



A Method for Single Particle Mass Spectrometry of Ice Nuclei

D. J. Cziczo,^{1,2} P. J. DeMott,³ C. Brock,^{1,2} P. K. Hudson,^{1,2} B. Jesse,³
S. M. Kreidenweis,³ A. J. Prenni,³ J. Schreiner,⁴ D. S. Thomson,^{1,2}
and D. M. Murphy¹

¹*Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado*

²*Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado*

³*Department of Atmospheric Science, Colorado State University, Ft. Collins, Colorado*

⁴*Max-Planck-Institut Für Kernphysik, Bereich Atmosphärenphysik, Heidelberg, Germany*

High altitude cirrus clouds play an important role in the terrestrial radiation budget. Cirrus clouds are composed of ice particles that generally form on only a small subset, from 1 in 10 to 1 in 10⁵, of the background aerosol. Ice particles may form due to the homogeneous freezing of aqueous aerosols or by the action of heterogeneous ice nuclei (IN). IN possess the ability to form ice at a higher temperature for a given vapor pressure of water than is required for homogeneous freezing. Apart from a few studies of refractory particles, the chemical composition of these climatically important particles remains largely unknown. Almost nothing has been reported about the semivolatile and volatile components of IN. One of the principal reasons is that collection of cirrus precursors ideally should take place immediately after ice formation, before significant alteration of the crystals due to particle and gas-phase scavenging. Here we describe a method to measure the concentration and activation conditions of aerosols by exposure to temperatures and relative humidities (RH) similar to those that initiate cirrus cloud formation in the atmosphere. Laser mass spectrometry was subsequently used to investigate only those particles that nucleated ice. With this technique we were able to differentiate particles known to act as IN from those that entered the ice phase

homogeneously. Deployment to study aerosol effects on ice formation in cirrus clouds is presented, although this method is applicable to the entire tropospheric mixed-phase and ice-phase regimes.

INTRODUCTION AND MOTIVATION

The indirect effects of aerosols on the Earth's radiation budget, for example, the increased frequency and persistence of clouds, are highly uncertain in both direction of forcing and magnitude (Houghton 2001). Cirrus clouds are of particular importance because they have wide coverage (30% of the Earth's surface) and alteration of their properties, for example, the concentration of particles on which they form, has a strong potential for altering the radiative balance. Very little is known about the composition of ice nuclei (IN), and it has therefore been impossible to determine if anthropogenic activities have increased their number density in the required region of the atmosphere. Further complicating this problem is that different particle types and nucleation mechanisms may dominate the formation of cirrus ice depending on atmospheric temperature, humidity, and cloud dynamics. Ice will not homogeneously form from pure solution droplets, no matter how dilute, at temperatures greater than about -38°C (Pruppacher and Klett 1998). Cirrus ice nucleated at warmer conditions therefore requires a heterogeneous nucleus upon which the initial ice embryo forms. Below this temperature either mechanism may dominate.

Two methods have been employed toward the goal of better understanding the composition of particles that form ice, and these represent the data now available in the literature. First, various workers have analyzed samples of cirrus crystals (Heintzenberg et al. 1996), ice in aircraft contrails (Petzold et al. 1998), and solid precipitation (Kumai 1961; Parungo et al. 1976). Residual components remaining after water was removed were analyzed using electron microscopy. These studies have at

Received 22 April 2002; accepted 28 August 2002.

This work was supported by NSF (grants ATM-9714177 and ATM-0124927; any opinions, findings, and conclusions expressed in this material are those of the authors and do not necessarily reflect the views of NSF) and NOAA base funding. We wish to thank Jose Jimenez for many helpful discussions relating to the aerodynamic lens used for these studies, Dave Rogers for his advice for the preparation of AgI particles in order to validate this technique, Erik Williams for his logistical support, and Randy Borys for his assistance with preparation and deployment of instruments at Storm Peak. Tony Prenni's participation was supported by the NOAA Postdoctoral Program in Climate and Global Change, administered by the University Corporation for Atmospheric Research.

Address correspondence to D. J. Cziczo, Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80305. E-mail: djcziczo@al.noaa.gov

least 2 major shortcomings: first, the uncertain history of the collected material could have included both gas-phase and particle scavenging events and second, no semivolatile or volatile information can be ascertained because these analyses require that samples be placed within a vacuum chamber. As a group these published data indicate a high frequency of crustal components. Tenberken-Potzsch et al. (2000) attempted to separate cloud ice from supercooled droplets at ground level by assuming that the crystals did not stick to an impaction plate. Capillary electrophoresis was used to report bulk concentrations of the inorganic cations ammonium, potassium, sodium, calcium, and magnesium for each group. Tenberken-Potzsch et al. (2000) indicate that the latter 4 cations are similar in both small ice crystals and cloud droplets but that considerably less ammonium is observed in the ice phase, which is consistent with crustal or fly ash material inducing ice formation. As with the other collection techniques, scavenging events could not be decoupled and, as has been shown for general atmospheric filter samples, the results correspond to a bulk material property.

The second method employed for understanding IN composition consists of formation of ice crystals on a background aerosol under controlled temperature and water saturation conditions using a continuous flow diffusion chamber (CFDC) (Chen et al. (1998) and references therein). These particles were impacted onto transmission electron microscope (TEM) grids and subjected to energy dispersive x-ray (EDX) analysis. This method eliminated possible scavenging events that could mask the actual composition of IN. This method requires that upper tropospheric aerosols are sampled and that collection occurs under conditions representative of the range under which cirrus clouds form. CFDC/TEM/EDX data are also limited by the need for sample preparation under vacuum conditions and therefore the loss of any semivolatile or volatile components. All of these studies required extensive analysis time in the laboratory after collections were made.

The last decade has shown the emergence of laser mass spectrometry as a technique for analysis of aerosol particle chemical composition both in situ and in real time. Single particle instruments vary in specific design, but the basic concept is common to most instruments (Middlebrook et al. 2002). Ambient particulate matter is detected and sized, normally using either single or dual visible laser beams. A subsequent laser beam of higher fluence illuminates the particle, ablating condensed-phase material and simultaneously ionizing it. A variety of techniques can then be used to detect the ions, with time of flight (TOF) mass spectrometry being the most prevalent. Single particle mass spectrometry has been used to study aerosols under a variety of conditions including clean marine (Murphy et al. 1998b), polluted urban (Middlebrook et al. 2002), and free tropospheric (Murphy and Thomson 1997; Murphy et al. 1998a). Among the important information provided by single particle instruments is the understanding that tropospheric aerosols are not homogeneous representations of the material collected in bulk filter

samples and are most often complex mixtures of both refractory and volatile components.

Here we present a method for the rapid chemical characterization of aerosols that form ice by combining a diffusion chamber with a single particle laser mass spectrometer. We validated this method using a dual population of aerosols comprised of a majority that do not nucleate ice under experimental conditions and a minority with a distinctly different mass spectrum that are known to act as effective IN. Finally, a detailed description of the deployment of this method for field studies within free tropospheric air is given.

