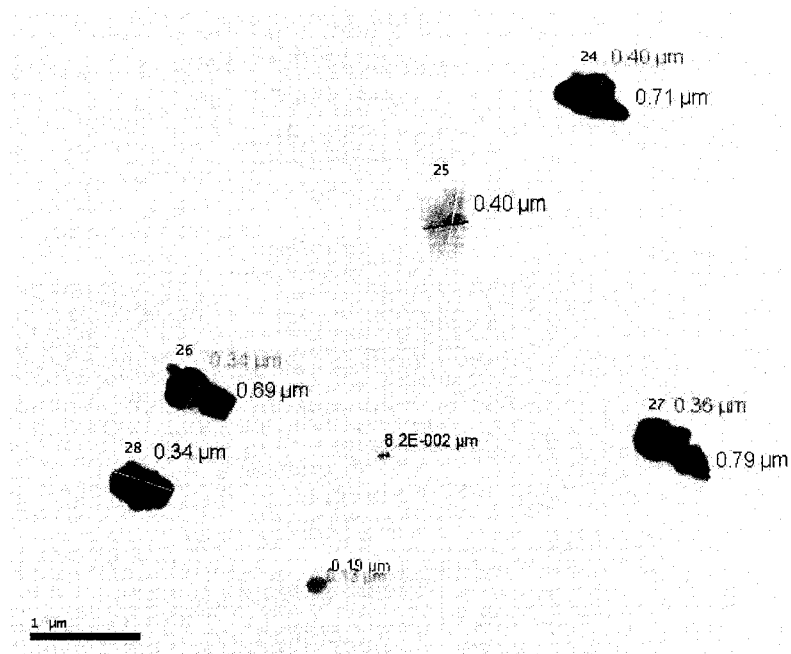


Figure 2.5: Scanning electron microscope image of size selected 300 nm Arizona test dust particles.

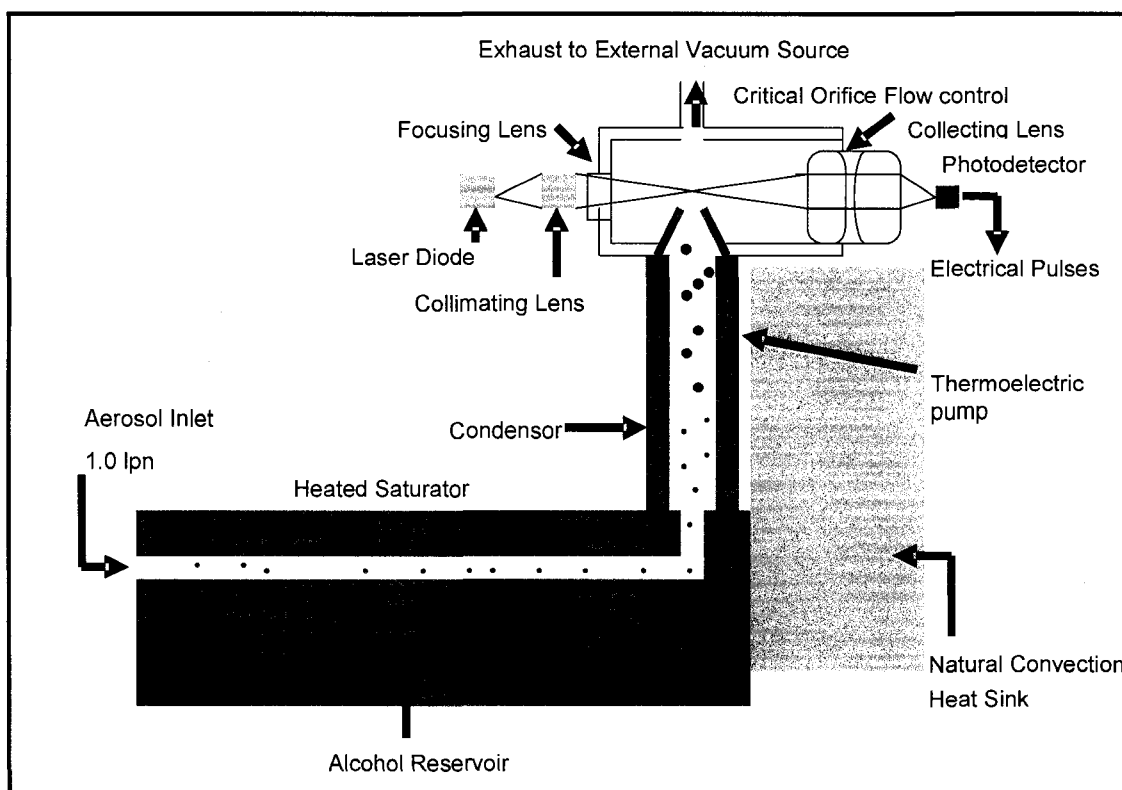


Figure 2.6: Schematic of Condensation Particle Counter (from TSI Model 3010 Condensation Particle Counter manual, 2002).

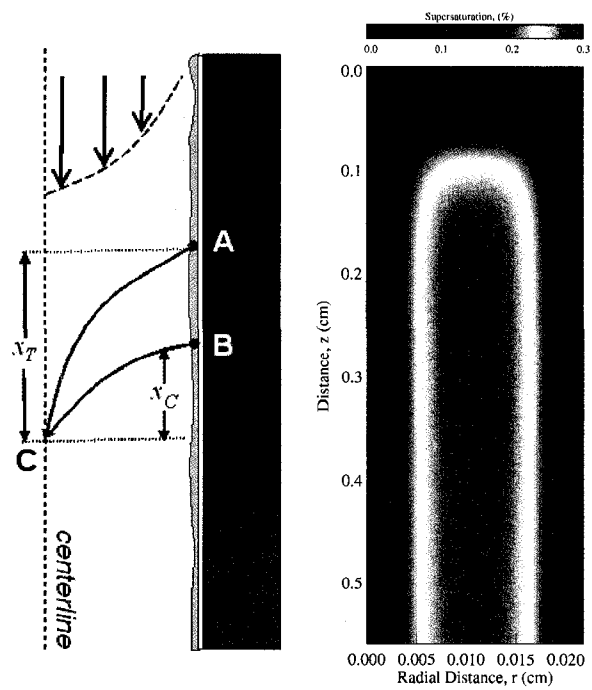


Figure 2.7: Droplet Measurement Technology CCNC diagram with supersaturation profile.

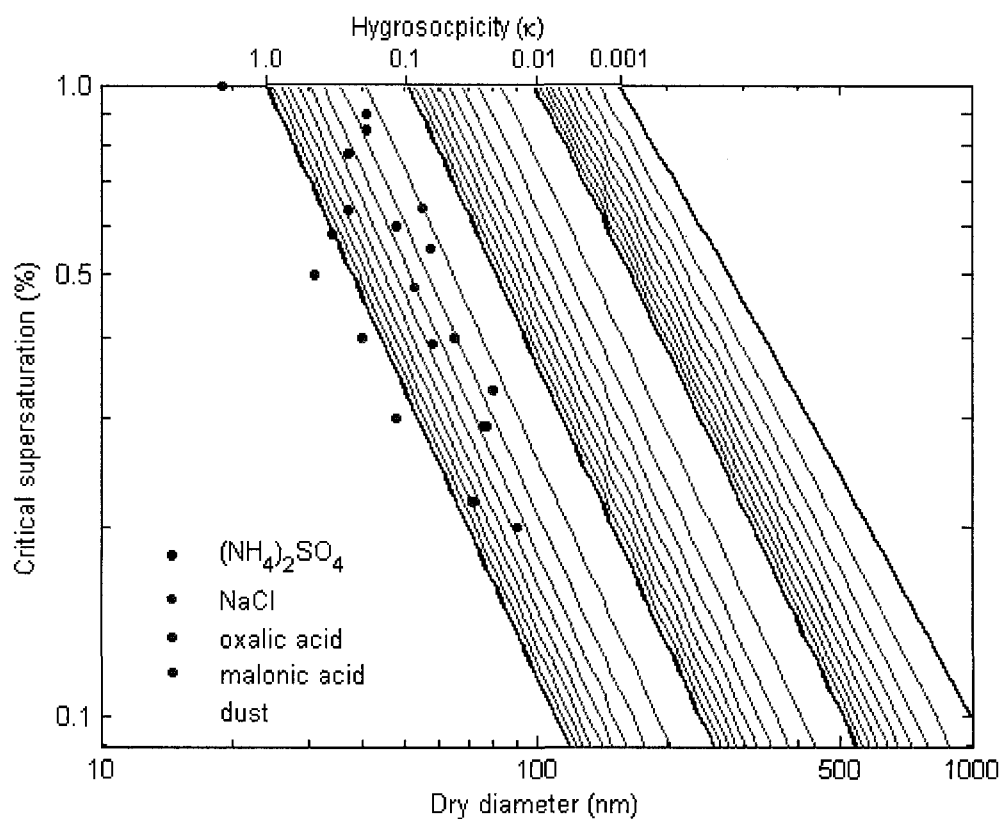


Figure 2.8: Calculated critical supersaturation for $0.001 < \kappa < 1$ computed at $T=298$ K. The gray lines are linearly spaced intermediates. Data points are taken from this work, Kumar et al. (2003), Giebl et al. (2002), Raymond and Pandis (2002), and Corrigan and Novakov (1999).

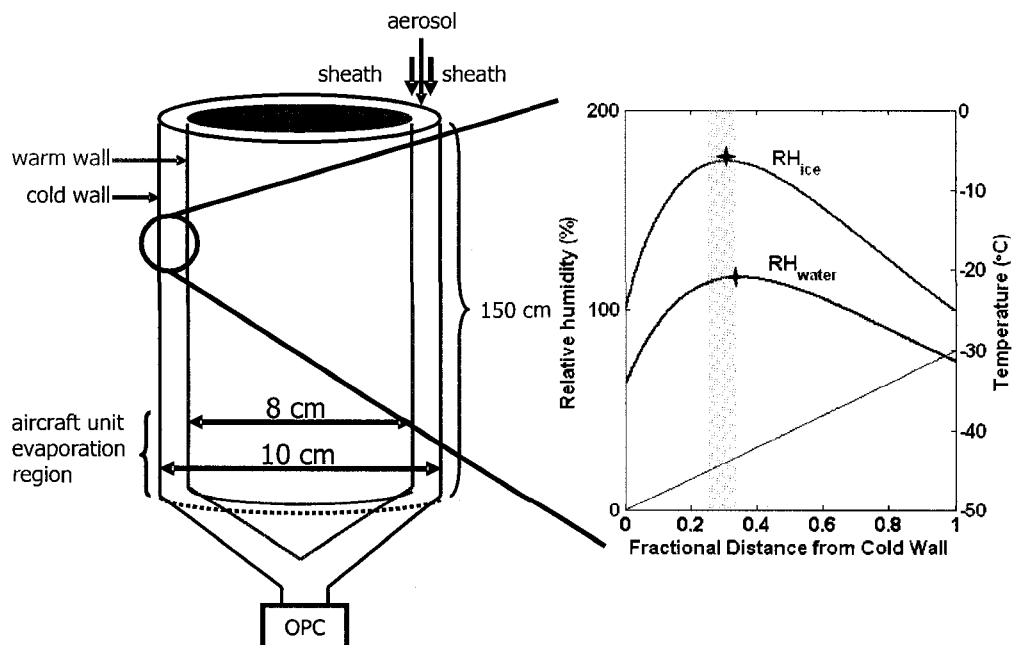


Figure 2.9: Continuous flow diffusion chamber schematic and steady-state temperature and saturation profile inside the CFDC for the given wall temperatures.

3. Theories Describing Homogeneous and Heterogeneous Ice Nucleation

3.1. *Homogeneous Ice Nucleation*

In supercooled liquid, the initiation of an ice embryo involves the breaking of water-water bonds and reforming of water-ice bonds. Supercooled water molecules are in constant contact with a growing ice embryo, but the water molecule must pass from one equilibrium position to another and these two positions are separated by the Gibbs free energy of activation for a water molecule to diffuse across the water-ice boundary. The following sections outline two theoretical descriptions of homogeneous freezing. The first section follows Pruppacher and Klett (1997) for classical nucleation theory of supercooled water. In the second section, two published parameterizations of homogeneous nucleation from a solution droplet are outlined.

3.1.1. Classical Theory of Homogeneous Ice Nucleation

Classical theory of homogeneous ice nucleation from a pure supercooled water droplet is analogous to the theory of homogenous nucleation from the vapor phase. The nucleation rate can be found by computing the diffusive flux density of water molecules

across an ice surface and plugging into the expression for the homogeneous nucleation rate, J_{hom} [$\text{m}^{-2} \text{s}^{-1}$], as:

$$J_{hom} = 2N_{wc} \left(\frac{\rho_w kT}{\rho_i h} \right) \left(\frac{\sigma_{i/w}}{kT} \right)^{1/2} \exp \left(-\frac{\Delta g}{RT} - \frac{\Delta F_g}{kT} \right), \quad (3.1)$$

where N_c is the number of water monomers in contact with the unit ice surface, ρ_w and ρ_i are the density of water and ice, respectively, k is Boltzmann's constant, h is Planck's constant, T is the temperature, $\sigma_{i/w}$ is the surface tension between the water and ice surface, R is the universal gas constant, Δg is the molar Gibbs free energy of activation for diffusion of water molecules across the water-ice boundary, and ΔF_g is the work of ice germ formation. To evaluate Equation (3.1) numerically, it is necessary to determine expressions for Δg and ΔF_g . Δg is generally unknown, but can be estimated from nucleation measurements. According to the classical model, ΔF_g is analogous to the work of liquid germ formation, and it must be assumed that densities, latent heats, and surface tensions are constant over the range of interest. However, homogeneous nucleation rates are only significant at temperatures colder than -35°C and these properties become a strong function of temperature in this region.

In atmospheric science, homogeneous freezing often refers to the freezing of ice in aqueous solution drops without the presence of a surface that participates in the ice nucleation process. While this phenomenon is not "homogeneous nucleation" in the strictest sense, since more than one molecule type is present, throughout this work, homogeneous freezing shall refer to this situation. A "classical" description in the 1950s and early 1960s was based on the stochastic hypothesis: that all drops of equal size had an equal probability of ice embryos of critical size forming within them. It was assumed that the presence of foreign molecules enhanced the efficiency of the random nucleation

process in a nonspecific way. The rate of change of unfrozen drops (dN_u) to frozen drops in a time interval (dt) for a given temperature was related to the rate determined for the pure water case:

$$-\frac{dN_u}{N_u} = V_d J_{\text{hom}}(T_{\text{sup}}) dt, \quad (3.2)$$

where the rate is a function of drop volume, V_d , and the nucleation rate is expressed as a function of supercooling, $J_{\text{hom}}(T_{\text{sup}})$, where $T_{\text{sup}} = 273.15 \text{ K} - T$ and T is the droplet temperature. From his experiments, Bigg (1953) represented $J_{\text{hom}}(T_{\text{sup}})$ as:

$$J_{\text{hom}}(T_{\text{sup}}) = B(\exp(aT_{\text{sup}}) - 1) \quad (3.3)$$

where a and B are constants specific to each solution. From Equations (3.2) and (3.3) if the volume of the drop or the supercooling increases, the fraction of unfrozen drops decreases. While experimental evidence has shown that homogeneous freezing does depend on the volume of the drop and is also exponentially dependent on the supercooling, data have shown that for a given temperature the fraction of drops frozen per unit time decreases exponentially, in contrast to the constant rate predicted by this stochastic mechanism. This indicates the need for a more complete description of solution droplet freezing.

3.1.2. Parameterizations of Homogeneous Ice Nucleation

3.1.2.1. Water Activity Based Parameterization

Koop et al. (2000) showed that, at least to a first order, the homogeneous freezing rate of solution particles was independent of the solute composition and depended only on the water activity of the solution. The water activity of a solution is defined as the ratio of the solution vapor pressure to the vapor pressure over pure water under the same

conditions. The melting and freezing temperatures of a solution are typically thought to depend only on the solute concentration, not the properties of the solute. However, this is false for very concentrated solutions due to non-ideality effects. If the melting or freezing temperature is expressed in terms of solute molality, there is considerable scatter depending on solute type for concentrated solutions (molality > 5 mol/kg), as shown in Figure 1 of Koop et al. (2000). However, if the freezing temperature is expressed in terms of the solution water activity, this scatter collapses more or less onto one line, which is a constant offset from the activity of water in a solution in equilibrium with ice. This lends strong support to the theory that homogeneous ice nucleation is dependent only on the water activity of the solution. Baker and Baker (2004) used a thermodynamic model to show that NaCl solutions with the same compressibility as pure water under increased pressure froze at the same temperature. This confirms that the impact of solute and pressure on the freezing of a solution is physically due to changes in the hydrogen bonding structure of the metastable liquid.

Koop et al. (2000) suggested the nucleation rate, $J_{hom} [\text{m}^{-2} \text{s}^{-1}]$, could be calculated by:

$$\log(J_{hom}) = -906.7 + 8502\Delta a_w - 26924(\Delta a_w)^2 + 29180(\Delta a_w)^3, \quad (3.4)$$

where Δa_w represents the offset from the water activity in equilibrium with ice line:

$$\Delta a_w = a_w(c, T) - a_w^i(T). \quad (3.5)$$

$a_w(c, T)$ is the composition and temperature dependent water activity of the solution and $a_w^i(T)$ is the activity of water in a solution in equilibrium with ice. Several formulations can be found in the literature for the temperature dependence of $a_w^i(T)$ (e.g. Koop et al., 2000; Murphy and Koop, 2005).

This parameterization has been compared to ice nucleation of various soluble species in the CFDC. The nucleation rate may be converted to a fraction of particles frozen, F_i , by:

$$F_i = \exp(-J_{\text{hom}}(T, a_w) \cdot V(a_w) \cdot \Delta t), \quad (3.6)$$

where $V(a_w)$ is the volume of the drop at a given water activity. The water activity of the solution is related to the ambient relative humidity via the Kelvin equation, but the difference between the water activity and the equilibrium relative humidity is negligible for droplets larger than ~ 200 nm. To use Equation 3.6, the equation must be solved for the given water activity and a nucleation rate of 0.1 s^{-1} to determine the conditions for which 1% of the particles nucleate ice crystals during the residence time, Δt , of about 10 seconds in the CFDC at the set point temperature. In this way, the nucleation rates can be compared for a variety of temperatures and the corresponding relative humidities that support this nucleation rate determined.

Chen et al. (2000) investigated the onset conditions for homogeneous nucleation of ammonium sulfate and sulfuric acid solution drops in the CFDC. Their study did not include a comparison to the Koop et al. (2000) parameterization, but the data have since been compared to the predictions and found to be in good agreement. Prenni et al. (2001) investigated freezing behavior for several dicarboxylic acids, which were generally also in good agreement with the parameterization, although low temperature water activity data are not available for these species. In this work, the performance of the CFDC is periodically evaluated using ammonium sulfate aerosol and data are compared to the Koop et al. (2000) parameterization for consistency. Figure 8.1 shows such a comparison with CFDC data for ammonium sulfate solution droplets at -50°C .

3.1.2.2. *Melting point depression parameterization*

Sassen and Dodd (1988) found from an aircraft measurement campaign in Colorado during 1983 that droplet freezing via the homogeneous mode was a function of temperature, time and drop volume. They expressed the probability that a droplet would freeze as a function of the effective freezing temperature (T^*):

$$T^* = T + \lambda \delta T_m, \quad (3.7)$$

where T is the drop temperature, δT_m is the melting point depression and λ is a parameter which relates the freezing and melting point depressions. The melting point depression is a function of the molality of the solution droplet. Experimentally-determined values for λ are generally around 1.7 as an average of all solutes, but values between 1.0 and 2.0 have been used in the literature (Lin et al., 2002). It is assumed that the nucleation rate of the droplet (J_{hom}) at the temperature T is equal to the nucleation rate of equivalently sized pure water droplets (J_w) at the effective freezing temperature, such that:

$$J_{hom} = J_w(T^*) \quad (3.8)$$

Many parcel model simulations have had success simulating homogeneous freezing in this manner (e.g. Lin et al., 2002). It is easy to show, parameterically speaking, that the water activity and melting point depression parameterizations give quite similar results.

3.2. *Heterogeneous Ice Nucleation*

The conditions in which homogeneous ice nucleation occurs in the atmosphere do not account for all the conditions in which ice crystals are observed (e.g. DeMott et al., 2003a; DeMott et al., 2003b; Sassen et al., 2003). Therefore, the occurrence of heterogeneous nucleation in the atmosphere appears as the only viable process to account for ice formation at warmer temperatures and lower relative humidities than are required

for homogeneous ice nucleation. In this section, properties of heterogeneous ice nuclei and the equations for the classical theory of heterogeneous ice nucleation will be presented. Finally, to overcome the limitations of the classical theory, some parameterizations of heterogeneous ice nucleation proposed in the literature will be presented.

3.2.1. Properties of ice nuclei

Heterogeneous ice nucleation has been thought to occur via four mechanisms: deposition mode, condensation freezing mode, immersion freezing mode, and the contact freezing mode (Pruppacher and Klett, 1997). In the deposition mode, ice deposits on the surface of an insoluble particle directly from the vapor phase. This mode theoretically only requires temperatures below 0°C and relative humidity conditions above ice saturation, although for any given substrate colder temperatures or higher relative humidities may be required for the initiation of the ice phase. The condensation freezing mode describes a particle, which contains an insoluble core mixed with soluble matter that forms a solution from which an ice germ subsequently freezes due to the presence of the insoluble core. In this mode temperatures below 0°C and water saturated conditions are required. The immersion freezing mode is similar to the condensation freezing mode, except the insoluble core is immersed into the drop or haze particle and initiates freezing at sufficiently cold temperatures. The contact freezing mode describes the situation in which an insoluble core comes in contact with a supercooled droplet surface, causing the droplet to freeze. Immersion freezing is generally found to initiate ice formation at similar temperatures to condensation freezing (Lohmann and Diehl, 2006), but it is generally expected that contact nucleation proceeds at faster rates under warmer

temperature conditions than the other three modes (e.g. DeMott, 1995 and references therein).

Insoluble cores that initiate ice formation are known as ice nuclei (IN) and their concentrations can be highly variable in time and space and depend on the temperature (T) and relative humidity (RH) of their environment. Many studies in the 1950s-1970s attempted to determine the composition of IN in the atmosphere. It was suggested that the production of dust and clay particles from arid regions was the major global source of IN (Roberts and Hallett, 1968; Schaller and Fukuta, 1979) along with combustion products (e.g. DeMott et al., 1999; Langer, 1968; Langer, 1970), and volcanic material (Hobbs et al., 1971; Isono et al., 1959; Schnell et al., 1982). Other sources of metal oxides such as steel mills, power plants, aluminum works and sulfide works were found to emit IN (e.g. Telford, 1960). Finally, it was shown that organic material such as leaf litter and bacterial particles could be active as IN at very modest supercoolings (Schnell and Vali, 1972; Schnell and Vali, 1973; Vali, 1968; Vali et al., 1976).

From these observations, requirements for a particle to serve as an IN were stated as follows by Pruppacher and Klett (1997):

1. Insolubility requirement: IN provide a rigid substrate for ice germ formation. The presence of salt ions would lower the effective freezing temperatures by forming a solution and inhibiting the ice germ formation.
2. Size requirement: It has been shown that the concentration of IN is proportional to the concentration of large particles (diameter $> \sim 0.3 \mu\text{m}$) and uncorrelated to the concentration of Aitken sized particles (diameter $< 0.1 \mu\text{m}$) (Edwards and Evans, 1960; Edwards et al., 1962; Georgii and Kleinjung, 1967; Richardson et al.,

2007). However, it is unclear if this simply is the result of changing chemistry with particle diameter (e.g. terrestrial aerosol such as mineral dust has a larger mode size than background sulfate aerosol). IN must be larger than the size of the critical ice embryo and are typically larger than 0.1 μm , supported by work by Chen et al. (1998) and Marcolli et al. (2007).

3. Chemical bond requirement: IN must have bonding similar to the O-H-O hydrogen bonds in the ice structure. Outward pointing hydrogen bonds allow for maximum interaction with oncoming water molecules. Fukuta (1966) also suggested that a hydrogen-bonding molecule on the IN surface should have rotational symmetry.
4. Crystallographic requirement: It is suggested that the geometric arrangement of bonds at the substrate surface may be as important as the chemical nature of the substrate. An arrangement similar to the structure of ice will facilitate the growth of ice at the surface. Small differences require the ice or the substrate to structurally deform to join, yielding elastic strain energy, and may result in dislocations in the structure of ice. The elastic strain raises the bulk free energy of the ice embryo and therefore reduces the nucleability of the substrate. The degree of misfit can be represented by the disregistry:

$$\delta = \frac{na_{o,n} - ma_{o,i}}{ma_{o,i}} \quad (3.9)$$

where $a_{o,n}$ is the crystallographic lattice parameter of the IN, $a_{o,i}$ is the crystallographic lattice parameter of ice and m and n are integer numbers chosen to minimize δ . It is assumed the ice embryo can be strained by an amount ε :

$$\varepsilon = (a'_{o,i} - a_{o,i}) / a_{o,i}, \quad (3.10)$$

where $a'_{o,i}$ is the strained ice lattice parameter. If it is assumed that the substrate strain is negligible, the misfit is $\delta\varepsilon$.

5. Active site requirement: IN contain sites which are able to adsorb water molecules and initiate ice nucleation. There are three known types of active sites:
 - a. Morphological surface inhomogeneities such as steps or cracks in the surface of the particle are high energy sites able to hold water molecules to their surface.
 - b. Chemical inhomogeneities are usually caused by the presence of a foreign, hydrophilic ion. Water molecules are attracted to this ion of spuriously high hydrophilicity by electric forces and a dipole moment develops between the water molecule and the foreign ion.
 - c. Electrical inhomogeneities are sharply defined boundaries between regions of different electric field sign or locations where the electric field vector is parallel to the substrate surface. Due to its molecular dipole, water molecules are attracted to these sites. Additionally, the diffusivity of the water molecules may be enhanced by the parallel electric field, enhancing the growth of water clusters.

Therefore, from these requirements it is clear that at any given T and RH conditions, only a fraction of ambient particles are able to serve as IN. It has been observed that as the temperature decreases, the fraction generally increases; although, measurements suggest sometimes only modest increases (e.g. Prenni et al., 2007b)

3.2.2. Classical theory of heterogeneous ice nucleation

The classical deposition nucleation theory is based on the work of Fletcher (1958; 1959; 1962). It is assumed an ice embryo can be described as a spherical cap on a curved substrate and the work of ice germ formation via freezing is described as (Pruppacher and Klett, 1997):

$$\Delta F_{g,s} = \frac{16\pi M_w^2 \sigma_{i,v}^3}{3[RT\rho_i \ln(S_i)]^2} f(m_{i/v}, x), \quad (3.11)$$

where $f(m, x)$ describes how a foreign surface lowers the barrier and all other parameters are as defined in Section 3.1.1. $f(m, x)$ accounts for the equilibrium vapor pressure required over the curved germ surface and is given by:

$$2f_{het}(m, x) = 1 + \left(\frac{1 - mx}{\phi} \right) + x^3 \left(2 - 3 \left(\frac{x - m}{\phi} \right) + \left(\frac{x - m}{\phi} \right)^3 \right) + 3mx^2 \left(\frac{x - m}{\phi} - 1 \right) \quad (3.12)$$

$$\phi = (1 - 2mx + x^2)^{1/2}; \quad m = \cos \alpha; \quad x = r_N / a_g$$

where α is the contact angle, r_N is the substrate radius and a_g is the germ radius. If the embryos grow by vapor deposition, then the heterogeneous nucleation rate, J_{het} , may be derived:

$$J_{het} \approx \frac{kT}{h} 4\pi r_N^2 c_{i,s} \exp\left(-\frac{\Delta g}{RT} - \frac{\Delta F_{g,s}}{kT}\right) \quad (3.13)$$

$$c_{i,s} = \frac{e}{(2\pi M_w kT)^{1/2} v_s} \exp(\Delta G_{des} / kT)$$

where $c_{i,s}$ is the concentration of single water molecules adsorbed on the surface, e is the vapor pressure, v_s is the frequency of vibration of an adsorbed molecule normal to the surface, g is number of water molecules in the ice germ, ΔG_{des} is the energy of desorption, and $\Delta F_{g,s}$ is defined as in Equation (3.11). Slightly different formulations are

used for deposition nucleation resulting from the difference in ice forming from the liquid or vapor phase (see Chapter 8).

From this expression for the nucleation rate, several conclusions may be drawn: for a given growth rate, there is little temperature dependence if r_N is greater than 0.1 μm , however the temperature dependence is strong for smaller IN sizes. The nucleation rate decreases rapidly with decreasing $m_{i/v}$ for a given particle size because this acts to increase the interfacial free energy between the ice and the substrate. Classical theory qualitatively matches some experimental results. First, it reproduces the result that there is decreased nucleability with decreasing particle size. Second, there is decreased nucleability for decreased $m_{i/v}$, however there is no quantitative information available on this effect since contact angles generally are not known for any substance and since it is not the macroscopic contact angle, which could potentially be measured, but instead the microscopic contact angle which is important for nucleation properties. However, this theory predicts that all particles of the same size and composition (and contact angle) should have the same nucleation efficiency, which has been shown not to hold for heterogeneous ice nucleation (Berezinski et al., 1988). Further, this theory cannot account for phenomena such as active sites, which appear to be crucial in heterogeneous ice nucleation. Marcolli et al. (2007) investigated heterogeneous freezing nucleation rates if particles were assumed to have varying contact angle distributions or a representation of active sites (see Chapter 8). Theories expanding on the classical theory can be found in Khvorostyanov and Curry (2000; 2004).

Problems arise in the practical application of the classical theory due to the large number of unknown parameters such as contact angles (θ), surface tensions (σ) and

energies (Δg , ΔG_{des} , etc.), and their temperature dependencies. Thus, to this point it has not been practical, and perhaps not accurate, to implement the classical theory into models. Khvorostyanov and Curry (2005) claim otherwise, but it is not yet clear that their theory is practically constrained to agree with existing IN measurements (personal communication with Paul DeMott). Therefore, many parameterizations have been developed in the literature for deposition as well as other freezing modes and some are presented in the following section.

3.2.3. Parameterizations of heterogeneous ice nucleation

Early work suggested that there was no systematic variation of IN with location and Fletcher (1962) suggested that IN concentrations, N_{IN} , could be represented as purely a function of the degree of supercooling:

$$N_{IN} = A \exp(\beta T_{sup}) \quad (3.14)$$

with $A=10^{-5} \text{ l}^{-1}$ and $\beta=0.6 \text{ }^{\circ}\text{C}^{-1}$ as suggested values. Later work (Huffman, 1973a; Huffman, 1973b) showed that N_{IN} also depends on RH and Meyers et al. (1992) developed a formulation still in use today in many models:

$$\begin{aligned} N_{IN} &= \exp(A + BS_i) && (\text{deposition and condensation freezing}) \\ N_{IN} &= \exp(a + bT_{sup}) && (\text{contact}) \end{aligned} \quad (3.15)$$

where S_i is the supersaturation with respect to ice, expressed as a fraction, and $A=-0.639$, $B=0.1296$, $a=-2.80$ and $b=0.262$. The deposition and condensation freezing nucleation parameterization was based on data collected over the temperature range -7 to -20°C and for ice supersaturations less than 25%, but has been extrapolated beyond this range (e.g. Lin et al., 2002). The contact freezing parameterization is based on data collected for temperatures between -5 and -20°C. Contact freezing cannot be effectively measured in

the CFDC and thus will not be discussed further here; however, it is important to remember that contact freezing can be occurring in the atmosphere via collisions of mineral dust particles with supercooled droplets and may initiate ice crystals at warmer temperatures than observed for deposition nucleation. Durant and Shaw (2005) found that contact freezing temperatures did not depend on if the IN was located outside the droplet and collided with the liquid or if the IN was located within the droplet and contacted the surface from inside. They suggested that this surface crystallization mechanism could describe the evaporation freezing observed in the evaporating edges of clouds. This suggests that contact freezing concentrations could be limited by the concentration of immersion freezing nuclei, but activation simply occurs via a different process and potentially at warmer temperatures.

Detwiler and Vonnegut (1981) investigated the ice nucleation of silver iodide and lead iodide particles between -6 and -67°C. Following classical heterogeneous ice nucleation from Fletcher (1969a, Equation (3.13)), the nucleation rate will be dominated by the exponential term which is temperature dependent. According to Fletcher (1969b), Equation (3.11) can be rewritten as:

$$\frac{\Delta F_{g,s}}{kT} = \frac{16\pi\sigma_{i,v}^3 V^2 N f(m, x)}{3R^3 T^3 \ln^2 S_i}, \quad (3.16)$$

where V is the molar volume of water in the ice phase and N is Avogadro's number. If one wanted to hold the right side of Equation (3.13) constant, while decreasing the temperature, then the cubic dependence on temperature would have to be compensated by an increase in the ice saturation ratio. Thus, to a first approximation:

$$\frac{\ln^2 S_{i,T1}}{\ln^2 S_{i,T0}} = \frac{T_o^3}{T_1^3}. \quad (3.17)$$

Equation (3.17) may be used to predict the saturation ratio required for nucleation at any temperature once the nucleation conditions have been determined for a single temperature. However, the equation only holds if all the other parameters in Equations (3.13) and (3.16) are constant with temperature, which is not a good assumption for many factors. This is primarily due to the decreased velocity of the impinging vapor molecules with decreasing temperature and to a lesser extent, a decrease in size of the critical ice embryo and lower vapor densities corresponding to the ice saturation ratio as the temperature decreases which alters the parameter $c_{I,S}$.

More recently, several formulations to predict number concentrations of heterogeneous freezing nuclei have been used in intercomparison studies; Lin et al. (2002) compare the methods of four different models that predict N_{IN} in various ways. The U.K. Met office model (UKMO, Spice et al., 1999) and the Goddard Space Flight Center (GSFC, Lin, 1997) model parameterize N_{IN} as only a function of maximum ice supersaturation (S_i):

$$N_{IN} = A(S_i - 1)^B \quad (\text{UKMO}), \quad (3.18)$$

where A and B are constants. The GSFC formulation is identical to the Meyers formulation, but slightly different constants are used to account for changes in aerosol concentration. These parameterizations are expected to give an upper limit of N_{IN} in the atmosphere as the predicted N_{IN} is not limited by observed or estimated number concentrations of insoluble particles in the atmosphere, and thus may exceed reasonable values of N_{IN} . At the very least, these expressions give “global” concentrations of IN since they are not tied to aerosol concentrations or properties. Parcel models developed at CSU (DeMott et al., 1994b; DeMott et al., 1998) and the University of Utah

(Khvorostyanov and Sassen, 1998; Sassen and Dodd, 1988) are based on the concept of the effective freezing temperature (T_{eff}) from Sassen and Dodd (1988):

$$\begin{aligned}
 N_{IN,k} &= \frac{a}{F_{>0.1\mu m}} (T_0 - T_{eff,k})^b & (CSU) \\
 \frac{dN_i}{dt} &= \sum_k A_{s0} B_s \exp(-A_z z) \exp[B_s (T_0 - T_{eff,k})^b] \frac{dT}{dt} & (UTAH)
 \end{aligned} \tag{3.19}$$

where T_0 is 273.15K, $F_{>0.1\mu m}$ is the number fraction of particles larger than 0.1 μm in diameter, z is the height, k is a given size bin and a, b, A, B are constants. Values for all constants may be found in Lin et al. (2002). Those authors found that accounting for heterogeneous nucleation in the four models (opposed to homogeneous freezing only) generally reduced ice crystal concentrations in cirrus clouds, particularly when updrafts were low, due to the reduction of water vapor available for initiating and growing crystals via homogeneous freezing. However, due to such different formulations of heterogeneous freezing parameterizations, the authors found it impossible to scrutinize the differences in N_{IN} predicted.

