PHYSICAL AND CHEMICAL IMPACTS ON THE ICE NUCLEATING PROPERTIES OF ATMOSPHERIC PARTICLES

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1. INTRODUCTION[1.]

Nucleation of ice particles in the atmosphere occurs by homogeneous freezing of liquid particles and by heterogeneous nucleation due to the action of insoluble ice nuclei (IN). Homogeneous freezing herein refers to spontaneous ice embryo formation within either dilute droplets or concentrated solutions at temperatures below about -36°C. Heterogeneous nucleation can occur via multiple ice formation mechanisms at all temperatures below 0°C, given a sufficiently effective ice nucleus. These two fundamental ice nucleation processes interact directly in the cirrus cloud regime. This particular regime provides the focus for much of the work reported in this paper, but the methodologies applied are currently being extended to cover all mixed phase (ice present with liquid) clouds.

Understanding the range of temperature and relative humidity conditions that can support cirrus cloud formation in the presence of diverse types of aerosol particles present in the atmosphere is critical to an assessment of the effects of these cold clouds on climate (e.g., Kärcher and Lohmann 2003). While some atmospheric measurements have been made to infer the activation conditions for homogeneous freezing and the presence or absence of heterogeneous nuclei around cirrus clouds (Haag et al. 2003), few direct measurements of these nuclei as functions of temperature and ice supersaturation exist.

Measurements of the concentrations and compositions of total aerosol particles and those active in homogeneous and heterogeneous ice formation processes are being made to investigate natural and anthropogenic influences on ice nuclei populations throughout the range of conditions relevant for tropospheric clouds. These studies are conducted for particles in free tropospheric air, as sampled from a mountaintop location (Storm Peak Laboratory, 3220 m MSL) in the western United States. Focused laboratory studies are also underway. Results from ambient particle measurements during three weeks in autumn (November 2001) are reviewed in this paper. New measurements in April to May of 2004 will further explore apparent influences of organic species on ice formation processes and the important roles of aerosol size distribution and mineral dust concentrations in determining the concentrations and activation conditions of heterogeneous ice nuclei. Preliminary new results will be presented at conference time.

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2. EXPERIMENTAL METHODS

The key experimental methods used in sampling natural aerosol particles effective in forming ice are shown in Figure 1 and are described further by Cziczo et al. (2003) and DeMott et al. (2003). Ice nuclei compositions are determined by processing submicron particles for selected cloud formation conditions in a continuous flow ice thermal diffusion chamber (CFDC), separating nucleated ice crystals from the flow using a laboratory counterflow virtual impactor (LCVI), and performing compositional analyses of individual evaporated residual nuclei by mass spectroscopy (PALMS instrument) and transmission electron microscopy (TEM).

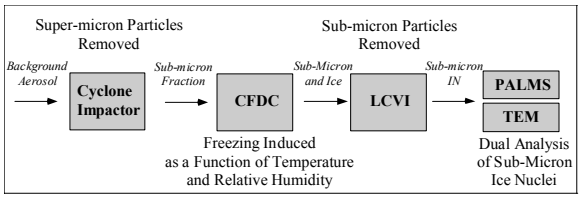

Figure 1 Experimental methods used during aerosol particle sampling in November 2001, as described in the text.

The CFDC instrument determines the concentration of aerosol particles that nucleate ice as functions of temperature and relative humidity. The Particle Analysis by Laser Mass Spectrometry (PALMS) instrument obtains complete positive or negative ion mass spectrum of the residual nuclei after laser ablation.

3. RESULTS

Key results from the first study have been reported by DeMott et al. (2003). Information was gained

concerning the onset conditions for homogeneous freezing on background particles, the apparent influence of particle chemistry on this phase transition, the concentrations of heterogeneous IN present at low temperatures in free tropospheric air, and factors influencing heterogeneous IN concentrations.

