Atmospheric Concentrations of Submicron Contact-freezing Nuclei

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ABSTRACT

Atmospheric concentrations of contact-freezing nuclei were measured using a technique primarily sensitive to submicron aerosol particles. Diffusion and phoretic forces were relied on for the capture of nuclei by supercooled drops of distilled water exposed to the sample air. Nucleus concentrations were deduced from the rate at which the drops were observed to freeze, interpreting that rate on the basis of a theoretical prediction of aerosol capture rate for different assumed sizes of the nuclei. Measurements at Laramie, Wyoming, yielded average concentrations of contact-freezing nuclei of 1.7 L^{-1} at −15°C and 3.1 L^{-1} at −18°C for an assumed radius of 0.01 μm for the nucleating particles.

1. Introduction

The origin and the development of ice in tropospheric clouds have been extensively studied since Wegener (1911), Bergeron (1935), and Findeisen (1938) identified the pivotal role that ice plays in precipitation processes. It is now known that the presence of ice in clouds also impacts radiative and chemical processes within the clouds. Much has been learned in the past decades about the occurrence of ice in clouds, how ice crystals grow and become precipitation elements, and how ice influences the radiative and chemical properties of clouds, but there are still major questions about the ways in which ice can originate in the atmosphere.

In general terms, it is now clear that ice crystals originate from either primary or secondary processes. The former refers to nucleation (homogeneous or heterogeneous), while the latter refers to ice particles being created as a result of interactions between preexisting ice particles and droplets (riming), or as a result of collisions between ice crystals. Of the various processes of ice formation, heterogeneous ice nucleation has proven to be the most difficult to fully characterize. The main reason for this difficulty is that heterogeneous ice nucleation can follow several distinct paths ("modes" of nucleation). So far, no way has been found to adequately reproduce natural conditions with respect to all of the paths in measuring devices, and theoretical understanding of the processes is also incomplete. Hence, from early attempts (e.g., Findeisen 1938; Rau 1953; Palmer 1949; Aufm Kampe and Weickmann 1951; Bigg 1958; Bird et al. 1961) to more recent ones (e.g., Zamurs and Jiusto 1982; Hussain and Saunders 1984; Rogers 1988; Rosinski et al. 1988), measurements of ice nuclei are known to be incompletely representative of natural conditions.

The adequacy of ice nucleus measurements was called into question when it became apparent that the nucleus concentrations measured were at times exceeded by factors of 10^3 or more by observed concentrations of ice crystals in clouds. The discovery and detailed study of secondary ice generation (or ice multiplication) mechanisms (Brownscombe and Thorndike 1968; Hallett and Mossop 1974; Vardiman 1978; Mossop 1985) showed that the discrepancy between ice crystal and ice nucleus concentrations (Murgatroyd and Garrod 1960; Koenig 1963; Braham 1964; Mossop and Ono 1969; Hobbs 1969, 1975; Harris-Hobbs and Cooper 1987) is due, in some clouds, to secondary ice generation. However, secondary processes require specific conditions for their operation. In the absence of those conditions, and when simple monotonic relationships are found between temperature and ice crystal concentrations, it is likely that the origin of ice is entirely, or predominantly, by heterogeneous nucleation. Also, secondary processes require some initial ice present, and that ice is, presumably, generated by heterogeneous nucleation in the majority of cases. Hence, there is considerable interest attached to heterogeneous ice nucleation in the atmosphere, as summarized in recent reviews (Knight 1979; Rosinski 1979; Vali 1985a; and Götz et al. 1991).

