The role of heterogeneous freezing nucleation in upper tropospheric clouds: Inferences from SUCCESS

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Abstract. A temperature spectrum of heterogeneous freezing nuclei concentrations in continental air in the upper troposphere was determined based on airborne measurements. Numerical model simulations incorporating ice formation by heterogeneous and homogeneous freezing of deliquesced soluble aerosol particles were performed to investigate the effect of the heterogeneous process on the microphysics of upper tropospheric clouds. Heterogeneous freezing nuclei were predicted to cause lower maximum concentrations of ice particles formed in clouds These nuclei also initiate the first ice formation and act to broaden ice crystal size distributions in upper tropospheric clouds. Observations of ice formation in an orographic wave cloud supported these predictions.

Introduction

Upper tropospheric clouds play an important role in intercepting radiation and controlling climate. The interaction of these clouds with radiation is determined by the phase, size, shape, and concentrations of particles composing the cloud. Understanding the processes by which aerosol particles lead to the formation of cloud particles is important for estimating natural and anthropogenic impacts on clouds and climate.

Ice formation at low temperatures in upper tropospheric clouds may result from both homogeneous freezing of solution droplets formed on soluble cloud condensation nuclei (CCN) and heterogeneous nucleation of ice by insoluble or partially insoluble particles. The former mechanism is thought to dominate below -40°C. The role of heterogeneous nucleation has been open to question due to a shortage of information on concentrations and properties of ice nuclei (IN) in the upper troposphere. A new ice nucleus measuring device for aircraft use was deployed during the SUbsonic aircraft Contrail and Cloud Effects Special Study (SUCCESS). This study focused on gathering data on the direct and indirect effects of aircraft exhaust on upper tropospheric clouds The measurements were based primarily over the south-central Great Plains of the United States during April-May 1996. In this paper, the data set was analyzed to determine the atmospheric concentrations of heterogeneous freezing nuclei as functions of temperature

and total particle loading. This information was used in a numerical model to compare versus observational data and to investigate the role of IN in cirrus ice formation.

Methodology

IN Measurements

Measurements of IN during SUCCESS were made using a real-time continuous flow diffusion chamber (CFD) mounted in the NASA DC-8 aircraft This new instrument and the sampling system used are described by Rogers et al. [1997]. In the CFD technique (Rogers, 1988), air flows vertically downward in the annular space (~1 cm) between two ice-coated cylinders that are held at different temperatures The temperature and humidity that particles are exposed to are determined by the temperatures of the walls For SUCCESS, sampling conditions ranged from -10 to about -40°C and from ice saturation to in excess of water saturation Ice crystal concentrations are determined by optical methods.

Determining a Freezing Nuclei Temperature Spectrum

Ice nuclei may form ice crystals by a number of mechanisms. In one important pathway at low temperatures in the troposphere [DeMott et al , 1997], the insoluble components of mixed aerosol particles lead to freezing during the condensation and growth of haze and cloud droplets. The IN data were analyzed to estimate the maximum concentration of such condensation-freezing IN versus temperature.

Freezing nuclei concentrations were estimated by cycling sample humidity (by a time-varying change in CFD wall temperatures) to determine [IN] versus percent water supersaturation (S_w) at constant processing temperatures. An example is shown in Figure 1 for an approximately 50 km flight segment above cirrus over Oklahoma. IN concentrations responded strongly to increased S_w, but above a certain S_w the [IN] remained constant All the particles that could act as freezing nuclei at the CFD temperature were probably immersed in dilute droplets at S_w above a few percent. The low [IN] noted below water saturation in Figure 1 suggested that nuclei that form ice directly from the vapor phase (deposition nuclei) were only a small fraction of the total IN population Also shown in Figure 1 are the concentrations of all particles above 12 nm in the sample air stream, measured using a condensation nuclei (CN) counter (TSI Model 3010).
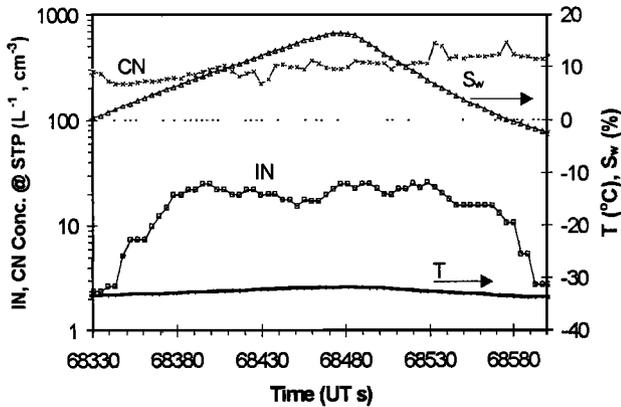
Figure 1. Time series of IN and CN (>12 nm) concentrations as a function of CFD operating temperature and water vapor supersaturation (S_w) on April 24, 1996. IN data are ~ 1 min. running averages. The DC-8 was flying above cirrus at 11.6 km, a pressure of 206 mb, and a temperature of -61°C.

