P4.6 SOME AEROSOL EFFECTS ON CIRRUS ICE FORMATION

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1. INTRODUCTION

This study reports on laboratory measurements to investigate homogeneous and heterogeneous ice nucleation involving various aerosol particle types in the environmental regime of cirrus clouds. The motivation for such studies is to determine the role of different natural and manmade aerosols in affecting cirrus microphysical properties and thereby potentially altering the radiative characteristics of cirrus. Current estimates of aerosol effects on radiative forcing of the climate system (Intergovernmental Panel on Climate Change 2001) do not yet consider the effects of aerosol changes on cirrus. These aerosol effects are certainly quite different than they are in warm, low altitude clouds. Numerical model studies have made clear that cirrus microphysics may be much less sensitive to aerosol particle increases than are warm clouds, but that this conclusion depends strongly on assumptions of the predominant nucleation mechanism for cirrus formation (DeMott et al., 1997; Jensen et al. 2001, Lin et al. 2002). The predominant ice formation mechanism could be homogeneous, involving soluble particles that deliquesce and dilute as relative humidity rises during lifting, or heterogeneous involving insoluble aerosol components. Which mechanism dominates depends both on the types of aerosols reaching cirrus altitudes and on the forcing dynamics of the clouds. Recent studies, including some summarized in this paper, have placed constraints on the effect of soluble aerosol composition on homogeneous freezing nucleation rates. These results make it difficult to explain the full range of observed conditions of cirrus formation (DeMott 2002), a point that will be reinforced in this paper.

There has been limited information published on the composition of natural ice nuclei (IN) in the upper troposphere. The primary information has come from studies of cirrus ice crystal residuals (Heintzenberg et al., 1996; Petzold et al., 1998) and from collections of IN from ambient air activated in a diffusion chamber (Chen et al. 1998). These studies clearly indicated the presence of refractory aerosols at cirrus levels that might act as heterogeneous nuclei for cirrus formation. However, Chen et al. did not reproduce cirrus conditions at temperatures below -40°C to validate the role of IN there. Some studies have correlated the presence of carbonaceous material from aircraft with ice crystal concentrations in cirrus clouds (Strom and Ohlson, 1998). However, insoluble aerosols may also enter cirrus crystals by scavenging processes.

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One approach to resolving the role of different aerosols in forming cirrus is to investigate in the laboratory the nucleation behavior, at the appropriate conditions, of particle types detected in the upper troposphere. An important aspect is to do such studies with aerosols of the most relevant sizes for the atmosphere. This paper describes the generation, physical and chemical characterization, and measurement of ice nucleation characteristics of such aerosols. The key measurements of ice nucleation are made using the continuous flow diffusion chamber technique (Rogers et al. 2001). To minimize the need for an exhaustive "survey" of all types of atmospheric aerosols in the laboratory, related new studies are being done to measure the activation conditions and compositions of atmospheric IN. Some of these new studies are reported elsewhere in this volume (DeMott et al. 2002).

2. METHODS

The approach used in this study includes development of methods for generating surrogate atmospheric aerosols, methods for characterizing their physical, chemical and hygroscopic properties, and methods for measuring their effects on ice nucleation. The ice nucleation device is first described.

Measurements of ice nucleation in this study use a continuous flow diffusion chamber (CFDC) operating at temperatures from -40 to –65°C. The CFDC processing device used in this study is described by Chen et al. (2000) and mimics many of the features of the airborne device described by Rogers et al. (2001). In this diffusion chamber, airflow is directed vertically between two concentric ice-coated cylinders held at different temperatures, creating an ice-supersaturated zone in the annular region. The sample air containing aerosol particles, representing 10% of the total flow, is focused between two particle-free flows of air in order to define processing conditions. Residence time is sufficient to grow activated ice particles to sizes greater than a few microns so that they may be optically detected as distinct from aerosol particles, even if the aerosol particles grow by water uptake. Additional details on this instrument are given at http://lamar.colostate.edu/~pdemott/cfdc/cfdc.html.