Zuberi et al. (2002) investigated whether the Koop et al. (2000) relationship between the freezing temperature and water activity would hold for ammonium sulfate solution droplets with mineral dust inclusions. Those authors found that using $\Delta a_w = 0.242$ for $-70 < T < -30$ °C gave good, but not perfect agreement to the data. The fit appears not to hold at higher water activities, for which the particles required colder conditions to freeze than the parameterization predicted. Kärcher and Lohmann (2003) suggested that the water activity parameterization for homogeneous freezing could be applied to heterogeneous freezing if Δa_w was allowed to vary with factors that control heterogeneous freezing, X_k , such that:

$$\Delta a_w = [S_{cr}^{hom} - S_{cr}^{het} \{X_k\}] a_w^i(T), \quad (3.20)$$

where S_{cr}^{hom} and S_{cr}^{het} are the freezing thresholds for homogeneous and heterogeneous freezing. In this way the nucleation rates, J_{het} and J_{hom} , for heterogeneous and homogeneous freezing are simply a function of the parameter Δa_w . Then the freezing for a mixed particle containing an IN is:

$$J_{mix} = A_c J_{het} + (1 - CVF) V_d J_{hom}, \quad (3.21)$$

where J_{mix} is the nucleation rate of the mixed particle, A_c is the surface area of the core IN, and CVF is the core volume fraction: the ratio of the core volume to the volume of the surrounding liquid. Sharp increases in ice crystal concentrations were found if S_{cr}^{het} was less than 1.3 and the freezing threshold is nearly constant for mixed particles at S_{cr}^{het} if $CVF > 10^{-5}$ for 250 nm particles. Thus this parameterization predicts that simply the presence and not the size of the immersed IN is critical in determining the nucleation rate of mixed particles. Therefore this parameterization predicts that heterogeneous freezing happens just like homogeneous nucleation, with a modified Δa_w , but does not account for differences in insoluble core properties.

Diehl and Wurzler (2004) developed a parameterization for immersion freezing based on the median freezing temperature, T_m , of drops with an insoluble core of a certain composition. They assumed the number of frozen drops was independent of the cooling rate and the number density of insoluble particles in the drop. They did allow for changes in the rate due to differences in insoluble core composition, however, through the parameter $B_{h,i}$, which increases with increasing efficiency of the particle and is applied in the equation:

$$-T_m = \frac{1}{a} \ln \frac{\ln 2}{B_{h,i}} - \frac{1}{a} \ln V_d, \quad (3.22)$$

where V_d is the volume of the drop and a is a constant. The change in the number concentration of unfrozen drops at the median freezing temperature ($N_u(T_m)$) with time is then:

$$\frac{dN_u}{dt} = N_u a B_{h,i} V_d \exp(aT_{\text{sup}}) \frac{dT}{dt}. \quad (3.23)$$

The parameterization was found to be in good agreement with freezing of ammonium sulfate droplets with mineral inclusions reported by Zuberi et al. (2002). However, the validity of applying a single value of $B_{h,i}$ for a given species is uncertain.

Lohmann and Diehl (2006) developed parameterizations for immersion and contact freezing for $-35 < T < 0^\circ\text{C}$:

$$\begin{aligned} N_i &= \frac{kTC_c}{3\eta r_m} m_{oi} 2r_l N_{a, \text{cnt}} \frac{N_l^2}{\rho q_l} & (\text{contact}) \\ N_i &= N_{a, \text{imm}} \exp(273.2 - T) \frac{dT}{dt} \frac{\rho q_l}{\rho_l} & (\text{immersion}) \end{aligned} \quad (3.24)$$

where r_l is the mean volume droplet radius, q_l is the cloud liquid water mass-mixing ratio, N_l is the number concentration of cloud drops, ρ is the air density, ρ_l is the density of water, m_{oi} is the mass of the ice crystal, and $N_{a, \text{cnt}}$ and $N_{a, \text{imm}}$ are the number concentration of contact or immersion nuclei, respectively. The first term in the top equation represents the Brownian aerosol diffusivity where η is the viscosity of air, C_c is the Cunningham correction factor and r_m is the aerosol mode radius. Distributions of $N_{a, \text{cnt}}$ and $N_{a, \text{imm}}$ are assumed input parameters and are allowed to vary with temperature to allow for differences between IN composition. Those authors found that for modest

changes in IN composition (kaolinite vs. montmorillonite) changes in global cloud cover and precipitation were observed resulting in differences in global net radiation of $\sim 1 \text{ W m}^{-2}$.

While this section is not meant to be an exhaustive list of all heterogeneous freezing parameterizations developed and published in the literature, it provides a look at the range of parameterizations used. It also demonstrates several features that these parameterizations lack: only one parameterization predicts IN concentrations as a function of particle size and few are a function of both temperature and supersaturation. In Chapter 7, a new parameterization will be proposed which accounts for all three variables and its applicability to the observations of the freezing behavior of the four dust samples will be examined.

4. Owens (dry) Lake Dust

4.1. *Introduction*

The parameterization of heterogeneous nucleation has faced many challenges in large scale models due to the lack of understanding of the factors controlling heterogeneous freezing and lack of experimental data (Kärcher and Lohmann, 2003). DeMott et al. (2003a) determined the composition of residual ice nuclei particles that were measured in a continuous flow diffusion chamber (CFDC) from free troposphere air sampled at Storm Peak Laboratories, located on Mt. Werner (3200 m above mean sea level), and found that while mineral dust particles comprised only around 1% of the total particles, they represented 33% of the heterogeneously nucleated ice crystals. Kärcher and Lohmann (2003) postulated that condensation or immersion freezing was likely the dominant pathway for heterogeneous freezing, as they believed that insoluble particles were unlikely to reach the upper troposphere without being coated by soluble material. Several studies have investigated the freezing behavior of sulfates with mineral dust inclusions (Archuleta et al., 2005; Hung et al., 2003; Zuberi et al., 2002) and found these mixed particle types could be active under many atmospherically relevant conditions. Therefore to accurately characterize heterogeneous nucleation, more information is needed on nucleation of pristine mineral dust as well as processes occurring on coated dust.

Sheehy (1992) suggested that the sizes of arid regions around the globe are increasing by millions of hectares per year due to changes in precipitation and anthropogenic disturbances and thus the role of dust in atmospheric processes may amplify in the future. One prominent example of dust source amplification by anthropogenic disturbance is the Owens Lake region in southeastern California. The Owens lakebed contained water continuously for the last 800,000 years until its source water was diverted to Los Angeles County in 1913. Within 15 years, the lake was completely dry, and the resulting alkaline, saline playa now is considered one of the largest sources of fine particulate matter (particles having diameters smaller than 2.5 μm , $\text{PM}_{2.5}$) in the western hemisphere (Gill and Gillette, 1991).

The mechanisms and consequences of formation of an erodible salt crust over portions of the playa, the surface of which has highly-variable composition, is discussed by Cahill et al. (1996), Reheis (1997), and Niemeyer et al. (1999), among others. Briefly, the playa receives moisture from an underlying brine pool and from frequent flooding during winter and spring; the depth to moisture is also shallow in many portions, and is recharged from regional aquifers (Cahill et al., 1996). When wetted, the surface salts hydrate forming a fragile, easily erodible crust. The dust flux from such playas, and potentially the salt content of the aerosol, is highly dependent on this crust formation, groundwater depth, wind speed, and location (Reheis, 2006; Reid et al., 1994). Owens Lake dust fluxes also show a seasonal dependence: during the summer, a harder, less erodible crust is formed that tends to persist through the fall into the higher precipitation season of the next winter (Niemeyer et al., 1999). Given the complex topography of the region, plumes can be lofted to 2 km, transported 250 km and extend to cover 90,000

square kilometers (Reid et al., 1994). Near-surface total suspended particulate dust loadings have been measured as high as $2600 \mu\text{g m}^{-3}$ 100 km south of the lake bed, and Niemeyer et al. (1999) measured aerosol optical depths as large as 4.5 during dust storm events in this region using a sunphotometer. For comparison, the 24-hour-averaged EPA standard for particulate matter with diameters less than $10 \mu\text{m}$ (PM_{10}) is $150 \mu\text{g m}^{-3}$.

The characteristics of airborne dusts collected in various parts of the Owens Valley were examined by Reheis (1997); mean grain size and composition varied with location and season. The analysis by Reheis (1997) determined organic matter content, total soluble salts and gypsum, total carbonate (calcite plus dolomite), and grain size. From 60-90% of the mass in the analyzed samples was contained in particles having diameters smaller than $10 \mu\text{m}$, and 10-50% of the mass was in particles smaller than $2 \mu\text{m}$. *In situ* measurements of Owens Lake dust during dust storms also showed that it is unusually fine grained compared to agricultural soils, with an observed bimodal volume distribution with mode sizes for suspended dust of 0.3 and $3.5 \mu\text{m}$ (Reid et al., 1994). Reheis (1997) determined that organic content represented 0.9-30.1% of the total mass, depending on season and location around the lake bed, but a clear trend with season was not observed. The soluble salt content varied between ~3-37% of the mass on an organic-matter-free basis. The dominant soluble salts in the playa crust are sodium sulfate, sodium carbonate, hydrates of those sodium salts (mirabilite, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; thermonatrite, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$; natron, $\text{Na}_2(\text{CO}_3) \cdot 10\text{H}_2\text{O}$; and trona, $\text{Na}_3\text{HCO}_3\text{CO}_3 \cdot 2\text{H}_2\text{O}$), and sodium chloride. Unanalyzed inorganic mass (40-75%) comprises minerals including calcite, smectites, illites, kaolinites, quartz and plagioclase feldspar (Niemeyer et al., 1999).

The high soluble-salt contents of Owens (dry) Lake dust, and the presence of minerals that have been shown to be active as heterogeneous ice nuclei (Pruppacher and Klett, 1997) suggest that particles derived from this source may be active in warm cloud formation in the region, as well as potentially influence regional concentrations of ice nuclei (IN). Further, studies have found that this soil contains various toxic metals in concentrations up to tens of parts per million (Gill and Gillette, 1991), and the hygroscopicity of this dust may strongly influence the lifetime and transport distances of these species in the atmosphere. However, the distribution of soluble species with particle size is unknown and probably highly variable, and the mixing state of individual particles is also not known. In this chapter, the water uptake, CCN activity and ice nucleating ability of submicron particles derived from samples of Owens (dry) Lake dust are presented.

4.2. *Experimental*

4.2.1. Sample Collection

Samples were obtained by the United States Geological Survey (USGS) from the Owens Lake region. Samples were collected from the top 3 cm of the dust at various locations around the dry lakebed. Particulate matter larger than 2 mm was removed from the bulk sample using a wind tunnel. USGS prepared elemental analyses and particle size distributions for the collected samples using a Malvern Mastersizer 2000. These analyses showed that the volume distribution was generally bimodal, with one peak at particle diameters between 6-9 μm and another between 200-300 μm . If the particles are assumed to be spherical, the size distribution lognormal, and the volume distribution is converted to a number distribution, 44% of the particles have diameters less than 0.58 μm . In the

bulk samples, the dominant elements reported in the analyses supplied to us were sodium, calcium, iron and potassium. In this work, because of experimental limitations described further below, only the very smallest particles (diameters ≤ 400 nm) in each sample were examined; it is unclear if the bulk elemental analysis is representative of our subset of particles. Hygroscopicity experiments showed similar results for measurements performed on several samples from each area of the lakebed; therefore it is not specified here which sample was used for each experiment.

4.2.2. Experimental Procedure

Initially the bulk sample was reaerosolized via atomization from water suspension. However, since both soluble and insoluble components were present in this dust sample, alteration of the potentially size-dependent particle composition may have occurred when the bulk sample was suspended in water and then atomized. Specifically, water soluble material was likely redistributed across the size distribution and insoluble particles that were not initially associated with soluble material may have been transformed into internally mixed particles. Therefore a fluidized bed was also used to generate Owens (dry) Lake particles directly from the bulk sample (dry generation), which is expected to be more representative of the process which lofts dust in the atmosphere. However, the formation of the fragile salt crust involves hydration and recrystallization of surface layers, and thus the generation of particles via atomization from solution may also produce compositions that could be observed in nature. Particles generated by the fluidized bed are often highly charged so the particles were charge-neutralized by passing through a bipolar diffusion charger (TSI Model 3077 and Aerosol Dynamics Inc., NRD Staticmaster 2U500) before size selection. At the time of the

experiment, the activity was 0.87 mCi for the ^{85}Kr sources and ~ 2 mCi for the ^{210}Po source. Aerosols generated by atomization were charge-neutralized in this way also.

Figure 4.1 shows the experimental set-up for the experiments described in this chapter. The humidified tandem differential mobility analyzer (HTDMA) was run in its typical configuration described in Chapter 2 and at a temperature of 30°C. To obtain sufficient number densities of particles for experiments with dry generation, it was necessary to use a flow ratio of 5:1 to allow a broader distribution of particles to exit the DMA. For DMA voltage settings corresponding to 100 nm mobility diameter particles, the 5:1 flow ratio yields a distribution of singly-charged particles having diameters from 90-113 nm; for nominal 400 nm particles, the singly-charged particles range from 352-473 nm. Particle sizes larger than 400 nm were not examined because of the increasing importance of multiply-charged particles, as well as the difficulty in producing sufficient number concentrations of those larger sizes with the DMA technique. Hygroscopicity is expressed in terms of the growth factor, $GF(RH_w)$, the ratio of the diameter after conditioning to the dry diameter measured at $RH_w < 10\%$ (Equation 2.1). Size distributions were fit to a theoretical model accounting for instrument transfer functions using the inversion algorithm of Zhou et al. (2002) to give values of $D_{wet}(RH_w)$.

Next, a cloud condensation nuclei counter (CCNC) was used to measure CCN concentration as a function of dry particle diameter and water supersaturation. Wet-generated aerosol was generated, size-selected and counted as in the sample stream for the HTDMA (see Figure 4.1), then introduced in the center of the CCN chamber. Dry-generated aerosol was not in sufficient number concentrations for this measurement and only wet-generated aerosol was examined. The supersaturation was increased in a

stepwise manner and the critical supersaturation was determined to be the supersaturation at which a minimum of 50% of the particles activated as cloud droplets. Factory calibrations of the CCNC supersaturations were applied to the data analysis. Ammonium sulfate was used to verify the calibration on a regular basis.

The continuous flow diffusion chamber (CFDC) was employed to study freezing behavior. Quasi-monodisperse particles with distributions centered at 100, 200, 300 or 400 nm were either wet- or dry-generated, size-selected and counted as described above (see Figure 4.1). The aerosol sample flow was transmitted to a pre-cooler at a temperature near -25°C that cooled the aerosol flow. After exiting the pre-cooler the sample flow was forwarded immediately to the CFDC. During a series of experiments, the RH_i in the CFDC was increased in a stepwise manner to map out conditions where particles began to nucleate and grow as ice crystals. By comparing the concentration of ice crystals measured in the OPC with the total counts measured by the CPC upstream of the CFDC inlet, the fraction of particles nucleating ice crystals was determined. The preferred definition of the onset conditions for ice formation is the temperature and relative humidity at which 1% of the input particles have nucleated ice. However, in these studies, using the laboratory unit and particularly for the larger particle sizes tested, the hygroscopic growth of the particles in the chamber prior to ice nucleation sometimes contributed to an enhanced OPC signal. This background was unambiguously distinguishable from the freezing signal when 5% of the particles had nucleated ice, and therefore those conditions are reported as freezing onset for the experiments using the laboratory system. This choice may be expected to lead to a slight overestimation of the RH_w at onset conditions. Results are presented as averages of at least three points per

temperature, with uncertainty bars representing the 95% confidence level, except that data for wet-generated 300 and 400 nm particles are shown as individual data points. Unlike the laboratory unit, the evaporation region in the aircraft unit (ACFDC- 1) permits operation above water saturation while ensuring the discrimination of ice crystals versus water droplets. This capability enabled freezing-onset conditions to be defined as those for which 1% of the particles nucleated ice, since hygroscopic growth of the particles was suppressed in the evaporation region. Individual data points are shown for measurements collected with this unit ($T > -40^{\circ}\text{C}$), as it is more difficult to reproduce equivalent processing temperatures in every experiment using the refrigeration compressors, and thus averaging would occur over a broader temperature range.

During experiments, a temperature gradient existed along the outer ice surface of the laboratory unit, which was configured such that the outer wall was colder than the inner ice surface, as described in Chapter 2. The inner cylinder had a nearly uniform temperature along the length of the wall, as measured by four thermocouples. There were also four thermocouples along the outer cylinder. Temperature readings from the two along the top half of the chamber were within $\sim 0.5^{\circ}\text{C}$ and readings from the two along the bottom half of the chamber were also within $\sim 0.5^{\circ}\text{C}$, with a $\sim 1.5^{\circ}\text{C}$ temperature difference between the two groups. The temperature was colder at the bottom half of the chamber, exposing the particles to colder temperatures and higher relative humidity just prior to the exit of the chamber. It is expected that sufficient time exists for the particles to reach equilibrium with the conditions in the lower half of the chamber, where ice nucleation and growth can continue. Therefore, using the average of the four thermocouple readings in the calculation of the aerosol location, which determines the

temperature and RH_i the particles experienced, was inaccurate, and data processing was modified to only include the two thermocouple measurements at the bottom of the chamber in the average temperature calculation. Results from freezing onset experiments for quasi-monodisperse ammonium sulfate particles were compared to predictions from the water activity based homogeneous freezing theory of Koop et al. (2000). Agreement between the data and theory was improved when the revised method was used to compute RH_i (See Appendix I).

A temperature gradient also existed along the axial direction of the inner (cold) wall in the aircraft system at the time of these studies. Since the temperature increased down the wall (in the direction of particle flow), the relative humidity at the exit of the unit was not as high as calculated using the average wall temperature. Richardson et al. (2007) determined a linear relationship between the measured cold wall temperature and an “effective” cold wall temperature for this case. Their relationship was applied to our data, allowing a new aerosol position to be calculated and a corrected RH_i computed.

4.3. Results

4.3.1. Hygroscopicity data

The GF values for particles generated from the Owens (dry) Lake dust samples are shown in Figure 4.2. There was no significant difference in hygroscopic behavior for 100 and 200 nm particles when the particles were generated via wet generation, so GF data for both sizes are shown in Figure 4.2 (circles). The data for dry-generated aerosol (triangles) are for 200 nm particles, as 100 nm particles are not efficiently generated by the fluidized bed. Predicted GF values of pure anhydrous sodium carbonate and sodium sulfate particles are shown in Figure 4.2 for comparison. These values were calculated

based on simplified Köhler theory (Pruppacher and Klett, 1997) in which the maximum dissociation ($v=3$) was assumed, which is equivalent to $\kappa=1.02$ for sodium sulfate and $\kappa=1.29$ for sodium carbonate (see Petters and Kreidenweis (2007)). The scatter indicates the degree of heterogeneity among similarly sized particles due to differences in the mixture of soluble species and the percentage of insoluble mass in each particle as experimental uncertainty is much smaller than the scatter observed. The wet-generated particles took up a small amount of water at $30\% < RH_w < 65\%$ ($GF < 1.1$). The phase diagrams of sodium sulfate (Flatt, 2002) and sodium carbonate (Vanderzee, 1982) show that both salts are stable in hydrated states for these RH_w values at the temperature of the measurements. This small growth at low RH_w is possibly indicative of the formation of a hydrated phase. Some of the wet-generated particles exhibited a deliquescence-like transition just before $70\% RH_w$, with about 90% of the particles falling into the more-hygroscopic mode. The deliquescence transitions were not sharp due to the heterogeneous nature of the sample and it is possible they occurred for $67\% < RH_w < 77\%$, with intermediate GF values observed through this RH_w range. Above $78\% RH_w$, the majority of the wet-generated particles experienced continuous growth, while the remaining particles ($\sim 10\%$) exhibited much smaller growth factors. The presence of more than one characteristic hygroscopic growth factor in submicron particles is not surprising, since Owens Lake dusts contain appreciable amounts of both insoluble minerals and soluble salts in this size range (Reid et al., 1994). Any individual particle may have a different fraction of these components. The thick black line shows the fit to the upper edge of the data envelope for the wet-generated particles, using Equation (2.11)

with coefficient values shown in the first row of Table 4.1. Fits for other subsets of the data are also listed in Table 4.1.

For particles that were generated dry (triangles, Figure 4.2), no hygroscopic growth was observed until a deliquescence-like transition near $\sim 70\% RH_w$. In contrast to the wet-generated sample, a smaller fraction of the particles were hygroscopic ($\sim 35\%$), but those particles took up more water than did the more-hygroscopic fraction produced by the wet generation method. The majority of the particles ($\sim 65\%$) remained either at their dry size, or exhibited small water uptake at high relative humidity ($RH_w > 80\%$), with GF values slightly smaller than the less-hygroscopic fraction of the wet-generated particles. The differences in water uptake between the wet- and dry-generated cases occur for the following reasons. When the particles are suspended in water for the wet generation procedure, the soluble material dissolves and is then redistributed among the insoluble dust cores during the droplet generation and drying; different proportions of hydrated salts than existed in the original sample may also form during this procedure. The redistribution of soluble material in effect normalizes the water uptake, with the less hygroscopic fraction taking up more water, and the more hygroscopic fraction taking up less water, than the comparable fractions in the dry-generated particle samples. The less-hygroscopic dry-generated particles also exhibited some GF values less than one (the lowest value was $GF = 0.96$), possibly due to slight changes in the shape of the particles with hydration (Mikhailov et al., 2004). As small amounts of water deposit on the surface of an irregular particle, the particle becomes more spherical and appears smaller in the DMA, due to the reduced drag force on the particle. The decrease in particle size could also be due to density and bound water mass changes as salt constituents of the

mixed particle changed hydrated state. Given the chemically heterogeneous nature of the dust, and the unknown particle morphologies, shape corrections were not applied to the data.

The differences in hygroscopic response between wet- and dry-generated particles are illustrated in Figure 4.3, showing distributions from the HTDMA at selected RH_w . Figure 4.3a shows the distributions for wet-generated particles and Figure 4.3b for dry-generated particles. In each case, the dry distribution at 5% RH_w is shown as a dashed line. The dry size distribution was broader for the dry-generated case because lower flow ratios in DMA1 were required to obtain the necessary particle concentrations. In Figure 4.3a, at 85% RH_w all of the wet-generated particles have shifted into larger sizes, yielding the bimodal distributions with the percentages in each fraction as indicated earlier. Comparison of the distributions at 85% and 90% RH_w shows the relatively stable size of the less-hygroscopic mode and the increased diameter of the more-hygroscopic mode as RH_w increased. In contrast, most of the dry-generated particles remained at their dry size at 85% RH_w and only a small fraction of the particles grew to the larger sizes, with the broad grown distribution lacking a clearly defined mode size for the more-hygroscopic fraction. Determining a grown size from data such as that shown in Figure 4.3b is somewhat subjective and a range of GF values is possible, but the maximum GF generally increased with increasing RH_w .

The hygroscopic growth of the range of particle types produced in both generation methods from the bulk Owens (dry) Lake sample is approximately captured by Equation (2.13) for $0.39 < \kappa < 1.07$. These bounds are shown as the shaded area in Figure 4.2. The primary difference between the particle types produced by the wet and dry generation

methods was in the fractions of particles falling into the more- and less-hygroscopic modes. While it is generally expected that the dry-generated dust is more representative of the dust that reaches the atmosphere, the wet-generated case could also be atmospherically-relevant, as it has been suggested that dusts with higher salt contents exist after precipitation events (Reid et al., 1994).

4.3.2. CCN activity

The activity measured by the CCNC for particles generated from the Owens (dry) Lake sample via wet generation is shown in Figure 4.4 (circles). Activation behavior is expressed in terms of the minimum supersaturation required to activate a particle having the indicated dry diameter. Unfortunately, the fluidized bed was unable to produce sufficient number concentrations of particles at sizes small enough to measure the critical supersaturations accessible in our instrument, so no direct comparisons can be made between the CCN activity of particles generated by the two methods.

Extrapolation of the hygroscopicity data using Equation (2.13) yielded the range of predicted CCN activity for Owens (dry) Lake dust shown as the shaded area in Figure 4.4, for $0.39 < \kappa < 1.07$, corresponding to the hygroscopic growth defined by the shaded region in Figure 4.2. Predicted s_c - D_{dry} relationships for sodium sulfate ($\kappa=1.02$) and sodium carbonate ($\kappa=1.29$) are shown in Figure 4.4 for comparison. Heterogeneity of composition with size is apparent in Figure 4.4. At the sizes corresponding to the HTDMA measurements, 100 to 200 nm, the CCN activity corresponded well to the smallest κ chosen, which best represented the smallest observed hygroscopic growth below 100% RH_w . Particles smaller than 100 nm were more CCN-active than the larger particles, and thus appeared to have relatively more hygroscopic material. It is possible

that smaller particles would have exhibited larger GF values in the HTDMA, similar to those observed for the dry-generated particles and more consistent with $\kappa=1.07$. Experimental verification of larger GF values for smaller particles was not performed. Indeed, it is uncertain if the smallest sizes contained any insoluble material.

Although it could not be measured directly, the CCN activity of the dry-generated particles can be inferred by comparing the hygroscopic growth data in Figure 4.2 with the CCN activities in Figure 4.4. A small fraction of the particles is likely to be more CCN-active compared to the majority of particles, with s_c - D_{dry} relationships between those estimated for sodium carbonate ($\kappa=1.29$) and sodium sulfate ($\kappa=1.02$). However, the majority of the dry-generated particles fell into the less-hygroscopic mode. We predicted the activity of the less-hygroscopic mode assuming $GF(RH=90\%) = 1.1$, equivalent to $\kappa=0.04$; the s_c - D_{dry} relationship is indicated in Figure 4.4 as “dust”. Small (< 70 nm) sized particles composed of this less hygroscopic material are not expected to significantly influence warm cloud formation. However, the size distribution of dust particles lofted in the atmosphere may include particles much larger than examined in our experiments. As seen in Figure 4.4, particles with $\kappa=0.04$ which are larger than 300 nm activate at supersaturations below 0.1%, and are much more active than insoluble but wettable particles, which must be several microns in diameter to activate at these low supersaturations. Even low number concentrations of the less-hygroscopic Owens (dry) Lake particles may represent significant contributions to the populations of hygroscopic large or giant cloud condensation nuclei (GCCN) (Pruppacher and Klett, 1997), and may be important to warm cloud formation and the development of precipitation, as shown by Rudich et al. (2002) and Johnson (1982).

4.3.3. Ice nucleation activity

Ice nucleation was investigated for the temperature range $-60^{\circ} \leq T \leq -30^{\circ}\text{C}$ and for ice relative humidities (RH_i) ranging from $140 \leq RH_i \leq 180\%$. Markedly different ice formation behavior was observed if the particles were generated wet or dry, but no significant activity as ice nuclei (IN) was observed for $T > \sim -37^{\circ}\text{C}$ in both cases. Data are shown in Figure 4.5: blue symbols represent 100 nm particles, red 200 nm, green 300 nm and black 400 nm. The solid blue line represents water saturation and the dashed blue line in panel (a) is 95% RH_w . Results for particles produced by wet generation are presented in Figure 4.5a. Particles nucleate ice below water saturation at temperatures colder than -40°C . Very little size dependence in the onset conditions for nucleation was observed for wet-generated particles, within the uncertainty of the measurement. For the wet-generated particles, there was a considerable decrease in the required RH_i for onset of ice formation as the temperature was increased from -60°C to -40°C , yet on a RH_w basis, the ice formation onset conditions for 100 and 200 nm particles were relatively independent of temperature. This behavior suggests either a condensation freezing process or homogeneous freezing of the solution surrounding the undissolved dust particle. Koop et al. (2000) concluded that homogeneous nucleation rates are independent of the nature of the solute and only depend on the water activity of the solution. Water activities derived from the fit to hygroscopic data shown in Figure 4.2 (Equation (2.11), values in Table 4.1, row 1), were applied in the parameterization described in Table 1 of Koop et al. (2000) to predict homogeneous nucleation rates of the solution droplet (see Chapter 3). The droplet was assumed to be spherical, and the calculations did not explicitly exclude the volume of any insoluble material. It is

assumed that the internal drop pressure was zero and that the water activity of the Owens (dry) Lake dust was independent of temperature, a generally good assumption. The conditions required to achieve a nucleation rate, J , were computed such that J approximated the number fraction of particles nucleated to crystals per second ($Fraction_{IN} = 5\%$) for the residence time in the CFDC chamber using Equation (3.6). The water activity corresponding to this nucleation rate was determined and converted to RH_w via the Kelvin equation (Equation 2.12). In the Kelvin term it is assumed that σ_{sol} is the surface tension for pure water, with the temperature dependency estimated from Pruppacher and Klett (1997):

$$\sigma_w(T) = 76.1 - 0.155 \cdot T. \quad (4.1)$$

where T is expressed in °C. The predicted onset of nucleation for 200 and 400 nm particles are shown in Figure 4.5 as solid and dashed black lines. The 200 nm prediction shows reasonable agreement with the observations at temperatures warmer than -50°C. However, the limited set of observations at ~-55°C suggest that the size dependence was larger for the wet-generated particles than predicted by the homogeneous freezing parameterization. This may be due to an increase in dust core size in larger particles, promoting heterogeneous freezing in a small number fraction of these particles. Another possibility is that freezing onset conditions are influenced by the number fraction of less hygroscopic particles, which may not receive a full coating of soluble material and are able to serve as heterogeneous IN before the remaining 90% of more hygroscopic particles initiate ice formation homogeneously. Since only 10% of the wet-generated particles are of the less hygroscopic mode, as opposed to 65% of the particles when dry-generated, to see a signal of 5% of the particles activated as ice crystals, a higher

percentage of this subset in the experiments on wet-generated particles must freeze, requiring a higher RH_i for a given temperature than would be required for the dry-generated particles (compare to Figure 4.5b).

For temperatures warmer than -40°C , there is a steep increase in required RH_i for nucleation with increasing temperature. For $100\% < RH_w < 110\%$, the variation in observed freezing-onset conditions may reflect the rapidly diminishing activity of IN with increases in temperature after all particles are immersed in drops. For $110\% < RH_w < 120\%$, the state of the particles cannot be unambiguously determined. The region $T > -35^{\circ}\text{C}$ and $RH_w > 120\%$ corresponds to conditions where water drops are known, from our prior studies, to have grown large enough to transmit through the evaporation region and be counted by the OPC. Thus, the data suggest that no ice formation occurred at temperatures warmer than $\sim -35^{\circ}\text{C}$ for either wet- or dry-generated particles.

When the particles were generated dry, as shown in Figure 4.5b, the Owens (dry) Lake dust particles were substantially more active as IN than the wet-generated particles at temperatures colder than -45°C . The colors refer to sizes as described for Figure 4.5a. No data were available for 100 nm particles because number concentrations were too low. The mode of activation appeared to be different for this generation method since below -40°C there was very little dependence of the activation RH_i on temperature, which means the RH_w was changing substantially. The onset of freezing was likely due to a heterogeneous deposition nucleation processes on insoluble dust particles. Since these particles did not receive the artificial soluble coating created during atomization, some of the particles likely had little or no soluble material adhered to the surface, and so the dust surface may have been exposed, allowing deposition nucleation of ice at RH_i well below

where homogeneous freezing was expected, particularly at lower temperatures. Figure 4.3 suggests that some particles did not grow at all at humidities as high as 90% RH_w . A bimodal fit to the distribution in Figure 4.3 found a less-hygroscopic mode with $GF > 1$ at higher RH_w for the dry-generated samples, as shown in Figure 4.2. A trimodal fit to the data in Figure 4.3 might produce an additional mode with $GF = 1$, but this was not attempted. Since this feature is the major difference between the hygroscopic response of the wet and dry-generated particles, we hypothesize that the non-hygroscopic particles in the dry-generated samples are responsible for the differences seen between Figures 4.5a and 4.5b. The freezing data thus indicate that nonhygroscopic, insoluble dust particles found in the Owens (dry) Lake sample had a significant influence on ice nucleation and, in the atmosphere, can impact cloud properties at temperatures where homogeneous nucleation is often assumed to be the dominant mechanism for ice formation. The data also exhibited stronger size dependence for freezing onset when the dust was dry-generated. Larger particles (400 nm) activated ice at several percent lower RH_i than did smaller particles (200 nm), with this effect more pronounced at lower temperatures perhaps due to the existence of more active sites on larger particles. As was the case for the wet-generated particles, the data obtained at warmer temperatures with the aircraft CFDC showed a very strong dependence on temperature, so individual data points are shown.

4.4. Comparison to Other Freezing Studies

Few previous studies on the freezing behavior of mineral dust aerosol have examined the size dependence. Archuleta et al. (2005) examined size selected pure and sulfate-coated mineral surrogates as well as a natural Asian dust sample, at temperatures

colder than -40°C . Over this range, the coated dust samples showed similar ice nucleation behavior to that observed for wet-generated particles in this study, which were shown to have a large fraction of soluble material. While several of the pure mineral surrogates showed increasing onset RH_w with increasing temperature, the Asian dust sample showed very little dependence of RH_w on temperature over this range, a behavior observed for the dry-generated dust in this work. However, the onset RH_w for the Asian dust was $\sim 15\%$ lower than the conditions required for ice formation with the dry-generated Owens Lake dust. It is unknown if the mineral dust surrogates or natural Asian dust sample investigated by Archuleta et al. (2005) were active as IN at temperatures warmer than -40°C .

Other studies which do not size select particles, have observed ice nucleation at temperatures much warmer than found in this study. Field et al. (2006) examined polydisperse Asian and Saharan dust samples (mode size $0.3\text{--}0.5\text{ }\mu\text{m}$, with an upper limit of $2\text{ }\mu\text{m}$) and found that while deposition nucleation was only active at temperatures colder than -40°C , ice nucleation on a small fraction ($< \sim 1\%$) was observed for temperatures as warm as -29°C for the Asian dust and -21°C for the Saharan dust. Kanji and Abbatt (2006) found that several polydisperse mineral surrogates, as well as a Saharan dust sample (particle diameters between $0.5\text{--}5\text{ }\mu\text{m}$) nucleated ice at very modestly ice supersaturated conditions for temperatures as warm as -10°C . Similar results were found by Knopf and Koop (2006) for the mineral dust surrogate Arizona Test dust when they examined particles as large as $10\text{ }\mu\text{m}$ at temperatures as warm as -13°C and by Salam et al. (2006) for mineral surrogates kaolinite and montmorillonite at temperatures as warm as -15°C . It may be that the presence of soluble material in our

samples prevents ice nucleation at the warm temperatures observed by the aforementioned studies or that the limited size range examined in this work prevents the observation of ice nucleation at warmer temperatures. However, Zuberi et al. (2002) examined the freezing behavior of mineral dust inclusions in concentrated ammonium sulfate droplets (10-55 μm). The size distribution of the inclusions is not well defined, but likely includes particles much larger than examined in this study, and each droplet may contain a number of inclusions. Yet those authors observed nucleation only for temperatures below -34°C , roughly consistent with the behavior observed in this study. However, since at temperatures warmer than $\sim 35^{\circ}\text{C}$, condensation freezing is generally expected to be the pathway for ice nucleation, requiring water saturated conditions, we do not expect the presence of soluble species, which would be greatly diluted at saturation conditions, to significantly impact the freezing of a particle population. We therefore believe, in light of warm temperature data by Field et al. (2006) in which 0.5% of particles were seen to nucleate ice at saturation for $\sim 20^{\circ}\text{C}$, that the size dependence is more important in determining the onset of ice nucleation than the presence of soluble species in the sample.

4.5. Conclusions

The experiments show that the Owens (dry) Lake dust ($D_p \leq 400 \mu\text{m}$) had at least two distinct particle types: one fraction that was hygroscopic and another fraction that appeared to have little hygroscopic material and was primarily composed of insoluble species. We speculate that the hygroscopic fraction can contribute significantly to atmospheric CCN and GCCN concentrations while the less-hygroscopic fraction is likely to represent a significant source of IN.