Data of the type shown in Figure 1, at different CFD temperatures, were accumulated for flight segments at altitudes between 9 and 12 km on three days. Flights selected were near cirrus over Kansas and Oklahoma and near wave clouds over New Mexico. The data used were collected in clear air regions containing spatially homogeneous CN concentrations. The value of S_w needed for complete activation of freezing nuclei varied at different times. A median value of 3% was determined for segregating data. IN concentrations were normalized by concurrent CN concentrations and fit to,

$$F_{IN/CN} = a\, T_s^b \qquad (1)$$

where $F_{IN/CN}$ is the ratio [IN]/[CN>12nm], T_s liquid supercooling, and a and b are constants. Although there is no reason to expect a general correlation of freezing nuclei with CN, normalization improved the fit (~ doubled r^2) to data. This correlation may reflect that regions of new particle formation or particle depletion were excluded from analyses.

Numerical Cloud Modeling

The measured heterogeneous freezing nuclei spectrum was used in an adiabatic parcel model [*DeMott et al*, 1994] to investigate the role of heterogeneous nuclei in ice formation in upper tropospheric clouds. The cloud model calculates nucleation and growth of droplets and ice crystals for a non-precipitating parcel of air in a constant updraft. Homogeneous freezing rates were computed assuming pure sulfuric acid CCN, based on the parameterization given in *DeMott et al.* [1997]. This parameterization uses the concept of an effective freezing temperature (T_{eff}) that accounts for the melting point depression (ΔT_m) due to solute [*Sassen and Dodd*, 1988].

$$T_{eff} = T + \lambda_{hom}\,\Delta T_m \qquad (2)$$

where T ($= -T_s$) is droplet temperature (all temperatures in degrees Celsius). The constant, λ_{hom}, was assumed to be 1 for H_2SO_4/H_2O, based on laboratory studies [e.g., *Bertram et al.*, 1996]. Effective freezing temperature was then used as droplet temperature in an expression for the classical nucleation rate of pure water [DeMott et al., 1994, Eq. (3)].

Heterogeneous freezing nucleation was incorporated into simulations by assuming that the effective freezing

temperature concept could be extended to the situation of heterogeneous freezing of highly supercooled droplets. Thus, T_s in (1) was replaced by $-T_{eff}$. It was further assumed that the proportionality constant for a heterogeneous freezing process, λ_{het}, is equal to λ_{hom}. There is no theoretical basis for the validity of this last assumption. There is also little data on heterogeneous freezing of concentrated solution droplets. Hoffer (1960) found that λ_{het} may be double λ_{hom} for some solutions at higher molality. Thus, it is possible that assuming $\lambda_{het} = \lambda_{hom}$ overestimates the effect of heterogeneous IN.

The extrapolation of the heterogeneous freezing spectrum to temperatures below the range of measurement is preliminary. Nevertheless, sulfuric acid solution droplets freeze homogeneously at a weight percent of about 26% at -60°C, where the freezing point depression due to the solute is about 20°C [*Bertram et al.*, 1996]. Thus the applicable heterogeneous freezing rate is that for dilute droplets at $T_{eff} = $ -40°C; e.g., only a modest extrapolation of data is needed.