As mentioned before, one of the features of heterogeneous ice nucleation is that there are several different modes (mechanisms) involved, depending on the parent phase (vapor or liquid) and on the sequence of events that bring together the heteronucleus and the metastable water phase. Nucleation is inherently time

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dependent, and can also be influenced by electric fields, the presence of other chemical species, previous exposure of the nucleus to different temperature or humidity regimes, and other factors. This complexity of ice nucleation in clouds makes realistic simulations of atmospheric conditions within measuring devices quite difficult and uncertain. An alternative to simulations of cloud conditions is to make measurements that focus on specific nucleation modes, and to model ice nucleation in clouds as the superposition of the component mechanisms. To carry out such calculations, information is needed on the sizes and other properties of the particles in addition to their ability to serve as nuclei of given modes. The difficulties inherent in securing such detail in aerosol characterization has rendered progress in the measurement of ice nucleation modes slow.

The study of one ice nucleation mode was the goal of the work reported in this paper: contact freezing, and more specifically, contact freezing by submicron particles in the atmosphere.

2. Contact freezing[1]

Contact freezing is the name given to the process in which freezing of a supercooled droplet results from the impact of an aerosol particle onto its surface (Rau 1950). This is different from condensation freezing or immersion freezing, where the active nuclei are surrounded by supercooled water, either due to condensation onto the particle at temperatures below 0°C, or due to the particle entering water at some time prior to the onset of freezing. Deposition nucleation is the formation of an ice germ on an aerosol particle from the vapor phase. The importance of contact freezing is associated with the observations that certain particles are more effective in this mode of nucleation than in the others.

Three theories have been offered to explain the effectiveness of contact freezing. Fletcher (1970) suggested that the character of active sites on a dry particle may change when the particle is immersed in water, reducing the freezing activity of the particle. Fukuta (1975) proposed that contact freezing is the result of a disequilibrium effect when the particle contacts the liquid. Immediately upon contact the interfacial energy between the particle and the liquid assumes a value higher than the equilibrium value, and this favors nucleation. Cooper (1974) pointed out that the critical size of an ice embryo is less for ice nucleation from the liquid than it is for ice nucleation from the vapor. Thus, a particle inactive as a deposition nucleus at some temperature may carry ice embryos large enough to nucleate a supercooled droplet at that same temperature. Regarding the sizes of the particles that might act as contact-freezing nuclei, thermodynamics-based calculations for freezing (without the additional effects just mentioned) indicate that sizes of the order 0.01 μm are needed for freezing at temperatures near −10°C (Fletcher 1958, 1969).

Empirical evidence for contact freezing is relatively extensive with artificial nuclei such as AgI. Such particles are found to be active as contact-freezing nuclei at significantly warmer temperatures than when the same particles are immersed in the liquid for some time (Gokhale and Goold 1968; Gokhale and Lewinter 1971; Sax and Goldsmith 1972; Fukuta 1975; and others). By tagging cloud droplets with a tracer and looking for the presence of the tracer in crystals initiated by AgI in a cloud chamber, Katz and Pilie (1974) observed that only small fractions of 0.005- to 0.025-μm radius particles produced contact freezing at temperatures warmer than −10°C; these tests delineate a limit for the efficacy of contact freezing. On the other hand, examinations of the rate of nucleation in a cloud chamber led DeMott et al. (1983) to conclude that the mode of nucleation, for the specific AgI compounds and complexes involved in those tests, was contact freezing. When ice crystals are generated by contact freezing, either in a cloud chamber or in atmospheric clouds, the rate of collisions between nuclei and droplets determines the time rate of freezing events.

There is some evidence from cloud observations that atmospheric concentrations of contact-freezing nuclei might be important in comparison with nuclei of other modes of activity. In all cases, the evidence is partial, since direct confirmation of the nucleation mode has not been possible so far. Young (1974) examined the collection rates of particles by cloud droplets, and argued that contact freezing is a viable possibility for explaining ice formation in clouds. Cooper and Vali (1981) observed in wintertime lenticular clouds that ice crystals form within the first 1–2 minutes after the onset of condensation, and that the concentration of crystals then remains nearly constant throughout the clouds. This pattern was ascribed to either condensation freezing or contact freezing. The observed rate of crystal formation is consistent with contact freezing caused by particles of order 0.01 μm.[2] Hobbs and Rangno (1985) called attention to the possible importance of contact freezing in the rapid glaciation of cumulus turrets. The efficiency of this process is enhanced

[1] In accordance with adopted nomenclature (Vali 1985b), the terms "contact freezing" and "contact-freezing nuclei" are used to describe the process and its initiators, respectively. The term "ice nuclei" is used when the distinction of nucleation mode is irrelevant. "Ice nuclei" or just "nuclei" are used for simplicity when the meaning is clear from the context.