The data presented here for Owens (dry) Lake dust hygroscopicity, CCN activity and ability to nucleate ice showed that Owens (dry) Lake dust has the potential to have a significant impact on cloud formation during dust storm events. The CCN activity of the hygroscopic particles in Owens (dry) Lake dust is similar to those of many other inorganic species in the atmosphere, implying that Owens (dry) Lake dust could enhance CCN concentrations in warm clouds and therefore might alter cloud properties by supporting nucleation of more, smaller cloud drops. This can have important implications for the radiative properties of the cloud as well as potentially suppressing precipitation formation. In cold clouds, the ability of the dust to nucleate ice at RH_i well below where typical aqueous atmospheric aerosol homogeneously nucleate ice can have an important impact on clouds and radiative budgets. For example, the presence of more efficient ice nuclei may actually lead to a decrease in ice crystal number density (DeMott et al., 1997b; Kärcher and Lohmann, 2003), an increase in crystal size, and a subsequent increase in sedimentation velocities in cirrus. The formation of ice may also increase the likelihood of precipitation formation in mixed phase clouds, although the ice nucleation activity of Owens Lake dust in this warmer temperature regime could not be confirmed for particles smaller than 400 nm. Implications for cloud development will be discussed further in Chapter 7.

Species	Percentage of particles in fraction	a	b	c	$\kappa (a_w = 0.9)$
Owens Lake Dust (wet), more-hygroscopic (upper range)	90%	8.02	-19.40	12.68	0.82
Owens Lake Dust (wet), more-hygroscopic (lower range)		5.99	-13.55	8.27	0.49
Owens Lake Dust (wet), less-hygroscopic	10%	0.24	0.03	-0.18	0.12
Owens Lake Dust (dry), more-hygroscopic	35%	15.35	-32.34	17.85	0.69
Owens Lake Dust (dry), less-hygroscopic	65%	-0.35	0.71	-0.30	0.05
sodium sulfate					1.02
sodium carbonate					1.29

Table 4.1: Fit constants to Equation (2.11) and Equation (2.13) for species relevant to this study.

Owens Lake Dust						
Laboratory Unit		Temperature				
	Size	-60	-55	-50	-45	-40
dry generation (1%)	200 nm		155.47±2.8	150.00±3.4	148.85±2.4	146.15±2.8
	300 nm		144.71±2.0	141.51±2.0	146.05±2.0	144.89±2.0
	400 nm		144.71±1.2	141.51±1.2	146.05±1.2	144.89±1.2
wet generation (1%)	100 nm	165.98±1.5	161.23±1.5	155.20±1.5	150.14±1.5	145.70±1.5
	200 nm	165.59±1.7	160.09±1.7	153.88±1.7	150.34±1.7	145.95±1.7

Table 4.2: OLD freezing results collected with the laboratory CFDC unit. Values represent the RH_i condition in which 5% of the particles, by the generation method and diameter indicated, nucleated ice. Error bars represent the 95% confidence interval using a pooled standard deviation.

Owens Lake Dust						
ACFDC-2	Particle Size					
	200 nm		300 nm		400 nm	
	T	RH_i	T	RH_i	T	RH_i
dry generation (5%)	-37.92	102.94	-32.27	106.76	-36.10	115.43
	-33.33	114.71	-40.78	100.76	-36.57	118.91
	-35.33	108.82	-35.81	108.01	-30.21	125.36
	-34.74	111.69	-36.22	102.82	-38.09	102.88
	-39.96	89.76	-35.42	109.16	-36.39	108.50
	-39.22	100.62	-36.44	106.57	-32.98	120.05
	-35.85	106.02	-35.61	110.98	-39.62	101.04
	-39.06	101.08	-39.67	97.42	-36.10	115.40
	-36.43	111.33	-34.39	114.03		
	-35.41	117.06	-30.71	118.09		
	-34.46	116.80				
	-32.75	117.60				
	100 nm		200 nm			
	T	RH_i	T	RH_i		
wet generation (5%)	-38.29	151.12	-37.54	150.42		
	-38.64	151.68	-30.84	173.50		
	-36.44	155.90	-38.26	150.17		
	-36.95	151.57	-37.52	150.90		
	-34.21	165.42	-40.90	149.86		
	-33.65	168.22	-37.00	151.70		
			-36.27	154.64		
			-34.33	164.53		
			-32.20	162.08		
			-29.73	157.20		
			-34.47	165.18		

Table 4.3: OLD freezing results collected with the laboratory CFDC unit. Values represent the T and RH_i condition in which 5% of the particles, by the generation method and diameter indicated, nucleated ice.

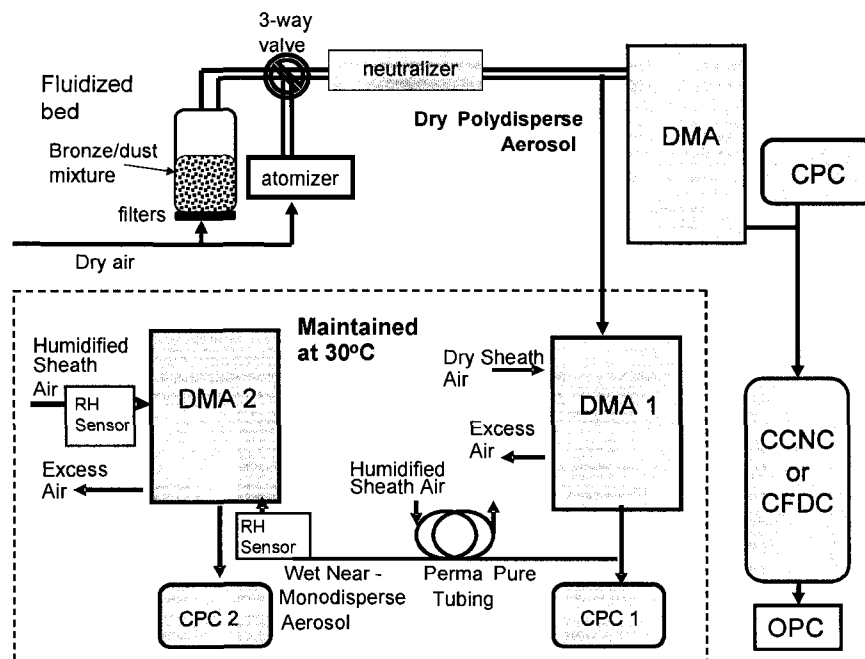


Figure 4.1: Schematic of experimental configuration, including particle generation.

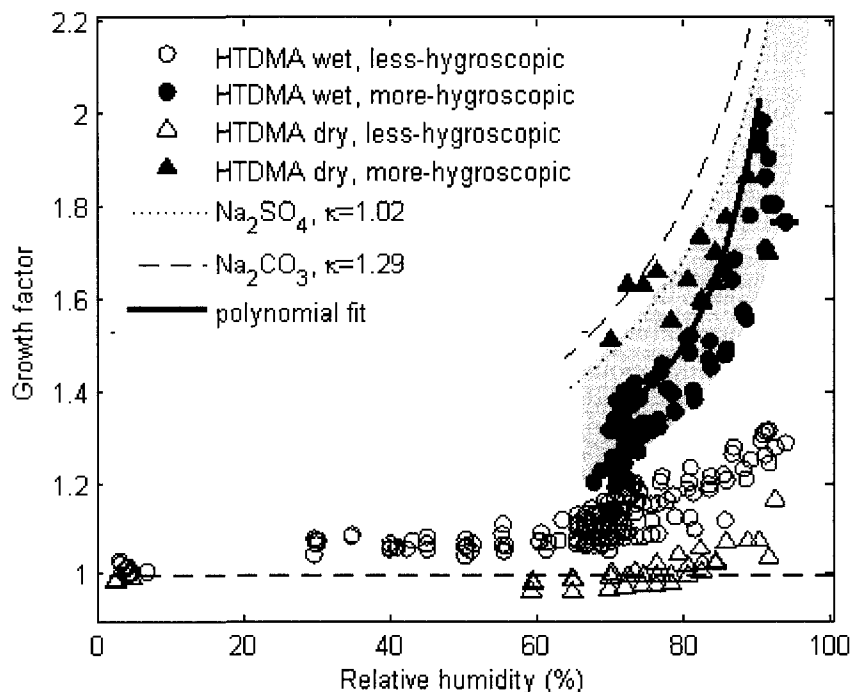


Figure 4.2: Hygroscopic GF of Owens (dry) Lake dust when aerosol is generated wet (circles) and dry (triangles). The shaded region represents the range of GF values corresponding to $0.39 < \kappa < 1.07$. The dotted and dashed lines are the predicted GF values of sodium sulfate ($\kappa=1.02$) and sodium carbonate ($\kappa=1.29$) particles. The thick black line is the polynomial fit to the data (first row, Table 4.1, valid for $70 < RH_w < 90\%$). Representative uncertainty bars for the HTDMA data are shown in thick black lines for one point ($RH_w \sim 90\%$, $GF \sim 1.8$), with the uncertainty in the RH_w measurement contained within the symbol size.

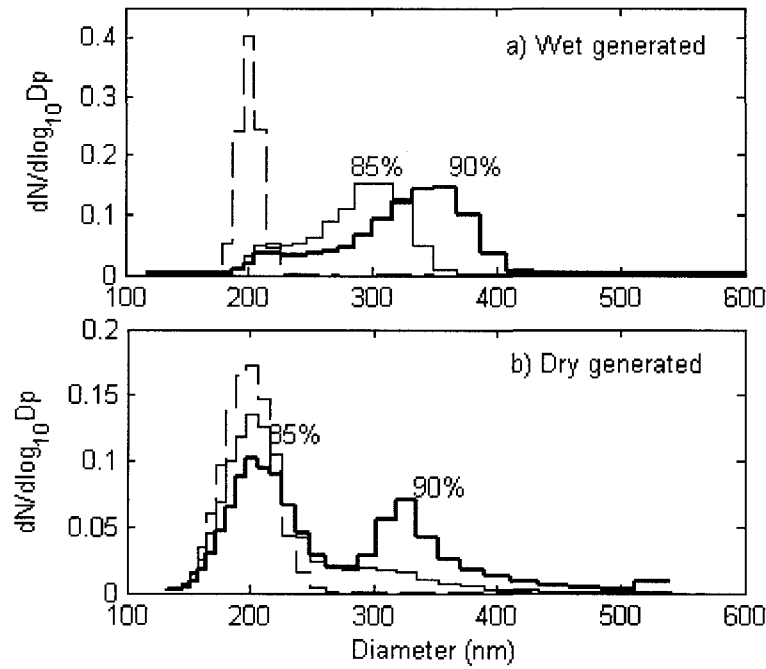


Figure 4.3: Normalized HTDMA size distributions for a) wet-generated and b) dry-generated Owens Lake dust particles. Dashed lines indicate the size distribution measured at 5% RH_w . Other distributions are at the RH_w indicated.

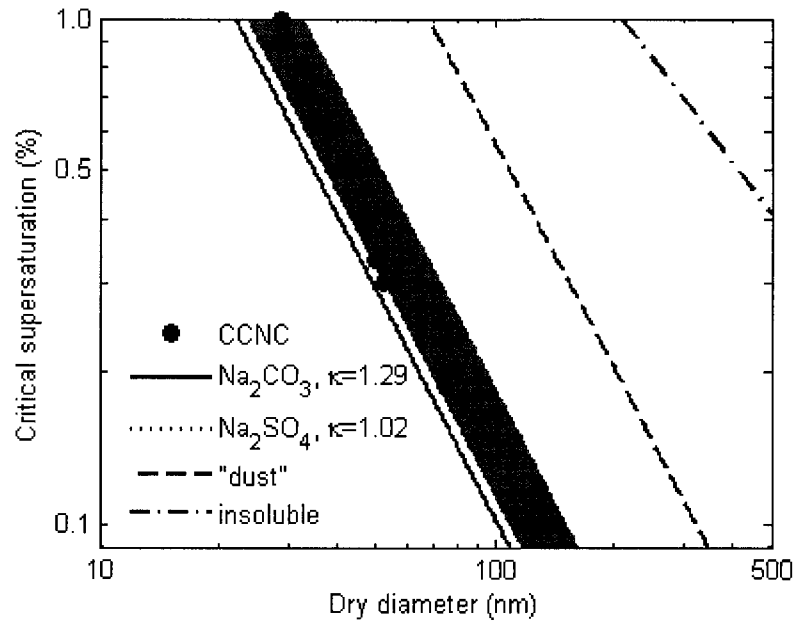


Figure 4.4: CCN activity of Owens (dry) Lake dust as measured by the CCNC (points for particles created by wet generation). The shaded region represents the range of critical supersaturation values corresponding to $0.39 < \kappa < 1.07$. The CCN activities of sodium sulfate ($\kappa=1.29$) and sodium carbonate ($\kappa=1.02$) are predicted according to simplified Köhler theory. The "dust" line represents a species with $\kappa=0.04$ (see text). The "insoluble" line is for an insoluble, wettable particle according to Kelvin theory ($\kappa=0$).

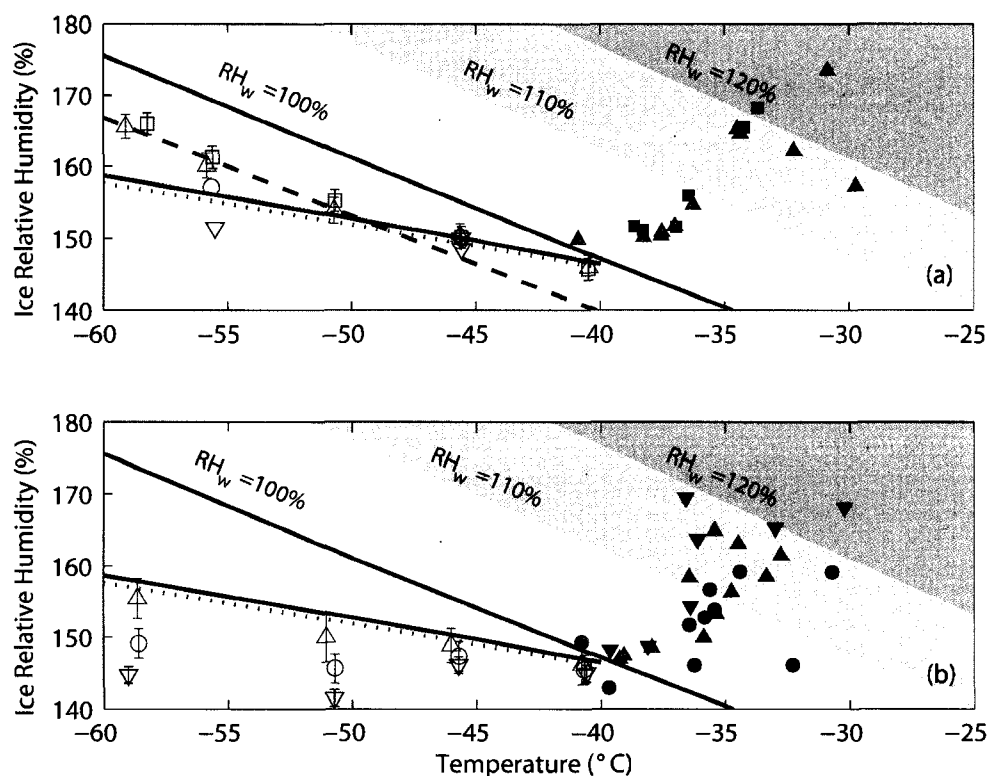


Figure 4.5: Ice nucleation data for Owens Lake dust. Blue symbols refer to 100 nm particles, red symbols to 200 nm particles, green symbols to 300 nm particles, and black symbols to 400 nm particles. Open symbols represent data collected using the laboratory unit (points indicate ice formation in 5% of particles) and filled symbols represent data collected using the aircraft unit (points indicate ice formation in 1% of particles). The solid blue line is water saturation, the dashed blue line is $RH_w = 95\%$. Light grey shading indicates the region between $110\% < RH_w < 120\%$ and the darker shading indicates the region of $RH_w > 120\%$. Panel (a) shows data collected when the particles were generated wet and panel (b) shows data collected when the particles were generated dry. The solid and dashed black lines are the homogeneous freezing prediction for 200 and 400 nm particles using derived water activities (see text).

5. The ability of Arizona test dust to initiate cloud development

5.1. *Introduction*

This chapter describes laboratory experiments with Arizona Test dust (ATD), a commercially produced, milled product (Powder Technologies, Inc.). Table 5.1 shows the elemental and mineralogical composition of the particles (from Möhler et al., 2006; Vlasenko et al., 2005). Water vapor interactions over a broad range of temperatures are measured to help predict the role of similar natural mineral dust aerosols in the atmosphere. Because ATD has a low content of soluble matter (Vlasenko et al., 2005), we anticipated that ATD would serve as a heterogeneous IN at modest ice supersaturations. This chapter will focus on the results for uncoated ATD; ice nucleation results for ATD coated with secondary organic material will be presented in Chapter 7.

Arizona test dust (ATD) is composed almost entirely of insoluble material (Vlasenko et al., 2005). Vlasenko et al. (2005), using energy dispersive X-ray analysis (EDX), found that ATD consists primarily of silicon, aluminum, and calcium (~91%) with several percent of sodium, magnesium, and potassium found in the powder. Those authors also investigated the water soluble composition of the submicron fraction of the ATD with a wet effluent diffusion denuder/aerosol collector (WEDDAC) system with anion chromatography and found that sulfate was the primary anion with small amounts

of phosphate, chloride and nitrate. They deduced that the water soluble fraction comprises about 2% of the mass. ATD is expected to be representative of dust in the southwest United States and has been used in several experimental studies on particle hygroscopicity and ice nucleation (Gustafsson et al., 2005; Mangold et al., 2005; Möhler et al., 2006; Vlasenko et al., 2005).

5.2. *Experimental*

Experimental methods are similar to those in Chapter 4 and are only discussed briefly here. The experimental setup is identical to that shown schematically in Figure 4.1.

5.2.1. Aerosol generation

In laboratory studies an atomizer (hereafter “wet generation”) is often used to reaerosolize a sample. However, due to the insoluble nature of this dust, it is possible that significant alteration of the particles or their surface properties can occur when the sample is suspended in water and then atomized, as was found for the Owens (dry) Lake dust presented in Chapter 4. Therefore, we also investigate particle hygroscopic and ice nucleating behavior for samples aerosolized by a dry generation method, using a fluidized bed (hereafter “dry generation”). Unfortunately, as noted in Chapter 4, the fluidized bed is inefficient at producing particles smaller than ~150 nm.

5.2.2. Experimental Procedure

The HTDMA was employed to measure the growth of particles due to water adsorption/absorption below water saturation. A narrow distribution of particles is selected according to their electric mobility diameter (D_{dry}) and counted using a CPC (Section 2.2.2). Since the dust particles are likely aspherical, this size can be

considerably different than the geometric size, as is seen in the Scanning Electron Microscope (SEM) image shown in Figure 5.1. It is clear from Figure 5.1 that many of the particles have at least one dimension of the particle greater than the selected size, which was 300 nm for the particles sampled in this image. The DMA (Section 2.2.1) selects a quasi-monodisperse stream of particles, and the width of the distribution depends on the sheath:sample flow ratio through the instrument. The use of the DMA to size select particles gives an upper size limit for a quasi-monodisperse sample stream of ~400 nm in this work. For particles generated by atomization, a 10:1 flow ratio was used in size selection (a nominal 200 nm monodisperse output stream will contain particles with diameters from 189-214 nm). The fluidized bed generates significantly lower particle concentrations than an atomizer, so a 5:1 flow ratio was necessary to obtain adequate particle concentrations for all experiments (a nominal 200 (400) nm size selection will allow particles 179-230 (352-473) nm to exit). The particle flow was then humidified up to ~90% RH_w . A second DMA (DMA2) scanned through mobility diameters and a second CPC (CPC2) counted the particles yielding a grown distribution for the elevated RH_w . Growth of the particles is expressed in terms of the growth factor (GF , Equation 2.1); no shape factor corrections were applied.

Using the hygroscopicity data and the procedure outlined in Section 2.3.1, GF values can be fit and extrapolated to water activities approaching one. D_{wet} for an assumed dry diameter can be calculated from the fit and the corresponding RH_w computed via Equation (2.12). By scanning a range of RH_w including supersaturated values, the Köhler curve is mapped out and the maximum RH_w , known as the critical supersaturation, $S_{crit} = (RH_{max} - 100) * 100$, is found. These predictions were then

compared to direct measurements of S_{crit} as a function of dry diameter from the CCNC. Quasi-monodisperse particle flows were obtained using a sheath:sample flow ratio of 10:2.5 in the DMA for CCNC experiments.

The laboratory and aircraft (ACFDC-1) CFDC units were operated as described in Chapter 4 to examine the nucleation ability of ATD between $-60^{\circ}\text{C} \leq T \leq -20^{\circ}\text{C}$. Quasi-monodisperse particle flows were obtained using a sheath:sample flow ratio of 10:1 in the DMA for wet-generated particles and 7:2.5 in the DMA for dry-generated particles during CFDC experiments. The RH_i was increased gradually, until a condition was achieved where 1% the particles nucleated and grew as ice crystals. All data collected using the laboratory unit are reported as averages of at least three repetitions and error bars represent confidence intervals at the 95% level. Due to difficulty in exactly reproducing experimental conditions in the aircraft system, averages are not taken and individual points are shown.

5.3. Results

5.3.1. Hygroscopicity and CCN Activity

Diameter growth factors measured by the HTDMA for both wet- and dry-generated particles are shown in Figure 5.2. There is no size dependence in the data. Very little water uptake was observed at any RH_w to the upper limit of the instrument, about 90% RH_w . For particles created by both generation methods, GF values less than one occurred between $RH_w \sim 50\%$ -80%. This was likely due to restructuring of the particles and/or a change in the shape factor of the particles. Gustafsson et al. (2005) found that 2 monolayers of water coated ATD particles at $\sim 50\%$ RH_w . As small amounts of water deposited on the surface of the irregularly shaped dust particles, they became

more spherical and appeared smaller in the DMA due to the reduced drag on the particle (Mikhailov et al., 2004). Vlasenko et al. (2005) used a TOPAS Solid Aerosol Generator to dry generate ATD particles and similarly used a HTDMA to measure diameter GF values. They observed $0.995 < GF < 1.005$ for $RH_w < 90\%$, and observed restructuring with $GF \sim 0.99$ for $RH_w > 90\%$. It is unclear why restructuring was observed at lower RH_w in our studies than was found by Vlasenko et al. (2005). Gustafsson et al. (2005) had a bimodal input distribution of particles generated from a water suspension and for the large mode with an average dry diameter of 250 nm found similar GF values ($0.98 < GF < 1.02$) as reported here, but found slightly larger GF values ($0.99 < GF < 1.08$) for the smaller mode having an average dry diameter of 56 nm. They concluded that the growth of the large particles is obscured by the width of the selected mobility, which is narrower for smaller particles, allowing for more precise measurement. Sheath:sample flow ratios used in the DMA by Gustafsson et al. (2005) were not reported.

Figure 5.3 shows measured CCN activity for both wet- (circles) and dry- (squares) generated particles. CCN activity of a typical inorganic aerosol (ammonium sulfate, $\kappa \sim 0.6$) is shown in Figure 5.3 for comparison. The wet-generated ATD particles, when compared to the CCN activity predicted for a wettable, insoluble particle ($\kappa = 0$, dashed line) according to Kelvin theory (Seinfeld and Pandis, 1998), had critical supersaturations closer to soluble particle types. Normalizing all points to the lowest observed GF yields, $GF(RH_w = 90\%) = 1.08$, equivalent to $\kappa = 0.03$ (Equation 2.13), to predict the CCN activity, the predicted critical supersaturation for a 100 nm dry particle is 0.64% supersaturation, over 3.5 times larger than the measured critical supersaturation for wet-generated ATD particles, but in good agreement with that found for the dry-

generated ATD particles. The best-fit κ to the critical supersaturation-dry diameter data in Figure 5.3 for dry-generated particles is $\kappa=0.025$ (blue line), very similar to that obtained from the *GF* measurements. As noted above, Vlasenko et al. (2005) found that 2% of the ATD mass was soluble and composed primarily of sulfate. If it is assumed that 2% of an otherwise insoluble particle ($\kappa=0$, $\rho=2 \text{ g cm}^{-3}$) is comprised of a sulfuric acid ($\kappa=1.19$, $\rho=1.8 \text{ g cm}^{-3}$) and using the condition that κ mixes linearly with volume fraction (Petters and Kreidenweis, 2007), the calculations yield $\kappa=0.026$, in excellent agreement to the measured critical supersaturations and best-fit κ for the dry-generated ATD particles.

In contrast, the best-fit κ for the measurements on wet-generated particles is $\kappa=0.35$ (red line). The higher hygroscopicity exhibited by the wet-generated particles in the CCNC, as compared with the deduced hygroscopicity from the HTDMA data, suggests the presence of soluble material that does not deliquesce until $RH_w > 90\%$, in addition to the small amount of hygroscopic material that was responsible for some water uptake below 90% RH_w . These results indicate that significant alteration of the particles occurred when they were suspended in water and atomized, as was also found for Owens (dry) Lake dust. Since the entire distribution of ATD is suspended in water, any soluble material on ATD particles will go into suspension. As the suspension is atomized, each dust core will be initially surrounded with solution. When the particles are dried, the soluble material will remain on the surface of the ATD. As only the smaller dust cores are capable of being atomized ($< \sim 0.5 \text{ }\mu\text{m}$), concentration of the soluble material on small atomized dust cores likely occurs. This enhanced fraction of soluble material ($\kappa=0.35$ suggests a soluble fraction of 32%, if it were to behave as sulfuric acid) is unnoticeable in

the HTDMA, but very evident in the CCN measurements. The chemical composition of material that would lead to these observations is uncertain.

Although the dry-generated ATD particles required much larger critical supersaturations for activation of a given diameter compared to the wet-generated particles, the measured critical supersaturations are well below the predictions for an insoluble particle. Dry-generated ATD particles are able to serve as CCN at critical supersaturations $<1\%$ for particles larger than 100 nm and therefore these particles can affect warm cloud microphysics.

5.3.2. Ice Nucleation Results

Ice nucleation results are summarized in Figure 5.4. All points represent the condition where 1% of the particles froze. Figure 5.4a is for ATD generated wet, while results for the samples created by dry generation are shown in Figure 5.4b. Sizes are denoted by symbol with 100 nm particles in squares, 200 nm particles in triangles, 300 nm particles in circles and 400 nm particles in inverted triangles. Included for reference on the figure is the water saturation line as the solid blue line and $RH_w=80\%$ as the dashed blue line. It is first noted that ATD, under many conditions, was an efficient IN, with the larger particles nucleating ice below 80% RH_w at $T<-55^\circ\text{C}$ by both generation methods. Under cirrus conditions ($T<-40^\circ\text{C}$), there was no temperature dependence for RH_i nucleation onset. There was, however, a size dependence; much stronger than is predicted for homogeneous nucleation of haze particles, particularly for the wet-generated particles. The conditions for onset of ice nucleation for Asian dust samples reported by Archuleta et al. (2005) are also qualitatively consistent with the present ATD results: both show little dependence of freezing onset RH_i with temperature for $T<-40^\circ\text{C}$,

and both indicate dependence on particle diameter. The wet-generated ATD particles activated at very similar RH_i as was observed for the Asian dust (also generated wet), but the dry-generated ATD particles were more active, with 200 nm particles nucleating ice on average 13% lower RH_i than 200 nm Asian dust particles. A small size dependence for onset conditions exhibited by the dry-generated particles was observed up through 400 nm, indicating that it is not related to the Kelvin term. It is not surprising that a size dependence was observed as larger particles, with larger surface area, are more likely to have active sites capable of initiating the ice phase; however, the size dependence may diminish with increasing size. The small size dependence, as well as the very low RH_w at which the ATD was seen to take up some adsorbed water in the HTDMA, leads us to conclude that deposition nucleation of ice on the surface on the insoluble dust particles is likely occurring at cold temperatures ($T \leq -40^\circ\text{C}$), but we cannot rule out immersion freezing.

When the particles were generated wet (Figure 5.4a), nucleation followed a nearly constant RH_i line from the coldest examined temperatures to warmer temperatures until water saturation was reached. At this point onset conditions follow the water saturation line and it appears unlikely that deposition nucleation was occurring, instead we conclude that condensation freezing took over, particularly considering the high deliquescence point of soluble material predicted from the HTDMA and CCNC measurements. This behavior was observed for mineral surrogates as early as 1968 (Roberts and Hallett, 1968; Schaller and Fukuta, 1979). From the measurements described in Section 5.3.1 we know that the ATD particles produced by wet generation were able to activate as CCN at RH_w slightly above water saturation. At sufficiently cold temperatures these activated

cloud droplets will freeze due to the presence of the insoluble core. The shift in freezing mechanism from deposition to condensation freezing occurs over the temperature range where the aircraft unit is being used ($T > -40^{\circ}\text{C}$, filled symbols). For $110 \leq RH_w \leq 120\%$ (light gray shading) the phase of the particles cannot be unambiguously determined. At $RH_w > 120\%$ (dark gray shading) it is known that liquid water grown CCN are large enough to survive the evaporation region and be counted by the OPC. The data in Figure 5.4a suggest that condensation nucleation occurred near water saturation from $T \sim -40^{\circ}\text{C}$ and warmer, until a threshold temperature was reached (T_{thresh}). For temperatures warmer than T_{thresh} , the dust appeared to lose its ability to nucleate ice. This manifests itself as a sharp jump in freezing onset conditions to near $120\% RH_w$ for a 1% detection signal in the OPC. Since we do not have a direct way to determine phase of the particles, it is possible that some small fraction of the particles ($\ll 1\%$) may still nucleate ice crystals. However, we believe that since there is such a sharp transition to the high RH_i at $T = -34^{\circ}\text{C}$ for 200 nm particles and $T = -27^{\circ}\text{C}$ for 400 nm particles that the increase in onset RH_i most likely represents the temperature where the particles are unable to nucleate ice (T_{thresh}). The temperature at which a particle shifts from being a deposition nucleus to a condensation freezing nucleus and T_{thresh} are known to be dependent on the material type (Schaller and Fukuta, 1979); this study shows that T_{thresh} can also be a function of size, with larger particles being able to nucleate ice 8°C warmer than the smallest particles studied.

When the particles were generated dry (Figure 5.4b), the particles similarly had a very small dependence of nucleation RH_i with temperature, however they nucleated ice at 12-20% lower RH_i than was found for the wet-generated particles. As the temperature

increased beyond -40°C , the dry-generated particles rapidly lost their ability to initiate the ice phase, nucleating ice at similar RH_i as was found for the wet-generated particles, indicating a shift to condensation freezing, as indicated by the increase in nucleation RH_i toward water saturation. The results show a somewhat smaller size dependence of T_{thresh} than was observed for the wet-generated data, with $T_{thresh} \sim -35^{\circ}$ for 200 nm particles and $T_{thresh} \sim -30^{\circ}\text{C}$ for the 400 nm particles. Also the data do not follow the water saturation line as clearly as the data for the wet-generated aerosol. The reason that the onset RH_i for the dry-generated particles above -40°C did not follow the water saturation line, as did the data for the wet-generated particles, is not clear, but may represent a decreasing ability of these particles to initiate the ice phase as the temperature increases or a water supersaturation required for water activation to initiate freezing.

We believe that when the particles were atomized then dried, small amounts of dry soluble species remain on active sites, preventing ice from depositing at these preferential locations. Since these are hydrophilic locations, it is not surprising that water and, upon drying, the soluble material would localize on these active sites. Therefore deposition nucleation must occur on sites that are less favorable for ice formation, or the soluble material may create a solution coating on the particle causing the particle to activate via the condensation freezing mechanism, resulting in an increase in RH_i required for onset of freezing.

5.4. Comparison to other freezing studies

Möhler et al. (2006) also studied ATD using the Aerosol Interactions and Dynamics in the Atmosphere (AIDA) cloud chamber. In this facility it is not possible to size resolve results; instead a nearly lognormal distribution of dry-generated particles

with a median diameter of 350 nm and a geometric standard deviation of 1.65 was used in experiments. Particles larger than 2 μm were removed from the sample with an impactor. Aerosol was generated dry using a rotating brush disperser. Similar to our findings, Möhler et al. (2006) found over the range $-75 \leq T \leq -50^\circ\text{C}$ the ATD particles nucleated ice at a nearly constant RH_i , although the onset of nucleation (8% of particles frozen) was observed at lower humidities than in our studies, between 101-110% RH_i . However, considering the size dependence found for freezing onset RH_i for the dry-generated particles in our study, it is probable that it is the largest particles in their distribution that are nucleating ice first. Since Möhler et al. (2006) control pumping rate and not supersaturation directly, it is instructive to compare the maximum RH_i the chamber experiences during an expansion experiment with the maximum fraction of particles nucleating ice, which occurs at roughly the same time. Integrating the lognormal distribution from the largest sizes to the observed fraction, we may obtain the minimum size likely nucleated at the maximum supersaturation conditions. Möhler et al. (2006) found that at -50°C with a maximum RH_i of $\sim 115\%$, 55% of the particles nucleated ice corresponding to particles as small as ~ 300 nm, which is consistent with the RH_i onset conditions determined for 300 nm particles nucleated ice in this work. At -63°C with maximum RH_i of around 115% they found a higher fraction of particles nucleated ice, corresponding to a minimum diameter of ~ 200 nm. This is $\sim 10\%$ RH_i lower than we found for 200 nm particles at this temperature.

Möhler et al. (2006) found that ATD nucleated ice at warmer conditions in the AIDA chamber than was found in this work (Dr. Ottmar Möhler, personal communication). At -20°C they found that 10% of the particles still nucleated ice at

$\sim 110\%$ RH_i . According to their lognormal distribution, 10% of the particles would correspond to a smallest activated diameter of around 650 nm, larger than the particles examined in this work. Knopf and Koop (2006) examined ATD particles as large as 10 μm using a low temperature stage method and found ice nucleation occurred at temperatures as warm as -13°C . Similar results were found by Kanji and Abbatt (2006) and Salam et al. (2006). The latter groups found that several polydisperse (particle diameters between 0.5-5 μm) mineral surrogate samples (e.g. kaolinite, montmorillonite, silica, alumina) nucleated ice at very modestly ice supersaturated conditions for temperatures as warm as -10°C and -15°C , respectively. The active freezing mechanism in all these studies was expected to be via the deposition mode.

Conditions for the onset of immersion freezing were reported for kaolinite as -10°C (Schaller and Fukuta, 1979) and -14°C (Pitter and Pruppacher, 1973) and for montmorillonite as -12°C (Pitter and Pruppacher, 1973). Marcolli et al. (2007) observed ATD particles to freeze via the immersion mode at temperatures as warm as -20°C and determined that freezing was a function of the dust particle size and number of immersed particles in each drop. Those authors suggested that the colder temperature required in their experiments as compared to the deposition mode investigated by Knopf and Koop (2006) may be due to the difference in mode of activation. Also a bias from the substrates used for the cold stage measurements by Knopf and Koop (2006) and Kanji and Abbatt (2006) cannot be ruled out. The model developed by Marcolli et al. (2007) which best agreed with observations suggested that only a small fraction of the surface of each particle is capable of serving to initiate heterogeneous freezing and that these “active sites” are more likely to exist on larger particles. In contrast to homogeneous

freezing, in which each particle of the same size and concentration has an equal probability of freezing, under this singular hypothesis, all particles are not equally good IN. They found continuous freezing from the onset temperature down to the temperature where homogeneous freezing of droplets without mineral inclusions occurred. Their findings are analogous to the observations presented here, in which activation happened over a much broader range of RH_w conditions for a given temperature than observed for homogeneous nucleation (see Chapter 8, Figure 8.1). It is likely that the discrepancies in the freezing data at warm temperatures between these cited studies (via the immersion and deposition modes) and those reported here are due to the limited sizes we were able to examine. It is also unclear if there are any morphological changes in particle surfaces that occur in the generation of these mineral surrogates, which may or may not be representative of mineral dust surfaces in the atmosphere.