APPARATUS DESCRIPTION

Overview

The methodology used to perform laser mass spectrometry of IN is shown in Figure 1a. Removal of supermicrometer aerosols was required at the onset for processing atmospheric IN with a CFDC because the growth of nucleated ice particles to supermicrometer sizes, as compared to nonnucleated dry or aqueous aerosols, was the basis for differentiating those particles that formed ice. After ice crystal formation, all submicrometer particles were eliminated and the temperature was raised to melt and desiccate the condensed-phase water. The remaining particles represented those submicrometer aerosols that effectively nucleated ice at the experimental conditions. These could then be analyzed by a traditional single particle mass spectrometry technique.

Figure 1b shows the experimental techniques used to analyze the aerosol via the processes in Figure 1a. Specifically, a cyclone impactor was used to remove all supermicrometer ambient particles before experimentation so that they were not confused with same-size ice crystals. The Colorado State University (CSU) CFDC instrument (Rogers et al. (2001) and references therein) was employed to create the low temperature/high humidity conditions required to nucleate ice. Submicrometer aerosols that did not induce freezing were removed using a laboratory counterflow virtual impactor (LCVI) developed at the National Oceanic and Atmospheric Administration (NOAA). Analysis was then performed on the IN using the NOAA particle analysis by laser mass spectrometry (PALMS) instrument. Alternatively, traditional TEM/EDX analyses were performed, although details are not included in this work.

Cyclone Impactor

Ambient particles were provided for these studies using a NOAA-designed inlet reaching ~ 10 m above ground level. A URG, Inc. PM_{2.5} cyclone impactor was employed to remove all supermicrometer aerosols from this distribution. The correct removal size was monitored using a Climet Model 208 particle analyzer (PA) that sizes particles 0.3–10.0 μm in diameter by white light scattering. For the purposes of this study, the PA was coupled with a Perkin-Elmer 306 data acquisition card to provide rapid particle size information. The flow through the cyclone

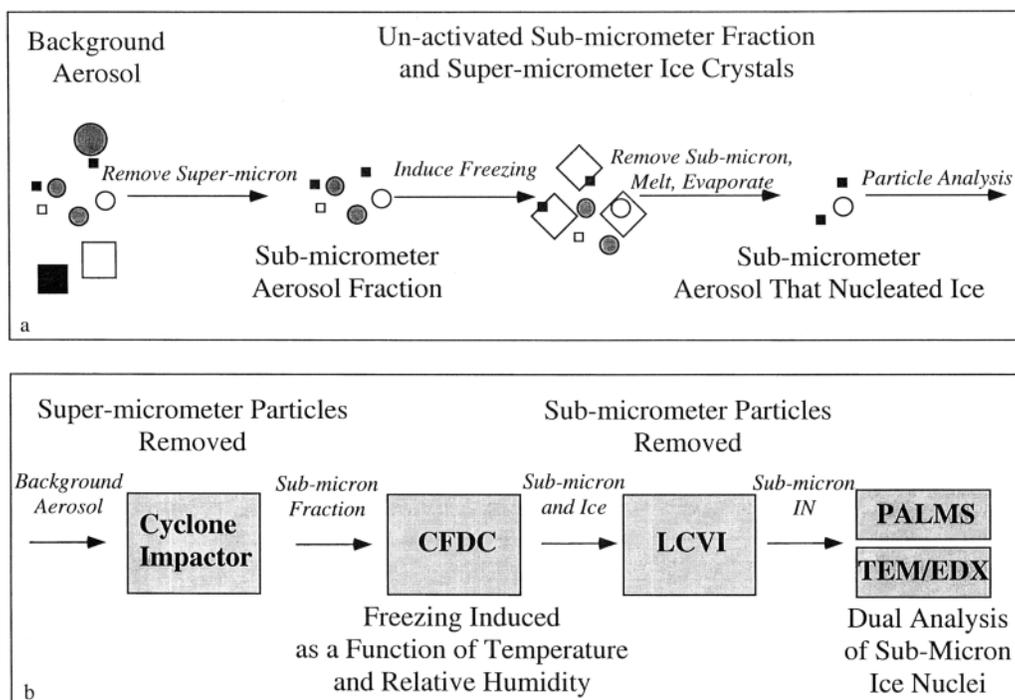


Figure 1. Methodology for the investigation of ice formation by atmospheric aerosols using single particle laser mass spectrometry (a) and a schematic representation of the instruments used to perform this study (b). Ambient supermicrometer diameter particles were removed with a cyclone impactor so they were not confused with ice crystals grown in the CSU CFD chamber. Submicrometer aerosols that did not nucleate ice under experimental conditions were removed using a LCVI. Retained particles that had nucleated ice were analyzed using the NOAA PALMS instrument or by TEM/EDX.

was set such that no particles larger than $1.0 \mu\text{m}$ in diameter were detected in 10 min samples each day of operation. The flow corresponded to a throughput of 15 volumetric liters per minute (vlpn) when attached to the isokinetic NOAA inlet. The PA showed complete retention of particles from 0.3 (the lower instrumental size limit) to $0.5 \mu\text{m}$, whereas particles greater than this size were partially depleted due to impaction.

CFDC

The CSU continuous flow diffusion chamber used in these studies functions by forming a controlled profile of ice supersaturated conditions in the space between 2 concentric ice-coated cylinders held at different temperatures. Only the central 10% of the flow between the cylinders contains aerosols. The remaining flow of dry, particle-free, N_2 forms a sheath both isolating the particle flow from direct contact with cylinder surfaces and ensuring that aerosols are exposed only to a narrow range of temperatures (0.7°C across lamina) and humidity (0.8% RH maximum variation). The CFDC was operated at a pressure of 0.5 atmospheres and a total flow of ~ 15 vlpn during these studies, resulting in a residence time of ~ 5 s. The selected flow rate and pressure were chosen for optimal operation of the LCVI (see next section). Pressure was maintained using a critical orifice on the ambient pressure side and pumps on the low pressure side. The CFDC used in this study enhanced the size difference

between liquid aerosols and nucleated ice particles by transitioning conditions toward the ice-frost point over the last third of the processing time. Those particles that formed ice remained stable and did not decrease in size, whereas aqueous particles that had not activated as ice shrunk due to evaporation. Ice crystals formed within the chamber as well as aerosols that did not activate were counted and sized at the outlet using a Climet Model 7350A optical particle counter (OPC). This version of the CFDC instrument, previously used for airborne studies, has been described in detail previously (Rogers et al. 2001). One significant change in the CFDC instrument was made for the experiments described here. Previous studies occupied the temperature range -10 to -38°C and from ice saturation to 20% RH greater than water saturation. This temperature regime is warmer than the conditions required for the homogeneous freezing of purely liquid sulfate aerosols that form the majority of the particulate matter in the free troposphere (Chen et al. 2000; Murphy et al. 1998a). A primary goal of this project was to study a large portion of the cirrus formation regime, including both where a heterogeneous nuclei was required to initiate ice formation and where homogeneous freezing was possible. A new cooling system was installed to accommodate a lower limit of -65°C . Thus we were able to investigate heterogeneous ice nucleation at temperatures above -38°C as well as both heterogeneous and homogeneous freezing as low as 27° below this temperature.