An uncertainty in predicting ice formation based on the normalized freezing nuclei spectrum was estimating what fraction of the IN active at high S_w were also hygroscopic (and CCN). Energy dispersive x-ray analyses (EDS) of IN residues indicated that 3 to 27% contained elements associated with soluble species [*Chen et al.*, 1997]. Since the EDS analyses were not able to detect soluble mass fractions smaller than about 10%, we assumed 1, 10 and 100% of IN behave also as CCN in different simulations to bound the estimates. This CCN-active fraction of the IN was multiplied by $F_{IN/CN}$ in numerical calculations. It was further assumed that: 1) all IN are > 0.1 μm diameter (reasonable, based on *Chen et al.*, 1997), 2) particles >0.1 μm are typically 10% of the total aerosol particle (CN) population; and 3) freezing nuclei had a soluble mass fraction of 0.5 (*Chen et al.*, 1997 inferred soluble volume fractions of 0.2 to 0.9). CCN dry sizes were inverted from a CCN (cm⁻³) spectrum of [CCN] = 200 $S_w^{1.5}$

Observations of Ice Formation in a Wave Cloud

Orographic wave clouds offer excellent opportunities for studying natural ice nucleation processes [e.g., *Heymsfield and Milosevich*, 1995]. Homogeneous freezing usually dominates ice formation in wave clouds because the updrafts
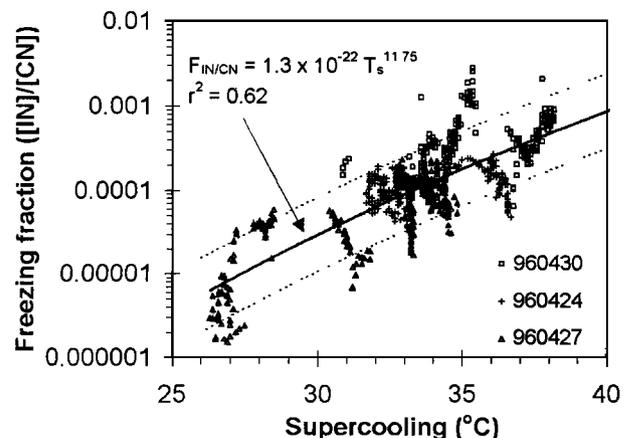

Figure 2. Freezing nuclei concentrations for S_w>3%, normalized by [CN], as functions of supercooling below 0°C for segments of three DC-8 flights (dates in legend) in the upper troposphere. The 1σ uncertainty of the power law fit (solid line) is indicated by the dashed lines.
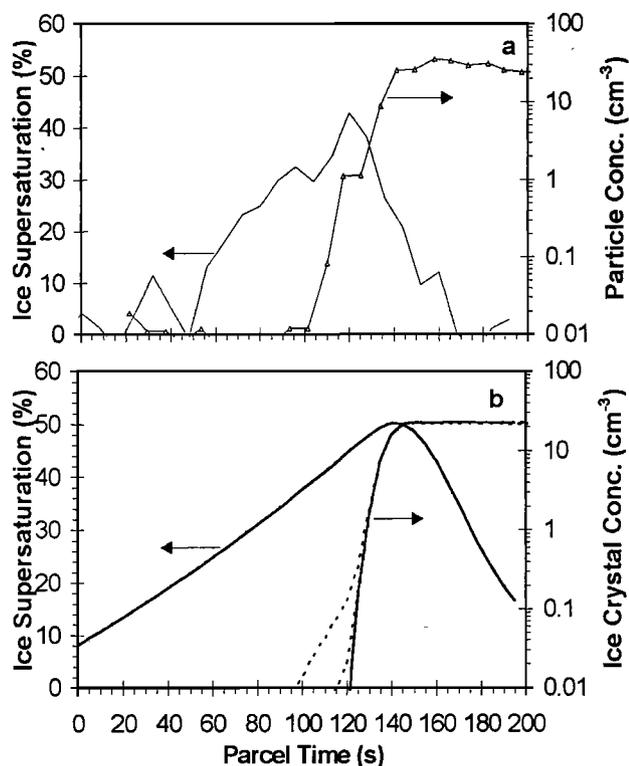
Figure 3. (a) Observed ice particle concentration and S_w for penetration of orographic wave cloud on April 30, 1996. (b) Parcel model simulations with ice formation by homogeneous freezing only (solid) and including homogeneous and heterogeneous freezing nucleation (dashed lines bracket uncertainty shown in Figure 2).

present (typically > 1 m s^{-1}) favor high parcel humidification. Nevertheless, it is expected that the first ice formed is from heterogeneous nuclei. We analyzed measurements from a wave cloud case (April 30, 1996) to investigate if the presence of heterogeneous freezing nuclei could be discerned.