5.5. Conclusions

Arizona Test dust is expected to be representative of dust with very low soluble material content in SW United States. Our studies of the water uptake and freezing behavior of ATD suggest that even with the low soluble mass fraction for the bulk samples reported by Vlasenko et al. (2005), significant alteration of the particles occurred if the sample was suspended in water prior to reaerosolization. Very low water uptake was observed in the HTDMA for particles generated either dry or from aqueous suspension, although restructuring observed from 50-80% RH_w suggested adsorption of water at these RH_w values occurred. The CCN activity showed that the particles which were wet-generated were significantly more hygroscopic than dry-generated particles. Both generation methods, however, produced particles which were more CCN active than

predicted for insoluble, wettable particles and their activity was such that sub-400 nm particles of ATD should readily serve as CCN at typical atmospheric supersaturations.

At cirrus conditions ($T < -40^{\circ}\text{C}$), particles studied by both generation types possibly serve as deposition IN, however, much lower ice supersaturations were required for the dry-generated particles than the wet-generated particles. As the temperature increased, the particles produced by both generation methods required water saturation conditions before initiating freezing, indicating a shift from deposition to condensation freezing at temperatures warmer than $\sim -40^{\circ}\text{C}$. Larger particles were able to serve as condensation freezing IN to warmer temperatures than observed for smaller particles. The experimental results were consistent with other studies of ATD reported in the literature, except some groups observed freezing activity at much warmer temperatures. We suggest that this was due to the use of much larger particles in those studies than we were able to generate, and that the size-dependence behavior of ATD is an important feature.

From Vlasenko et al. (2005)		From Möhler et al. (2006)	
Element	Elemental composition expressed in % of atoms	Mineral	Mineralogical composition expressed in weight % of bulk samples
Al	15.9±0.3	Al ₂ O ₃	13.8
Ca	4.8±0.2	CaO	4.3
Fe	4.9±0.1	FeO	4.0
K	3.1±0.2	K ₂ O	3.8
Mg	4.7±0.2	MgO	2.9
Na	2.9±0.2	Na ₂ O	2.7
Si	63±1	P ₂ O ₅	0.2
		SiO ₂	57.4
		TiO ₂	0.6

Table 5.1: Elemental composition of submicron ATD by inductively couple plasma optical emission spectrometry (ICP-OES) as reported by Vlasenko et al. (2005) and mineralogical composition of bulk ATD X-ray fluorescence analysis (XRF) as reported by Möhler et al. (2006).

Arizona Test Dust						
Laboratory Unit		Temperature				
	Size	-60	-55	-50	-45	-40
dry generation (1%)	200 nm	125.67±5.5	118.38±5.5	116.71±5.5	122.03±4.7	127.44±4.7
	300 nm	116.05±3.8	110.54±4.7	109.67±4.7	118.34±3.8	116.42±3.8
	400 nm	113.70±2.7	115.42±2.7	109.90±2.1	110.80±1.8	111.50±1.8
wet generation (1%)	100 nm	153.42±0.9	156.00±1.1	154.61±0.8	151.38±1.0	151.11±0.8
	200 nm	135.95±0.9	139.41±1.1	135.49±0.9	134.90±0.9	138.61±0.6

Table 5.2: ATD freezing results collected with the laboratory CFDC unit. Values represent the RH_i condition in which 5% of the particles, by the generation method and diameter indicated, nucleated ice. Error bars represent the 95% confidence interval using a pooled standard deviation.

Arizona Test Dust								
ACFDC-1	Particle Size							
	100 nm		200 nm		300 nm		400 nm	
	T	RH_i	T	RH_i	T	RH_i	T	RH_i
dry generation (5%)			-39.21	145.76	-36.25	142.55	-33.07	141.28
			-39.10	144.58	-39.33	143.65	-35.94	141.30
			-39.06	145.23	-35.76	143.96	-39.01	140.25
			-38.17	144.84	-39.40	144.13	-36.56	141.92
			-37.92	155.80	-36.96	142.62	-33.92	144.51
			-37.22	148.84			-30.31	146.42
			-37.21	149.91				
			-36.74	151.77				
			-36.18	147.64				
			-35.71	155.57				
			-34.20	158.74				
			-32.16	146.46				
wet generation (5%)	-22.5	151.62	-12.6	136.83	-24.4	147.81	-21.1	141.37
	-29.2	159.48	-16.1	140.24	-25.6	169.55	-25.3	146.53
	-39.4	143.38	-18.5	137.29	-28.7	138.45	-25.3	143.47
	-39.8	145.27	-19.0	143.58	-29.1	136.63	-28.6	132.47
	-40.9	146.60	-23.8	151.94	-30.2	136.07	-29.3	132.24
			-24.9	146.59	-30.2	134.13	-30	132.02
			-29.6	151.06	-32.2	133.97	-32.4	134.26
			-31.8	148.20	-34	138.31	-32.6	135.50
			-32.8	141.39	-34	136.17	-32.9	135.27
			-33.2	140.77	-38.1	143.51	-33.2	135.06
			-34.1	146.88	-38.8	138.27	-38.3	182.47
			-34.6	138.84				
			-35.4	140.36				
			-38.7	139.53				
			-39.8	139.09				

Table 5.3: ATD freezing results collected with the aircraft CFDC unit ACFDC-1. Values represent the T and RH_i condition in which 5% of the particles, by the generation method and diameter indicated, nucleated ice.

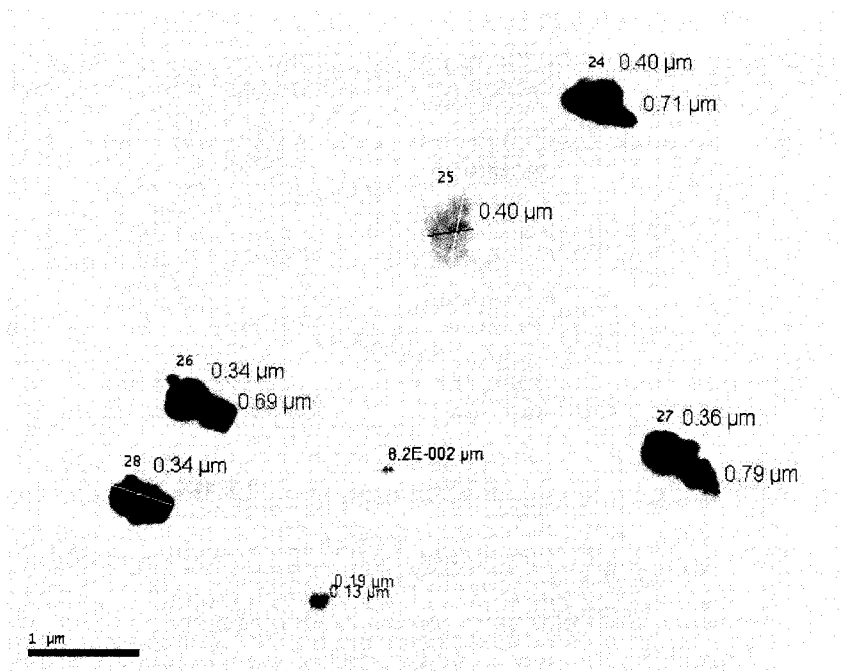


Figure 5.1: SEM images of size selected Arizona Test dust (300 nm).

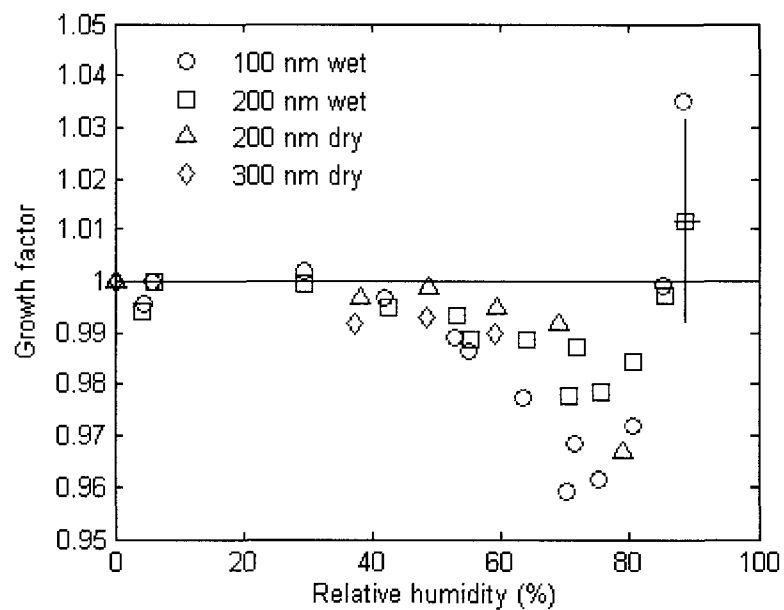


Figure 5.2: Hygroscopic growth factors for 100 nm and 200 nm Arizona Test dust particles by wet generation and for 200 nm and 300 nm particles by dry generation.

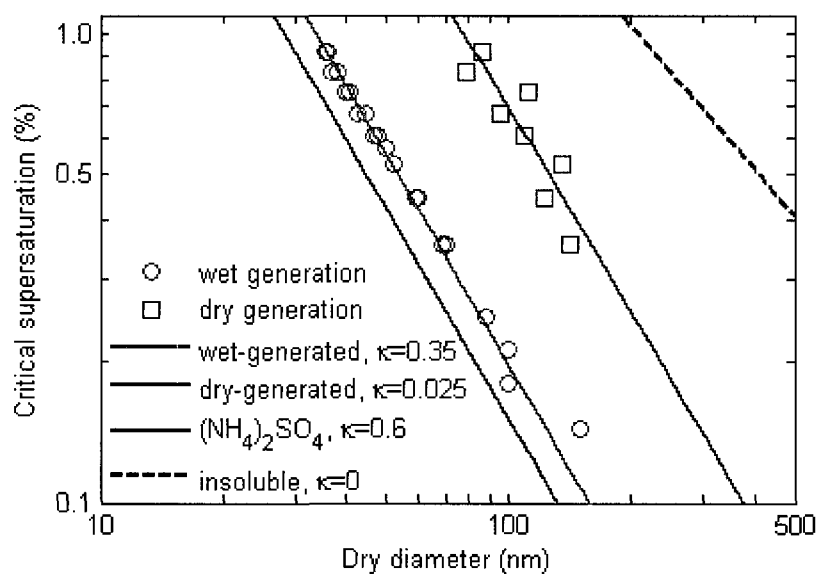


Figure 5.3: CCN activity of Arizona Test dust particles compared to a typical inorganic particle (ammonium sulfate); a theoretical insoluble, wettable particle; and best fit lines for the data by generation type, with $\kappa=0.35$ and $\kappa=0.025$. Measurements for dry-generated particles were only possible for diameters <200 nm due to insufficient number concentrations of larger particles.

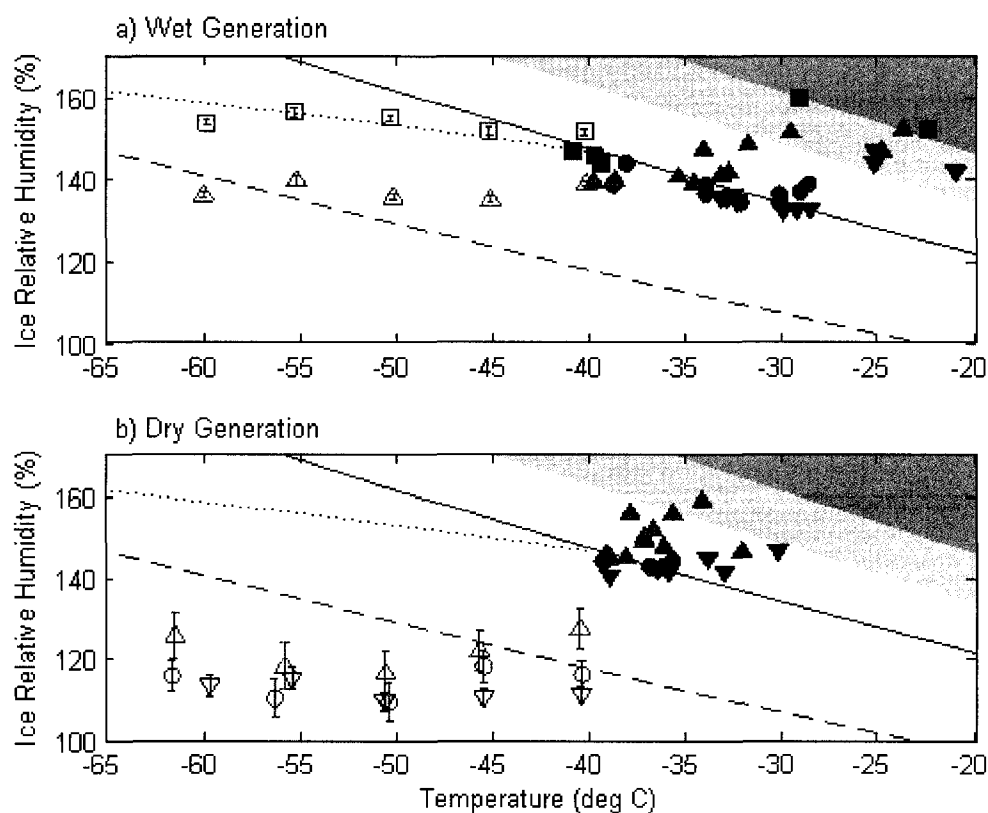


Figure 5.4: Ice nucleation results for (a) wet generation and (b) dry generation. Squares represent 100 nm data, triangles for 200 nm data, circles for 300 nm data and inverted triangles for 400 nm data. Points represent 1% of the particles activating as ice crystals. Open symbols refer to data collected with the laboratory unit, filled symbols refer to data collected in the aircraft unit. The solid blue line is water saturation and the dashed blue line is $RH_w = 80\%$. The dotted black line is homogeneous freezing of 250 nm ammonium sulfate particles as predicted by the parameterization of Koop et al. (2000). Light grey shading indicates the region between 110 120% RH_w and the darker shading indicates the region of $RH_w > 120\%$.

6. Measurements of Saharan dust interactions with water vapor and implications for cloud development

6.1. *Introduction*

The Saharan desert is the largest source of aeolian mineral dust on Earth (D'Alemeida, 1986; Swap et al., 1996). Aeolian dust has an impact worldwide on biogeochemical cycles, from providing nutrients such as iron to the world oceans (Talbot et al., 1986) to fertilizing jungles as far away as the Amazon (Swap et al., 1992). It has also been implicated in transporting disease carrying spores, which contribute to coral reef die-off (Shinn et al., 2000). While in the atmosphere, these particles degrade visibility and have the potential to serve as cloud condensation nuclei (CCN) or ice nuclei (IN) and impact cloud development, which can influence the climate. Most of the North African dust emissions are known to come from localized depressions such as the Bodélé depression, which is the remains of Mega-Lake Chad (Giles, 2005). At points in the past when the Saharan region was wetter, such as the Holocene pluvial during the Last Glacial Maximum, this lake contained water and diatoms thrived. Diatoms are unicellular organisms with a cell wall composed of SiO_2 . As the lake dried out, sediments contributed by these species were left behind which are now deflated as dust

(Washington et al., 2006). Washington et al. (2006) found that the topography of the region was a necessary component of the large dust fluxes achieved in this region due to the erosive winds of the Bodélé Low Level Jet. In simulations where the surrounding mountain ranges were not included, wind peaks were 30% slower and Aeolian dust concentration were much lower. This study, and others, showed that the areas of most intense dust emissions are localized, and depend on many factors such as soil moisture and topography. Another large North African source area is a region covering eastern Mauritania, western Mali and southern Algeria (Goudie and Middleton, 2001). Both of these regions have little impact from anthropogenic activities.

Saharan dust has been observed to nucleate ice at fairly low relative humidities and warm temperatures compared with typical background aerosol based on experimental (Field et al., 2006; Kanji and Abbatt, 2006; Möhler et al., 2006) and field observations (DeMott et al., 2003b; Sassen et al., 2003). DeMott et al. (2003b) measured IN concentrations up to 1 cm^{-3} , the highest ever recorded, at temperatures warmer than the conditions required for homogeneous freezing of sulfates, in Saharan dust plumes near Florida. Sassen et al. (2003) found that Saharan dust was able to glaciate clouds at temperatures as warm as -5.2°C . Yet it is often neglected that dust particles can impact warm cloud formation as well by serving to enhance CCN and giant CCN (GCCN) concentrations. While many studies assume that dust particles are not capable of serving as CCN unless coated by soluble material such as sulfates (e.g. Levin et al., 2005; Yin et al., 2002), the CCN activities of these particles have not been measured. Additionally, in light of higher number concentrations of large ($>500 \text{ nm}$) dust particles as compared to the background aerosol, the potential for dust particles to serve as GCCN should be

considered. In this chapter the interaction of two Saharan dust samples with water vapor are examined covering a wide range of temperature and saturation conditions.

We examine samples collected from the surface soil layer from two locations in the Saharan region. The first was collected near the town of Mala on the Canary Island of Lanzarote (hereafter, CID). While this island is not a major source of dust to the atmosphere, it is in the path of dust transport from the African continent and receives large annual deposits of Saharan dust, and presumably has for thousands of years. The most intense region of Saharan dust transport is between 10°-25°N and shifts with season; Lanzarote, at 29°N, is in the primary dust path during July, August and September (Goudie and Middleton, 2001). However, Saharan dust transport can also occur in the Northern Hemisphere winter, and persists over 30% of that season (Criado and Dorta, 2003). Dust concentrations in excess of $600 \mu\text{g m}^{-3}$ (Chiapello et al., 1999) and an annual dust flux of 20 g m^{-2} (Criado and Dorta, 2003) have been measured on nearby Tenerife Island, approximately 250 km west of Lanzarote. The CID sample also likely contains beach sand and small ancient coral. No processing or sieving of the sample was done prior to experiments.

The second surface sample was collected outside Cairo, Egypt (hereafter, SD). Studies have been performed on this sample previously at the Aerosol Interactions and Dynamics in the Atmosphere (AIDA) cloud chamber facility (Field et al., 2006; Linke et al., 2006; Möhler et al., 2006). Optical and mineralogical composition measurements for a similar sample (“Cairo 2”) have been performed in this chamber and SiO_2 and CaO were found to be the dominant minerals (Linke et al., 2006). Prior to being shipped to our laboratory it was sieved to contain only particles smaller than $75 \mu\text{m}$. During the

spring, Sharav cyclones pass over this region of Egypt and can transport large quantities of mineral dust to the Eastern Mediterranean (Alpert and Ganor, 2001; Kubilay et al., 2000) and as far as East Asia (Tanaka et al., 2005). Alpert and Ganor (2001) reported that during an extremely large dust event on 15-17 March 1998 in Israel, concentrations of particulate matter with diameters less than 10 μm (PM_{10}) exceeding $8000 \mu\text{g m}^{-3}$ were reported. Snow also occurred during the dust washout, an extremely rare event in mid-March (Alpert and Reisin, 1986).

While our samples are not from regions expected to be the primary sources of North African dust to the atmosphere, Schütz and Sebert (1987) found that the mineralogical compositions of aeolian and surface mineral dust with diameters less than 10 μm are quite homogeneously mixed throughout North Africa and are in crustal proportions. A few notable exceptions were kaolinite, which showed increasing concentrations to the south; calcite concentrations which were higher in the north; and enrichment of feldspars and depletion of montmorillonite, compared to surface soils (Schütz and Sebert, 1987). Kaolinite and montmorillonite are known to initiate the ice phase at temperatures as warm as -15°C (Roberts and Hallett, 1968; Salam et al., 2006) and thus changes in their concentration could impact the ice nucleability of dust material.

6.2. *Experimental Procedure*

Experimental methods are similar to those in Chapters 4 and 5 and are only discussed briefly here. CID particles were created by wet (atomization) and dry (fluidized bed) generation. Wet generation, while giving higher and steady number concentrations for a size selected, submicron aerosol, likely alters the surface properties of the particles. We expect dry generation to be more representative of how particles

reach the atmosphere from wind erosion and thus wet generation was not used for the SD sample. All experiments used a Differential Mobility Analyzer (DMA, TSI Model 3071A) to produce a quasi monodisperse aerosol flow. Due to low number concentrations, particularly from dry generated aerosol, it was often necessary to use flow ratios (sheath:aerosol) as low as 7:2.5 in the DMA for CID and occasionally even lower for SD. In this case, selection of a nominal 200 nm particle size can produce a sample stream containing singly-charged particles having diameters between 162-269 nm, and selection of a nominal 400 nm particle size will produce a sample stream containing singly-charged particles having diameters between 323-557 nm. Errors in data interpretation due to the presence of multiply charged particles are also more likely for the data obtained for particles created by the dry generation process, which produces higher concentrations of larger particles. While the size-selected samples are not as monodisperse as usually desired for HTDMA (10:2.0 lpm flow ratio), CCNC (10:2.5 lpm flow ratio) and CFDC (7:2.5 or 4:2.5 lpm flow ratio) experiments, no other size-resolved measurements for Saharan dust ice nucleation exist in the literature. Experiments on wet-generated particles were usually performed on quasi-monodisperse samples produced from a 5:1 DMA flow ratio, for which a nominal 200 nm selection yields a distribution from 177-230 nm and nominal 400 nm cut yields a distribution from 351-472 nm. Interactions with water vapor were measured using our three systems which cover a non-continuous temperature range from $-60 < T < 30^{\circ}\text{C}$ and range of relative humidity with respect to water (RH_w) from $\sim 5\%$ to well above water saturation.

The HTDMA and CCNC were run under their typical configurations as discussed in Chapters 2, 4, and 5. The experimental setup is identical to that shown in Figure 4.1.

The CFDC was operated as described in Chapters 2 and 4. Laboratory unit data were processed as described in Chapter 2. All aircraft CFDC data were obtained using the unit in which the lower portions of both walls of the chamber are held to the same temperature and are ice coated (ACFDC-2). The threshold where the state of the grown particles cannot be unambiguously determined is not rigid, but generally varies between 106-108% RH_w . In this work, we define the threshold as 105% RH_w for this unit to provide a conservative estimate of ice formation conditions and is denoted by a gray shaded region in ice nucleation plots.

As was found in Chapter 4, in these studies the width of the quasi-monodisperse distribution of particles for dry generation, particularly for the large sizes, often contributed to an enhanced background OPC signal. This background was unambiguously distinguishable from the freezing signal when 5% of the particles had nucleated ice, and therefore we report those conditions as freezing onset for our experiments. We note that this choice may be expected to lead to a slight overestimation of the RH_w at onset conditions. For experiments with CID and in which the laboratory unit was used, results are presented as averages of at least three points per temperature, with uncertainty bars representing the 95% confidence level and are for the standard sizes: nominal 200, 300 and 400 nm. Due to difficulties in exactly reproducing temperature conditions in each repeat experiment using the aircraft unit, individual points are shown for these data. Data collected with the laboratory unit were obtained for particle streams produced from DMA flow ratios at 7.0:2.5 lpm and for the aircraft unit at 7.0:3.2 lpm. While this contaminated the sample supplied to the aircraft unit with more large particles than in the sample used in laboratory unit experiments, we do not expect

this to influence the results significantly as size effects were not observed at temperatures warmer than $\sim -40^{\circ}\text{C}$. For experiments with the SD, due to the small bulk sample mass and difficulties in producing sufficient number concentrations from the fluidized bed, flow ratios in the DMA were generally set to 7.0:2.5 lpm, but on occasion were reduced to 4.0:2.5 lpm to obtain higher number concentrations. Therefore, individual points and separate series are shown for the different flow ratios. The aircraft unit data were also size selected by the DMA with flows of 7.0:3.2 lpm.

6.3. Results

6.3.1. Canary Island Dust

6.3.1.1. Hygroscopicity

Diameter GF for size-selected CID were measured by the HTDMA when the dust was generated wet and dry and results are shown in Figure 6.1. While no size effect was observed, very different behavior was observed for particles generated by the two methods. For $RH_w < 70\%$, the GF values were small by both methods. At higher RH_w , the wet generated particles started to exhibit hygroscopic growth, while the dry generated particles had GF values less than ~ 1.1 , for all RH_w . The scatter in GF for the dry generated particles was partially due to the small number concentrations from the fluidized bed, making the grown particle size distributions less smooth and making it more difficult to define a peak, and also may represent real heterogeneity within the sample.

Fits were applied to the data for 100 nm wet-generated particles in two ways. Following the method described in Section 2.3.1, the fit to Equation (2.11) for the CID yields: $a = 0.865$, $b = -2.593$, and $c = 2.013$ and is shown as the black line in Figure 6.1

denoted “polynomial fit”. The single parameter fit represented by Equation (2.13) did not represent the data well. Instead of being constant, the best fit κ was a strong function of a_w . Values of κ ranged from ~ 0 to 0.26 at the highest RH_w value. Figure 6.1 shows the fit for $\kappa=0.26$ as the blue line denoted the “kappa=0.26 fit”. This fit greatly over-predicts GF values for $RH_w < 90\%$, but merges with the polynomial fit at $RH_w > 90\%$.

Since the dust sample was scooped off the ground and not sifted, a small fraction of large particles likely dominates the mass. If these large particles have soluble material associated with them, either in the form of inorganic salts, possibly sea salt or organic material, this soluble material will go into the atomizer solution. Since the large insoluble particles cannot be atomized, the soluble material is redistributed to the smaller insoluble cores, increasing the hygroscopicity of the wet-generated aerosol over that generated from the fluidized bed. Based on the GF data in Figure 6.1, the maximum κ expected from the dry-generated particles would correspond to $GF(RH_w=90\%) = 1.1$, equivalent to $\kappa = 0.037$.

6.3.1.2. CCN activity

CCN activity could only be measured for the wet-generated particles since concentrations of dry-generated particles small enough for CCN measurements were too low. Results are shown in Figure 6.2. CCN activity can be predicted from the fits to the hygroscopicity data as described earlier. The CCN activity of the wet-generated particles is in good agreement with the hygroscopicity estimated from the HTDMA data using the polynomial fit (black line, Equation (2.11)) or the kappa fit (blue line, Equation (2.13)) for the largest observed $\kappa=0.26$. While $\kappa=0.26$ is an overestimation of the growth for $RH_w < 90\%$, it represents the GF near 90% RH_w and also predicts the observed CCN

activity quite well. This suggests that κ does not change significantly between $a_w = 0.9 - 1$. However, the hygroscopicity data for the dry generated particles shows similar scatter but less restructuring ($GF < 1$) than was found for submicron Arizona test dust particles (Chapter 5). We expect similar CCN activity of the dry-generated CID particles as was found for the dry-generated ATD particles, which exhibited $\kappa = 0.024$; this representation is included in Figure 6.2 for reference. While this value is small, it is considerably more active than a pure insoluble particle ($\kappa = 0$) and may have implications for warm cloud development. The CCN activity for ammonium sulfate, $\kappa = 0.61$, and an insoluble particle, $\kappa = 0$ (Petters and Kreidenweis, 2007), are shown for comparison.

6.3.1.3. *Ice nucleation*

Ice nucleation measurements for CID are shown in Figure 6.3. Each point indicates the conditions for which 5% of the particles nucleated ice crystals. Data for wet-generated particles are shown in part (a) and dry generation in part (b) with 100 nm data represented by squares, 200 nm by triangles, 300 nm by circles, and 400 nm data by inverted triangles. Water saturation is shown as the solid blue line and $RH_w = 90\%$ as the dashed blue line. The shaded region indicates $RH_w = 105\%$ and in this region ice particles cannot be unambiguously distinguished from CCN droplets. The ice nucleation of CID shows a behavior similar to that observed for the Owens (dry) Lake dust (Chapter 4). When the dust was wet generated, its ice nucleation onset conditions were similar to those predicted by homogeneous nucleation parameterizations (Koop et al., 2000). Homogeneous freezing conditions for 200 nm ammonium sulfate particles are shown as the dotted black line for comparison. Since the wet-generated CID particles showed large hygroscopic growth and were readily activated in the CCNC, requiring only tenths of a

percent larger supersaturation for activation than ammonium sulfate particles at a given size, it appears that the soluble coating on the wet generated CID particles was freezing homogeneously. Homogeneous freezing is not predicted to occur at significant rates at temperatures colder than -36°C , but a heterogeneous freezing signal was observed at $\sim -35^{\circ}\text{C}$, however. Significant nucleation is not observed at warmer temperatures for any size.

Nucleation onset conditions for dry-generated dust show very little dependence on RH_i for $T < -40^{\circ}\text{C}$ and, despite the fact that low flow ratios were used in the DMA, yielding broad size cuts, a strong size dependence was observed. All sizes showed onset of ice nucleation at considerably lower ice supersaturations than are required for homogeneous freezing of ammonium sulfate. However, at $\sim -35^{\circ}\text{C}$ the size dependence is no longer apparent and water saturated conditions are required for ice formation. At -30°C , the 5% nucleation point falls close to the threshold where ice nucleation can no longer be unambiguously determined from CCN activation. This likely indicates a decreasing ability of the particles to nucleate the ice phase with increasing temperature and it is likely that a small fraction of the particles are initiating the ice phase, while others only activate as CCN. By -25°C no significant ice nucleation is occurring for the limiting conditions required to define threshold ice formation ($>5\%$ at $RH_w < 105\%$).

6.3.2. Saharan Dust

6.3.2.1. Hygroscopicity and CCN Activity

Figure 6.4 shows *GF* data for two sizes of dry-generated SD: atomization was not used to generate SD particles. The results presented in Chapter 4, 5 and the previous section well establish that the suspension of dust particles in water prior to

reaerosolization causes significant changes to the particle hygroscopicity. Neither size tested (200 and 300 nm) shows appreciable water uptake to the upper limit of the instrument. No fit is possible with the observed low growth factors, but the largest measured $GF(RH_w=92\%)=1.015$ corresponds to $\kappa=0.004$ (Equation 2.13).

Despite the low hygroscopicity observed at subsaturated conditions, these particles were able to serve as CCN at much lower supersaturations than are predicted for either insoluble particles ($\kappa=0$, thick black line) or $\kappa=0.004$ (dashed red line) as suggested by the HTDMA data, as shown in Figure 6.5. CCN activity of the dust particles was measured at supersaturations from 0.3 to 1%, but data for critical supersaturations greater than $\sim 0.65\%$ could not be captured because the fluidized bed does not produce sufficient concentrations of particles with diameters smaller than ~ 100 nm. Due to the low number concentrations from the fluidized bed, the flow ratio in the DMA was approximately 7.0:1.5 lpm. This gives fairly broad size selections and the activation curves are not as steep as observed for salts. However, some of this breadth may be due to the heterogeneity of the sample, if all particles of the same size do not have the same composition nor CCN activity. Activation occurred at lower supersaturations than were predicted for the less-hygroscopic fraction of the Owens (dry) Lake dust (Chapter 5) and lower than measured for dry generated Arizona Test dust ($\kappa=0.024$, shown for comparison). A fit to the CCN data yields $\kappa\sim 0.054$. Following the discussion in Section 5.3.1 this corresponds to a soluble fraction, if it is assumed to be composed of pure sulfuric acid ($\kappa=1.19$), of 4.5% if the remainder of the particle is characterized by $\kappa=0$. This suggests that there is some material on the surface of these particles which does not

deliquesce in the HTDMA, but contributes to water uptake as water saturation is approached.

6.3.2.2. *Ice Nucleation*

Results of ice nucleation measurements for the Saharan dust are shown in Figure 6.6 and represent 5% of the particles activating as IN. For flow ratios in the DMA of 7.0:2.5, the standard labeling convention used in Figure 6.3 was used. Additional series were added when flow ratios were 4.0:2.5. At these flow ratios, when nominal sizes of 300 and 600 nm were chosen, particles of 216-619 and 472-860 nm were selected, respectively. These are shown in black with 300 nm data in pluses and 600 nm data in stars. The series for 600 nm particles shows that the size dependence observed for 200-400 nm particles continues to larger sizes, yet is slightly smaller than the size dependence observed for the CID. Indeed the series sort by the maximum diameter allowed to exit the DMA for each selected size and flow ratio.

As was seen for CID and ATD, little dependence of RH_i with increasing temperature at $T < -40^\circ\text{C}$ was observed, although the individual data points shown in Figure 6.7 have more scatter than the averages shown for the other samples. At temperatures warmer than -40°C , water saturation was required to initiate the ice phase. Between $-35^\circ\text{C} < T < -30^\circ\text{C}$, increasing RH_w was required to initiate ice formation, likely indicating a decreasing ability of the particles to initiate ice with increasing temperature. At temperatures warmer than -30°C , the required RH_w increased to $\sim 110\%$ for all sizes, indicating that water droplets which had grown large enough to survive the evaporation region, and not ice crystals were likely to be responsible for the OPC signal. These

features are qualitatively consistent with those observed for both of the other insoluble dusts, ATD and CID.

A direct comparison of the ice nucleation results for either dust presented in this chapter with Figure 5.4 for ATD particles is not appropriate since Figures 6.3 and 6.6 represent 5% of the particles activating as IN and Figure 5.4 is for 1% activation. However, the conditions supporting 1% activation of CID and SD can be determined for the 200 nm particles because there is little influence of the dry or haze particles on the OPC signal for these smallest particles studied. Figure 6.7 shows that 1% of the 200 nm SD particles activated as IN (stars) at very similar RH_i as observed for the CID (squares). It is observed that ~6-18% higher RH_i conditions are required for a given temperature for the CID and SD than ATD (triangles) at temperatures colder than -40°C, however all three dust types require water saturated conditions at -35°C. It is unclear if the lower supersaturations required for onset of ice formation for ATD, as compared to the Saharan region samples, are due to differences in chemical composition or if the milling process used in production of the ATD creates more active sites than are found on natural mineral dust aerosol.

6.4. *Comparison to other freezing studies*

The similarity in ice formation onset conditions for CID and SD particles observed in our studies is consistent with the findings of Schutz and Sebert (1987) that mineral dust compositions in the Saharan region are homogeneous for submicron particle sizes. While differences were observed between particles created by wet and dry generation, we expect this to be an artifact of the water suspension required to wet generate the dust. This observation is consistent with our findings for both Owens (dry)

Lake and Arizona Test dusts and confirms that studies attempting to investigate the interactions of dust particles with water vapor should not immerse the particles in water prior to sampling unless immersion/condensation freezing are the only modes of interest.

Field et al. (2006) and Möhler et al. (2006) studied ice nucleation on Saharan dust, a different subset of the sample provided to us, in the AIDA chamber. In those studies, they were not able to size resolve ice nucleation. Instead they used a nearly lognormal distribution of particles with an average mean diameter of 0.35 μm and an average standard deviation of 1.85, with particles larger than 2 μm removed by an impactor prior to entering the chamber. In those studies dry generation by rotation brush was used, which we expect to yield particles with composition and morphology similar to those created in fluidized bed generation. Field et al. (2006) report conditions for which 0.5% and 8% of the particles nucleate ice; but due to the polydisperse distribution of particles, a direct comparison to our data is difficult. However, those conditions generally bound the conditions observed for ice nucleation onset in this chapter indicating reasonable agreement between the two methods. We expect that nucleation occurs in or on the largest particles first and as the ice supersaturation increases, smaller particles initiate ice. Thus we expect Field et al. (2006) to see freezing onset at several percent lower RH_i than we observed. This was the case for some temperatures, but similar onset RH_i values were observed at other temperatures. Field et al. (2006) also observed $\sim 1\%$ of the SD particles nucleating ice at temperatures as warm as -20°C , much warmer than observed in this work. Assuming the largest particles are nucleating ice first and integrating the given size distribution to the activated fraction, only the very largest particles are activated at this warmest temperature; much larger than examined in our

studies at the warm temperature range. Möhler et al. (2006) provide maximum nucleation fractions and the corresponding ice supersaturation for which this maximum nucleation occurred. We assume, as in Chapter 5, that the largest particles nucleate ice first and the given size distribution may be integrated down from the largest sizes to the activated fraction to find the minimum diameters corresponding to the reported maximum supersaturations. For similar conditions in our chamber, these diameters were roughly consistent with those observed in our chamber at -52°C (minimum diameter = 540 nm at 145% RH_i), but somewhat smaller than observed in our chamber at -60°C (minimum diameter = 345 nm at 124% RH_i) and are included in Figure 6.6 for comparison. However, it appears that the findings in the AIDA chamber are generally consistent with the findings in this study considering the difficulty in directly comparing a distribution of particles with a size selected aerosol flow.