LCVI

CVI have been used extensively on aircraft to separate large cloud particles—both ice and droplets—from unactivated background aerosols (Ogren et al. 1985). The operational principle is to counter an incoming aerosol flow with an opposing, low-velocity flow of warm, particle-free, dry gas so that only those particles with sufficient inertia efficiently transit the CVI, exiting as a sample flow. The rate of counterflow gas is used to set the inertial cutsize of particles desired for analysis. Particles smaller than this size have insufficient inertia to transit the stagnation zone and, unable to reach the sample flow, are pumped away. Sampled aerosols lose condensed-phase water as they exit the CVI due to high temperature and low relative humidity of the counterflow. Large particle concentrations can be enhanced by a factor proportional to the ratio of the incoming aerosol flow to the outgoing sample flow.

The design of the laboratory CVI used in these studies is detailed elsewhere (Murphy et al. 2002). Specific LCVI system pressure, aerosol, and sample flow were empirically determined for these studies in order to maximize supermicrome-

ter but minimize submicrometer aerosol transmission. A fritted bubbler was used to produce aerosols from a 30 weight percent (wt %) solution of ammonium nitrate ($\rho = 1.725 \text{ g/cm}^3$) dissolved in distilled water. The bubbler was operated at a pressure of 0.5 atmospheres and produced a distribution, observed using a Climet Model 208 PA, of particles up to $\sim 4.5 \mu\text{m}$ aerodynamic diameter. For an input aerosol flow of 10.0 vlp, 1.5 vlp counterflow, a sample flow of 1.0 vlp and pumping to a reservoir at 305 torr, the dashed-dotted distribution shown in Figure 2 was produced. For the given rates and pressures, enhancements in particle concentration up to a factor of 4 were observed for particles $>1.5 \mu\text{m}$ in size. Particles $<1.0 \mu\text{m}$ diameter were transmitted with an efficiency of <0.002 (i.e., $<0.02\%$ of the submicrometer particles exited the LCVI), where this value is an upper limit due in part to optical undersizing and misclassification of supermicrometer particles properly transmitted by the LCVI. The cut-size of $1.5 \mu\text{m}$ was set based on the observation that the CFDC grew ice crystals above $1.5 \mu\text{m}$ for the cyclone impactor cut-size used and the processing conditions in this study. In order to further facilitate transmission of

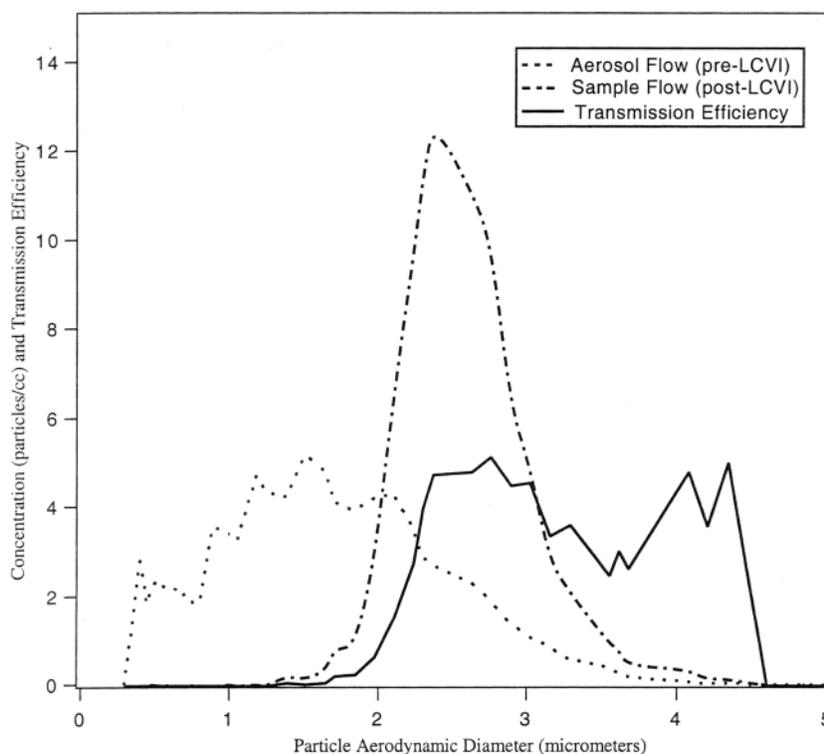


Figure 2. Transmission efficiency of the LCVI used in this work. The dashed line represents the concentration of particles, as a function of aerodynamic diameter, produced by a fritted bubbler. The bubbler contained 30 wt % NH_4NO_3 and the output was observed during a 60 s period using a Climet Model 208 particle analyzer. The dashed-dotted line represents the aerosol concentration after the LCVI as measured by the same instrument. Small particles had been removed and large aerosols enhanced (see text for explanation). The solid line indicates the transmission efficiency, where 1.0 is equivalent to 100% and greater values indicate enhancement of particles. Average transmission efficiency from ~ 2.5 to $4.5 \mu\text{m}$ was 4.0. The variability in this 60 s transmission curve is due to random changes in particle output by the bubbler. The upper limit of particle size is due to minimal production of aerosols larger than this size using this method and is not indicative of a reduction of transmission efficiency.

ice crystals, the region about the LCVI was actively cooled to $\sim 0^{\circ}\text{C}$ during these studies to minimize melting and evaporation before size selection. To our knowledge this was the first successful operation of a CVI in a laboratory.

PALMS

Ambient aerosols are drawn by vacuum into the NOAA PALMS instrument. Some fraction pass through a continuous Neodymium:Yttrium-Aluminum-Garnet (Nd:YAG) laser beam ($\lambda = 532\text{ nm}$). Scattered light from this beam is used to give a rough indication of particle size and to trigger an excimer laser ($\lambda = 193\text{ nm}$) that simultaneously ablates the aerosol and ionizes the material. A complete positive or negative mass spectrum from particles $0.3\text{--}3.0\ \mu\text{m}$ in diameter is produced using a TOF mass spectrometer. Specific details of this instrument have been previously published (Thomson et al. 2000).