[2] Cooper and Vali assumed that in the presence of freshly formed cloud droplets the collision rates of droplets with aerosol particles can be calculated as for random molecular motion. If the collision rate is calculated assuming a steady-state concentration gradient, then the sizes of the nuclei would have to be <0.01 μm.

by phoretic forces when droplets evaporate in entraining cloud tops. Small nuclei would be needed for rapid nucleation.

Direct measurements of atmospheric concentrations of contact-freezing nuclei have been attempted in a number of different ways. Ohtake (1971) used an isothermal settling chamber, in which a dense cloud of small droplets was produced to promote the likelihood of contact-freezing events via the diffusion of particles to the droplets. Vali (1974, 1976) utilized an electrostatic precipitator to force charged aerosol particles onto supercooled drops supported on a cold stage. Cooper (1980) allowed supercooled droplets to fall onto micropore filters on which atmospheric aerosols have been previously collected. The results of these various measurements are in rough agreement, generally indicating concentrations of 2 to 10 L^{-1} at −20°C; these values are also similar to what has been obtained for other modes, and even for cloud chamber simulations (Vali 1985a). However, these agreements might be fortuitous, as the measurements were made at different locations and times, and the ranges of variability in all measurements are large. Furthermore, each technique has some shortcomings. Several modes of nucleation may be operating in Ohtake's chamber, not only contact freezing, and particle collection rates depend on aerosol size. In Vali's instrument, the sampling efficiency decreases rapidly for particles approaching 0.005-μm radius, due to the size dependence of charging efficiency (Whitby and Liu 1966). For the filters Cooper used the influence of penetration of nuclei to the interior of the filter (especially important for small particles), the clustering of nuclei near the pores, and the degree to which droplets reach into the filter structure have not been evaluated.

Determinations of the sizes of ice nuclei, and of contact-freezing nuclei in particular, have been attempted in a number of ways. Particles, when present near the geometric centers of snow crystals, were found by electron-microscopic examination to be roughly in the size range of 0.1 to 1.0 μm (Kumai 1951; Kumai and Francis 1962; Rucklidge 1965; and others). Large fractions of freezing nuclei in rain samples were found (Vali 1966) to pass through micropore filters of 0.01-μm pore size. In contrast, Georgii and Kleinjung (1967) found that cloud chamber measurements of atmospheric ice nucleus concentrations had a high correlation with the number of large (>0.1 μm) aerosol particles and poor correlation with the number of small particles (Aitken nuclei). Interpreting the observations of Blanchard (1957) on the freezing of drops suspended in a wind tunnel, Young (1974) calculated that if contact-freezing nuclei are assumed to have radii of 0.5 μm, their concentrations would have to be several hundreds per liter to account for the observed rates of nucleation. If the assumed size is changed to 0.05 μm, the required concentrations reduce to 20 to 600 L^{-1} for temperatures of −4°C and −17°C, respectively. These concentrations are still somewhat high in comparison with measured values, so that perhaps yet smaller nuclei were involved.

In view of the remaining uncertainties regarding the concentrations and sizes of contact-freezing nuclei, and because the rate of ice formation by these nuclei in clouds is a strong function of their sizes, the experiments described here were designed to determine whether contact-freezing nuclei of submicron sizes exist in the free atmosphere, and in what concentrations. A method of testing was devised that was inherently sensitive to small particles. The technique was not as specific as might have been accomplished with size-classified aerosol, but was simpler and was intended as an initial step toward more comprehensive experimentation.