Kanji and Abbatt (2006) examined a Saharan dust sample on their cold stage system and found that ice nucleation occurred between $100 < RH_i < 105\%$ for temperatures between 220-260 K. Activation was observed to much warmer temperatures than found in this work; however their studies included particles as large as 5 μm , even larger than studied in the AIDA chamber. We expect differences in ice nucleation activity between our work and theirs are due to the larger particles they used and possibly due to interactions with the substrate used for the cold stage measurements.

Measurements of IN concentrations during the CRYSTAL-FACE campaign showed significant concentrations in Saharan dust layers for $T = -36^{\circ}\text{C}$ and $RH_i = 123\%$ (DeMott et al., 2003b). This is in reasonable agreement with the CID observations, especially when it is considered that particles much larger than studied in this work were

likely contained in these plumes. Further comparison to IN data from field campaigns may be found in Chapter 8.

6.5. Conclusions

The ability of two dry-generated samples of mineral dust from the Saharan region to take up water at subsaturated conditions and serve as CCN and IN was investigated. Both dust samples showed nearly zero water uptake at subsaturated conditions in the HTDMA, yet were able to serve as CCN at supersaturations lower than required for the activation of an insoluble particle. Both samples showed the ability to initiate the ice phase at modest ice supersaturations for temperatures colder than $\sim -30^{\circ}\text{C}$. At cirrus temperatures ($T < -40^{\circ}\text{C}$) both particle types were able to initiate ice at supersaturations considerably lower than required for homogeneous freezing of the background aerosol (e.g. sulfates) and at a nearly constant RH_i with decreasing temperature for a given size. A strong size effect was observed at cirrus temperatures for both samples. These results indicate that dust particles from the Saharan region likely influence cloud development over a widespread area of the North Atlantic and possibly worldwide. Atmospheric implications will be discussed further in Chapter 7.

Canary Island Dust				
Laboratory Unit		Temperature		
	Size	-50	-45	-40
dry generation (5%)	200 nm	146.21 $\pm$ 2.7	142.54 $\pm$ 2.7	141.46 $\pm$ 2.7
	300 nm	137.42 $\pm$ 6.1	135.89 $\pm$ 6.1	132.63 $\pm$ 6.1
	400 nm	130.43 $\pm$ 7.4	125.57 $\pm$ 7.4	134.19 $\pm$ 7.4
wet generation (5%)	100 nm	157.08 $\pm$ 2.1	153.84 $\pm$ 2.1	149.81 $\pm$ 2.1
	200 nm	155.93 $\pm$ 2.1	152.00 $\pm$ 2.1	148.85 $\pm$ 2.1
	300 nm	151.30 $\pm$ 3.0	148.67 $\pm$ 3.0	147.10 $\pm$ 3.0

Table 6.1: CID freezing results collected with the laboratory CFDC unit. Values represent the RH_i condition in which 5% of the particles, by the generation method and diameter indicated, nucleated ice. Error bars represent the 95% confidence interval using a pooled standard deviation.

Canary Island Dust						
ACFDC-2	Particle Size					
	200 nm		300 nm		400 nm	
	T	RH_i	T	RH_i	T	RH_i
dry generation (5%)	-35.74	142.04	-35.57	142.65	-35.05	143.64
	-35.41	141.75	-35.21	141.87	-35.66	140.88
	-31.06	142.12	-30.16	141.32	-29.64	140.86
	-30.92	144.84	-30.67	145.08	-29.49	141.73
	-24.81	148.20	-24.44	147.46	-24.24	146.25
	100 nm		200 nm		300 nm	
	T	RH_i	T	RH_i	T	RH_i
wet generation (5%)	-35.85	147.93	-35.61	147.03	-36.18	143.52
	-35.59	147.79	-35.38	146.80	-35.34	144.24
	-31.07	149.76	-30.89	148.57	-30.34	143.35
	-31.00	150.37	-30.62	149.15	-29.52	143.21
	-30.89	149.74	-25.50	149.82	-25.32	148.14
	-29.65	147.38	-25.25	149.07	-25.09	146.54
	-26.25	142.28	-19.03	135.75	-19.20	137.50
	-25.90	141.34				

Table 6.2: CID freezing results collected with the aircraft CFDC unit ACFDC-2. Values represent the T and RH_i conditions in which 5% of the particles, by the generation method and diameter indicated, nucleated ice.

Saharan Dust Ice Nucleation (5% Activation)								
Laboratory Unit	200 nm		300 nm		400 nm		600 nm	
Flow Ratio	T	RH_i	T	RH_i	T	RH_i	T	RH_i
7.0:2.5	-35.08	141.55	-35.14	141.70	-35.56	141.17		
7.0:2.5	-39.65	142.55	-39.67	141.24	-39.57	140.22		
7.0:2.5	-44.47	143.15	-44.51	140.32	-44.25	137.93		
7.0:2.5	-48.82	143.18	-49.17	140.13	-44.47	135.62		
7.0:2.5	-52.57	147.13	-50.65	132.87	-49.62	132.86		
7.0:2.5	-57.43	157.41	-52.73	143.84	-49.82	137.63		
7.0:2.5			-57.41	141.40	-53.45	140.19		
7.0:2.5					-55.70	137.07		
4.0:2.5			-35.77	138.16			-37.01	139.18
4.0:2.5			-41.17	137.81			-41.44	136.28
4.0:2.5			-47.88	129.88			-45.40	130.63
4.0:2.5			-51.61	130.67			-47.24	128.14
4.0:2.5			-57.33	138.51			-51.80	129.84
4.0:2.5							-56.36	137.05

Table 6.3: SD freezing results collected with the laboratory CFDC unit. Values represent the T and RH_i condition in which 5% of the particles, by the generation method and diameter indicated, nucleated ice. The left hand column gives the flow ratio used in the DMA to select particle sizes. The top half of the table with higher flow ratio will have a sharper size cut than the bottom half of the table with the lower flow ratio.

Saharan Dust						
ACFDC-2	Particle Size					
	200 nm		300 nm		400 nm	
	T	RH_i	T	RH_i	T	RH_i
dry generation (5%)	-24.95	141.11	-24.70	140.41	-20.01	133.94
	-28.53	144.95	-28.82	145.97	-25.31	140.77
	-33.13	143.89	-30.46	143.23	-25.59	142.88
	-33.59	142.06	-33.10	143.02	-28.89	146.90
	-33.98	143.87	-33.36	143.74	-30.40	149.49
	-35.35	142.53	-34.17	143.43	-33.37	144.05
	-36.73	142.43	-35.83	143.20	-34.21	142.82
	-38.43	144.09	-37.77	144.46	-36.62	142.41
			-38.38	143.61	-37.33	145.66
					-39.04	143.27

Table 6.4: SD freezing results collected with the aircraft CFDC unit ACFDC-2. Values represent the T and RH_i conditions in which 5% of the particles, by the generation method and diameter indicated, nucleated ice.

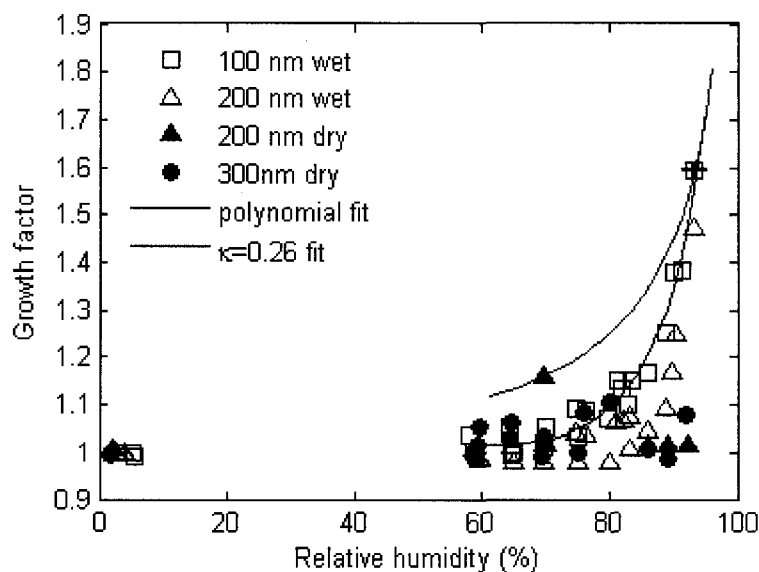


Figure 6.1: Measured GF values for CID with sizes as shown. Fits by Equations (1, black line) and (2, blue line) are included. Representative error bars are shown on one point with the highest GF .

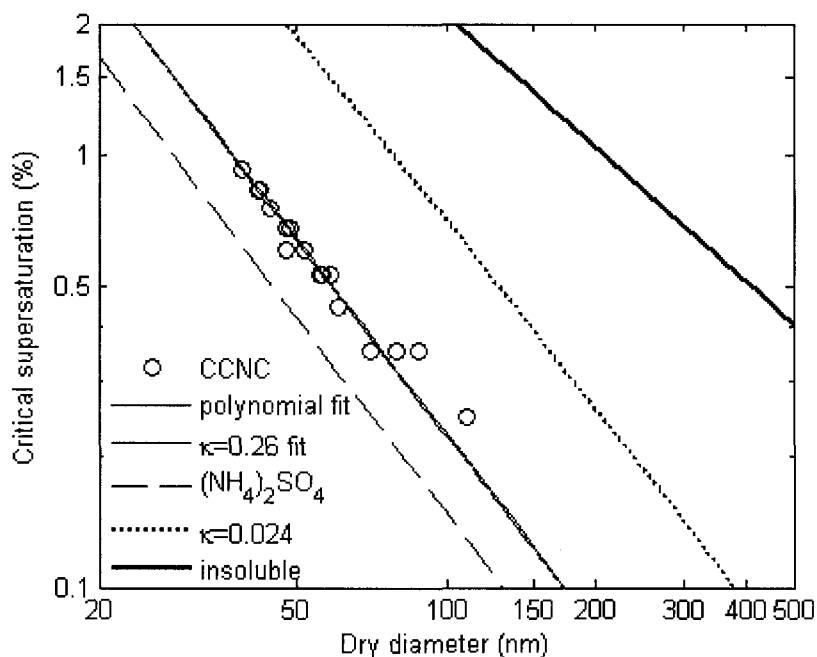


Figure 6.2: Measured CCN activation for CID (circles, wet generation) with the fits by Equation (1), black line and Equation (2), blue line. The activation for $(\text{NH}_4)_2\text{SO}_4$ ($\kappa=0.61$), Arizona Test dust ($\kappa=0.024$), and an insoluble particle ($\kappa=0$) are shown for comparison.

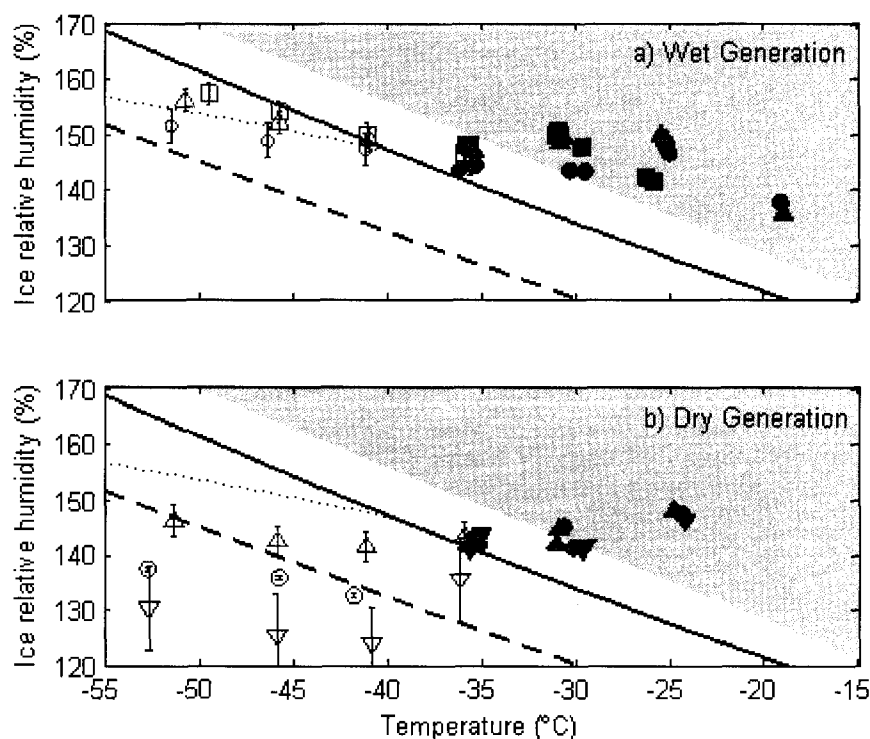


Figure 6.3: Ice nucleation results of CID for particles created by (a) wet generation and (b) dry generation. Squares represent 100 nm data, triangles for 200 nm data, circles for 300 nm data and inverted triangles for 400 nm data. Points represent 5% of the particles activating as ice crystals. Open symbols refer to data collected with the laboratory unit, filled symbols refer to data collected in the aircraft unit. The solid blue line is water saturation and the dashed blue line is $RH_w = 90\%$. The dotted black line is homogeneous freezing of 200 nm ammonium sulfate particles. The shaded region indicates $RH_w > 105\%$, the region in which ice crystals cannot be unambiguously distinguished from CCN droplets.

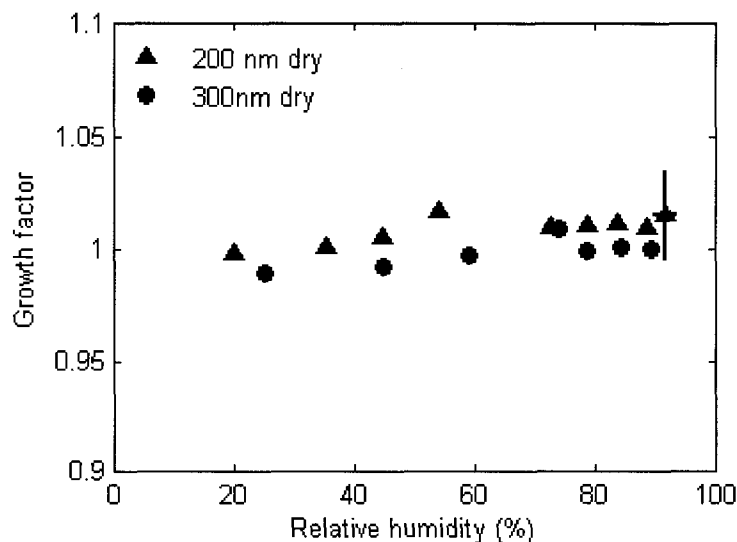


Figure 6.4: Measured GF values for dry-generated SD with sizes as shown. Representative error bars are shown on one point with the highest GF .

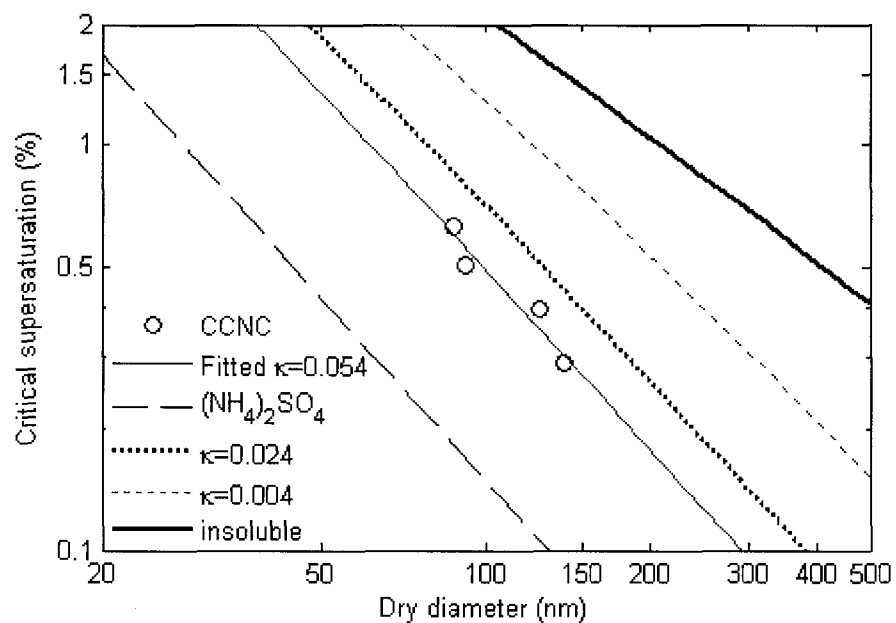


Figure 6.5: Measured CCN activation for SD (circles, dry generation) with the best fit as represented by $\kappa=0.054$. The activation for $(\text{NH}_4)_2\text{SO}_4$ ($\kappa=0.61$), Arizona Test dust ($\kappa=0.024$), the activity predicted from HTDMA data ($\kappa=0.004$) and an insoluble particle ($\kappa=0$) are shown for comparison.

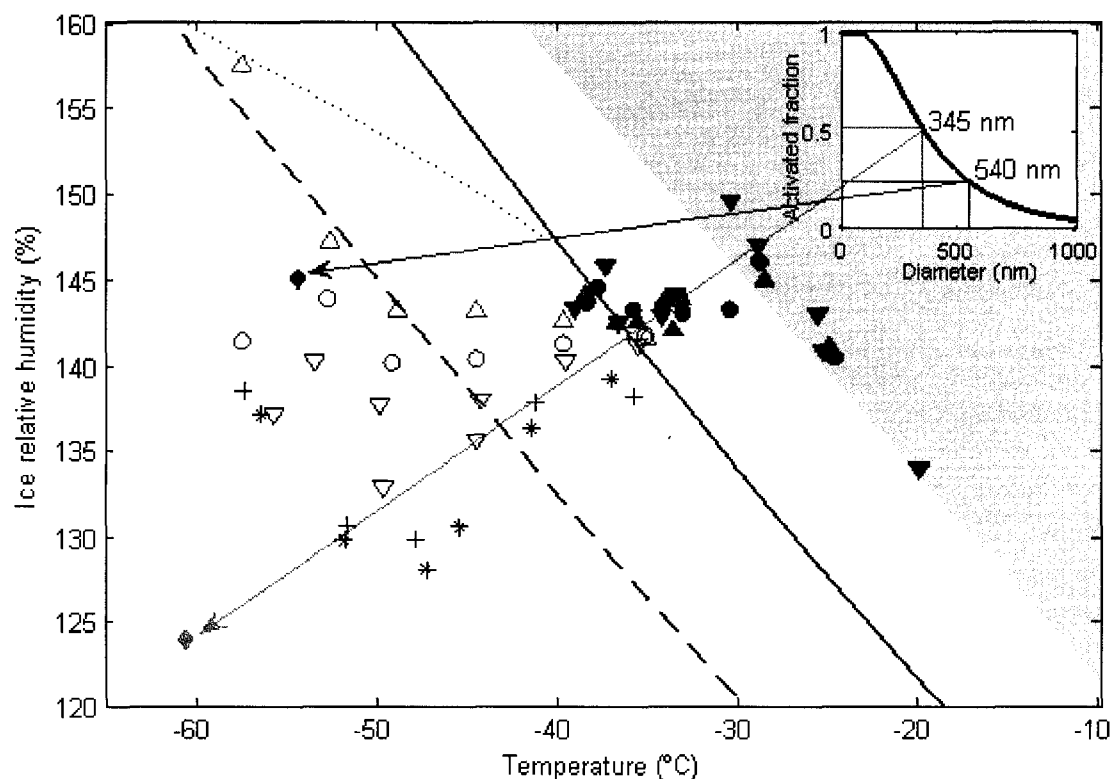


Figure 6.6: Ice nucleation results for dry-generated SD. Triangles represent data for 200 nm particles, circles for 300 nm particles and inverted triangles for 400 nm particles with flow ratios of 7.0:2.5 lpm in the DMA. Pluses are for 300 nm and stars for 600 nm data with flow ratios of 4.0:2.5 lpm in the DMA. Points represent 5% of the particles activating as ice crystals. Open symbols refer to data collected with the laboratory unit, filled symbols refer to data collected in the aircraft unit. The solid blue line is water saturation and the dashed blue line is $RH_w=90\%$. The dotted black line is homogeneous freezing of 200 nm ammonium sulfate particles. The shaded region indicates $RH_w > 105\%$, the region in which ice crystals cannot be unambiguously distinguished from CCN droplets. Results from Mohler et al. (2006) are shown in blue and orange diamonds for comparison. The inset shows the cumulative size distribution from largest particles to smallest particles used in these chamber studies. The maximum fraction activated in the chamber was used to determine a minimum diameter activated for these points (see text).

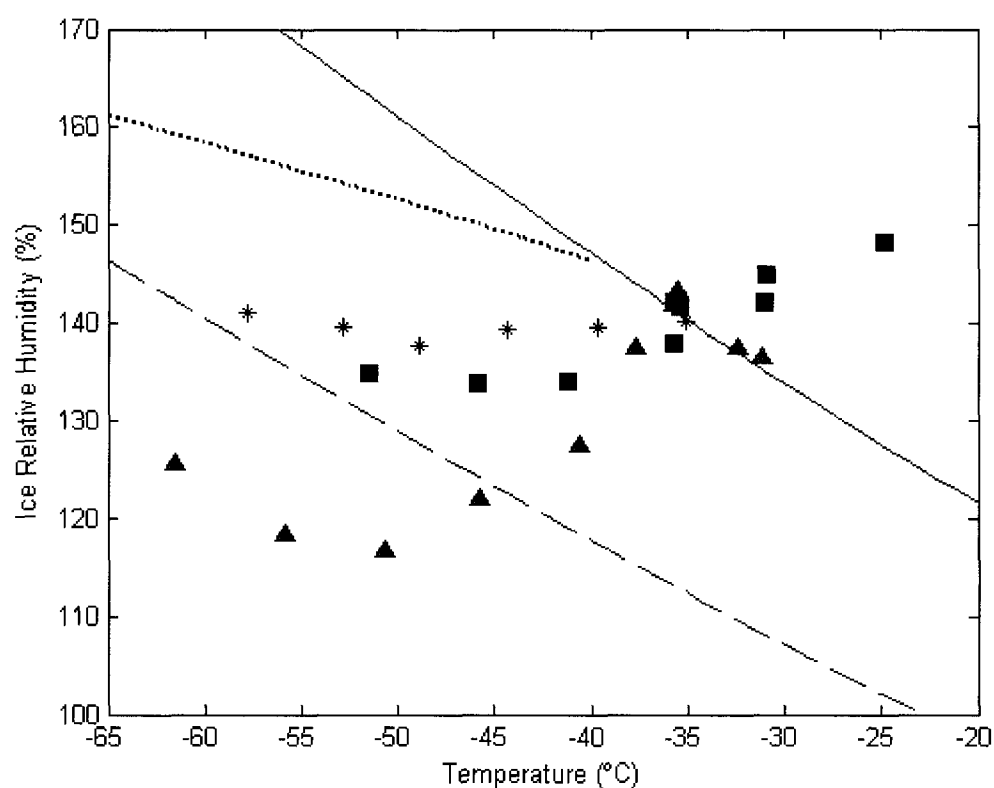


Figure 6.7: Comparison of onset conditions for 1% activation of particles as IN by ATD (red triangles), CID (blue squares) and SD (black stars). The solid blue line is water saturation and the dashed blue line is $RH_w = 80\%$. The dotted black line is homogeneous freezing of 200 nm ammonium sulfate particles. The shaded region indicates $RH_w > 105\%$, the region in which ice crystals cannot be unambiguously distinguished from CCN droplets.

7. Comparison and Climate Impacts of Dust

Types

7.1. *Higher κ vs. lower κ dusts*

Two broad classifications of dust types can be proposed from the measurements presented here: those which contained appreciable soluble material and those that did not. Dry-generated Arizona Test dust (ATD), Canary Island dust (CID) and Saharan dust (SD), as well the wet-generated ATD and likely the less hygroscopic mode of dry-generated Owens (dry) Lake dust (OLD) are included in what we will call the *lower κ dust*, and is defined as dust having $\kappa < 0.01$ deduced from CCN measurements. While the CCN activity of the dry-generated CID dust could not be measured, based on its hygroscopic and ice nucleating behavior, we expect this dust to fall in the lower κ category. Wet-generated OLD and CID and the more hygroscopic fraction of dry-generated OLD fall into the *higher κ dust* category, defined as dust having $\kappa > 0.01$ deduced from CCN measurements. Comparison of behaviors of these dust types as they pertain to warm and cold clouds will be examined in the following sections. The potential impact these dust types can have on the climate system will be discussed in Section 7.3.

7.1.1. Warm clouds

Figure 7.1 shows all measurements of CCN activity in this study. While measurements of CCN activity of all the lower κ mineral types were not possible due to limitations in aerosol generation, it is clear that there are two broad groupings of activation behavior, and the blue line indicating $\kappa=0.01$ separates these two groups as defined above. The higher κ dust types are enveloped in the light blue shading with $0.2 < \kappa < 1.1$, with the black line indicating the behavior of ammonium sulfate aerosol ($\kappa=0.61$). The lower κ dust types are bounded by the gray shading with $0.01 < \kappa < 0.08$. It is expected that most natural mineral dust from regions with low soluble contents will fall in the gray shaded region. However, dust from desiccated playa regions, such as Owens (dry) Lake may have a subset of highly soluble particles with CCN activity falling within the blue shaded region.

The lower κ particles showed no appreciable hygroscopic growth at $RH_w < 92\%$, yet were able to serve as CCN at lower supersaturations than are required for completely insoluble particles. Natural mineral dust particles likely have been exposed to small amounts of soluble material while either on the surface or suspended in air, and have surfaces which are capable of serving as sites for heterogeneous reactions of gas phase species such as sulfuric and nitric acid (Gibson et al., 2006a; Gibson et al., 2006b; Krueger et al., 2004; Laskin et al., 2005; Usher et al., 2003). The ability of submicron particles of this type to serve as CCN at relatively low supersaturations also limits their lifetime in the atmosphere because a fraction of activated CCN are removed during precipitation events. Given the relatively efficient CCN activity of these mineral dust

particles ($0.01 < \kappa < 0.08$), we expect that these particles can contribute to CCN and also giant CCN (GCCN) concentrations in the atmosphere.

The higher κ mineral dust particles are able to serve as CCN at very similar supersaturations as are required for typical inorganic atmospheric aerosol constituents like ammonium sulfate. Thus concentrations of even very small (diameters less than 100 nm) particles of this type can contribute to warm cloud development. Subsaturated hygroscopic growth can also contribute to visibility problems in areas with heavy dust loadings of this type, such as the Owens Valley.

Dust particles could potentially fall anywhere in the critical supersaturation-dry diameter space, depending on the mixing state of the particles. It is also possible, as observed for the Owens (dry) Lake sample, that multiple modes of particles, with different soluble contents associated with each, are possible.

7.1.2. Cold clouds

All freezing onset data collected for 200 nm particles are shown in Figure 7.2 at the 1% freezing level. In this figure the distinction between the behaviors of higher κ and lower κ dust particles are clear at temperatures colder than -40°C . Higher κ particles (wet-generated OLD and CID particles) activate very near the homogeneous nucleation line of 250 nm ammonium sulfate particles at temperatures colder than -40°C (dashed black line, Koop et al., 2000), while the lower κ particle types have much lower nucleation onset relative humidities at colder temperatures. The gray shaded region indicates $RH_w > 105\%$ and in the atmosphere it likely limits a reasonable range of relative humidity values observed, therefore we do not expect that particles which require higher RH_w to activate to contribute significantly to IN concentrations under those temperature

conditions. It appears, for the sizes studied, that the higher κ dust particles are active, for threshold activation conditions defined, at $T < -35^{\circ}\text{C}$ and lower κ particles are active at $T < -25^{\circ}\text{C}$, with variations between samples.

At temperatures below 0°C , the lower κ dust particle types generally showed a size dependence. The data exhibited very little temperature dependence for the humidity required at onset of nucleation at temperatures below -40°C and freezing mode transitioned from deposition to condensation freezing at $\sim -40^{\circ}\text{C}$. Some showed a strong size dependence for the threshold temperature of freezing, $T_{thresht}$, the warmest temperature in which nucleation was observed. However, none exhibited significant ice nucleation at temperatures warmer than -25°C , for the sizes examined.

Higher κ dust particles, however, generally initiated ice formation at conditions similar to those required for homogeneous freezing of sulfates. We expect that this indicates that when the particles contain sufficient soluble material to cover the particle surface with a liquid solution, active sites are prevented from serving as deposition nucleation sites. Although nucleation was observed at $\sim -35^{\circ}\text{C}$, above the limit of homogeneous freezing, but it was not observed at any warmer temperatures for the higher κ dust samples. These observations also seem to hold for some coated lower κ dusts (see Section 7.2), but may depend on the insoluble and soluble material.

7.2. Comparison of higher κ dust vs. coated dusts

This section will describe measurements in which dry-generated Arizona Test dust (ATD) particles were coated with secondary organic material to estimate the effect of coating during atmospheric transport of these particles. The system employed for coating the particles will be described in Section 7.2.1. Section 7.2.2 will present the data

and Section 7.2.3 will compare and contrast these measurements for ice nucleation activity of coated and higher κ dust with measurements from previous studies.

7.2.1. Description of coating system

The coating system consisted of a mixing tank (11.5 L) with controlled ozone, α -pinene and dry generated ATD aerosol flows. Ozone is known to react with α -pinene gas to form secondary organic products with low enough vapor pressures to partition to the particle phase (Docherty et al., 2005). Terpenes, such as α -pinene contribute substantially to the organic carbon aerosol in the atmosphere. Heald et al. (2006) estimated the source of SOA aerosol from terpenes to be 0.81 Tg C over North America during July-August, twice as large as the SOA source due to isoprene oxidation. The entire ATD particle distribution (i.e., no size cuts after generation by the fluidized bed) was sent to the mixing tank to provide as much existing surface area as possible to take up organic vapors and prevent nucleation of pure secondary organic aerosol (SOA) particles. The conditions in the tank were highly saturated with ozone; therefore, the products produced may not be representative of SOA products produced in the atmosphere. The hygroscopicity of pure SOA generated by this method was represented by $\kappa \sim 0.1$ (Prenni et al., 2007b). Due to dilution by the ozone and α -pinene flows, low number concentrations of size-selected particles prevented accurate measurement of hygroscopicity (HTDMA) or CCN activity. It was hoped that CCN measurements could be made to estimate the SOA mass deposited on the particles, but low number concentrations made these measurements impossible. Therefore no quantitative information on the thickness of the coating is available. Thus only size selected ice nucleation measurements (using DMA flow ratios of 9.6:2.6) are presented, as low

number concentrations are less of a barrier to this experimental set-up. The size of the selected particles is the coated size and includes the dust and coating.

7.2.2. SOA-coated dust results

The SOA-coated ATD had dramatically different freezing behavior as compared to the uncoated, dry-generated ATD particles. The results are shown in Figure 7.3. The data represent 1% of the particles nucleating ice crystals and each point from the laboratory unit (open symbols) is the average of three measurements with error bars indicating the confidence interval at the 95% level. Data collected with the aircraft unit (filled symbols) are shown as individual data points. The selected sizes are slightly different than used for the uncoated cases. Squares represent 160 nm particles, triangles represent 250 nm and circles represent 340 nm coated ATD. Data for the uncoated, dry-generated ATD are repeated in black for comparison, with the symbols as defined in Figure 5.4. The coated ATD required 30-45% higher RH_i for the same temperature to initiate the ice phase. Further, instead of requiring a constant RH_i at temperatures below -40°C , the temperature dependence of RH_i resembles the trend expected for homogeneous freezing. The dotted line shows the predicted onset of homogeneous freezing for 250 nm ammonium sulfate particles, calculated using the water activity based parameterization developed by Koop et al. (2000). Data at temperatures warmer than -40°C were collected using the second generation aircraft unit in which ice crystals cannot be distinguished from liquid grown CCN at $RH_w > \sim 105\%$ (gray shading). We are therefore confident that the points colder than -25°C are ice. The point right at -25°C is very close to this limit, therefore we cannot be sure of the state of the particles. Since nucleation occurs at temperatures warmer than those for which homogeneous freezing

can occur, at temperatures warmer than $\sim -36^{\circ}\text{C}$ the observed freezing must be heterogeneous and due to the presence of the dust core. It also appears that the larger particles have ice nucleation activity at warmer temperatures than do the smaller particles.

7.2.3. Comparison with other freezing measurements

The freezing-onset behaviors of SOA-coated dusts more closely resemble the data for higher κ dust particles than for the uncoated, lower κ ATD particles. This can be seen by comparison of Figures 7.2 and 7.3: the data for the coated dust fall in line with those for the 200 nm wet-generated OLD and CID. It appears that soluble material, either present as a component of the dust, or deposited on the dust surface through gas phase reactions, acts to coat the active sites on the lower κ dust. At temperatures below -40°C , it appears that deposition nucleation is inhibited by the presence of the SOA and some other soluble materials, so either the solution coating freezes homogeneously or the dust initiates freezing through immersion freezing at much higher RH_w than was observed for deposition nucleation of the uncoated ATD.

Archuleta et al. (2005) coated metal oxide particles with diameters between 50-200 nm with sulfuric acid and found that, depending on core type, the treatment either increased, lowered or did not change the required RH_i for ice nucleation. Those authors suggested only several monolayers would be sufficient to promote a liquid coating on the metal oxide particles and change the freezing process to either condensation freezing or homogeneous freezing of the surrounding solution. Archuleta et al. (2005) found that coatings of sulfuric acid on manufactured amorphous alumina-silicate particles in some cases inhibited ice formation and concluded that the sulfate promoted a liquid layer

covering the alumina-silicate substrate which was detrimental to ice formation as compared to the hydrophobic surface. Bassett et al. (1970) hypothesized that if water forms in clusters on active sites, that this water will be less organized than an oriented liquid layer on a polar surface, and only short-range ordering of the cluster is required to form the ice embryo, which is less of a barrier to freezing than for the liquid layer. Further, DeMott et al. (2003a) found that analyzed ice crystal residue particles with organic ionic fractions required significantly higher RH_i than other residue types. Archuleta et al. (2005) found for the smaller particle sizes (50-100 nm) that the results were indistinguishable from predictions of homogeneous freezing for similarly sized pure sulfuric acid particles, but the 200 nm particles in all cases showed a lower onset RH_i indicating a heterogeneous process was occurring. In this study, it is unclear how thick the SOA coatings were, and because the SOA may be much less hygroscopic than sulfuric acid, we cannot necessarily assume a liquid coating exists on the particles from a low RH_i . However, the inhibition of the deposition mode of ice nucleation indicates that a similar process is occurring on the coated ATD particles as observed in the experiments of Archuleta et al. (2005). While none of the sizes showed clear freezing onset at lower RH_i than predicted by homogeneous freezing at temperatures colder than -40°C , the ability of the coated dust to initiate the ice phase at temperatures warmer than $\sim -36^{\circ}\text{C}$ does indicate that ATD initiates heterogeneous freezing at warmer temperatures.