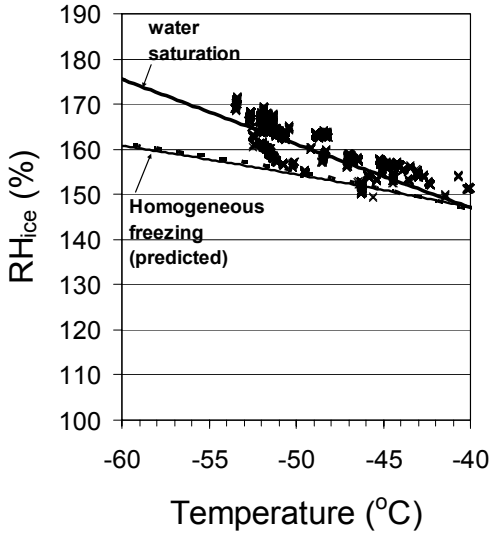

Figure 2 Approximate onset ice relative humidity (RH_{ice}) versus temperature conditions for apparent homogeneous freezing observed for natural aerosol particles in the CFDC. The data shown span a range of freezing conditions representing 0.05 to 1 % of all ambient particles above 100 nm freezing (ice particle concentrations from 0.125 to 5 cm^{-3} represented). The expected conditions for homogeneously freezing 1% of 100 nm pure ammonium sulfate particles based on Koop et al. (2000) and Chen et al. (2000) are shown as dashed and thin solid lines, respectively.

3.1 Homogeneous freezing by natural aerosol particles

Examples of time series of experimental data are given elsewhere (Cziczo et al. 2003; DeMott et al. (2003). These demonstrate the transition from relatively small numbers of particles nucleating as IN at lower relative humidity to homogeneous freezing of soluble and partially soluble particles as water saturation is approached and exceeded. These data were used to construct Figure 2, which shows the onset conditions (as defined in the figure caption) required for homogeneous freezing of ambient particles. The major findings are that the lowest onset ice relative humidity (RH_{ice}) versus temperature for activating homogeneous freezing is in good agreement with some laboratory studies of sulfate particle freezing. Nevertheless, as pointed out by DeMott et al. (2003), much higher RH_{ice} is sometimes required and this appears associated with the presence of organic species in aerosol particles.

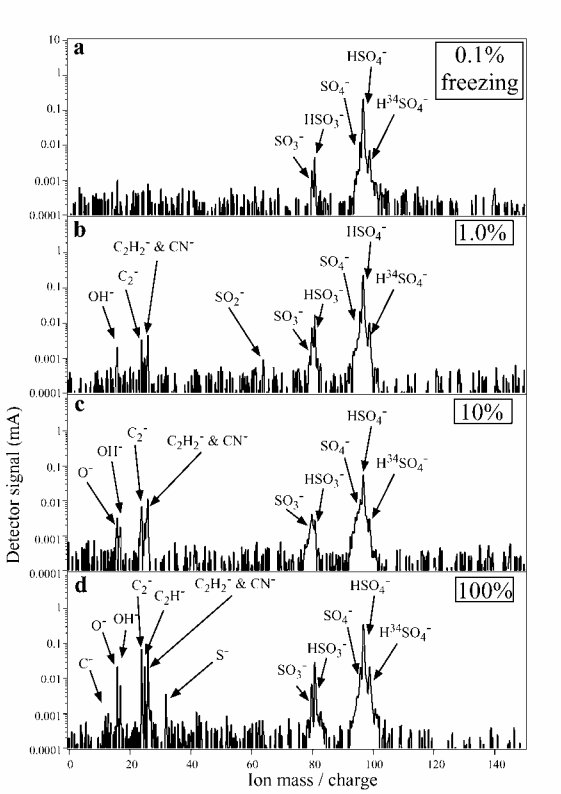

Figure 3 PALMS negative ion mass spectra showing the increasingly organic nature of particles as the fraction of particles (above 100nm, as a reference) freezing homogeneously increases from panels **a** to **d**. From Cziczo et al. 2004b).