IN are rare in the upper troposphere, with number concentrations ranging only from 10^{-4} to 0.1 cm^{-3} (Rogers et al. 1998). During these studies all supermicrometer particles were intentionally eliminated, including any that may have acted as IN. It is worth noting that Chen et al. (1998) found a mode size for heterogeneous IN at $0.2\ \mu\text{m}$ and suggested that the $0.1\text{--}1\ \mu\text{m}$ range contains most atmospheric IN. Unintentional particle losses through the inlet, cyclone, and experimental system were $\sim 30\%$. All these factors reduced the number density

of IN and therefore the data acquisition rate. The PALMS instrument operates using a capillary inlet to quickly draw particles into the instrument in order to minimize volatile component loss (Thomson et al. 2000). A transmission efficiency, defined as the probability that an ambient particle transits the PALMS inlet, is detected by the Nd:YAG and illuminated by the excimer laser, and ultimately produces a mass spectrum of 10^{-4} for submicrometer particles, typical using this inlet (Figure 3). For common free tropospheric number densities of $0.3\text{--}3.0\ \mu\text{m}$ diameter particles this has resulted in rapid data acquisition. For this study the combination of the low number density of ice-forming particles and system losses required more efficient transmission. One important improvement to the PALMS instrument was therefore made: an aerodynamic lens (AL), based on the design presented by Liu et al. (1995), was adapted to the PALMS instrument. Transmission studies were performed using polystyrene latex (PSL) spheres. As shown in Figure 3, an efficiency of 0.1 (i.e., 10% of 0.3 to $1.0\ \mu\text{m}$ incident particles produced a mass spectrum) was attained using the AL at a throughput of 0.3 vlpm at 0.5 atmospheres. Liu et al. (1995) showed that nonspherical particles were transmitted with a lower efficiency, due to lift force effects, than were spherical aerosols using this inlet. Transmission studies were not performed with nonspherical particles nor was shape factor or morphology monitored during these studies.

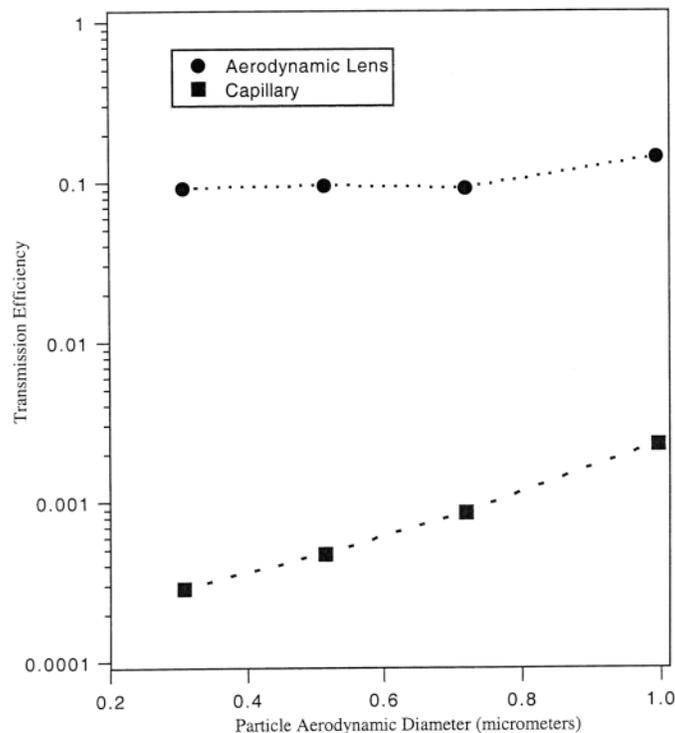


Figure 3. Transmission efficiency of particles through the PALMS instrument using a capillary inlet (squares) as a function of aerodynamic diameter using PSL spheres ($\rho = 1.05\text{ g/cm}^3$). Note that particles smaller than $0.3\ \mu\text{m}$ were not efficiently detected. An aerodynamic lens employed for these studies provided several orders of magnitude better transmission such that $\sim 10\%$ (a transmission efficiency of 0.1, see text for further details) of all particles were detected and analyzed (circles).

VALIDATION

Components listed in the schematic in Figure 1b were individually tested, but an important task was to verify that the composite method functioned as a whole. To validate the complete technique, laboratory studies were conducted under simulated atmospheric conditions, with a small fraction of IN mixed with particles known to be incapable of ice nucleation under the experimental conditions. The particle types were spectroscopically distinct so that they were not confused at the analysis stage.

Laboratory Validation

A well-known IN is silver iodide. AgI has a crystalline structure similar to that of water ice and, depending on how aerosols are produced, can efficiently nucleate this phase at temperatures below -5°C . Because of this property AgI is often used in atmospheric cloud seeding experiments. For laboratory studies, Vali et al. (1978) showed that submicrometer AgI particles can be produced by dissolving silver iodide in a concentrated ammonium iodide solution and then forcing precipitation by rapid addition of this mixture to distilled water.

Three distinct experiments were performed to validate the CFDC/LCVI/PALMS technique. First, ammonium nitrate, a particle type shown to be incapable of ice nucleation at experimental temperatures $> -30^{\circ}\text{C}$ (Cziczo and Abbatt 2001), was produced by passing dry N_2 through a fritted bubbler using a 30 wt % solution prepared from reagent grade solute and distilled water. A NOAA-designed differential mobility analyzer (DMA) was used to select aerosols of $0.4\ \mu\text{m}$ diameter. Particles were then passed through the combined instruments. The CFDC OPC verified that no large ice crystals were formed at a chamber temperature of -30°C . PALMS was operated with a LCVI counterflow to verify that no submicrometer aerosols were able to transit the system. Intermittently during the experiment the LCVI counterflow was intentionally shut off in order to allow transmission of all particles. The positive mass spectrum shown in Figure 4a was produced during one such event. The dominant peaks in this spectrum are fragments of the nitrate ion, specifically NO^+ and NO_2^+ . The ammonium cation is evident at mass 17 and 18. C^+ , possibly resulting from a small amount of organic material in the bubbler or sample lines, is also indicated.

The second validation experiment was performed by producing AgI particles from a solution prepared according to the Vali et al. (1978) method using a BGI Inc. 1-Jet collision nebulizer and selected at $0.4\ \mu\text{m}$ diameter using a DMA. AgI and NH_4I from reagent grade material and distilled water were used for aerosol production. The particles were passed through the combined system at a CFDC temperature of -30°C and the OPC verified that ice crystals were being formed. The LCVI was operated using the parameters detailed in the previous section and PALMS showed that particles were able to transit the combined system. A positive mass spectrum obtained under these conditions is shown in Figure 4b. The dominant high mass peaks are assigned to the isotopes of silver as well as this element complexed with iodine. The ammonium ion, used for AgI dissolu-

tion during preparation, is evident. The AgI impurities sodium, potassium, and iron were also observed. The distinct differences between the mass spectra of these 2 particle types precludes misidentification.

The final laboratory validation experiment was the simultaneous production of ammonium nitrate and silver iodide particles in a 4:1 number concentration ratio after DMA selection at $0.4\ \mu\text{m}$. This was done to test the ability to discriminate in situations where only a minor fraction of the aerosols nucleate ice. Similar studies to demonstrate the IN selectivity of the CFDC technique have been performed previously (Rogers 1994; Kreidenweis et al. 1998), but never with real-time validation of IN composition. At a CFDC temperature of -30°C only AgI particles were analyzed by the PALMS instrument during 10 h of experimentation as long as the saturation remained below 112% RH with respect to liquid water. During this time a concentration of $\sim 30\ \text{NH}_4\text{NO}_3$ particles cm^{-3} were present in the input flow to PALMS. At water vapor pressures higher than 112% RH, the OPC indicated that a few percent of the high number density NH_4NO_3 aerosols activated as droplets but did not evaporate to sizes below $1.5\ \mu\text{m}$ before exiting the CFDC. Under these loadings of large aerosols at extreme CFDC saturation conditions some ammonium nitrate spectra, identical to the one shown in Figure 4a, were obtained. This indicated that transit of large, dilute droplets was possible if a high CFDC humidity was set. The condition was evident when the median particle diameter, as indicated by the OPC, grew to supermicrometer size. This diagnostic was used to preclude experimentation under these conditions during field operation.