The continuous flow nature of the ice nucleation device necessitates the use of methods for continuous aerosol generation. Continuous aerosol generation systems have been constructed to produce surrogate upper tropospheric particles having various relevant compositions. These include:

1) Pure sulfates of varied neutrality have been generated (Chen et al. 2000) by atomizing solutions (ammonium sulfate and ammonium bisulfate) and drying the particles, and by a vapor condensation method (sulfuric acid). A differential mobility analyzer (DMA) is used to select particles at sizes from 20 to 200 nm. Sulfates are a dominant component of the background upper tropospheric aerosol (e.g., Murphy et al. 1998) and can serve as haze particles for homogeneous freezing.

2) Pure organic aerosols from the dicarboxylic acid series have been generated by solution atomization and drying (Prenni et al. 2001). Particles with diameters of 50 and 100 nm have been used in experiments. These particles were selected to represent a particular class of (natural and anthropogenically produced) atmospheric organics possessing a range of solubilities. Atmospheric observations (e.g., Murphy et al. 1998) suggest that organics sometimes contribute as strongly as sulfates to the composition of single particles in the upper troposphere and lower stratosphere.

3) Mixed solute particles (50 to 200 nm) composed of mixtures of sulfates and nitrates or mixtures of sulfates and organic species have been generated by solution atomization and drying. These particles are intended to represent the more typical atmospheric solute particle and to explore the effect of mixed compositions on the conditions of homogeneous freezing.

4) Black carbon particles have been produced at sizes from 50 to 700 nm using agitation (DeMott et al. 1999) and solution atomization/drying processes. These particles represent primary carbonaceous aerosols produced by combustion processes. These could be important as heterogeneous ice nuclei. Since these particles may be coated with condensed sulfates in the atmosphere, systems for coating these particles with sulfuric acid have been used.

5) Aerosols produced from the combustion of jet fuel have been simulated using a laboratory combustion generator. These particles could be important as heterogeneous IN in cirrus due to their concentrated injection at cirrus altitudes. Particles were selected using a DMA at size appropriate for aircraft-produced particles.

7) Pure dust-like particles (metal oxides) have been generated using the spray pyrolysis methods of Martin et al. (2000). Sizes from 50 to 500 nm are considered in ice nucleation studies. Mixed dust/sulfate particles have been studied using a linear temperature gradient tube furnace to coat flowing particles with sulfuric acid.

In order to understand the relation of aerosol particle water mass, and thus particle composition, to ice nucleation results, water uptake measurements have been conducted on most of the particle types. These measurements of water activity have included measurements of CCN supersaturation spectra and measurements of hygroscopic growth using a humidified tandem differential mobility analyzer (HTDMA). The CCN counter is a static thermal gradient diffusion chamber (DeMott et al. 1999). The CCN critical supersaturation determined for mixed particles is used with Köhler theory to determine the soluble content of coated particles used in ice nucleation experiments. An example is given for iron oxide (hematite) particles in Figure 1. The HTDMA system has been described by Prenni et al. (2001). This method used two DMA's to measure the hygroscopic growth of size-selected particles as a function of their exposure to relative humidity between 5 and 95%.

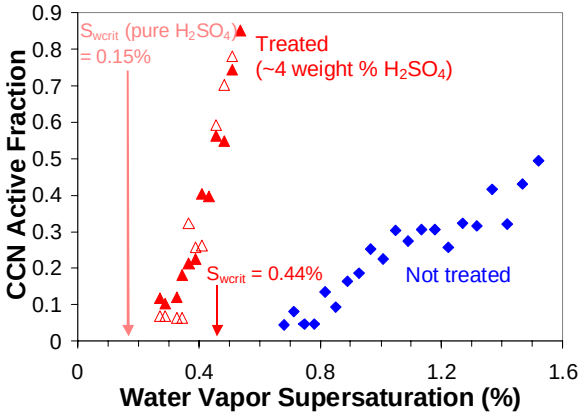

Figure 1. The effect of sulfuric acid coatings, produced by H_2SO_4 vapor condensation, on the CCN critical supersaturation of 100 nm diameter hematite particles (produced by spray pyrolysis). These measurements were used to infer the noted soluble content of test aerosols. The critical supersaturation of a pure 100 nm sulfuric acid droplet is indicated for reference.