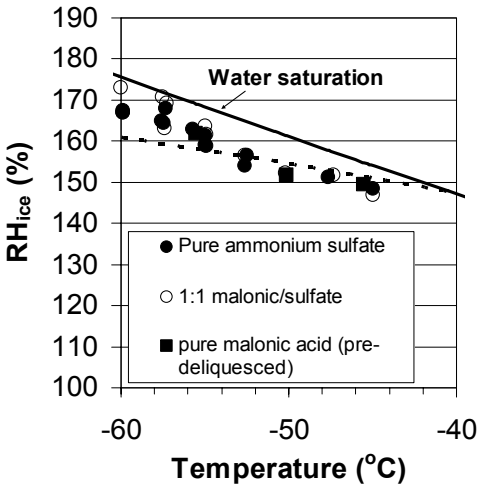

Figure 4 Laboratory measurements of the conditions for homogeneously freezing liquid particles formed on pure ammonium sulfate, pure malonic acid and 1:1 mixtures of these by mass. All particles are 100 nm at their dry size and freezing conditions represent 1% of particles nucleating in 12 s. The dashed line is the predicted homogeneous freezing condition.

This latter point is demonstrated in Figure 3. Particles freezing at the lowest RH_{ice} onset freezing conditions, as shown in Figure 2, are primarily sulfates. Particles include more and more organic fragments as the fraction of particles freezing (or nucleation rate) increases. This result does not occur simply because smaller particles, enriched in organics, freeze at higher nucleation rates (Cziczo et al. 2004b). Rather, these results demonstrate a clear fractionation of composition versus nucleation rate in the CFDC. This suggests a kinetic influence of certain organics on nucleation. We cannot state with certainty that these influences will occur on the time scale of cirrus cloud formation, but recent field measurements support that they do (Cziczo et al. 2004a).

Experiments have been done in the laboratory to explore organic effects on homogeneous freezing. Some recent results for mixtures of sulfates and dicarboxylic acid particles suggest no impact on the freezing conditions of particles of 100 nm initial (dry) size in the cirrus regime (Figure 4). Organic impacts must involve other soluble or surface active organic species.

3.2 Heterogeneous ice nucleation by natural aerosol particles

Concentrations of heterogeneous ice nuclei measured during the November 2001 campaign were modest, but significant as regards cirrus cloud forming in synoptic lifting or in the lower cooling rates thought to be present in subvisual cirrus (DeMott et al. 2003). Average concentrations as a function of ice supersaturation are summarized in Figure 4 for data within two different temperature regimes. At temperatures warmer than -35°C, ice formation is solely by heterogeneous nucleation in the CFDC. At below -38°C, heterogeneous ice nucleation is detectable up until the onset conditions for homogeneous freezing, where strong homogeneous nucleation masks the more selective process. These data suggest a difference in the way the heterogeneous nuclei population activates in the different temperature regimes, although the greatest differences occur in the ice saturation regime that includes water supersaturated conditions in the warmer regime. This may reflect differences between deposition and freezing nucleation mechanisms. IN concentrations during the 2001 study were much lower than those extrapolated on the basis of the IN parameterization of Meyers et al. (1992). This parameterization has been used extensively in cloud modeling, but is clearly inappropriate for the location of this study and the time of year. The solution to the inadequacies of this type of parameterization may be in explicitly recognizing the additional relation of IN concentrations to changes in the aerosol particle size distribution, particularly the apparent relation with the concentration of accumulation mode aerosol (DeMott et al. 2003). It will also be important to account quantitatively for IN sources and seasonal cycles.

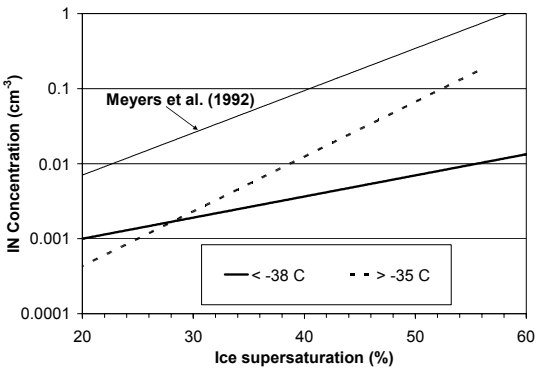

Figure 4 Average ice nuclei concentrations in the heterogeneous nucleation regime during the November 2001 study, distinguished for temperatures above -35°C and below -38°C. Also shown are IN concentrations predicted by extrapolating the IN versus ice supersaturation relation given by Meyers et al. (1992).