Field Validation

Upon completion of the laboratory validation experiments the combined CFDC/LCVI/PALMS system was deployed to the Desert Research Institute's Storm Peak Laboratory. This facility is located 10,560 ft (3220 m) above sea level on Mt. Werner near Steamboat Springs, Colorado (Borys et al. 1997). It was selected because it resides in free tropospheric air for long periods, confirmed by a low particle number density. Free tropospheric conditions were considered critical for attaining the major goal of the field deployment, which was to ensure sampling from aerosol populations representative of those on which cirrus clouds form. A comprehensive description of the results of this measurement campaign will be published separately.

A typical experiment was initiated by flowing dry, filtered air through the CFD chamber while operating at a stable, low relative humidity ($\sim 80\%$ wrt liquid water) and at a predetermined temperature between -35°C and -65°C . The PALMS instrument was used to sample ambient particles before connection to the CFDC/LCVI in order to characterize the chemical composition of the background aerosols for comparison to the subset that nucleated ice. Several thousand particles were typically analyzed before and after each experiment at both positive and negative polarities and from both the submicrometer and total ambient particle distribution (the cyclone impactor in-line and off-line,

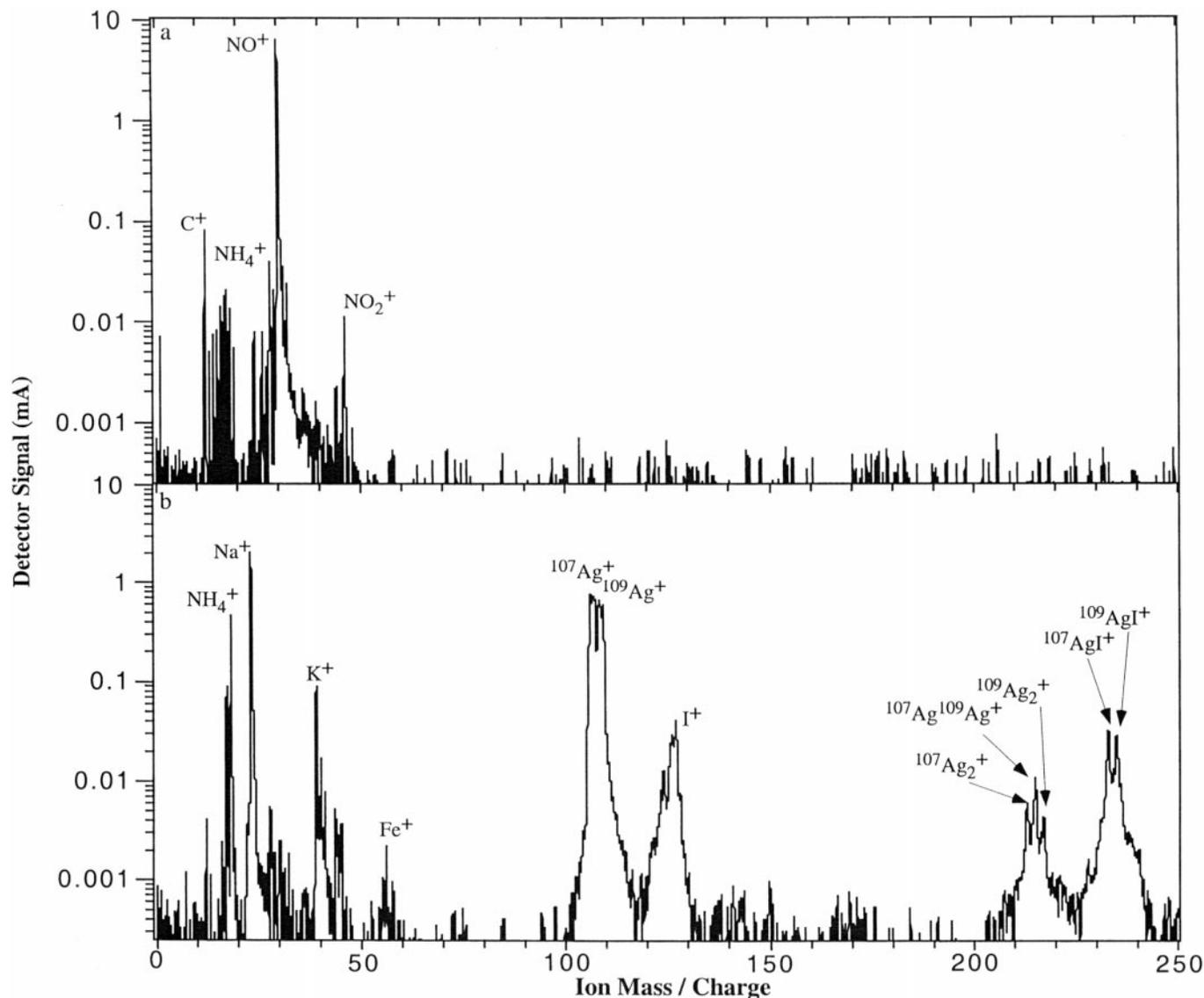


Figure 4. Positive spectrum of a $0.4\ \mu\text{m}$ diameter NH_4NO_3 particle analyzed using the PALMS instrument during a validation experiment with no LCVI counterflow such that all particles, regardless of size, were transmitted (a). Spectrum of a $0.4\ \mu\text{m}$ AgI particle that nucleated ice and grew to supermicrometer size in the CFD chamber and was transmitted through the LCVI with counterflow operating and was analyzed using the PALMS instrument (b). Notice the spectral differences between these particle types, especially the distinct silver isotopes at mass 107 and 109 in panel (b).

respectively). After the CFDC reached the selected experimental conditions and the background aerosol was characterized, the PALMS instrument was connected to the LCVI. All experimental flows and pressures were set for optimal formation and transmission of IN. At the beginning of, and sporadically throughout, experimentation the CFDC OPC was used to monitor the experimental flow while ambient particles were removed by a filter in order to verify that a minimal ice crystal signal was present under control conditions. Background concentrations of 1–2 ice crystals per liter were typical throughout these

studies and were probably due to frost material falling from the CFD chamber. Infrequent, but more intense, frost events produced particles that were detected and analyzed by the PALMS instrument. The residue of these particles was almost exclusively copper, aluminum, and iron, probably from the CFDC walls or due to frost particle impaction followed by liberation of material within the OPC or LCVI. Due to the unambiguous mass spectral characteristics of the contaminant particles, they were eliminated from the set of spectra analyzed during the field studies.