Zuberi et al. (2002) examined the freezing behavior of mineral dust inclusions in concentrated ammonium sulfate droplets (10-55 μm). The size distribution of the inclusions was not well defined, but likely included particles much larger than examined in this study, and each droplet may have contained multiple inclusions. The particles

were isolated from the ambient RH_i in the instrument and so the concentration of ammonium sulfate in the droplets was fixed prior to cooling; droplets were sealed with a halocarbon grease to maintain a fixed concentration. Upon cooling, the concentration was then converted to an ice supersaturation. Those authors observed nucleation at lower RH_i for the particles containing mineral inclusions than for pure ammonium sulfate particles. Koop et al. (2000) suggested that homogeneous freezing occurs at conditions which are offset by a constant water activity (Δa_w) from the water activity of the solution in equilibrium with ice. This relationship was still observed by Zuberi et al. (2002) for droplets with mineral inclusions; however a Δa_w of 0.242 was used to fit the data with mineral dust inclusions, compared to Δa_w of 0.305 for pure ammonium sulfate particles. This indicates a ~6% reduction in RH_w (a_w is approximately equal to RH_w for particles greater than 200 nm) for freezing compared to the pure ammonium sulfate particles. Archuleta et al. (2005) found a similar shift in Δa_w for metal oxide particles treated with H_2SO_4 with values ranging from 0.23-0.26 for 200 nm treated particles. Both indicate a much larger shift than was observed for the SOA coated ATD, as compared to ammonium sulfate in this study. This shift may be a strong function of the chemical species coating the dust material.

7.3. *Potential Climate Impacts*

The data presented in this work allow us to suggest potential impacts these mineral dust particles will have on cloud development and the potential impacts on climate due to changes in cloud microphysical properties. Section 7.3.1 will discuss general impacts due to mineral dust and Sections 7.3.2 and 7.3.3 will focus on impacts specific to the lower κ and higher κ dust types, respectively.

7.3.1. Mineral dust impacts

Although Figure 7.1 shows that the higher κ dust types are able to activate cloud droplets at significantly lower supersaturations than the lower κ dust types, all samples studied showed activation of cloud droplets at lower supersaturations than completely insoluble, wettable particles ($\kappa=0$). The extrapolated CCN activity suggests that less-hygroscopic submicron particles larger than ~ 300 nm can readily serve as CCN at typical cloud supersaturations. While most continental aerosol distributions (by number) consist of predominantly inorganic and organic particles with diameters less than ~ 300 nm (Seinfeld and Pandis, 1998) the size distribution of the dust particles will contain higher number concentrations of these larger particles, up to several microns in diameter. Therefore, dust particles can contribute to increased atmospheric CCN concentrations and lead to higher cloud drop number concentrations, and thus smaller diameters of the cloud drop distribution, retarding precipitation formation and possibly enhancing cloud lifetimes (Albrecht, 1989). On the other hand, if a distribution of dust particles includes giant CCN (GCCN), the GCCN can serve to broaden the cloud droplet distribution, enhance collision-coalescence processes and initiate precipitation earlier in the lifecycle of the cloud, reducing its lifetime (e.g. Hobbs et al., 1970). Maring et al. (2003) found that particles smaller than $7.3\mu\text{m}$ were not preferentially removed in plume transport across the Atlantic Ocean, indicating the likely presence of GCCN sized particles in dust plumes. They found that Stokes gravitation settling must be counteracted by an upward velocity of 0.33 cm s^{-1} to accurately model the transport of dust aerosol. They suggested that solar heating of the dust or intermittent turbulence in the Saharan air layer, similar to

as in the boundary layer, could be important contributors to the hypothesized upward force.

The role of large and giant CCN on cloud formation is a complex subject. It is typically assumed that GCCN cause initial broadening of the CCN spectrum and enhance collision-coalescence processes, leading to increased precipitation formation earlier in the lifecycle of the cloud (e.g. Hobbs et al., 1970). Feingold et al. (1999) found that the addition of GCCN could cause a previously non-precipitating stratocumulus cloud to evolve into a precipitating cloud. However, some studies have found while precipitation may form sooner in the lifetime of the cloud, the total rainfall considered after the full lifecycle of the cloud can actually be reduced, or may depend on the concentration of CCN present in the atmosphere (Saleeby and Cotton, 2005; Van den Heever et al., 2006; Van Den Heever and Cotton, 2007). The radiative properties of the cloud will also be changed if GCCN are present, particularly if the supersaturation is depleted quickly and many of the particles that would have activated without the presence of the dust GCCN remain unactivated. Van den Heever et al. (2006) assumed that all GCCN activated as cloud droplets for any water supersaturated conditions. In some of the studies which examine the impacts of GCCN, it is specified that dust particles do not act as GCCN unless sulfate has deposited on the surface of the particle from cloud processing (Yin et al., 2000; Yin et al., 2002). However, even an insoluble particle will act as a CCN if it is sufficiently large for the given supersaturation. For example, at a supersaturation of 0.3%, any ammonium sulfate particles larger than $D = 70$ nm would activate while any insoluble but wettable particles larger than $D = 670$ nm would also activate. Even modest hygroscopicity ($\kappa=0.04$) can greatly reduce the required supersaturation for activation (D

= 158 nm at 0.3% critical supersaturation). In areas affected by high dust loadings it may be necessary for climate simulations to consider the role of dust aerosol as contributors to warm cloud formation.

Several studies have examined the role of GCCN in cloud simulations and have found that dust concentrations can either increase or decrease the total precipitation, depending on the dynamics and background aerosol conditions (Levin et al., 1996; Rosenfeld et al., 2001; Saleeby and Cotton, 2005; Van den Heever et al., 2006; Van Den Heever and Cotton, 2007). For example, the works of Levin et al. (1996) and Yin et al. (2002) note that an addition of soluble material to dust particles will convert the particles into GCCN. These studies were conducted in the Mediterranean region, where the dust plumes mixed with pollution from the European continent. Yin et al. (2002) further stated that these dust particles may go through several growth and evaporation cycles within the clouds and that in each cloud cycle, more sulfate would be deposited on the dust particles until they grew to the size of GCCN, broadening the initial continental aerosol distribution and enhancing precipitation formation. On the other hand, if the African dust plume heads west over the Atlantic Ocean, it will remain with relatively clean maritime air masses, which already have a high precipitation efficiency. Therefore increasing CCN concentrations due to dust advection served to decrease droplet diameters, reducing the efficiency of collision-coalescence processes and decreasing the precipitation efficiency, as observed from satellite measurements (Rosenfeld et al., 2001). Teller and Levin (2006) concluded that while GCCN enhanced the total precipitation in polluted clouds, there was no noticeable effect in cleaner clouds. Van den Heever et al. (2006) used the Regional Atmospheric Modeling System (RAMS) to model a dust event

off the coast of Florida during the CRYSTAL-FACE campaign and found that if increased aerosol concentrations (as CCN, GCCN and/or IN) due to dust are included, precipitation processes were suppressed as compared to the “clean” case and there was a reduction in total precipitation reaching the ground. They found this to be true even if only the GCCN concentrations were increased. They argue that the GCCN are washed out relatively quickly compared to the CCN and the ratio GCCN/CCN becomes too small too quickly. Therefore, it appears that the conclusion of an individual study depends on many properties of the cloud system and the state against which the dust impact is referenced.

Although it has been known for some time that dust can contribute to cold or mixed phase cloud formation at relatively warm and dry conditions, many studies do not include this effect (Yin et al., 2002) or do so in a simplified manner. Many models use the Meyers et al. (1992) formulation to model ice nucleation (Saleeby and Cotton, 2005). This parameterization assumes a constant number of IN everywhere at all times where conditions are the same and this supply is never depleted unless the model is configured to deplete them with height or time. Van den Heever et al. (2006) modified the Meyers formulation to match the maximum concentration of IN available at their study location based on measurements, allowing this concentration to decrease with time as they are removed from the atmosphere. Lohmann and Diehl (2006) also related ice crystal concentrations to dust concentrations, subject to atmospheric removal processes at temperatures warmer than -35°C , examining contact and immersion freezing modes only. Their model allowed dust to be composed of either kaolinite or monmorillonite, and found significant differences in cloud cover, ice water path, and even a sign change of the

longwave radiative forcing depending on the mineral type assumed. However, natural mineral dust will not be composed entirely of a single mineral type, and the types of measurements presented in this study are crucial for realistic simulations of mineral dust aerosol influences on clouds. Their model also does not represent dust activation by freezing, as is suggested by Marcolli et al. (2007)

The ability of dust aerosol to serve as CCN, GCCN and IN can influence convective development as well (Van den Heever et al., 2006). Van den Heever et al. (2006) found for their enhanced dust conditions that there were stronger updrafts and thus greater amounts of liquid water in the cloud. Updrafts were increased due to the greater amounts of latent heat released when condensation (liquid and ice) forms on an increased number of aerosol particles. This was initially due to the increased CCN concentrations, but as the system matured the IN had the largest contribution to the increased updraft velocities. The other consequence of higher liquid water contents was that graupel was more rapidly grown into hail. Van den Heever and colleagues noted that in addition to increased updraft velocities, there was an increased area of convection.

7.3.2. Lower κ dust

Particles of the lower κ dust type were found to activate to cloud droplets at supersaturations below the Kelvin limit, despite negligible water uptake at $RH_w < 92\%$. This result is consistent with the conclusions of Kelley et al. (2007) who found that even small fractions of soluble coatings, such as $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, formed via heterogeneous reaction of Ca^{2+} or Mg^{2+} with NO_2 or SO_2 , could significantly lower the critical supersaturation of insoluble quartz cores. In their parcel model, even a 2% by mass coating on a relatively low number concentration of

dust particles, compared to the background ammonium sulfate aerosol, was sufficient to lower the maximum supersaturation reached in the cloud and reduce the cloud droplet number concentration, particularly at low updraft velocities (Kelly et al., 2007). It is likely that all atmospheric mineral dust particles, having been exposed to these gases, have some small fraction of these or other soluble species associated with the particle surface. The ability of the lower κ dust particles to serve as CCN at atmospherically relevant supersaturations for particles larger than ~ 200 nm, and the larger mean particle size of mineral dust aerosol as compared to the background aerosol, indicate that these particles can alter cloud droplet concentrations and impact the cloud radiative properties and potentially the generation of precipitation and lifetime of the cloud (Pruppacher and Klett, 1997). Therefore, while many modeling studies neglect the activation of mineral dust to CCN unless it has undergone appreciable coagulation with sulfate (e.g. Yin et al., 2002), this assumption may constitute severe underestimation of CCN concentrations in airmasses with high dust loadings. Also, the ability of submicron dust to participate in droplet formation and eventually be subject to wet deposition reduces the lifetime of this species in the atmosphere (Fan et al., 2004).

At temperatures colder than -35°C , lower κ dust particles were found to initiate ice at much lower RH_i than SOA coated ATD particles. Heymsfield and Miloshevich (1995) parameterized threshold RH_i requirements as a function of temperature for cirrus formation. Lower κ dust particles were observed to nucleate ice at lower RH_i than their expected requirements for most conditions with particle diameters 200 nm and larger; this is not surprising since those conditions were expected to be for homogeneous nucleation in the absence of many IN, but did not exclude possible heterogeneous mechanisms.

Therefore, it can be expected that these particles would alter cold cloud formation compared to conditions that would exist with only background aerosol. While it may be hypothesized that most dust particles do not reach the upper troposphere in their pure state (Kärcher and Lohmann, 2003), their efficiency in nucleating ice at low RH_i makes even a small number concentration of pristine dust IN relevant to cloud formation. DeMott et al. (2003a) and Cziczo et al. (2004) found that dust particles examined off the coast of Florida during the CRYSTAL-FACE experiment were generally externally mixed with sea salt and other soluble particle types. Also, DeMott et al. (2003b) found that only about 25% of the examined dust particles (evaporated ice crystals) sampled from free tropospheric air on Mt. Werner, Colorado (elevation 3200 m) contained measurable sulfate and organic material, thus the relevance of the pristine dust to the atmosphere must be considered.

Kärcher and Lohmann (2003) found for a constant freezing threshold of 130% RH_i that ice particle concentrations were strongly dependent on updraft velocity. When updraft velocities were greater than 30 cm s^{-1} , ice particle concentrations were about a factor of 2 higher than was found for homogeneous freezing only. At lower updraft velocities, large (up to a factor of 10) decreases in ice crystal concentration were observed. Our work suggests that dust could potentially initiate ice formation at an even lower freezing threshold than $RH_i \sim 130\%$ (as found for ATD particles and is predicted for larger ($D > 0.5 \text{ }\mu\text{m}$) CID and SD particles). As nucleated particles start to grow and deplete the water vapor in the atmosphere, the maximum saturation achieved in the cloud will be lowered and even lower ice crystal concentrations would result. If the saturation maximum is below the homogeneous freezing onset conditions of the background aerosol

(e.g. sulfates), then small numbers of large ice crystals can develop (DeMott et al., 1994a). This leads to very different radiative properties than would be found for the homogenous freezing case; however, the impact on cloud lifetime is still uncertain (DeMott et al., 1997a).

It must be noted that the ATD, the most IN active dust type studied, is a milled product and not necessarily representative of the particles that reach the atmosphere from natural desert regions. The milling potentially creates more or less effective active sites than natural dust and may have a different nucleation response than natural dust at varying temperature. Möhler et al. (2006) found that ATD nucleated ice similarly to natural Saharan and Asian dust samples at $\sim -60^{\circ}\text{C}$, but was more efficient than the Saharan and Asian dusts at $\sim -50^{\circ}\text{C}$. Sassen et al. (2003) found that Saharan dust was able to glaciate clouds as warm as -5°C , much warmer than ATD was seen to initiate ice formation in this study. Furthermore, Sassen (2002) found that cirrus in Asian dust layers were warmer than typical midlatitude cirrus clouds over a ten year period. DeMott et al. (2003b) found very high IN concentrations during the CRYSTAL-FACE measurement campaign operating at -36°C and $86.5\% RH_w$ in Saharan dust layers. This implies that sufficient concentrations of larger particles ($D > 0.4 \mu\text{m}$) exist in these clouds, and that the size dependence of T_{thresh} persists to large sizes.

7.3.3. Higher κ dust

The unique composition of the higher κ dust samples, Owens (dry) Lake and wet-generated Canary Island dust, allows these particles to be potentially important in both warm and cold cloud formation. This discussion will focus on observations for OLD, which is expected to be representative of dust from playa regions worldwide. The

relatively high soluble content of OLD dust and its significant water uptake can lead to an increased visibility impact near the ground when the RH_w is greater than $\sim 70\%$. In water supersaturated environments a subset of these particles have CCN activities similar to commonly-detected soluble and hygroscopic species in the atmospheric aerosol (e.g., sodium chloride). The less-hygroscopic subset of these particles is not as effective at forming cloud droplets as some inorganic particles, but their potential influence as large or giant CCN must be considered (see Section 7.3.1). Although we could not measure the CCN activity of particles larger than ~ 150 nm directly, if the HTDMA experiments have adequately captured the hygroscopicity of the less-hygroscopic fraction, we can use the results to predict CCN activity for larger-sized particles than were experimentally accessible, as discussed in Section 2.3.1. Niemeyer et al. (1999) measured size distributions of Owens (dry) Lake dust with a high-volume inertial impactor during 13 dust storm events in the region and found an average volumetric geometric mean diameter of $3.5\ \mu\text{m}$ and an average geometric standard deviation of 2.2. Although changes in this size distribution with height are uncertain, it is likely that in this region clouds with even modest supersaturation will activate some number of the large dust particles along with smaller soluble particles.

This study did not find substantial activity of the tested Owens Lake dust particles as heterogeneous ice nuclei in the convective cloud regime warmer than -36°C , the regime in which homogeneous ice nucleation does not occur. However, in this study we can only observe deposition and condensation freezing. While immersion freezing is generally found to initiate ice formation at similar temperatures to condensation freezing (Lohmann and Diehl, 2006), it is possible that contact nucleation could be efficient under

warmer temperature conditions. Further, it is unclear if larger sized particles would be efficient at initiating the ice phase at warm enough temperatures to influence the precipitation formation in mixed phase clouds as well as the GCCN effect. Figure 4.5b does not indicate a clear trend with size at temperatures warmer than $\sim -40^{\circ}\text{C}$.

The higher κ dust particles initiated the ice phase at similar conditions as are found for pure soluble particles (Koop et al., 2000). Therefore, these particles should not dramatically impact the generation of cold clouds. This can change the radiative properties and potentially the lifetime of these clouds (DeMott et al., 1997b). Our measurements show that a dust particle which acquires a hygroscopic coating requires larger relative humidities at the same temperature to nucleate ice with the same efficiency. Therefore, the impact of the dust on cold cloud formation may depend on the way freshly emitted dust ages in the atmosphere. Processes in which a dust plume mixes with hygroscopic material, such as from an anthropogenically polluted air mass or air masses over a large forest which contain hygroscopic secondary organic aerosol, may condense onto dust thereby reducing its ice nucleation activity.

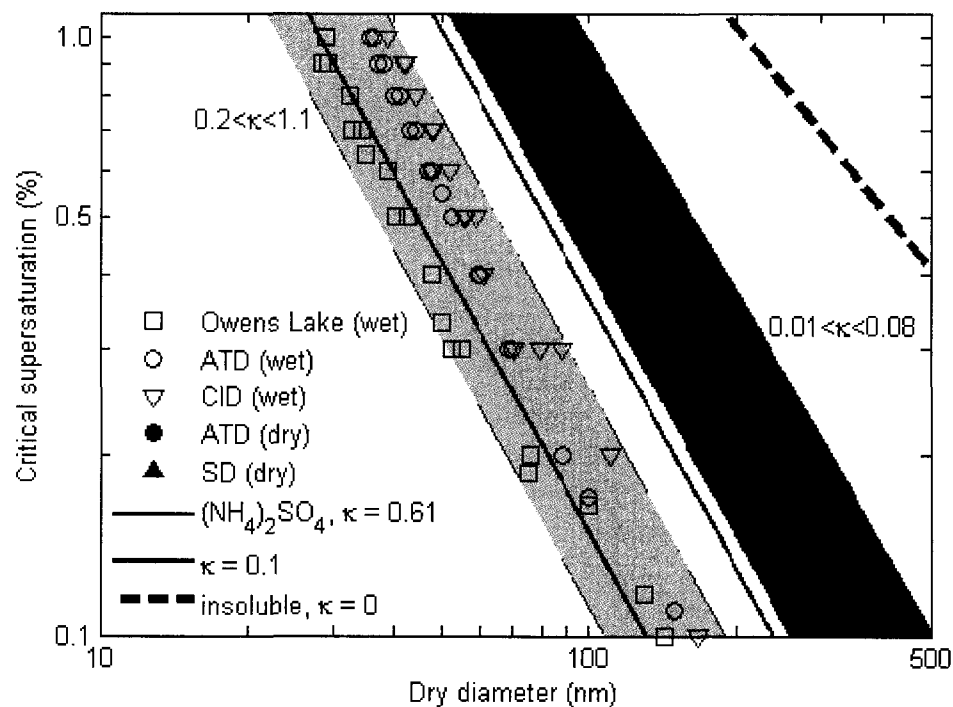


Figure 7.1: CCN activity of all measured dust samples, as labeled in the legend. The light blue shading indicates for $0.2 < \kappa < 1.1$ and the gray shading indicates $0.01 < \kappa < 0.08$. The blue line at $\kappa = 0.01$ denotes the partition from the more hygroscopic and less hygroscopic dust.

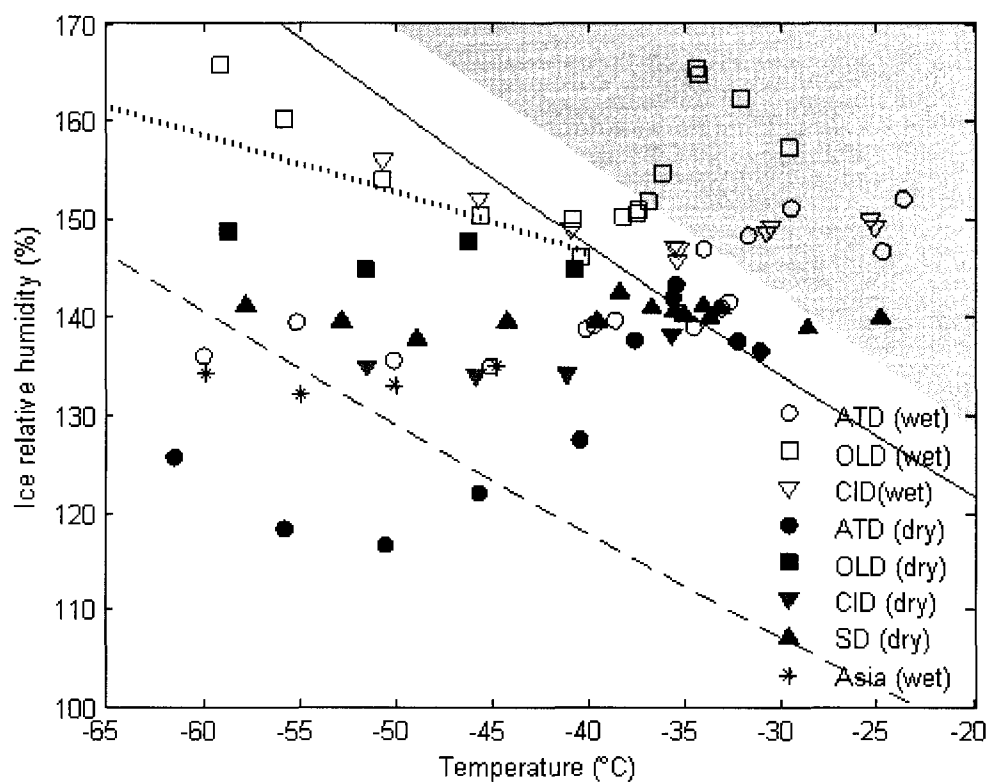


Figure 7.2: IN activity of 200 nm particles at the 1% freezing threshold for all samples. The solid blue line is water saturation and the dashed blue line is $RH_w = 80\%$. The dotted black line is homogeneous freezing of 250 nm ammonium sulfate particles. The shaded region indicates $RH_w > 105\%$.

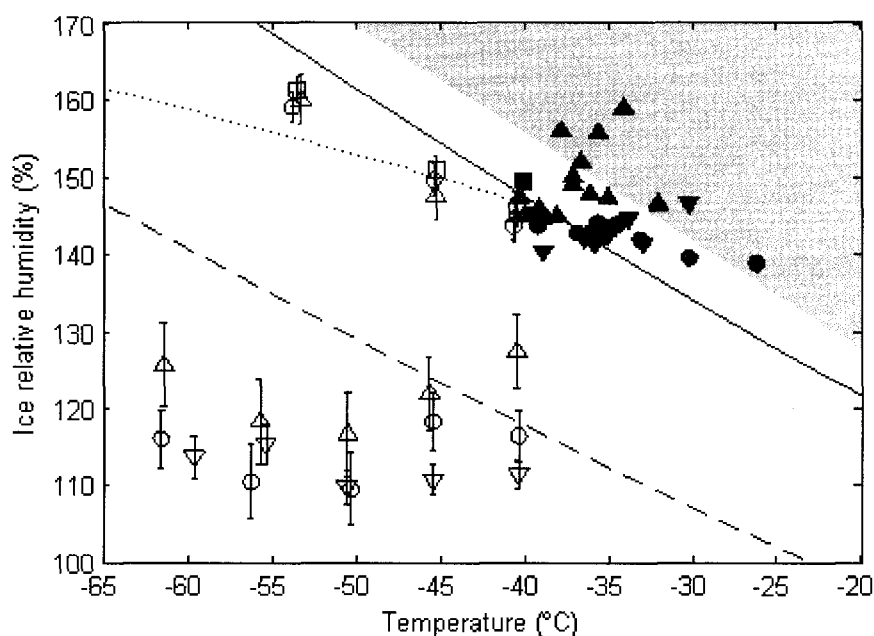


Figure 7.3: Ice nucleation results of coated ATD particles. Squares represent 160 nm data, triangles for 250 nm data and circles for 340 nm data. Points represent 1% of the particles activating as ice crystals. Open symbols refer to data collected with the laboratory unit, filled symbols refer to data collected in the aircraft unit. Black symbols are uncoated, dry-generated ATD with symbols as described in Figure 5.4. The solid blue line is water saturation and the dashed blue line is $RH_w = 80\%$. The dotted black line is homogeneous freezing of 250 nm ammonium sulfate particles. The shaded region indicates $RH_w > 105\%$, the region in which ice crystals cannot be unambiguously distinguished from activated cloud droplets.

8. Development and applicability of parameterization

8.1. Development of parameterization

This chapter seeks to develop a parameterization to fit the freezing data at temperatures colder than $\sim -30^\circ\text{C}$ for the dry-generated dust types. Some of the data for wet-generated particles and for coated dust particles (higher κ dust types) appear to be well represented by predictions for homogenous freezing and thus are not parameterized separately here. At temperatures colder than $\sim -30^\circ\text{C}$ (depending on the sample), the dry-generated particles are expected to freeze by the deposition mode and the parameterization will be based on the classical theory for deposition nucleation following Pruppacher and Klett (1997), with some modifications. The nucleation rate of an ice crystal from the vapor phase, J_{het} , is given by (Pruppacher and Klett, 1997):

$$J_{het} = \left(\frac{\pi a_g^2 Z_s e}{(2\pi \dot{m}_w kT)^{1/2}} \right) c_{l,s} \exp(-\Delta F_g(T, S_i, \alpha) / kT), \quad (8.1)$$

where a_g is the radius of the ice germ, $\dot{m}_w$ is the mass of a water molecule, Z_s is the Zeldovich factor, e is the vapor pressure of water, k is Boltzmann's constant, T is the temperature, and $c_{l,s}$ the number of vapor molecules adsorbed on the surface of the ice germ. Approximate values for $Z_s=0.01$ and $c_{l,s}=10^{28}$ are found in Pruppacher and Klett (1997). The germ radius is a function of T and ice saturation ratio S_i and is given by:

$$\alpha_g = \frac{2M_w \sigma_{i,v}}{RT\rho_i \ln(S_i)} \quad (8.2)$$

where M_w is the molar mass of water, $\sigma_{i,v}$ is the surface tension of the ice/vapor interface (105 erg cm⁻²), R is the universal gas constant and ρ_i is the density of ice (0.917 g cm⁻³). ΔF_g describes the work of ice germ formation and is given by Equation (3.11) including the compatibility function, f_{het} , describing how the surface lowers the energy barrier given by Equation (3.12).

Nucleation rates given by Equation (8.1) are very strong functions of $S_{i,v}$; however for mineral dust, it was observed that nucleation occurs over a broad range of RH_w conditions, even for a size-selected aerosol flow. Figure 8.1 shows activation curves for Canary Island dust (CID, red squares) and ammonium sulfate (black squares), both for 200 nm particles at -40°C measured in the CFDC. Each point is an average over ten seconds of data. The black line is the homogeneous freezing representation for ammonium sulfate given by Koop et al. (2000); details on this parameterization may be found in Section 3.1.2.1. The red line is the representation of deposition nucleation given by Equation (8.1) with a contact angle, $\alpha = 28^\circ$, assumed. It is clear that the experimentally-observed activation by homogeneous freezing is a very strong function of RH_w , with complete activation occurring over 2-4% RH_w in the CFDC and is well represented by the water activity based parameterization. However, the classical theory for deposition nucleation predicts activation curves which are also very steep, whereas activation of the CID was observed to occur over >10% RH_w . Changes in the assumed value of α simply shift the curve described by Equation (8.1) in the RH_w space, but do not change the slope of the curve. Similar behavior was observed by DeMott et al. (2003a) who measured IN concentrations on top of a mountain in Colorado (Storm Peak

Laboratory) and found that at temperatures warmer than -35°C (heterogeneous ice nucleation regime), the nucleated concentration increased much more slowly with increasing saturation ratio than for temperatures below -38°C , where homogeneous nucleation was likely the dominant mechanism of ice formation. Given these observations, it was necessary to modify the classical theory to accurately predict the shallow activation curves observed for mineral dust.

Marcolli et al. (2007) observed immersion freezing of polydisperse Arizona Test dust (ATD) particles using differential scanning calorimetry (DSC). In these experiments, latent heat release is measured from freezing droplets. It was observed that there was a continuous freezing signal over ~ 20 K as the droplets were cooled. Those authors similarly found that using the classical theory of immersion freezing that assuming all particles had a uniform α was not sufficient to describe the freezing behavior observed.

Marcolli et al. (2007) investigated two other representations of the particle surfaces. First, they assumed that the particles had a distribution of α values. Each particle was assumed to have a constant α over its entire surface, but a lognormal distribution of α across the particle population. They suggested a mean α of 76° with a geometric standard deviation of 1.083 to represent a wide range of IN qualities that broaden the freezing curve. Second, Marcolli et al. (2007) suggested that particles might be better represented if the surfaces of the particles were assumed to have active sites, represented by small regions of low α (large nucleation rate). They determined a probability function which gave each size of particle a fractional area corresponding to each α , and activation was assumed to occur only on these sites. It was found that the

data were best represented if the probability of an active site was low and decreased strongly with decreasing α . This representation means that larger particles are better IN because they have more and better active sites.

The complex representation of particles by Marcolli et al. (2007) may be more realistic than assuming the entire particle surface initiates the ice nucleation, as some works have suggested that active sites are crucial for an accurate representation of heterogeneous freezing (Pruppacher and Klett, 1997). However, applying this concept to deposition nucleation proved to be a large challenge. For immersion freezing, Marcolli et al. (2007) represented f_{het} as only a function of α . In deposition nucleation, the nucleation rate is far more sensitive to the assumed α . Further, f_{het} strictly is a function of IN size and T and $S_{i,v}$ through the ice germ radius. If it is assumed that only the active site area contributes to the ice formation, this area, not the size of the IN, should be used in the computation of f_{het} and f_{het} is a strong function of the assumed area of the active site. Figure 8.2 shows values of f_{het} , calculated according to Equation (3.12) for varying $m_{i,v}=\cos(\alpha)$ and diameter of the active site (assuming a circular active site) at -50°C and $S_{i,v}=1.1$. It is clear that for small active sites, f_{het} rapidly approaches unity, for any assumed contact angle. Thus, when this method was applied to our data, it did not produce variation in activation behavior between particles and steep activation curves were still maintained. This suggests that deposition nucleation is limited to larger active sites ($>0.01\text{ }\mu\text{m}$).

In the following we examine the behavior of Equation (8.1) to determine how best to represent the mineral dust particles activation behavior. It was found that for deposition nucleation, onset occurs over a very small range of α values, where lower

values of α nucleate all particles as ice and at larger α values, particles do not nucleate ice at all. This onset α value is a function of both temperature and particle size. Figure 8.3 shows the fraction of particles activated as a function of size and contact angle at water saturation for three temperatures: -60°C, -50°C and -40°C. Figure 8.4 shows the critical α value, α_{crit} , for which 50% of the particles of a given size and at a given temperature (at water saturation) nucleate ice. From this plot it is clear that while α_{crit} is a function of size and temperature, it is a rather weak function of both, with $\alpha_{crit} = 32.5 \pm 3.5$ over the range of interest. The contact angle is expected to be a fundamental property of the material, and thus should be constant; however, it was found that to accurately capture the nucleation curves it was necessary that α_{mean} be a function of both size and temperature. Pruppacher and Klett (Pruppacher and Klett, 1997) compiled values of α for various materials and showed that surface soil has $65.2 < \alpha < 68.9$. From Figure 8.3 it is clear that particles of this α would never nucleate via the deposition mode. Therefore, we suggest that due to inhomogeneities on the particle surface, nucleation is controlled by a contact angle that may vary with the particular surface features active at a given temperature, which is not captured by standard classical theory. Since we have no direct way to estimate the fraction of the particle surface that is active at a given temperature, the entire surface area of the particle is used in all calculations. Based on this knowledge, the data in this work were best fit by representing particles as having a normally distributed range of α , but with the entire surface of a single particle being represented by a single α . The mean contact angle, α_{mean} , was allowed to be a function of the particle diameter and temperature, such that more particles fall into the small α (high nucleation) side of this threshold α_{crit} when particle size is large and temperature is cold. In this way,

the condition that larger particles are more likely to have lower α values is maintained. The width of the distribution, α_{std} , was assumed to be fixed for each sample.

For each nominal size studied (200, 300 and 400 nm) a normal distribution of α was applied and an activated fraction, $\hat{N}_{IN}$, calculated by:

$$\hat{N}_{IN} = 1 - \exp[-J_{het}(T, S_{i,v}, D, \alpha(T, D)) * A_d(D) * t], \quad (8.3)$$

where J_{het} is given by Equation (8.1), A_d is the area of the dust particle and t is the time. Best fit values for α_{mean} and α_{std} were found by minimizing the sum squared error, SS_E , between the parameterization and CFDC data collected for multiple sizes and temperatures, where:

$$SS_E = \sum_{i=1}^N (N_{IN,i} - \hat{N}_{IN}) / n_i, \quad (8.4)$$

where N_{IN} is a measured ice crystal concentration at a given temperature and RH_w conditions for a given size and $\hat{N}_{IN}$ is the predicted ice crystal concentration for the same conditions and particle size, and n_i is the total number of points in the given data series (scan of increasing RH_w at a given temperature). Errors are summed for all i data series. $\hat{N}_{IN}$ has been calculated with a time of 1 s, but the time dependence will be explored later in this chapter. Several studies have found that nucleation is not strongly dependent on time or cooling rate (DeMott, 1990; Möhler et al., 2006), so this is not expected to strongly influence the development of the parameterization. The total number activated for a temperature and saturation condition is the sum of $\hat{N}_{IN}$ over all α and sizes. The parameterization is only anticipated to be valid at temperatures colder than $\sim -30^\circ\text{C}$ (depending on sample type), where it is expected that deposition nucleation occurred on the mineral dust particles studied. It is intended that this parameterization would merge

with an immersion freezing parameterization for temperatures in which water saturation is required for freezing and thus extrapolation of this parameterization to warmer or colder temperatures than the data used to constrain the parameterization is not recommended.

8.2. *Application to lower κ mineral dust*

The method described above was first applied to the data for dry-generated ATD. To represent the observed behavior, it was necessary that α_{mean} increase with decreasing size and increasing temperature. So the functional form:

$$\alpha_{mean} = a + b \frac{1}{D} + cT^2, \quad (8.5)$$

was used, where D is the particle diameter in cm, T is the temperature in Kelvin and a , b , and c are constants. Values for a , b , c and α_{std} that minimize SS_E were found and are listed in Table 8.1 for all mineral dust types created by dry generation. For ATD, SS_E was minimized when $\alpha_{std}=6$, $a=-15.8$, $b=1.1 \times 10^{-4}$ and $c=9.6 \times 10^{-4}$ based on the subset of data shown in Figure 8.5. Figure 8.5 shows the parameterization (lines) along with several measured activation curves for multiple sizes and temperatures. Sizes are denoted by color with 400 nm particles in black, 300 nm particles in green and 200 nm particles in red. Different symbols simply indicate different runs of the experiment and the panels are for temperatures of -60°C, -50°C, and -40°C. Data shown are averages over ten or sixty second intervals in the CFDC. Reasonable agreement could be found at temperatures colder than -40°C if α_{mean} was not a function of temperature, but this assumption predicted far too many particles nucleating ice crystals at warmer temperatures. The squared dependence on temperature yields lower activated fractions nucleated than predicted without the temperature dependence, which are more consistent

with observations at $T > -40^{\circ}\text{C}$. For example, the parameterization predicts that 2.4% of 400 nm particles nucleate ice at -35°C and water saturation, in good agreement with the measurements which found $\sim 5\%$ of 400 nm particles frozen at these conditions.

Figure 8.6 shows the parameterization and activation curves for dry-generated CID. Sufficient cooling was not possible for points at -60°C , so only activation curves at -50°C and -40°C are shown. Data are shown with the same color representations as in Figure 8.5. More scatter exists in these data, but the fit does a reasonable job of capturing the behavior of CID. It predicts that 11.2% of 400 nm particles nucleate ice crystals at -35°C and water saturation, compared to $\sim 5\%$ in the observations.