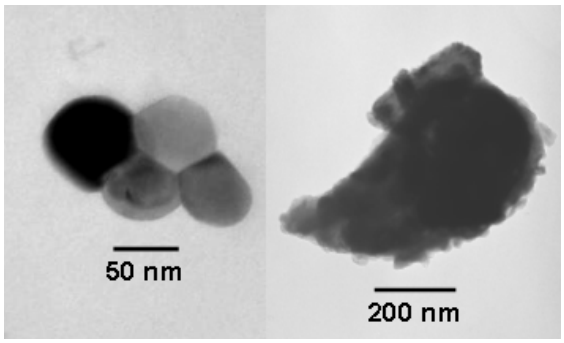

Figure 5 Images of two particles categorized as being of mineral or fly ash origin. The particle on the left is primarily composed of titanium and likely of anthropogenic origin from a high temperature process. The particle on the right that also includes Si, Na, Mg, Fe and S is more typical of a natural mineral dust particle and represented 80% of particles categorized as mineral dust/fly ash.

The compositions of heterogeneous IN measured in this study suggest important global sources. Ion mass spectra of IN indicated a predominance of particles representative of mineral dust, fly ash and metallic elements (DeMott et al. 2003). Furthermore, TEM analyses of particle morphologies and elemental compositions indicated that although particles of anthropogenic origin contributed significantly to the IN population, mineral dust sources were likely responsible for 80% of all such particles.

4. FUTURE WORK: SPRING 2004 STUDY

New studies during April and May 2004 will be done to sample free tropospheric air from the mountaintop site during what is expected to be the peak transport season for Asian dust particles to the site in the Western U.S. (VanCuran and Cahill, 2002). Figure 6 confirms the typical increase in soil dust concentrations at the site in spring compared to

concentrations closer to the annual minimum during the first study. Table 1 lists the suite of measurements for the next study. Included will be an additional aerosol mass spectrometer (AMS) with improved capabilities to quantify sulfate and organic particle content (Jimenez et al. 2003), improved size resolved composition with both mass spectrometers, new measurements of particle hygroscopicity, gas phase chemistry to correlate with IN measurements. Daily fine and coarse particle aerosol analyses will also be obtained from an IMPROVE (Interagency Monitoring of Protected Visual Environments) particulate monitoring network filter sampler.

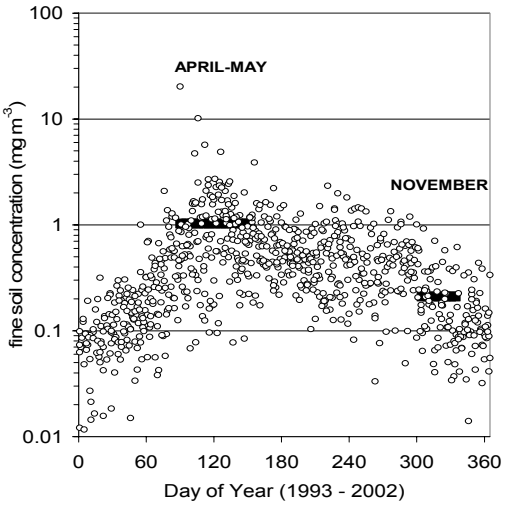

Figure 6 Annual cycle of fine soil dust at an IMPROVE network site located 10 km northwest of the study site and at approximately the same elevation. This indicates the expected difference between dust concentrations in the previous (November) and planned (April to May) study periods.

Table 1. Measurement Suite for 2004 Study

MEASUREMENT	INSTRUMENT
IN concentration	Continuous flow diffusion chamber
Aerosol and IN chemistry	AMS PALMS TEM grid collections
Bulk aerosol mass and chemistry	IMPROVE filters (24 hours integrated)
Water uptake (size resolved)	HTDMA
CCN	Thermal gradient diffusion chamber
Aerosol particle size	DMA (12 to 350 nm) OPC (100 to 2000 nm) APC (540 to 20000 nm)
Gas Phase	SO_2 O_3 CO

5. ACKNOWLEDGEMENTS

This research was supported by the U.S. NSF grants ATM0071321, ATM0124927, ATM0334228 and NOAA base funding. Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the authors. Special thanks to Brian Jesse and David Rogers for assistance during this study.

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