Measurements were made within an isolated field of thin wave clouds over eastern New Mexico. The specific flight plan designed to characterize cloud microphysics involved penetrations oriented along the direction of the wind and through upstream and downstream cloud edges. Logistical considerations on this day prevented the proper conduct of this plan The cloud penetration we discuss was from ~70915 to 70940 s UT, when the DC-8 turned into the leading edge of the clouds (along the wind direction) from an initial path perpendicular to the cloud field. The cloud was at 8.9 km (313 mb) and -42.5°C. Wind speed (3-D) was determined by the DC-8 meteorological measurement system [*Chan et al.,* 1997]. Relative humidity was measured with a cryogenic hygrometer [*Heymsfield and Milosevich,* 1995]. Ice particle concentrations were based on residual particle measurements from a counterflow virtual impactor (CVI) that isolated cloud particles larger than 3.5μm [*Twohy et al.,* 1997]. Particle size data are also reported from a Multiangle Aerosol Spectrometer Probe (MASP) that measures the size and concentration of particles 0.3 to 40μm diameter by laser light scattering.

Horizontal wind and aircraft speed were used to convert the measurements to air parcel times for comparison to model simulations. Air parcel trajectories were not followed exactly, but the relative position error was assumed small over the horizontal extent of the cloud formation region (~1 km).

Model simulations were initialized with a vertical motion representative of the cloud (2.5 m s^{-1}). The smallest model ice crystal diameter (3.2 μm) was similar to the CVI "cutoff" size.

Results

Freezing Nucleus Spectrum

The freezing nucleus temperature spectrum determined from the selected time periods is shown in Figure 2, along with a power law regression (± 1σ) for the data. IN concentrations ranged from 1 L^{-1} at warmest temperatures to 100 L^{-1} at coldest temperatures. The slope of this freezing nuclei spectrum has about a one order of magnitude increase in freezing efficiency for every 6 degree temperature decrease.

Ice Formation in an Orographic Wave Cloud

Data from a segment of the wave cloud penetration on April 30 are shown in Figure 3a. Time zero (parcel time) was selected to be where humidity just exceeded ice saturation on a trajectory entering the cloud. Ice supersaturation increased to a level of 40 to 45 % in the wave The saturation ratio to fell to ice saturation during rapid crystal formation and growth.

Parcel model simulations of this cloud are shown in Figure 3b. Separate simulation results are presented with and without heterogeneous ice nucleation. A constant IN fraction (0.1) capable of acting as CCN was assumed for simulations including heterogeneous nucleation. These simulations also considered the uncertainty in [IN]/[CN] shown in Figure 2. The model results emulated observed parcel humidity and ice formation quite well. High ice supersaturations were required to initiate ice formation, and parcel humidity fell to ice saturation as ice formed. Predicted maximum crystal concentrations (22 cm^{-3}) , ice water content (0.06 g m^{-3}), and average crystal radius (8 8 μm) gave excellent agreement with observations (H. Gerber, personal communication, 1997].

Two interesting behaviors were noted in the simulations including heterogeneous nucleation. First, ice formation began earlier and slower than in the simulation including only homogeneous freezing. These first freezing events were due to
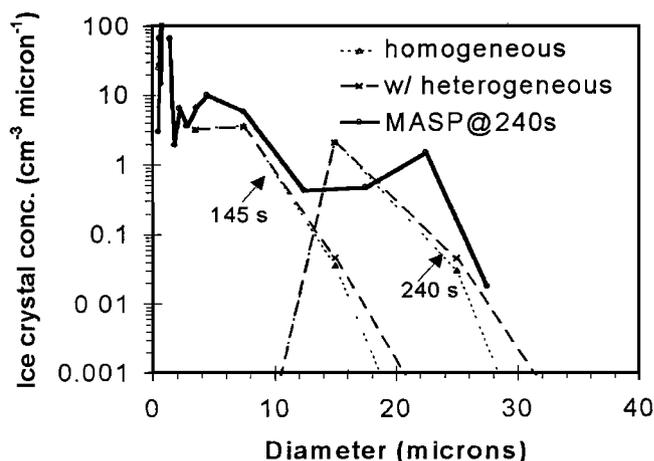