The parameterization of dry-generated Saharan dust, SD, is shown in Figure 8.7 for data obtained at -55°C , -50°C and -40°C and size representations as in Figure 8.5. Data at -55°C were used to help constrain the parameterization for this sample because cooling was not sufficient to yield activation curves at -60°C . The parameterization fits the data well at -50°C and -55°C , but appears to over-predict concentrations of ice crystals at low saturation ratios ($RH_w < 90\%$) at -40°C . The parameterization predicts that 2.3% of 400 nm particles nucleate ice crystals at -35°C and water saturation, similar to observations ($\sim 5\%$).

The parameterization of the freezing behavior of dry-generated Owens (dry) Lake dust, OLD, is shown in Figure 8.8 with the same temperature and size representations as in Figure 8.5. The parameterization fits the data fairly well at -60 and -50°C , however at -40°C , the signal looks much more like homogeneous nucleation, with very sharp activation curves at near water saturated conditions, indicating a likely change of nucleation mechanism. This may indicate that deposition nucleation is not active for this

dust sample at -40°C , as concentrations are overpredicted by the parameterization at $RH_w < 90\%$. The parameterization predicts 0.5% of 400 nm particles freezing at -35°C and water saturation, consistent with the data where less than 1% of particles initiated the ice phase at -35°C (see Figure 4.5), but it is not recommended that this parameterization be used for temperatures of -40°C and warmer, as the mode of ice nucleation is not expected to be deposition nucleation in this regime.

By comparing Figures 8.6 and 8.7 with Figures 6.3 and 6.6 it is clear that while the onset conditions were very similar for dry-generated CID and SD, the full activation had slightly different behavior. The CID had small activated fractions from much lower RH_w than were observed for SD. ATD had small activated fractions from even lower values of RH_w than CID. OLD behaves qualitatively similar to the other samples at -60°C and -50°C , yet has a very different activation signal at -40°C . The representation proposed in this chapter is able to reproduce the shallow activation curves of mineral dust, but caution should be used in applying this representation at warmer temperatures where water saturation is required for ice nucleation and where deposition nucleation may not be active. The temperature dependence of α_{mean} has been added to improve agreement with the data at temperatures warmer than -40°C , and produces agreement with the observations within a factor of ~ 2 for the ATD, CID, and SD samples; however for temperature conditions for which water saturation is required for freezing onset, it is recommended that an immersion freezing parameterization be used, such as the parameterization by Marcolli et al. (2007). No quantified comparison between the results found in this study and those by Marcolli et al. (2007) can be made and further, that

parameterization is not likely applicable to other mineral dust types. Therefore, additional studies on the ice nucleation at warmer temperatures are merited.

8.3. *Atmospheric Implications*

To estimate the atmospheric concentration of mineral dust IN active via deposition nucleation, it was assumed that atmospheric dust concentrations could be represented by a lognormal distribution with a median diameter of 0.8 μm , a standard deviation of 2 (Phillips et al., submitted), and a total dust concentration of 1 L^{-1} such that the activated concentration is also the fraction activated and can be scaled by any assumed dust concentration. The parameterization developed for ATD was applied to this distribution of particles and activated fractions were summed over all sizes and α . Figure 8.9 shows the concentration of ice crystals (IN) predicted per liter. The black line indicates water saturation and it should be noted that saturation ratios much higher than water saturation generally do not exist in the atmosphere at these temperatures ($T < -38^\circ\text{C}$) because homogeneous freezing of aqueous sulfate solution droplets will deplete the water vapor in the atmosphere. The parameterization predicts low activated fractions for all T at $S_{i,v}$ below ~ 1.2 . It also predicts that not all particles are activated approaching water saturation, as opposed to many other models which activate all dust particles at water saturation even at very modest supercoolings (e.g. Khvorostyanov and Curry, 2004; Liu and Penner, 2005; Lohmann and Diehl, 2006). This parameterization should be merged with an immersion freezing parameterization at water saturation, but care should be taken that the combined parameterizations yield activated fractions similar to those found in this work at similar sizes. Artificially nucleating too many dust particles as ice

crystals in a model depletes the ambient water vapor and may unrealistically lower the maximum ice supersaturation predicted for the cloud.

Figure 8.10 shows the difference in activated fraction predicted between ATD and CID particles, computed for the same lognormal distribution of dust particles. At low saturation ratios, the CID parameterization predicts similar concentrations as found for ATD, but at higher saturation ratios the CID parameterization predicts higher concentrations than were predicted by the ATD parameterization. This, however, may be a consequence of the lack of data for ATD at high RH_w values. For $-60 < T < -40^\circ\text{C}$ and $1 < S_{i,v} < 1.7$, the two parameterizations are within 20% of each other. Figure 8.11 shows the difference in activated fraction predicted between ATD and SD. The parameterization for ATD predicts up to 81% of the particles nucleating ice for a lognormal distribution at $T = -60^\circ\text{C}$ and water saturation, 12% larger than is predicted for SD (69%), but at warmer temperatures and water subsaturated conditions the ATD and SD parameterizations predict similar fractions of particles activated. These three representations of deposition nucleation predict activated fractions within a factor of ~ 2 of each other for $-60 < T < -40^\circ\text{C}$ and for saturations from ice to water saturation. Implementation of these parameterizations into a parcel model would be required to estimate the effect of these small differences on cloud microphysics and is beyond the scope of this work.

For a lognormal distribution of OLD, much lower activated fractions are predicted than for the other three lower κ dust types (note the difference in scale between Figures 8.12 and 8.9). Figure 8.12 shows the activated fractions as a function of T and $S_{i,v}$ for OLD with the same assumed size distribution as for the other dusts. The model-predicted

maximum activated fraction at -60°C and water saturation is 64%, similar to that found for SD, but the activated fraction is only 5% at -40°C and water saturation, less than half the number of SD or ATD particles activated at these conditions. This is likely due to the fact that a large fraction of the OLD particles contain hygroscopic material, and therefore while some of the particles may act in the deposition mode, others may develop water coatings, and freeze by another mechanism. The heterogeneous nature of this sample makes it very difficult to model.

Figure 8.13 shows the time dependence of the fraction of particles activating as crystals for a distribution of ATD particles according to the parameterization at -60°C , -50°C , and -40°C . The time dependence is rather small between 1 second and 10,000 s (~ 2 hrs 45 min), increasing activated concentrations about 5% over this time period. In cirrus with low updrafts, ice nucleation could take place over several hours, but this parameterization will not produce a strong change in crystal concentrations over this time period. Figure 8.14 shows the fraction of ATD particles activating at water saturation as a function of size and temperature. While at the coldest temperatures, nearly all of the largest particles ($\sim 10\text{ }\mu\text{m}$) nucleate ice, this fraction drops rapidly with increasing temperature and also decreases with decreasing size. At -60°C , for particles larger than $\sim 0.2\text{ }\mu\text{m}$, at least 50% of the particles will nucleate ice in one second. At -50°C , particles must be larger than $\sim 0.8\text{ }\mu\text{m}$ for at least 50% of the particles to nucleate ice. By -40°C , 50% of the particles do not nucleate for any size of atmospheric interest.

Figure 8.15 compares the parameterization developed in this chapter with IN concentrations from various field campaigns and parameterizations from the literature, where all IN concentrations are reported at STP. The blue line shows the

parameterization of ATD at water saturation for the temperature range over which the parameterization is expected to be valid. The parameterization is scaled by the noted assumed dust concentrations. The dashed line is the parameterization by Meyers et al. (1992, Equation 3.15) where the temperature dependence is determined by assuming S_i is at water saturated conditions. The dotted line is the parameterization from Fletcher et al. (1962). In this figure the IN concentration from field campaigns is shown only as a function of temperature and can represent saturation ratios from ice saturation to water saturation. Many of the field campaigns only have data for temperatures warmer than $\sim -30^\circ\text{C}$, and these are shown in red symbols. These include First ISCCP Regional Experiment- Arctic Cloud Experiment (FIRE-ACE, Lawson et al., 2001) and the Mixed-Phase Arctic Stratus Experiment (MPACE, Prenni et al., 2007a), both taking place in the arctic during spring and fall, respectively, and the Winter Icing Storms Project (WISP, Rasmussen et al., 1992). Measurements shown from those works indicate that deposition nucleation is not likely to be active in this temperature regime.

The INSPECT I and II field campaigns collected IN data on Mt. Werner in western Colorado and these studies contain the most measurements in the temperature range where deposition nucleation is expected to be relevant. Both sets of measurements were made on the ground at Storm Peak Laboratory (3200 m ASL) and conditions are expected to be representative of background dust IN concentrations in the atmosphere. Dust concentrations of $0.09\text{--}0.41\ \mu\text{g m}^{-3}$ were measured on the ground; this corresponds to a loading of $18\text{--}81\ \text{L}^{-1}$, assuming the lognormal distribution of dust applied above and a particle density of $2.3\ \text{g cm}^{-3}$. IN concentrations were measured between $1\text{--}11\ \text{L}^{-1}$, in

good agreement with the ATD parameterization developed here for the limiting dust concentrations measured during INSPECT.

IN concentrations were measured during aircraft flights during the Cirrus Regional Study of Tropical Anvils and Cirrus Layers – Florida Area Cirrus Experiment CRYSTAL-FACE campaign (DeMott et al., 2003b) in Saharan dust layers and during the Pacific Dust Experiment (PACDEX) in Asian dust layers (P.J. DeMott, personal communication). Very high IN concentrations were observed during CRYSTAL-FACE even for water subsaturated conditions; up to 1000 L^{-1} , 20-100 times higher than are normally measured. Dust loadings on the ground were measured as high as $30 \mu\text{g m}^{-3}$. Assuming the lognormal distribution of dust applied above and a particle density of 2.3 g cm^{-3} , this corresponds to a loading of $\sim 5.9 \times 10^3 \text{ L}^{-1}$. Concentrations of large ($D > 0.5 \mu\text{m}$) particles were found to be fairly constant with height from near ground through the dust layer on these days. IN concentrations were nearly as high during the PACDEX campaign at water saturated conditions. Reasonable agreement is found with the measurements from these campaigns using the dust loading calculated above.

Figure 8.16 shows the same data and parameterizations as in Figure 8.15 except as a function of ice supersaturation (the Fletcher et al. (1962) parameterization, which is solely a function of temperature is omitted). Campaigns conducted at temperatures warmer than -30°C are shown in red symbols and likely do not represent deposition nucleation processes. The solid blue line is the parameterization for ATD for -40°C and a dust concentration of 18 L^{-1} and the solid green line for -60°C and a dust concentration of 81 L^{-1} . The parameterization developed here gives good agreement for many of the measurements, particularly for the INSPECT projects using these limiting cases.

Measurements from the PACDEX campaign are in reasonable agreement with the parameterization calculated at -40°C and for a dust loading of $5.9 \times 10^3 \text{ L}^{-1}$ (dashed green line), but the parameterization underestimates IN concentrations from the CRYSTAL-FACE campaign.

Figure 8.15 and 8.16 show that the formulation Meyers et al. (1992), which is used in many model simulations, and that by Fletcher et al. (1962) tend to overpredict IN concentrations, particularly for large supercoolings and ice supersaturations, except in cases of very high dust loadings. However, it should be noted that any IN concentrations due to immersion or condensation freezing are not captured by the new parameterization.

Dust sample	a	b	c	α_{std}
ATD	-15.8	1.1×10^{-4}	9.6×10^{-4}	6.0
CID	-15.7	1.25×10^{-4}	9.0×10^{-4}	7.4
SD	-15.0	1.7×10^{-4}	9.6×10^{-4}	7.1
OLD	-15.45	1.7×10^{-4}	1×10^{-3}	6.2

Table 8.1: Values of parameterization constants for the four dust samples by dry generation.

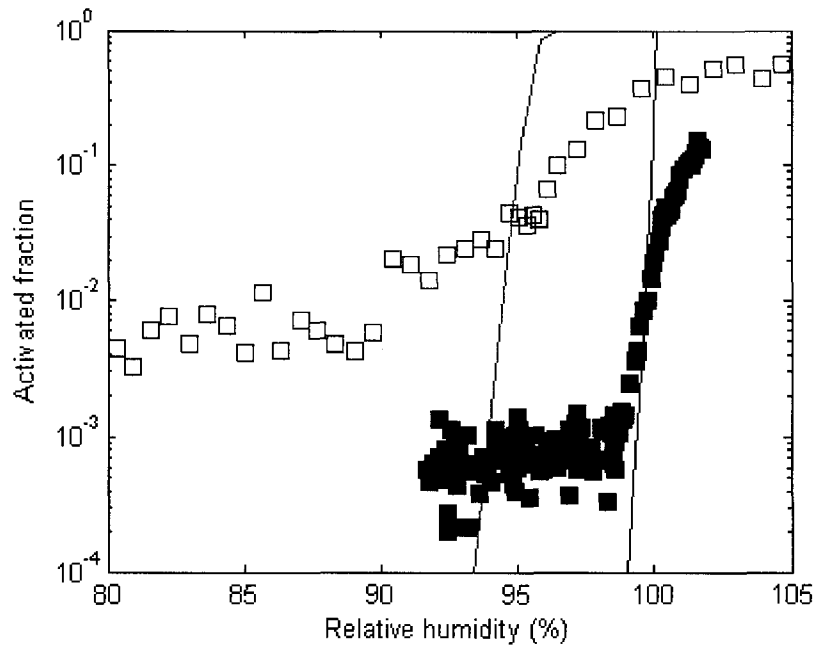


Figure 8.1: Activation curves of 200 nm dry-generated CID (red squares) and 200 nm ammonium sulfate (black squares) at -40°C . The black line is the activation of ammonium sulfate predicted by the Koop et al. (2000) parameterization and the red line is the activation predicted by Equation (8.1) with $\alpha = 28^{\circ}$.

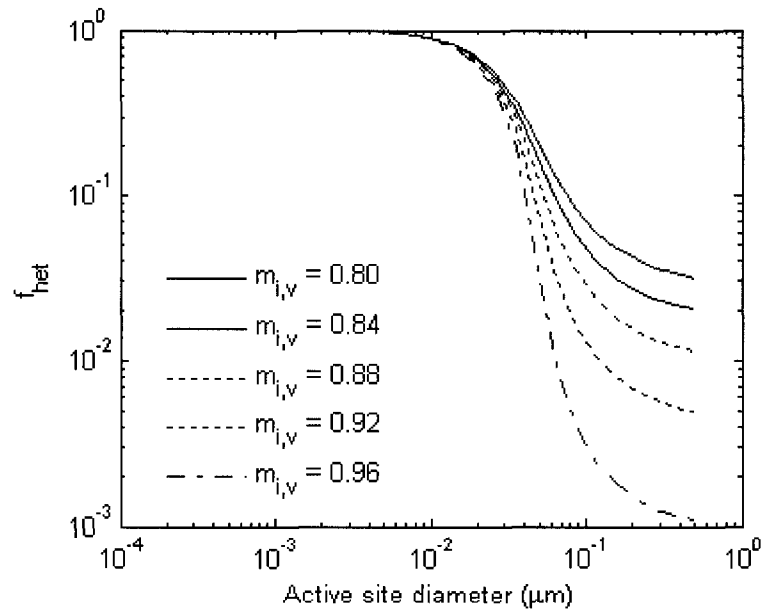


Figure 8.2: Compatibility function, f_{het} , for varying $m_{i,v} = \cos(\alpha)$ and active site diameter.

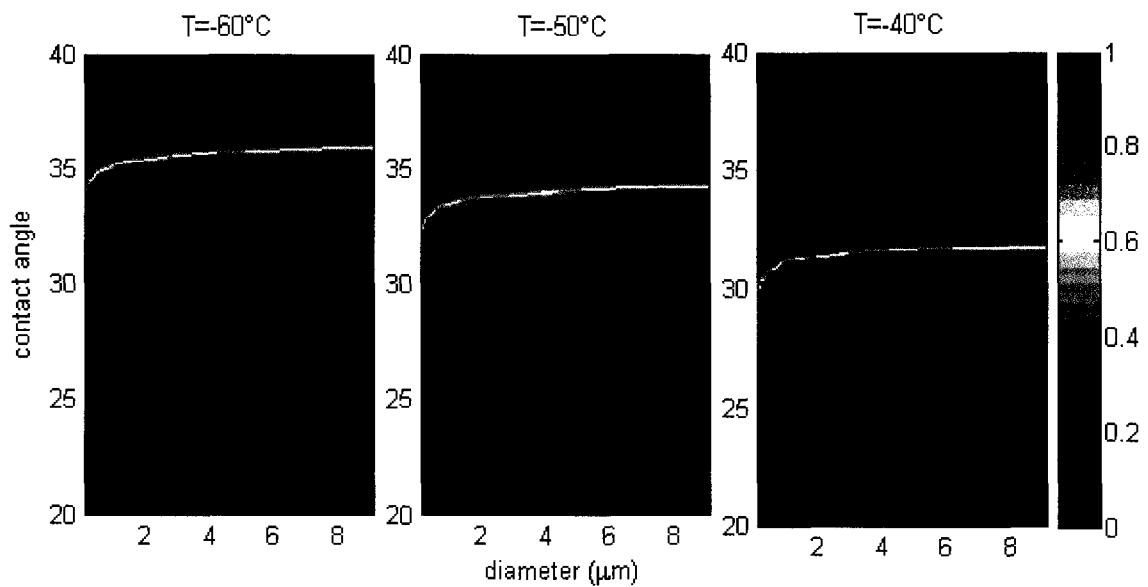


Figure 8.3: Fraction of particles nucleating ice as a function of particle diameter and contact angle for three temperatures: -60°C , -50°C , -40°C at water saturation. Each particle is assumed to have a constant contact angle over its entire surface.

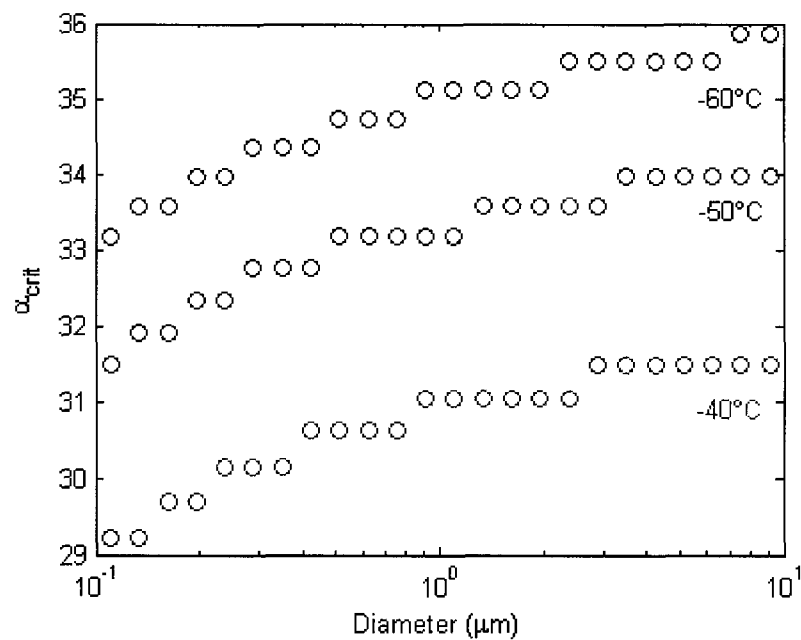


Figure 8.4: Critical α values for three temperatures: -60°C , -50°C , -40°C (at water saturation) as a function of particle diameter.

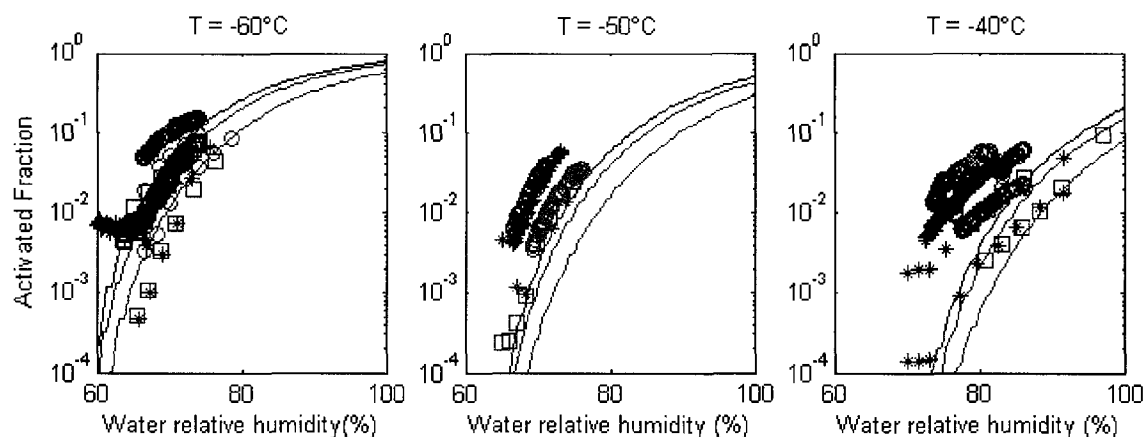


Figure 8.5: Parameterization (lines) for dry-generated ATD for three sizes: 400 nm (black), 300 nm (green) and 200 nm (red). Symbols show activation data for several runs. Data are grouped by temperatures: $T=-60^{\circ}\text{C}$; $T=-50^{\circ}\text{C}$; $T=-40^{\circ}\text{C}$.

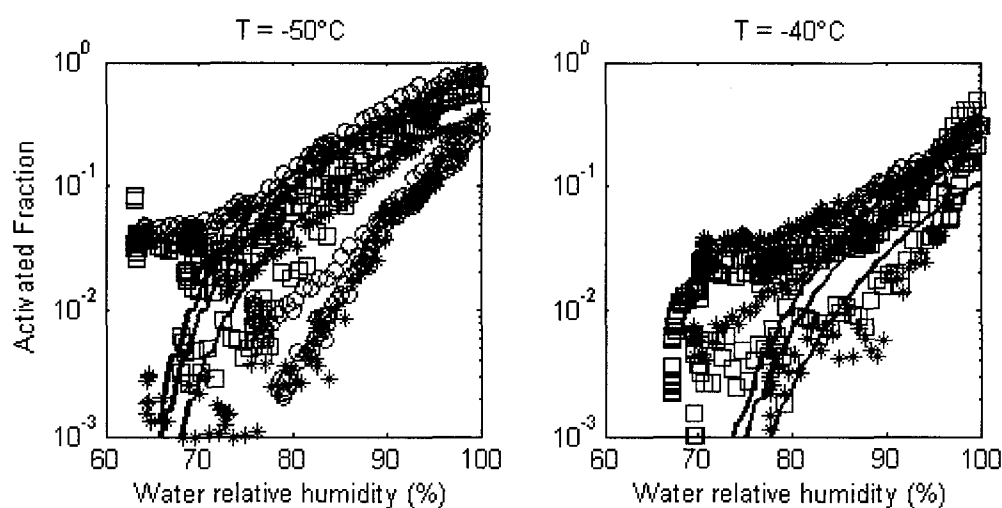


Figure 8.6: Parameterization (lines) for dry-generated CID for three sizes: 400 nm (black), 300 nm (green) and 200 nm (red). Symbols show activation data for several runs. Data are grouped by temperatures: $T=-50^{\circ}\text{C}$; $T=-40^{\circ}\text{C}$.

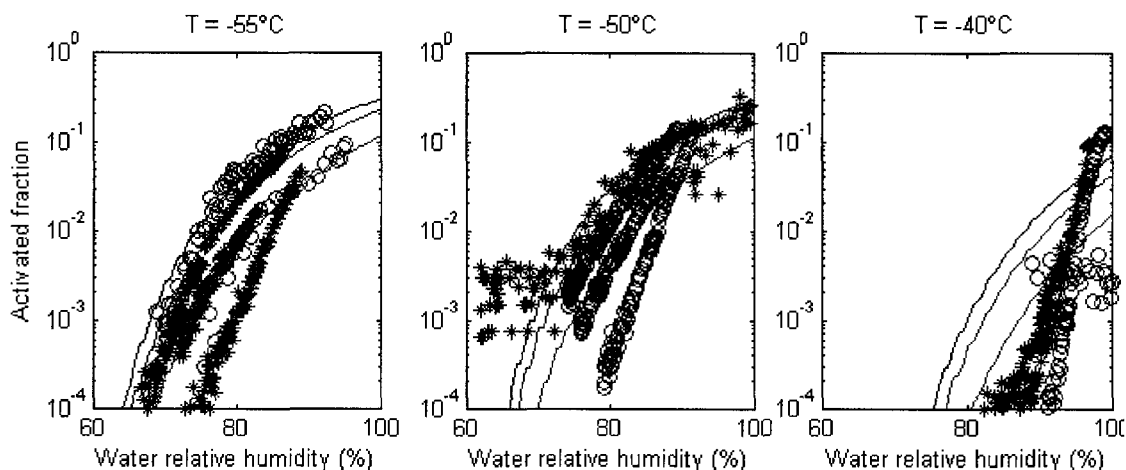


Figure 8.7: Parameterization (lines) for dry-generated SD for three sizes: 400 nm (black), 300 nm (green) and 200 nm (red). Symbols show activation data for several runs. Data are grouped by temperatures: $T=-55^{\circ}\text{C}$; $T=-50^{\circ}\text{C}$; $T=-40^{\circ}\text{C}$.

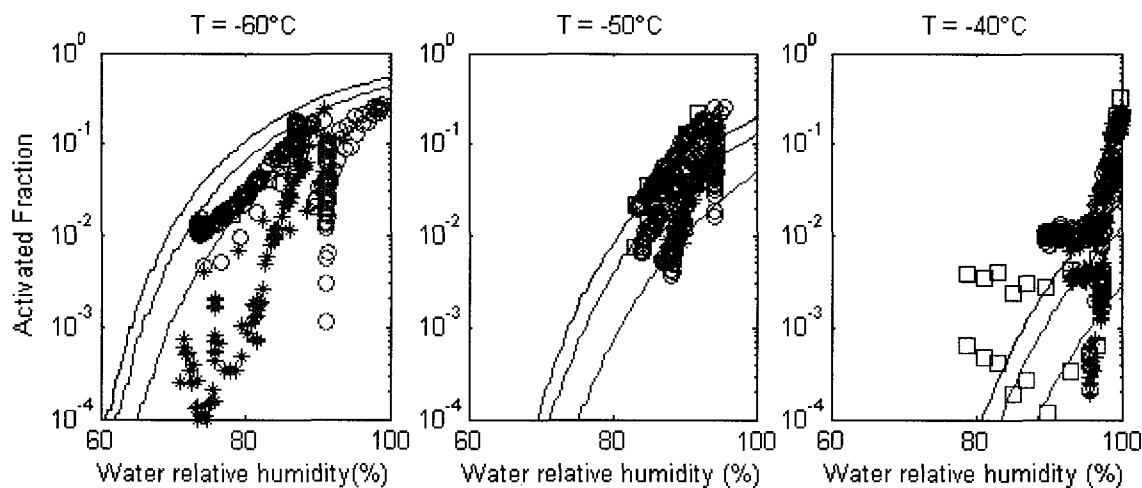


Figure 8.8: Parameterization (lines) for dry-generated OLD for three sizes: 400 nm (black), 300 nm (green) and 200 nm (red). Symbols show activation data for several runs. Data are grouped by temperatures: $T=-60^{\circ}\text{C}$; $T=-50^{\circ}\text{C}$; $T=-40^{\circ}\text{C}$.

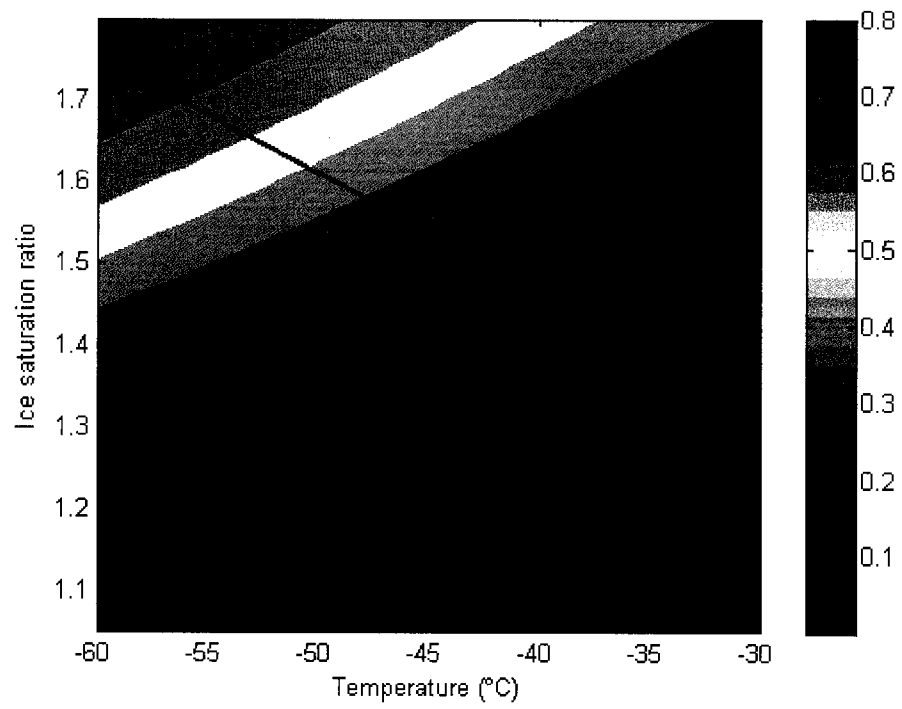


Figure 8.9: Predicted ice crystal concentrations in L^{-1} (or fraction) for an assumed particle size distribution of ATD. The solid black line indicates water saturation.

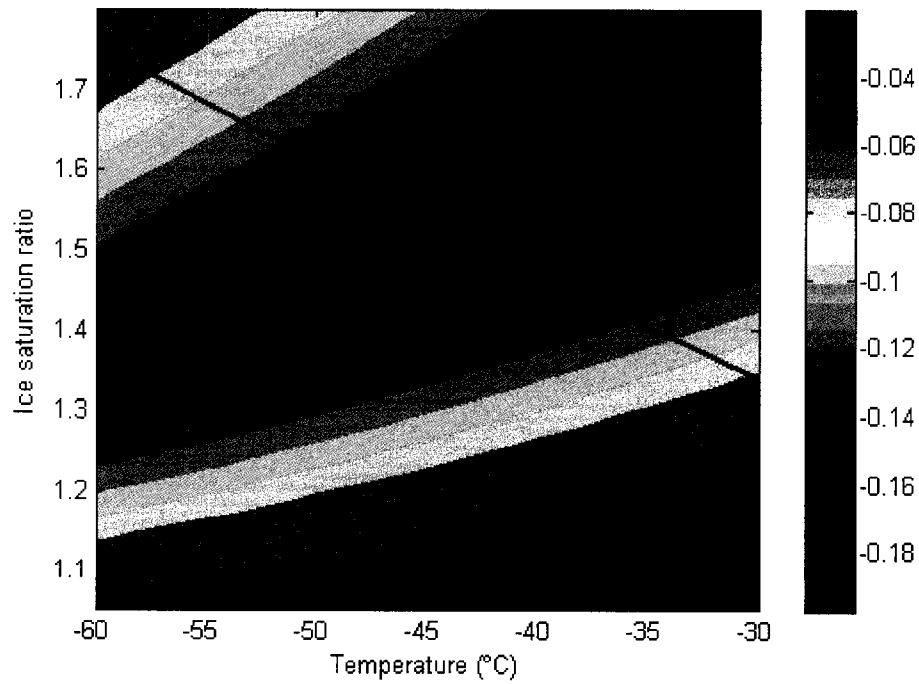


Figure 8.10: Difference in activated fractions in L^{-1} (or fraction) for an assumed particle size distribution between ATD and CID parameterizations. The solid black line indicates water saturation.

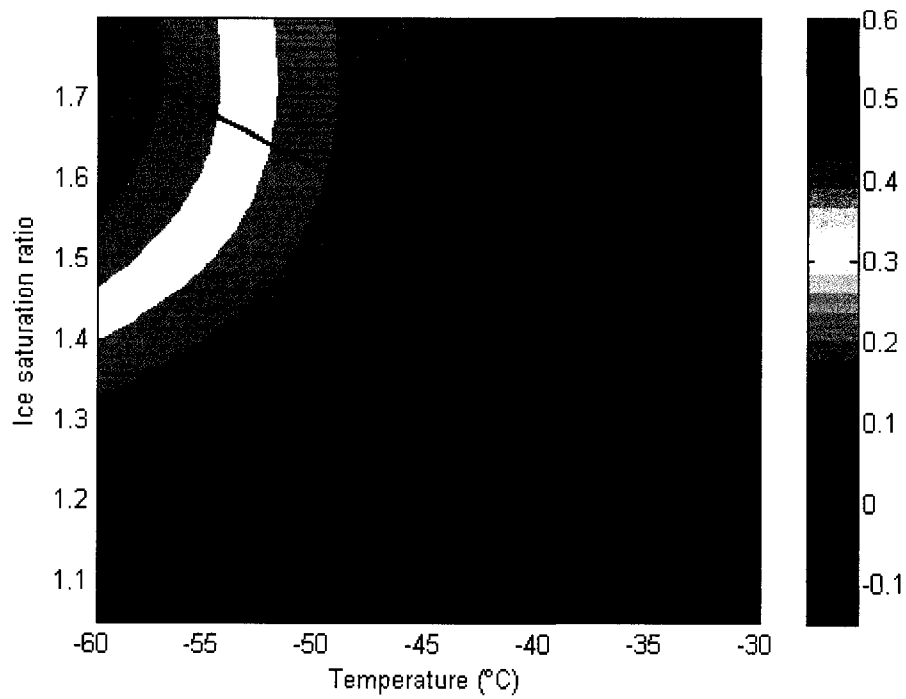


Figure 8.11: Difference in activated fractions in L^{-1} (or fraction) for an assumed particle size distribution between ATD and SD parameterizations. The solid black line indicates water saturation.

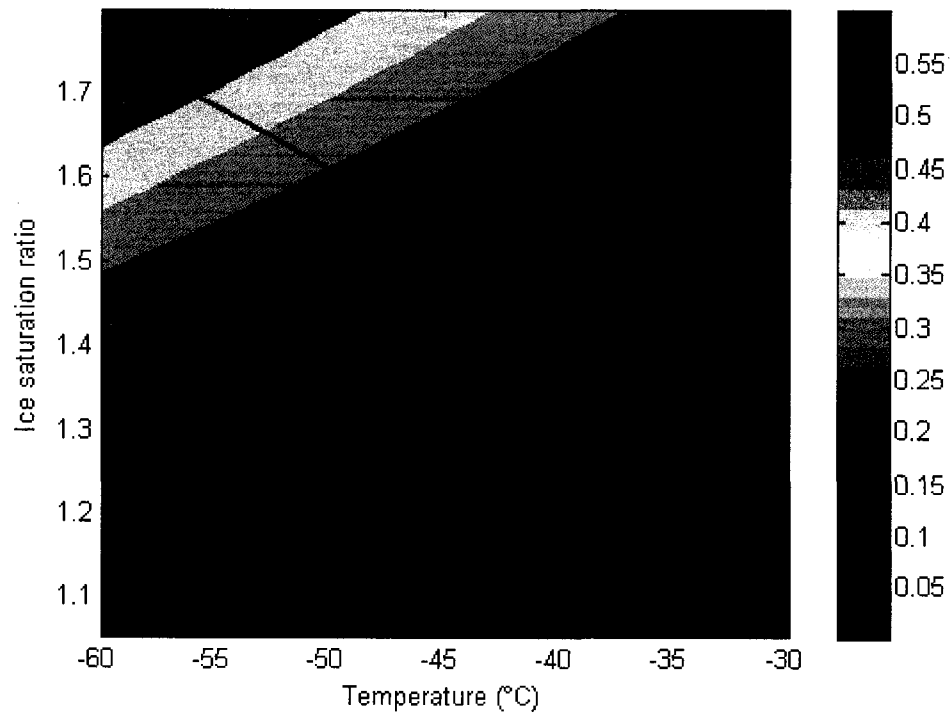


Figure 8.12: Predicted ice crystal concentrations in L^{-1} (or fraction) for an assumed particle size distribution of OLD in L^{-1} (or fraction). The solid black line indicates water saturation.