3. RESULTS

The results of this study will be presented in poster form during the conference. Selected results are given here.

Results on the homogeneous freezing conditions of pure sulfate particles were given by Chen et al. (2000). These indicated no significant difference in the homogeneous ice formation rate as a function of relative humidity for liquid sulfate aerosols of different neutrality. Alternately, the homogeneous freezing point depression coefficient (DeMott 2002) did not depend on the degree of ammoniation. The homogeneous freezing conditions of H_2SO_4 and $(NH_4)_2SO_4$ aerosol particles are shown in Figure 2.

Figure 2 also summarizes some of the results on pure organic aerosol freezing from Prenni et al. (2001) and a recent experiment on the conditions of ice formation in organic/sulfate solution droplets. Prenni et

al. demonstrated that some dicarboxylic acids inhibit both water uptake at higher relative humidities and solute crystallization at lower relative humidities. The generally lower water uptake compared to sulfates leads to inhibition of ice formation at low temperatures. Consequently, higher ice relative humidities are required to initiate homogeneous freezing in slightly soluble pure organic aerosols, as shown in Figure 2. When such organics acids are mixed with sulfates in particles in certain mass ratios, the effects on solute crystallization, water uptake and ice nucleation are transferred to the mixed aerosol particle. Thus, sulfate/oxalic acid particles with a 10:1 mass ratio of the individual components were found to retain a liquid phase state to relative humidities below the crystallization RH of ammonium sulfate. Such particles will then take up water continuously as RH rises in a lifting process (i.e., there is no deliquescence limitation). However, the effect of the organic acid on water uptake by the particles appears to inhibit their homogeneous freezing, as indicated by the requirement of water saturation for ice nucleation in the mixed particles.

Various studies of heterogeneous ice formation at cirrus conditions are underway. Figure 3 shows that carbonaceous and metal oxide aerosols do not require soluble coatings to activate ice formation. Such refractory aerosol particles are sometimes found in the atmosphere without significant sulfate or condensed components, especially away from urban areas. These particles are hydrophobic, showing poor CCN activity and virtually no water uptake as measured by the HTDMA system. Nevertheless, some form of surface nucleation of ice is initiated on these particles at conditions that make this nucleation process competitive with the conditions under which pure sulfates are found to homogeneously freeze. Nevertheless, these ice activation conditions cannot explain the conditions under which some cirrus clouds are known to form (Heymsfield and Miloshevich, 1995).

DeMott et al. (1999) have shown that coating black carbon particles with sulfuric acid does not necessarily lead to heterogeneous condensation freezing under less stringent conditions than those where the diluted solute should freeze homogeneously. Only larger black carbon aerosols nucleated ice when coated with sufficient sulfuric acid. These results are reproduced in Figure 4, along with other experiments on black carbon containing particles from the combustion of jet fuel. The smaller aerosols, which were 10% soluble based on CCN measurements, did not indicate heterogeneous ice nucleation activity. Instead, approximate water saturation conditions were required for ice formation. These latter results were found consistent with experiments, not shown here, on size-selected acid and sulfate coated black carbon particles.

Ice nucleation studies of mixed particles are continuing and additional results will be presented at the conference.