Figure 4. Model ice crystal size distributions at 145s (peak RH) and 240 s (ice saturation) in Figure 3b. The simulation including heterogeneous freezing nucleation produces over 100 L^{-1} of larger ice crystals compared with the simulation excluding heterogeneous nucleation. Observations from the MASP probe (solid line) are also shown.
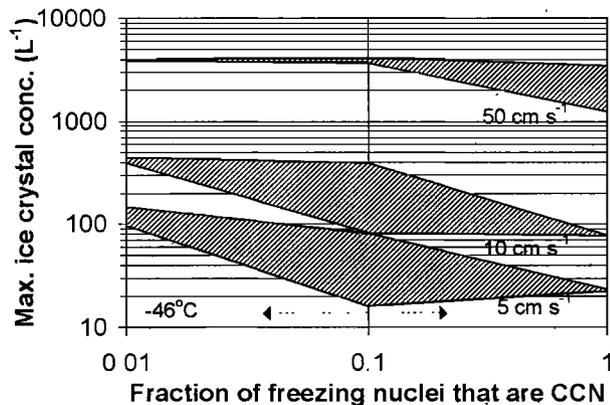
Figure 5. Maximum predicted concentrations of ice crystals forming in cirrus parcels by heterogeneous and homogeneous ice nucleation as functions of the fraction of freezing nuclei that are also CCN. The range of fractions of IN containing soluble matter, based on TEM studies, is given by the arrow. Initial parcel temperature was -46°C. Shaded regions at three vertical velocities bound the ice crystal concentrations formed when employing the uncertainties to the fit of Figure 2.

heterogeneous nuclei. We speculate that this explains the slower increase in ice formation observed in the actual cloud. This feature was also observed in a wave cloud on May 2, 1996 as reported by *Jensen et al.* [1997]. The second characteristic of the simulations with heterogeneous freezing was the production of a large size tail to the ice crystal spectrum (Figure 4) This feature is in the appropriate direction to explain the larger crystals observed by the MASP. The implication of the large ice crystal mode is that the heterogeneous freezing nuclei get a "head start" on growth and could be the first crystals to precipitate from high clouds.

Inferences to Ice Formation in Cirrus Clouds

Model results for cirrus clouds initialized at -46°C, ice saturation, 300 mb, and three constant vertical velocities are shown in Figure 5. Inclusion of heterogeneous freezing nuclei decreases the maximum ice crystal concentration formed ·compared with a singular homogeneous freezing process (far left side of Figure 5). Concentrations are reduced up to one order of magnitude, with less of an impact at higher updrafts. The uncertainty in what fraction of freezing nuclei were also active as CCN (x-axis in Figure 5) leads to a large uncertainty in their expected impact on ice formation. Nevertheless, the typical value of 10% of IN being CCN inferred from chemical analyses, is in the region of maximum impact. Heterogeneous freezing nuclei had a progressively smaller impact on ice concentrations at lower temperatures, with little effect in simulations below -65°C (not shown). The results shown in Figure 5 reflect the competition between nucleation and ice crystal growth, and the different rates and conditions of ice formation by heterogeneous and homogeneous nucleation. These factors have been discussed by *DeMott et al.* [1997].

Summary

An upper tropospheric heterogeneous freezing nuclei spectrum has been estimated from new in-situ measurements. This spectrum was used in numerical studies to infer that

heterogeneous freezing nuclei lower the concentrations of ice crystals formed in some cirrus clouds. Evidence for the presence of heterogeneous freezing nuclei was supported by observations of ice formation in wave clouds. Numerical process simulations also suggested an important role for heterogeneous nuclei in broadening ice crystal size distributions in upper tropospheric clouds. Confirmation of the conclusions of this study will require measurement of freezing nuclei below water saturation at temperatures below -40°C.

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