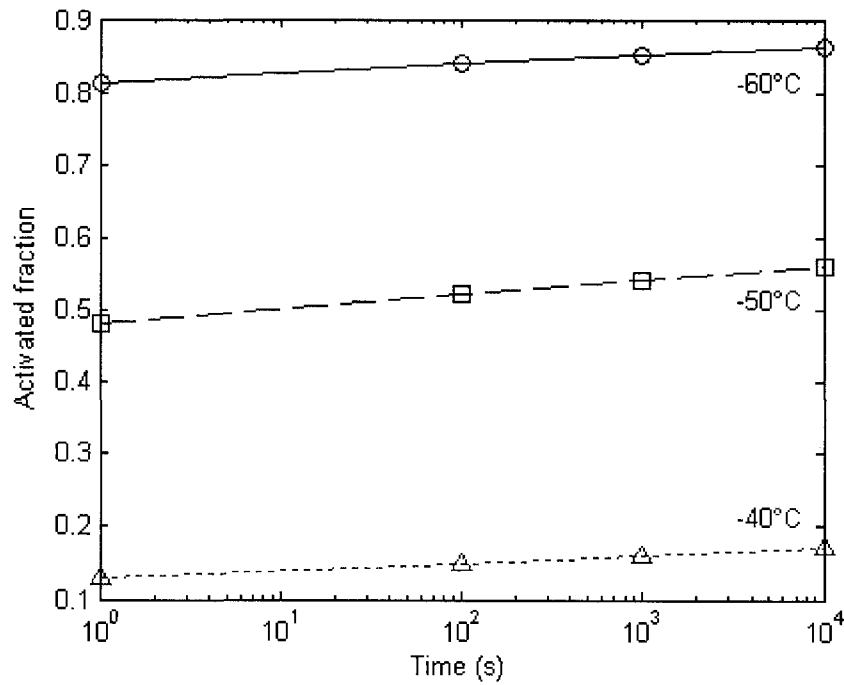


Figure 8.13: Time dependence of activated crystal fraction for dry-generated ATD parameterization at three temperatures: -60°C, -50°C and -40°C for a polydisperse distribution of dust.

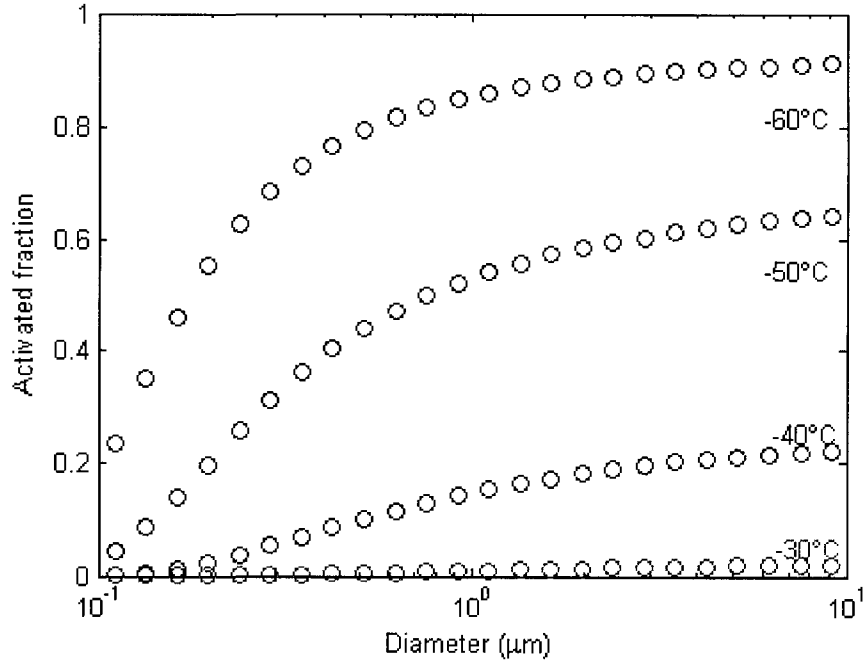


Figure 8.14: Fraction of dry-generated ATD particles nucleated as ice crystals as a function of particle diameter at four temperatures: -60°C, -50°C, -40°C and -30°C.

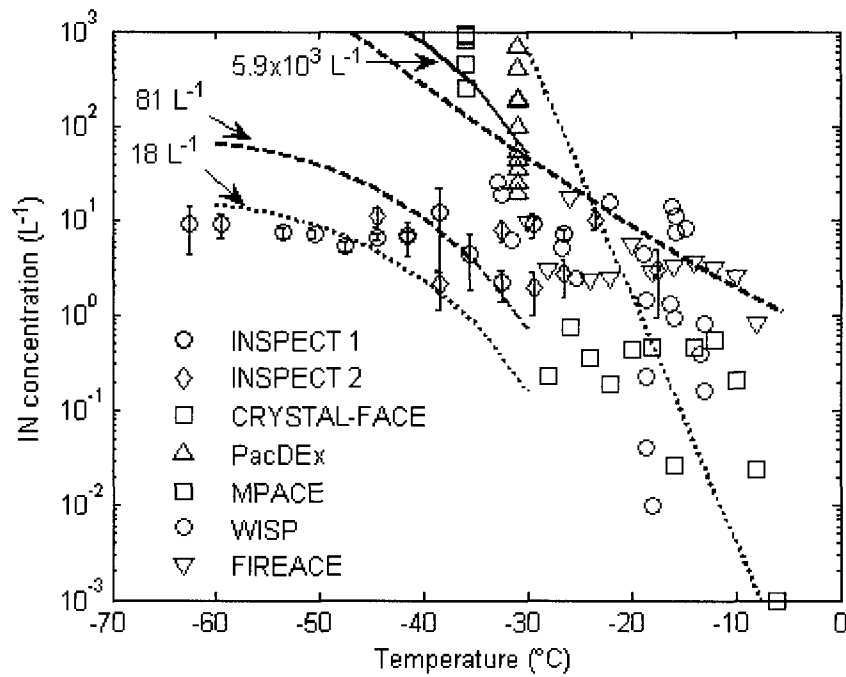


Figure 8.15: IN concentrations (at STP) from various field campaigns and parameterizations from the literature (see text) as a function of temperature. The parameterization developed for ATD is shown in the blue line at water saturation.

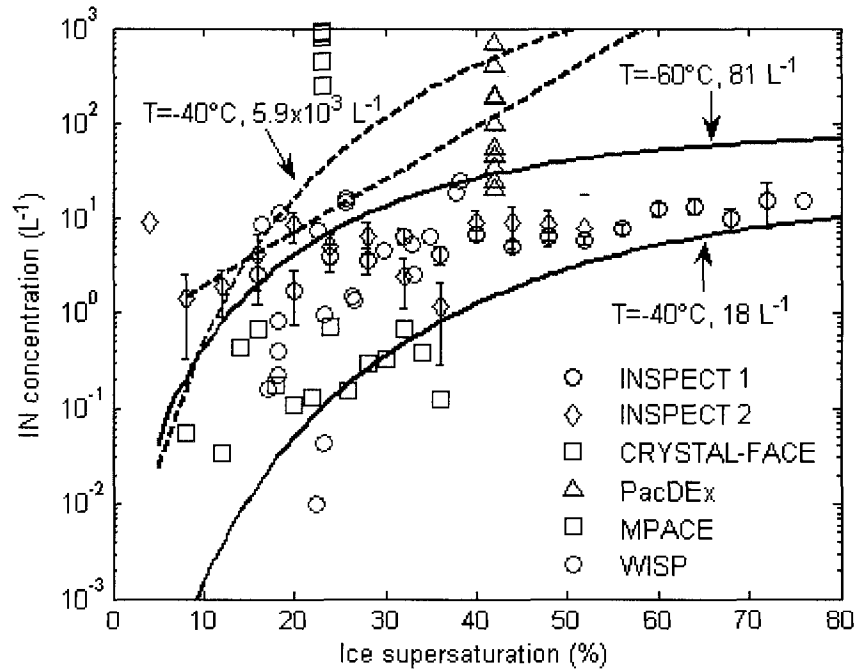


Figure 8.16: IN concentrations (at STP) from various field campaigns and parameterizations from the literature (see text) as a function of ice supersaturation. The parameterization developed for ATD is shown in the blue ($T=-40^{\circ}\text{C}$) and green ($T=-60^{\circ}\text{C}$) lines.

9. Conclusions and Recommendations for Future Work

9.1. Conclusions

Interactions of four mineral dust samples with water vapor over a wide range of temperature and humidity conditions were investigated. Three instrument systems, the humidified tandem differential mobility analyzer (HTDMA), cloud condensation nuclei counter (CCNC) and continuous flow diffusion chamber (CFDC), were employed to measure subsaturated hygroscopic growth, cloud condensation nuclei (CCN) activity, and ice nuclei (IN) activity, respectively. The HTDMA and CCNC measurements reported here provide some of the first data estimating the hygroscopicity of natural mineral dusts, which are often assumed to be completely insoluble (e.g. Yin et al., 2002). These measurements are also the first particle size-resolved ice nucleation measurements, adding a missing level of complexity to the current knowledge. Chapter 8 presented a parameterization of the ice nucleation data for use in parcel models. From the measurements the following conclusions can be drawn:

- The method of particle generation is very important in experiments with mineral dust. It was found that suspending the dust samples in water prior to generation via atomization caused significant changes in the soluble content and potentially the surface properties of the particles, even if the particles are

carefully dried after generation. By suspending the sample in water, intensification of the soluble material associated with the entire distribution of particles occurred on the smallest dust cores which were atomized. This led to generally larger hygroscopic growth, CCN activation at lower supersaturations and higher saturations for ice initiation. We expect that generating the particles dry, for example using a fluidized bed, creates particles which are more representative of how mineral dust particles reach the atmosphere during dust storm events.

- A mineral dust surrogate, Arizona Test Dust, was found to require the lowest RH_i conditions to initiate ice formation at a given temperature; onset RH_i values were at least 10% lower for Arizona Test Dust than for any other investigated sample. However, for the sizes investigated, ice formation was not observed at temperatures warmer than $\sim -30^\circ\text{C}$. At colder temperatures, it is uncertain if the efficiency of ice nucleation by these particles is due to differences in particle composition between this sample and the natural dust samples, or if the milling procedure used to produce the small particle diameters characteristic of this sample produced very efficient active sites, which might not be representative of dust in the atmosphere. These particles, when dry-generated, were found to have low hygroscopicity but served as CCN at lower supersaturations than required for the activation of an insoluble, wettable particle according to Kelvin theory, and had estimated $\kappa=0.02$.
- Dust from playa regions, represented here by the Owens (dry) Lake in California, contains a significant fraction of soluble material. These particles

were externally mixed, with one mode of particles which contain a high fraction of soluble material and are highly CCN active ($\kappa \sim 1$). This fraction initiated ice formation at similar conditions as predicted for similarly sized, fully soluble particles. The other mode was primarily insoluble with relatively low CCN activity ($\kappa \sim 0.04$) but initiated the ice phase heterogeneously at lower RH_i conditions than are required for homogeneous freezing at temperatures colder than -40°C . None of the particles were observed to freeze heterogeneously at temperatures warmer than $\sim -35^\circ\text{C}$.

- Two samples from the Saharan region, collected outside Cairo, Egypt and on the Canary Island, Lanzarote, were found to have similar hygroscopicity, CCN activity and IN activity, although the samples were collected over 4000 km apart. These particles showed little hygroscopic growth below water saturation, yet were able to serve as CCN at lower supersaturations than required for insoluble, wettable particles according to Kelvin theory. Their estimated $\kappa = 0.05$. These particles were able to initiate the ice phase at RH_i values much lower than required for homogeneous freezing and exhibited a strong dependence of ice initiation on particle size. This indicates that these particles can impact cloud development by potentially limiting the peak supersaturation in a cirrus cloud by depleting water vapor and changing ice crystal concentrations. These changes can lead to dramatic changes in the radiative properties of the clouds and can potentially alter cloud lifetimes (DeMott et al., 1997b). However, for the sizes studied, none of the particles initiated ice at temperatures warmer than -25°C , but it is expected that larger

particles may be able to serve as IN at warmer temperatures. It is also possible these particles act as contact IN at warm temperatures, a process which cannot be measured in the CFDC.

- Dry-generated Arizona Test dust particles were coated with secondary organic material formed via ozone oxidation of α -pinene. It was found that these particles required similar conditions to initiate ice formation as are required for homogeneous freezing of soluble particles. We believe that soluble material, when it deliquesced, formed a liquid layer surrounding the particle at low RH_i and prevented the particles from freezing via the deposition mode, even at higher RH_i . These coated particles, however, appeared to freeze heterogeneously at temperatures warmer than which homogeneous freezing occurs.
- Dust samples were grouped into two types: lower κ dust samples and higher κ dust samples. The lower κ dust samples included the dry-generated Arizona Test dust, Canary Island dust, Saharan dust, and the less hygroscopic mode of Owens (dry) Lake dust. Wet generated samples, the more hygroscopic mode of Owens (dry) Lake dust and the coated dust are the higher κ dust samples, which showed very different behavior from the lower κ dust types. The lower κ dust had low hygroscopicity with $0.01 < \kappa < 0.08$ and initiated ice formation at low ice supersaturations. The higher κ dusts were quite hygroscopic with $0.2 < \kappa < 1.1$ and froze at conditions similar to those required for homogeneous nucleation, although in some cases ice nucleation was observed at warmer temperatures where homogeneous nucleation is not active.

- Ice crystal formation by mineral dust does not occur over a sharply defined range of RH_w , as observed for pure soluble particles, such as ammonium sulfate. Typically, at a given temperature, ice nucleation occurred over 15-30% RH_w , whereas all ammonium sulfate particles are activated by homogeneous freezing in 2-4% RH_w . Results indicate that in numerical model simulations in which mineral dust is treated, all particles should not activate ice formation in a nearly step function, as this does not represent the behavior of real dust aerosols. Simulations may otherwise activate too many ice crystals, leading to overestimates of changes in the cloud microphysics.
- A parameterization for ice nucleation by deposition nucleation of the lower κ dust was developed. Slow activation over a broad range of RH_i was represented by a normally distributed range of contact angles across the particles. The mean α of the distribution was allowed to be a function of size, such that larger particles were more likely than smaller particles to have a fraction with low contact angle. The parameterization is able to predict the slow activation of mineral dust in the atmosphere and even at water saturated conditions for temperatures between -60 and -40°C, but does not predict complete activation of a lognormal distribution of mineral dust. This parameterization is only expected to be valid at temperatures colder than -30°C where it appears that the mineral dust particles nucleates ice by the deposition mode. It may over-predict IN concentrations of playa dust at the warm end, where it is uncertain if deposition nucleation, immersion freezing, or homogeneous nucleation of a liquid coating is occurring.

9.2. *Recommendations for Future Work*

One important conclusion from this work is the strong size dependence observed for onset conditions of ice nucleation. Due to the current detection method, which uses size alone to determine the presence of ice, only dry particles smaller than $\sim 0.5 \mu\text{m}$ could be examined in this study. The CFDC system should be modified so that larger particles can be examined to determine if the size dependence continues to larger sizes and to observe if larger particles are capable of serving as IN to warmer temperatures, as has been found by other groups (e.g. Field et al., 2006; Kanji and Abbatt, 2006; Knopf and Koop, 2006). This can be accomplished using the Small Ice Detector (SID) to determine the presence of ice instead of particle size alone. The SID uses high sensitivity detectors at six scattering angles to determine the shape, as well as the size of particles. This detector will be able to distinguish small ice crystals from haze droplets by the change in the shape of the particles for particles with diameters between 1-80 μm .

Experiments should also examine the possible dependence of the residence time in the CFDC. The residence time a particle is exposed to controlled temperature and saturation conditions is dependent on the flow rate through the chamber. The residence time can be increased by decreasing the flow through the instrument, but this is limited by a sufficiently high flow to counteract buoyancy driven circulations within the chamber. These experiments may also help validate the stochastic or singular hypotheses for heterogeneous ice nucleation (Pruppacher and Klett, 1997). The stochastic hypothesis assumes that nucleation is random and for a constant cooling rate, the fraction of droplets of a given volume frozen per unit time is constant. The singular hypothesis assumes that there is a characteristic freezing condition for an aerosol particle and therefore the

number of droplets of a given volume that freeze is independent of cooling rate (or increasing relative humidity). If the fraction of particles freezing in the CFDC is found to be a strong function of residence time in the chamber, this would suggest that the stochastic hypothesis is valid.

IN residuals should also be examined to further elucidate the role of soluble material and mineralogy in the activation of these particles. While some measurements of individual mineral species exist in the literature (Archuleta et al., 2005; Hung et al., 2003; Kanji and Abbatt, 2006; Knopf and Koop, 2006; Roberts and Hallett, 1968; Salam et al., 2006; Schaller and Fukuta, 1979) it is unclear how changes in mineralogy influence the ability of these particles to initiate ice in the atmosphere.

While secondary organic coatings were found to increase the required RH_i for ice nucleation in this study, Archuleta et al. (2005) found that sulfuric acid coatings in some cases decreased, increased or did not change the ice nucleation onset conditions for coated metal oxide particles. Thus, all coatings may not behave the same on all particles, and studies should examine the role of various coatings and the potential for gas phase reactions on the surface of these particles to alter the ice nucleability of dust. Coating systems should try to reproduce realistic conditions in the atmosphere of reactive gaseous species to get an accurate prediction of aging in the atmosphere.

The CFDC is able to make measurements of deposition, condensation and immersion freezing, as well as homogeneous nucleation but new methods should be developed to examine contact freezing. A system in which particles are free flowing, yet the number of collisions can be accurately measured or estimated is needed to quantify the role of this process.

An attempt should be made to obtain samples from the most prevalent dust source regions, such as the Sahel and Bodélé depression regions, for the most accurate representation of these species in the atmosphere. With these samples a suite of measurements, such as made in this study, as well as chemical composition, mineralogy, optical properties and reaction rates with atmospheric gases should be obtained. These data could be used to further constrain the myriad postulated roles of mineral dust in the atmosphere and in climate. Further, aircraft missions could attempt to follow dust plumes and examine chemical and morphological changes as the plume crosses polluted regions over the ocean.

Finally, this data suggests that more work should be done to accurately represent ice nucleation of dust in numerical simulations in both cirrus and mixed-phase clouds. Modeling studies using laboratory and field data of mineral dust ice nucleation should be extended to global models to provide a more realistic representation of dust ice nucleation in these simulations. Parameterizations such as developed by Marcolli et al. (2007) for warmer temperature ($T > -30^{\circ}\text{C}$) should be evaluated against more laboratory and field measurements for applicability in this regime, including potential variations with particle size.

Appendix I

Over the course of this work, several alterations to the laboratory CFDC were made to improve performance. Freezing experiments on Owens (dry) Lake dust generated by atomization were done in September through October 2003 and experiments using Arizona test dust (ATD) generated by atomization were done in November through December 2003. Work resumed on ATD generated in the fluidized bed in November and December 2004. Beginning in May 2005 it became apparent that problems were occurring with the CFDC laboratory instrument. Experiments with malonic acid particles showed difficulty reaching equilibrium conditions and activated fractions were found to decay with time while temperature and saturation conditions were held fixed. It was also difficult to reach 100% activation with the steep activation curves predicted for homogeneous freezing (zero activation to full activation should occur over a $\sim 2\text{-}4\%$ increase in RH_w). Prior experiments had found maximum activated fractions (number of IN per number of total particles) for nucleation experiments typically between 50-70%. It was assumed that losses through the inlet and CFDC system accounted for the missing particles. In these experiments, maximum activated fraction was much lower and turbulence was suggested as a possible reason for slow activation and increases in losses through the system. In an attempt to determine if turbulence was occurring in the system, flow controllers were placed on the inlet of the instrument to be able to independently

control the sheath flows. Instead of the sheath flow being equal on either side of the aerosol lamina, this allowed the flow to be varied on each side. This changed the width of the aerosol lamina and its position in the chamber. Establishing a fixed temperature gradient between the walls at high enough RH_i for ice crystals to be nucleated, the lamina was moved around the chamber but there was no apparent change in the ice crystal nucleation. As the lamina moves, particles should experience a significant change in RH_i , causing more or less ice crystals to be nucleated. Since this did not occur, it was deduced that turbulence existed in the chamber and that aerosol was likely distributed throughout the gap between the plates.

In addition to the turbulence, it was also observed during an experiment that if the RH_i was set to a high enough value to observe ice crystals, that the fraction of particles forming crystals decreased with time much more quickly than the ice was expected to be depleted from the walls. For the experiment shown in Figure A1.1 it is clear that while the RH_w (blue curve) remains quite constant, the activated ice crystal fraction (green curve) decreases steadily with time. Normally experiments were allowed to progress for four to five hours without concern for depletion of the ice surface.

In order to determine the quality of the ice surface along the walls, the walls were iced individually by cooling only one wall, pumping water through the chamber, then immediately turning off the cooling and collecting the melt water. Melting the ice on the outer wall produced ~80 ml of water while melting the ice on the inner wall only yielded ~20 ml. This was very surprising because the outer wall has only 25% more surface area than the inner wall. The melt water corresponds to an approximate ice coating of ~215

μm along the outer wall and $\sim 40\ \mu\text{m}$ along the inner wall. Initial studies (Rogers et al., 2001) estimated the ice coating to be several hundred microns on each wall.

The other possible explanation for the decay in ice crystal signal during an experiment is due to the cone at the bottom of the outer wall. While the cone at the bottom of the inner wall which helps direct the flow to the OPC is made of delrin, a hydrophobic material that will not be coated with ice, the outer wall cone was made of copper, like the rest of the chamber. This section is not actively cooled by refrigeration, but is noticeably cooler than room temperature and likely received an ice coating during the icing procedure. When the flow, which was previously determined to be turbulent, flowed down into the cone section, a supersaturation could have been established, activating CCN that were erroneously counted by the OPC as ice crystals. As the experiment proceeded, the ice on the cone section would be depleted lowering supersaturation in this region and decreasing the concentration of activated CCN. To verify the cone-section as the cause of the problems, experiments were performed in which heating tape was applied to the chamber, slightly above the cone section. This prevented ice from depositing on the surface of the cone. These experiments suggested it was indeed the cone-section which produced a supersaturation in the bottom of the chamber and accounted for the large volume of water collected along the outer wall.

The investigations described above led to the following CFDC modifications. It was first suggested that the bottom section of the outer wall be replaced with a PVC tube that had been made for the chamber during its construction. The PVC will not coat with ice and should remove the spurious-supersaturation artifact by establishing an evaporation region similar to what is used in the aircraft unit, except longer. This

required completely disassembling the CFDC. During the disassembly the upper portion of the outer wall was examined. By cooling it and pouring water down the center of the tube, it was very clear that a smooth ice surface was not obtained and instead ice was forming in patches on the surface on the copper. This could have serious implications for the calculated RH_i in the chamber. Therefore the surface of both walls was re-ebonized. In the ebonization process, the copper is reacted with a caustic solution to form a thin surface layer of cupric sulfide crystals, which helps create a wettable surface along the copper wall to aid in the formation of a smooth ice surface, as well as preventing oxidation of the copper.

After reassembly, it was found that extremely high supersaturations with respect to water could be established without forming ice crystals or detecting CCN in the OPC. It was postulated that the new evaporation region shortened the residence time in the ice supersaturation region enough to prohibit growth to detectable sizes. Therefore the unit was disassembled again and the cone portion of the outer copper wall was cut off and replaced with a Delrin cone, similar to that in the aircraft unit. Upon reassembly, the unit could be operated for a substantial period of time (several hours) without decay in the ice signal at constant RH_i . We hypothesize that the decrease in ice crystal concentrations as observed in Figure A1.1 was due to the depletion of the ice on the copper cone, since it was not actively cooled and subject to ice loss faster than the wall surfaces, but the inconsistent ice surface on both walls likely amplified this problem.

After these modifications onset of nucleation for ammonium sulfate particles occurred between 104-106% RH_w (Figure A1.2, circles) at $T=-50^{\circ}\text{C}$. Yet onset of homogeneous freezing of ammonium sulfate particles, predicted by the equations in

Table 1 of Koop et al. (2000, see section 3.1.2), should occur around 96% at -50°C and have a size effect as shown in the colored lines of Figure A1.2. The black line is for 200 nm, the red for 100 nm and the blue line for 50 nm particles. This size effect was not observed after the reassembly. It was suggested that an error in the temperature measurement of ~ 1 K would account for the error in the RH_w . However, before reassembly all thermocouples were compared with the temperature reading from a thermometer (Cole Palmer, Platinum RTD) and found to be in good agreement with each other and the PRT. Another thermocouple was added directly in the flow of the refrigerant as it exited the outer wall. This temperature measurement agreed precisely with the thermocouples along the outer wall, also indicating that unaccounted for errors in the temperature measurement were unlikely.

The ammonium sulfate particles are introduced to the CFDC as dry particles. While some studies have found heterogeneous nucleation of dry ammonium sulfate particles at low RH_w (Abbatt et al., 2006), it was postulated that if the ammonium sulfate did not deliquesce until they had passed most of the way through the chamber, then the particles were too small at the outlet to be detected until cloud droplets formed and froze. However, the observed activity is still at much higher RH_w values than the expected CCN activity of ammonium sulfate particles, which should occur at water supersaturations less than 1% for the sizes examined. In contrast to ammonium salts, sulfuric acid will take up water from very low RH_w , so any potential problems due to deliquescence barriers should be eliminated for this compound. Accordingly, some experiments were done where sulfuric acid was homogeneously nucleated by heating a bulk solution and allowing the vapor to condense into particles. These studies found similar supersaturations required

for ice nucleation by sulfuric acid as for ammonium sulfate, indicating that deliquescence was not a contributing factor to the observed high RH_w for freezing onset.

Throughout these experiments we believed that turbulence was still likely, perhaps due to a misalignment or morphing of the inlet. The inner wall hangs on the inlet, which could cause misalignment and torqueing of the narrow holes drilled in the inlet. Misalignment could cause not only dispersion of the aerosol through the chamber, but potentially could cause the aerosol to be injected not in the center but at an angle toward one of the walls. By examining the inlet during each disassembly of the instrument, we were not able to visually observe any irregularity with the inlet. Since the RH_i profile is skewed between the walls, it was hypothesized that if the aerosol was being directed toward the area where the RH_i is low, that could explain why we had to reach large supersaturations before ice nucleation was observed.

Thus it was suggested to swap the configuration of the walls, such that the outer wall is the cold surface and the inner wall is the warm surface. If the aerosol stream was being directed toward the region of low RH_i , swapping the temperatures of the walls should send the aerosol stream to a region of higher RH_i . Under this configuration the onset of nucleation was found to occur at much lower relative humidities, in fact several percent RH_i lower than predictions (Figure A1.2, squares). With the outer wall as the cold wall, even adding extra insulation, it was difficult to maintain a uniform wall temperature and a temperature gradient developed along the outer wall. The coolant was flowed such that the bottom half of the chamber was the coldest and hence the particles are exposed to the highest ice supersaturation at the bottom of the chamber, prior to being counted by the OPC. We expected that the time the aerosol was exposed to the higher

RH_i conditions in the lower half of the chamber was sufficient to nucleate ice crystals, and so we corrected the outer wall temperature average to only include the bottom two thermocouple measurements. This increased the calculated RH_w and gave good agreement with water activity based predictions for homogeneous nucleation onset for ammonium sulfate (Figure A1.2, filled triangles). We also get very steep nucleation curves, as expected for homogeneous nucleation. Therefore, it appears that the modifications made to the laboratory CFDC unit during 2005 and early 2006 have improved instrument reliability and accuracy.

All data shown in this work are obtained under the current configuration: the outer wall is the cold surface, but only the bottom two thermocouples are used in the temperature calculation; the inner wall is the warm surface and there is good agreement between all thermocouples on the wall, so each is included in the inner wall average temperature. All experiments completed prior to January 2006 were repeated with the new configuration.

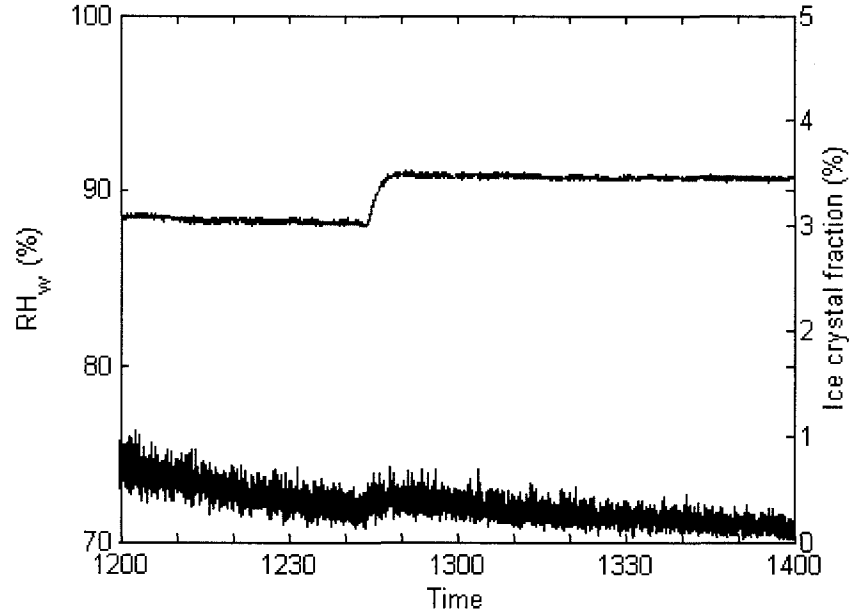


Figure 0A1.1: Fraction of ice crystals (right axis), for an approximately constant RH_w (left axis) with time, from May 26, 2005.

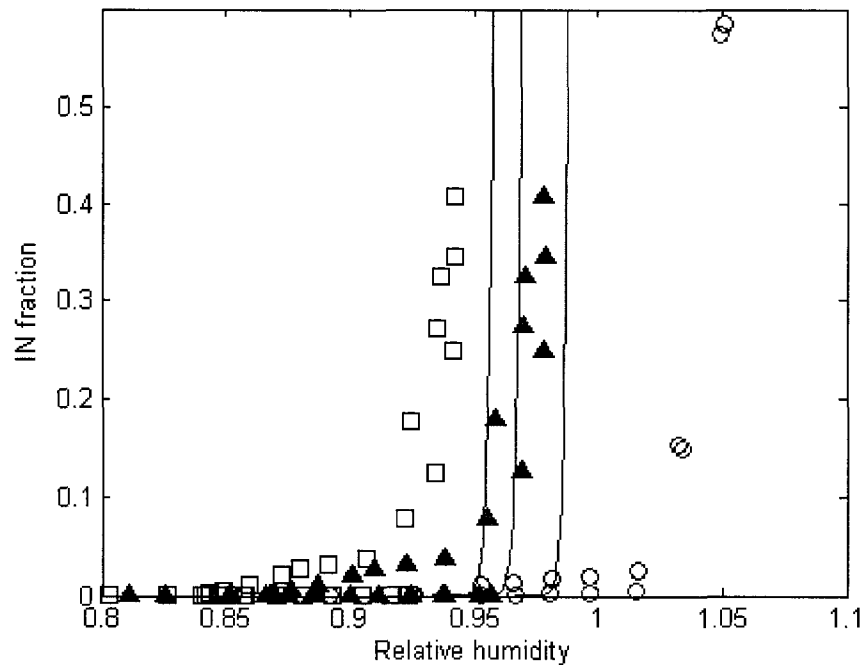


Figure A1.2 Activated fraction of IN activated for different configurations of the CFDC at -50°C . Circles represent data from December 16, 2005 with the outer wall being the warm surface and the inner wall being the cold surface. Squares represent data from January 9, 2006 with the outer wall being the cold surface and the inner wall being the warm surface. Filled triangles are the data from January 9, 2006 corrected to only use the bottom two thermocouples on the outer wall in the temperature calculation.

Appendix II

This Appendix will describe the procedure used to calibrate the CCNC. The supersaturation in the instrument is controlled by the gradient along the ceramic, wetted wall. The temperature gradient, ΔT is imposed and controlled along the outer wall of the column. Yet it is the temperature gradient along the inner, ceramic wall, $\Delta T'$ that controls the supersaturation. $\Delta T'$ will be some fraction of the imposed ΔT , and this loss of heat through the ceramic surface is known as the thermal efficiency (Lance et al., 2006). The thermal efficiency is calibrated by the manufacturer prior to shipping, but can drift and should be recalibrated after moving the instrument or after long periods without use.

In practice, the CCNC is calibrated using ammonium sulfate aerosol over a broad range of the supersaturations in the instrument, usually 0.1-1%. Calibration at higher supersaturations is not possible because of the very small particle diameters required to trace out the activation curve at higher supersaturations for the hygroscopic ammonium sulfate aerosol ($\kappa=0.6$). Particles with diameters smaller than ~ 20 nm are not produced in sufficient number concentrations from the atomizer. Ammonium sulfate particles are generated by atomization and dried and size-selected in the DMA using sheath:sample ratios of 10:1 to provide a narrow range of diameters exiting in the quasi-monodisperse aerosol stream. The CCNC is held at a fixed supersaturation and diameters of

ammonium sulfate particles are scanned, tracing out the activation curve. The curve is fit using a sigmoidal curve and the 50% activation diameter, D_{50} , is found. This procedure is repeated for supersaturations between 0.1-1%. The activation behavior of ammonium sulfate aerosol is well known, so for each D_{50} computed, the critical supersaturation corresponding to that diameter is calculated. Then a third order polynomial is fit to the ΔT and the known critical supersaturation for each D_{50} measured. This polynomial is used to determine the actual supersaturation in the instrument from the imposed ΔT .

Figure A2.1 shows the activation behavior of ammonium sulfate using the manufacturer calibration and a calibration performed in our laboratory. Activation behavior of ammonium sulfate ($\kappa=0.6$, black line) is shown for reference. While the laboratory calibration does not dramatically shift the points in supersaturation space at supersaturation greater than 0.3%, the laboratory calibration more closely follows the $\kappa=0.6$ line for critical supersaturations between 0.2-1%. The unit has the most error for the lowest supersaturation measured, 0.1%.

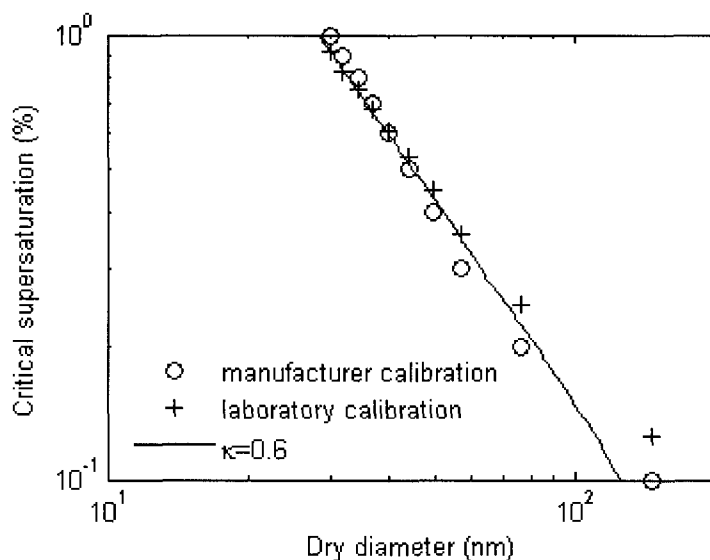


Figure A2.1: Ammonium sulfate aerosol CCN activation data using the manufacturer and laboratory calibration.

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