After a background count was obtained, unfiltered ambient air from the cyclone impactor was passed through the system. The CFDC relative humidity was slowly raised from $\sim 80\%$ toward water saturation through a region where only effective IN formed crystals. This was termed the “heterogeneous nucleation regime” and is evident in Figure 5 for an experiment performed at -50°C . The region was typified by a relatively constant number of IN, typically a few to 100 per liter. The transition from ice formation by efficient IN to nucleation by a large fraction of the background aerosol took place as water saturation was approached. In the case of the experiment shown in Figure 5, the “transition region” began at $\sim 96.5\%$ RH and was indicated by a dramatic increase in crystal concentration detected at the OPC. This rapid increase in ice number density is consistent with the onset of homogeneous freezing of a large fraction of the aqueous sulfate particles that formed the majority of the background aerosol load during these studies. We therefore re-

fer to this region as the “homogeneous nucleation regime.” It should be noted that we cannot definitively determine the mechanism that led to ice formation on a per particle basis. This is because most atmospheric particles are complex internal mixtures of soluble and insoluble components and it is impossible to know with certainty where ice nucleation occurred.

Two points are indicated along the ice crystal concentration line in Figure 5. These correspond to particles analyzed by the PALMS instrument at the given experimental conditions and which were typical of these regimes. Corresponding mass spectra are shown in Figure 6. Specifically, Figure 6a is used to show the mass spectrum of a particle analyzed at -50°C and $\sim 95.5\%$ RH at which a concentration of ~ 10 IN per liter was present. This positive spectrum is dominated by peaks at mass 28 and 44, which are attributed to Si^+ and SiO^+ because of the intensity of the peaks and the presence of both features. Organic material is indicated by the C^+ peak at mass 12. This type of particle is

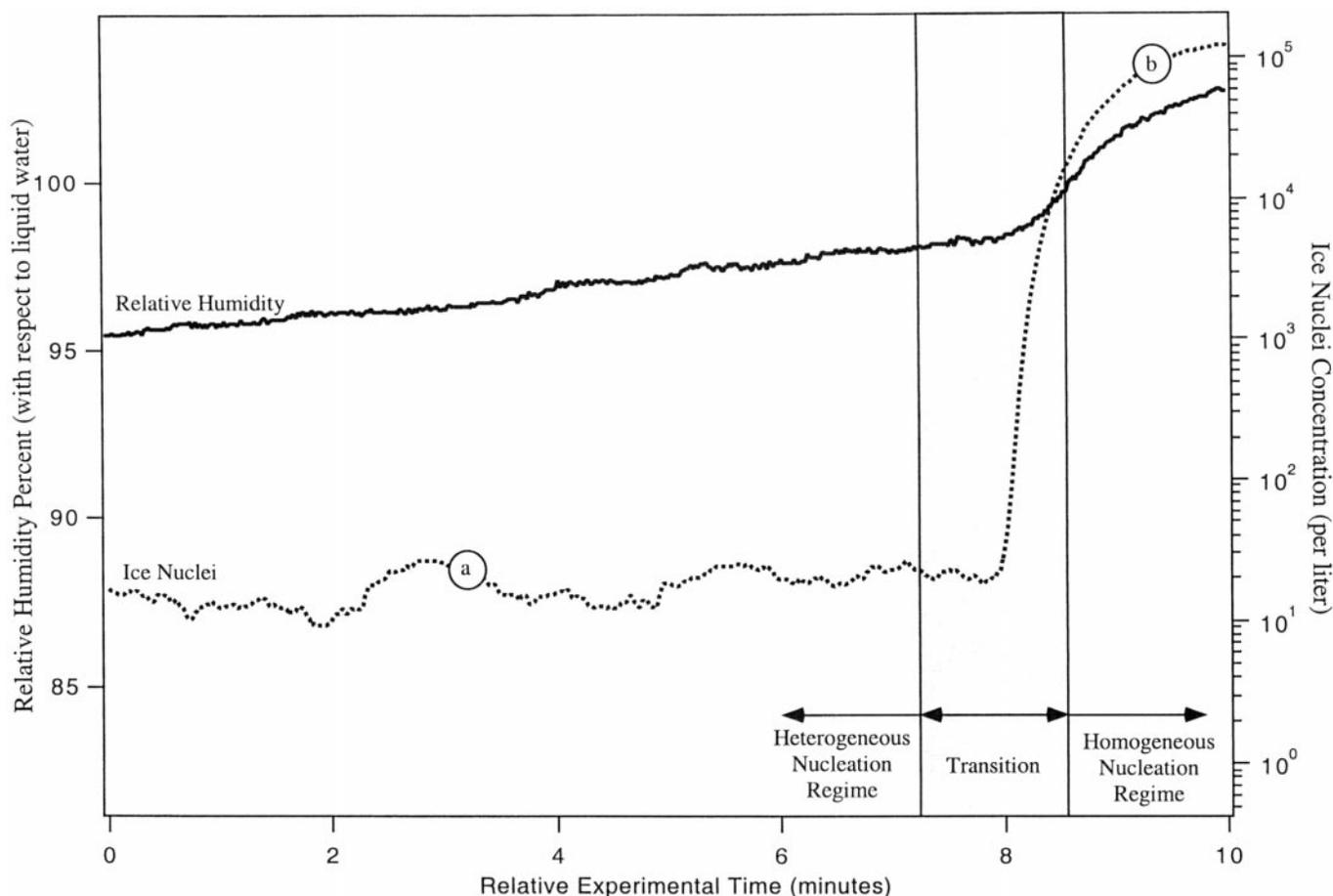


Figure 5. Ice nucleus concentration as a function of time detected by the CFDC optical particle counter during an experiment performed at -50°C . Relative humidity was slowly raised and ice crystal concentration remained steady at ~ 10 per liter until several orders of magnitude more particles (i.e., a significant fraction of the background aerosol) began to nucleate this phase starting at $\sim 96.5\%$ RH. Points (a) and (b) denote spectra, shown in Figure 6, typical of the low and high ice crystal concentration regimes, respectively.