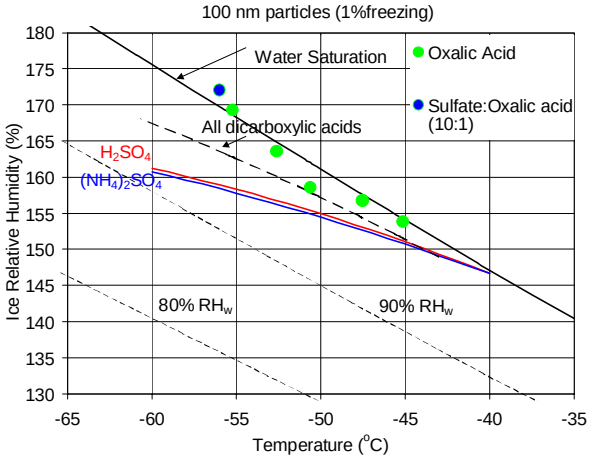

Figure 2. Summary of CFDC ice formation conditions (temperature versus ice relative humidity) for sulfates (Chen et al. 2000), dicarboxylic acids (Prenni et al. 2001) and a recent experiment using mixed sulfate-organic aerosol particles. RH_w is the relative humidity with respect to water. Ice nucleation results are for 100 nm (dry size at 1% RH_w) particles and the conditions plotted are where 1% of the particles were observed to freeze.

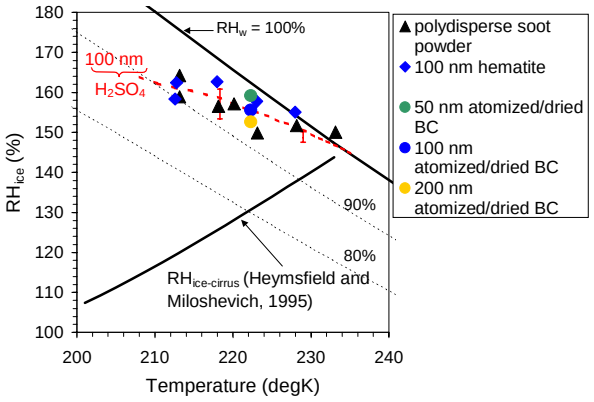

Figure 3. Heterogeneous ice nucleation conditions (RH_{ice} versus temperature) of various pure insoluble particle types (see legend). RH_w conditions are shown by dashed curves. BC indicates black carbon particles. The conditions for homogeneous freezing of 100 nm sulfuric acid aerosols (generated at 1% RH_w) are shown for comparison. The curve labeled $RH_{ice\text{-}cirrus}$ is based on observations of cirrus formation conditions by Heymsfield and Miloshevich (1995).

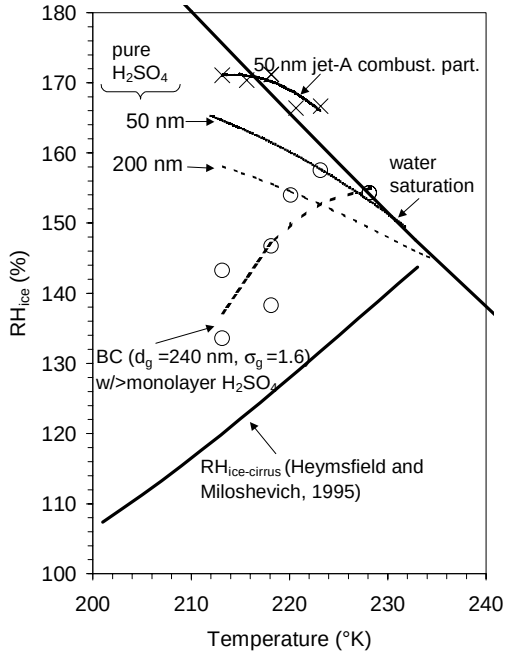

Figure 4. Conditions for the formation of ice on 1% of soluble-component containing carbonaceous aerosol particles. Certain larger black carbon aerosol particles were found to act as heterogeneous freezing nuclei when coated with sufficient amounts of sulfuric acid (BC curve in figure, from DeMott et al. 1999). In contrast, small carbon-containing but partially soluble aerosols from combustion of jet fuel did not show significant heterogeneous ice nucleation activity.

4. CONCLUSIONS

Continuing studies are elucidating the varied effects of different surrogate atmospheric particles on the formation conditions of ice in the cirrus cloud regime. This information should be of utility for focusing atmospheric studies and for developing numerical model formulations to investigate scenarios of aerosol effects on cirrus clouds.

5. ACKNOWLEDGMENTS

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