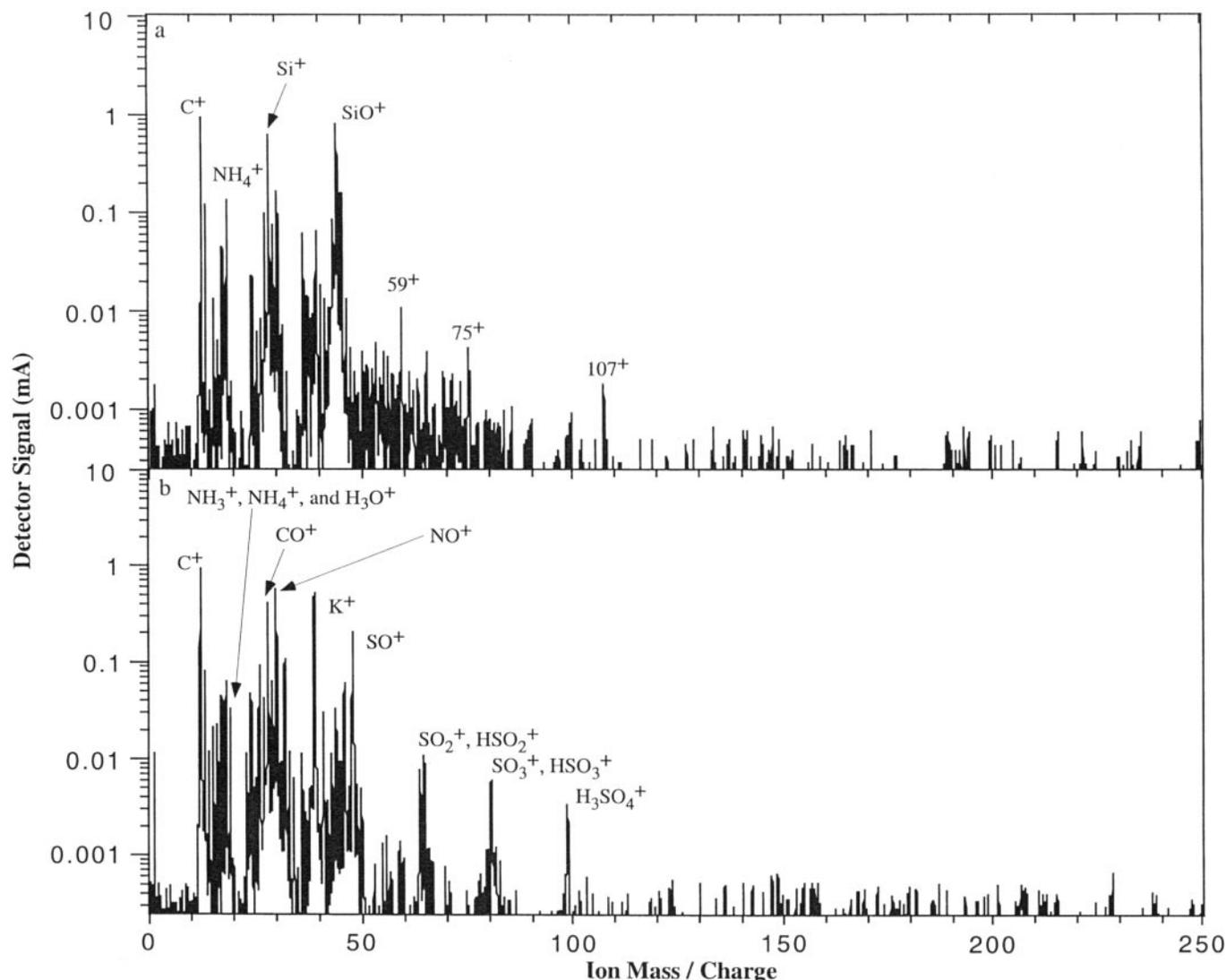


Figure 6. Positive spectrum of an aerosol that nucleated ice at -50°C and 95.5% RH (i.e., ~ 10 ice crystals per liter) where the dominant mass peaks correspond to Si^{+} and SiO^{+} (a). Spectrum typical of particles acquired when a significant fraction of the background aerosol was nucleating ice, in this case at -50°C and 101.5% RH (b). The dominant mass peaks are sulfate fragments. K^{+} , possibly indicating sulfate condensation on a small biomass burning fragment, is evident. Organic material is present and ammonium ions indicate that the sulfate was neutralized to some extent.

probably either of crustal or fly ash origin and has been observed using the PALMS instrument previously (Lee et al. 2002). This spectrum was typical of aerosols that nucleated ice in the heterogeneous freezing regime but is representative of $<1\%$ of the particles analyzed in the background distribution of aerosol by the PALMS instrument during the course of the field studies. Unlike the vast majority of atmospheric aerosols sampled during these studies ($\sim 90\%$), there is no indication of sulfate on this particle.

Figure 6b shows the positive mass spectrum of an aerosol analyzed at the same experimental temperature but a relative humidity of 101.5% (i.e., in the homogeneous nucleation regime). This spectrum is dominated by several fragments of the sulfate

ion as well as some amount of organic material in the form of C^{+} and CO^{+} . CO^{+} and Si^{+} ions share a common mass and can contribute to the same peak (Murphy et al. 1998a). The lack of a clear SiO^{+} feature in Figure 6b is the basis for our peak assignment of CO^{+} in this case. The sulfate in this particle was neutralized, to some extent, by the ammonium ion indicated at mass 17 and 18. The peak at mass 39 indicates the presence of potassium, which may have been the result of a small, insoluble biomass burning inclusion in a predominantly sulfate particle. This aerosol type dominated the background distribution, corresponding to $\sim 80\%$ of the submicrometer particles in the air mass on the day of this experiment.

Limitations and Uncertainties

There are several noteworthy limitations of the CFDC/LCVI/PALMS technique. First, mass spectra produced by single particle instruments, such as PALMS, provide qualitative data except in the case of aerosols that can be extensively studied in the laboratory (Thomson et al. 1997). The principle reason is that common aerosol components can have considerably different laser ionization potentials such that different signals are created by identical concentrations (Thomson et al. 1997). Difficult to ionize substances may not be apparent in a mass spectrum, whereas another component, present at the same concentration, can represent the dominant peak. The phase and matrix of an aerosol can also affect the ablation and ionization process so that an identical abundance of a substance can create different signals depending on the particle. For these reasons the data presented here offer a qualitative, not quantitative, understanding of IN composition.

Second, an undetermined fraction of the IN that existed in the background atmosphere during experimentation was eliminated from these studies both intentionally and unintentionally. The need to inertially separate ice crystals from unactivated aerosols required that all supermicrometer particles be eliminated before experimentation. Although Chen et al. (1998) found that most atmospheric IN are submicrometer in diameter, the requirement that all supermicrometer aerosols be removed doubtless resulted in a loss of some IN. Unintentional aerosol loss through the system, including potential IN, was $\sim 30\%$, a value derived from the difference of the concentration of particles at the cyclone inlet and LCVI outlet using a Climet Model 208 PA.

Finally, the PALMS instrument had a lower particle size detection limit of $\sim 0.3 \mu\text{m}$ diameter during these studies. Any IN that were smaller than this size would have induced ice formation in the CFDC and been transmitted through the LCVI. The particles, however, would not have been detected in the PALMS instrument due to insufficient light scattering from the Nd:YAG laser beam. It is our intention to quantify these losses by analyzing the IN size distribution using TEM/EDX during future studies.

SUMMARY AND DISCUSSION

We have shown that the combined CFDC/LCVI/PALMS instrument represents a viable technique for the real-time in situ analysis of aerosols that nucleate ice in the atmosphere. Supermicrometer ambient aerosols were removed from the sample flow using a cyclone impactor so that they were not confused with ice crystals formed in the CSU CFDC instrument. A NOAA-designed laboratory counterflow virtual impactor was used to separate and enhance the crystals before condensed phase water was removed in a flow designated for single particle analysis. The PALMS instrument provided complete positive or negative mass spectra of approximately 10% of the IN $0.3\text{--}1.0 \mu\text{m}$ in diameter by using an aerodynamic lens for improved particle detection.

The method presented here will improve our ability to understand the climatic effects of high altitude cirrus clouds for 3 reasons. First, the CFDC instrument is capable of creating conditions similar to those that induce the formation of cirrus clouds in the atmosphere. This is important because ice particles that form and are sampled in the atmosphere may have undergone gas-phase and particle scavenging events prior to measurement. Such events would reduce the certainty of what specific material initiated ice formation. In addition, the CFDC instrument is able to scan across a wide range of temperatures and relative humidities, providing a transition through regimes that are dominated by different ice nucleation mechanisms. Second, the PALMS instrument is able to provide information about volatile and semivolatile as well as refractory components of particles. Almost all previous studies of IN composition used vacuum techniques that eliminated nonrefractory species. Third, particle analysis using this technique is completed in situ and in real time, whereas previous studies required complex and time-consuming laboratory analyses with the possibility of sample contamination during transport and handling.

REFERENCES

- Borys, R. D., and Wetzel, M. A. (1997). Storm Peak Laboratory: A Research, Teaching and Service Facility for the Atmospheric Sciences, *Bulletin. Amer. Meteorol. Soc.* 78:2115–2123.
- Chen, Y., DeMott, P. J., Kreidenweis, S. M., Rogers, D. C., and Sherman, D. E. (2000). Ice Formation in Sulfate and Sulfuric Acid Aerosol Particles Under Upper Tropospheric Conditions, *J. Atmos. Sci.* 57:3752–3766.
- Chen, Y., Kreidenweis, S. M., McInnes, L. M., Rogers, D. C., and DeMott, P. J. (1998). Single Particle Analyses of Ice Nucleating Aerosols in the Upper Troposphere and Lower Stratosphere, *Geophys. Res. Lett.* 25:1391–1394.
- Cziczo, D. J., and Abbatt, J. P. D. (2001). Ice Nucleation in NH_4HSO_4 , NH_4NO_3 , and H_2SO_4 Aqueous Particles: Implications for Cirrus Cloud Formation, *Geophys. Res. Lett.* 28:963–966.
- Heintzenberg, J., Okada, K., and Strom, J. (1996). On the Composition of Non-Volatile Material in Upper Tropospheric Aerosols and Cirrus Crystals, *Atmos. Res.* 41:81–88.
- Houghton, J. T., Ding, Y., Griggs, D. J., Noguera, M., van der Linden, P. J., Dai, X., Maskell, K., and Johnson, C. A. (eds) (2001). *Intergovernment Panel on Climate Change, Climate Change 2001. The Scientific Basis*. Cambridge University, Cambridge, pp. 291–335.
- Kreidenweis, S. M., Chen, Y., Rogers, D. C., and DeMott, P. J. (1998). Isolating and Identifying Atmospheric Ice-Nucleating Aerosols: A New Technique, *Atmos. Res.* 46:263–278.
- Kumai, M. (1961). Snow-Crystals and the Identification of the Nuclei in the Northern United States of America, *J. Meteorol.* 18:139–150.
- Lee, S. H., Murphy, D. M., Thomson, D. S., and Middlebrook, A. M. (2002). Chemical Components of Single Particles Measured with Particle Analysis by Laser Mass Spectrometry (PALMS) during the Atlanta SuperSite Project: Focus on Organic/Sulfate, Lead, Soot, and Mineral Particles, *J. Geophys. Res.* 107(AAC1):1–13.
- Liu, P., Ziemann, P. J., Kittelson, D. B., and McMurry, P. H. (1995). Generating Particle Beams of Controlled Dimensions and Divergence: II. Experimental Evaluation of Particle Motion in Aerodynamic Lenses and Nozzle Expansions, *Aerosol Sci. Technol.* 22:314–324.
- Middlebrook, A. M., et al. (2002). A Comparison of Particle Mass Spectrometers during the 1999 Atlanta Supersites Project, *J. Geophys. Res.*, in press.
- Murphy, D. M., and Thomson, D. S. (1997). Chemical Composition of Single Aerosol Particles at Idaho Hill: Negative Ion Measurements, *J. Geophys. Res.* 102:6353–6368.

- Murphy, D. M., Thomson, D. S., and Mahoney, M. J. (1998a). In Situ Measurements of Organics, Meteoritic Material, Mercury, and Other Elements in Aerosols at 5 to 19 Kilometers, *Science* 282:1664–1669.
- Murphy, D. M., Thomson, D. S., Middlebrook, A. M., and Schein, M. E. (1998b). In Situ Single-Particle Characterization at Cape Grim, *J. Geophys. Res.* 103:16,485–16,491.
- Murphy, D. M., et al. (2002). Design of a Laboratory Counterflow Virtual Impactor, *Aerosol Sci. Technol.*, in preparation.
- Ogren, J. A., Heintzenberg, J., and Charlson, R. J. (1985). In-Situ Sampling of Clouds with a Droplet to Aerosol Converter, *Geophys. Res. Lett.* 12:121–124.
- Parungo, F. P., Ackerman, E., and Proulx, H. (1976). Natural Ice Nuclei, *J. Rech. Atmos.* 10:45–60.
- Petzold, A., Strom, J., Ohlsson, S., and Schroder, F. P. (1998). Elemental Composition and Morphology of Ice-Crystal Residual Particles in Cirrus Clouds and Contrails, *Atmos. Res.* 49:21–34.
- Pruppacher, H. R., and Klett, J. D. (1998). *Microphysics of Clouds and Precipitation*, 2nd ed., Kluwer Academic Publishers, Netherlands, pp. 205–211.
- Rogers, D. C. (1994). Detecting Ice Nuclei with a Continuous-Flow Diffusion Chamber—Some Exploratory Tests of Instrument Response, *J. Atmos. Oceanic Technol.* 11:1042–1047.
- Rogers, D. C., DeMott, P. J., Kreidenweis, S. M., and Chen, Y. (1998). Measurements of Ice Nucleating Aerosols during SUCCESS, *Geophys. Res. Lett.* 25:1383–1386.
- Rogers, D. C., DeMott P. J., Kreidenweis, S. M., and Chen, Y. (2001). A Continuous-Flow Diffusion Chamber for Airborne Measurements of Ice Nuclei, *J. Atmos. Oceanic Technol.* 18:725–741.
- Tenberken-Potzsch, B., Schwikowski, M., and Gaggeler, H. W. (2000). A Method to Sample and Separate Ice Crystals and Supercooled Cloud Droplets in Mixed Phased Clouds for Subsequent Chemical Analysis, *Atmos. Environ.* 34:3629–3633.
- Thomson, D. S., Middlebrook, A. M., and Murphy, D. M. (1997). Thresholds for Laser-Induced Ion Formation from Aerosols in a Vacuum using Ultraviolet and Vacuum-Ultraviolet Laser Wavelengths, *Aerosol Sci. Technol.* 26:544–559.
- Thomson, D. S., Schein, M. E., and Murphy, D. M. (2000). Particle Analysis by Laser Mass Spectrometry WB-57F Instrument Overview, *Aerosol Sci. Technol.* 33:153–169.
- Vali, G., Rogers, D. C., Gordon, D., Saunders, C. P. R., Reischel, M., and Black, R. (1978). Aerosol and Nucleation Research in Support of NASA Cloud Physics Experiments in Space, *NASA Final Report*, pp. 1–86.