3. Experimental concept

Aerosol particles of <0.1-μm diameter have high mobilities at atmospheric pressures and temperatures, and hence have large diffusion velocities in a concentration gradient. This leads to efficient collection of such aerosol by sinks such as water drops. In fact, additional forces (electric or aerodynamic) can increase those collection rates by only small factors. In the measurements we report, collection of the aerosol was by diffusion, thus giving emphasis to the smaller particles.

Supercooled drops were suspended in a chamber through which aerosol samples were passed and the presence of ice nuclei in the aerosol was inferred from the freezing of the drops. The concentrations of contact-freezing nuclei were calculated from observations of the drop freezing rate.

As long as the fraction of drops frozen is small, the number of nuclei collected in an interval of time can be equated to the number of drops frozen. The probability that a second nucleus contacts an already frozen drop can also be accounted for, but was negligible in our tests. The rate at which the drops freeze is given by

$$dn_c/dt = KI(n_s - n_c),$$

where n_c is the number of sampling drops frozen, n_s the total number of sampling drops, I the number of nuclei per unit volume of air, or concentration, and K the collection kernel, or volume from which aerosols are scavenged for each sampling drop per unit time. Integrating over the sampling time, t, and solving for I gives

$$I = \ln[n_s/(n_s - n_c)]/Kt. \quad (1)$$

The collection kernel, K, was calculated taking into account Brownian diffusion, thermophoresis, and diffusiophoresis. Theoretical expressions for the collection kernel considering these forces have been given by, among others, Slinn and Hales (1971), Young (1974), and Wang et al. (1978). The collection kernel is defined

as $K = J/N_0$, where J is the rate of particle flux to the collector drops and N_0 is the ambient aerosol concentration. The expression given by Wang et al. (1978) for the collection kernel can be written as

$$K = \frac{4\pi a^2 V_s}{\exp(aV_s/D) - 1}, \quad (2)$$

where a is the radius of the collector drop, V_s the sum of the velocities produced by the action of the phoretic forces, and D the particle diffusion coefficient. For V_s and D the study here uses the expressions presented by Deshler (1985), which account also for the effects of ventilation. The expression used for V_s is appropriate for particles in the transition regime, between approximately 0.006- and 0.2-μm radius.

Experiments using aerosol particles and collector droplets small enough that inertial effects could be ignored have been reported by Wang and Pruppacher (1977) and Beard (1974). The results of these measurements have been compared with the theory presented here and found to agree well (Deshler 1985). In addition, Deshler presented measurements of K using fluorescent dye aerosols of 0.03-, 0.06-, and 0.13-μm radius that also confirmed the theory presented here to within a factor of 2. The dye experiments are particularly relevant to this work, since they tested the collection kernel for the same experimental arrangement as that used here to sample ice nuclei. For the range of conditions used for the sampling of nuclei, that is, temperatures of $-11°$ to $-18°$C, and humidities of 50% to 90%, and for particles of 0.005- to 0.05-μm radius, the corresponding values of the collection kernel are approximately 10^{-3} to 10^{-4} cm^3 s^{-1}.

4. Experimental methods

a. Procedure

Contact-freezing nuclei were sampled by allowing diffusion, and the phoretic forces, to transport nuclei from the air to sampling drops suspended on thermocouples in a chamber through which aerosol could be passed. A schematic diagram of the sampling apparatus is shown in Fig. 1. The end of each thermocouple was formed into a loop to hold a drop. The thermocouples were connected in series and their output monitored with a recording voltmeter. A freezing event was indicated by a voltage pulse as the thermocouple sensed the latent heat of freezing. The chamber was cooled by a circulating liquid. Two additional thermocouples, one dry and one suspending a drop, were included in the sampling chamber to measure the air temperature and humidity. To reduce frost formation and the chance of ice fragments entering the air stream, aerosol samples passed through a diffusion dryer before entering the sampling chamber. Aerosol concentrations at the outlet of the chamber were monitored with an Aitken nucleus counter.

A coating was applied to the thermocouples to pre-

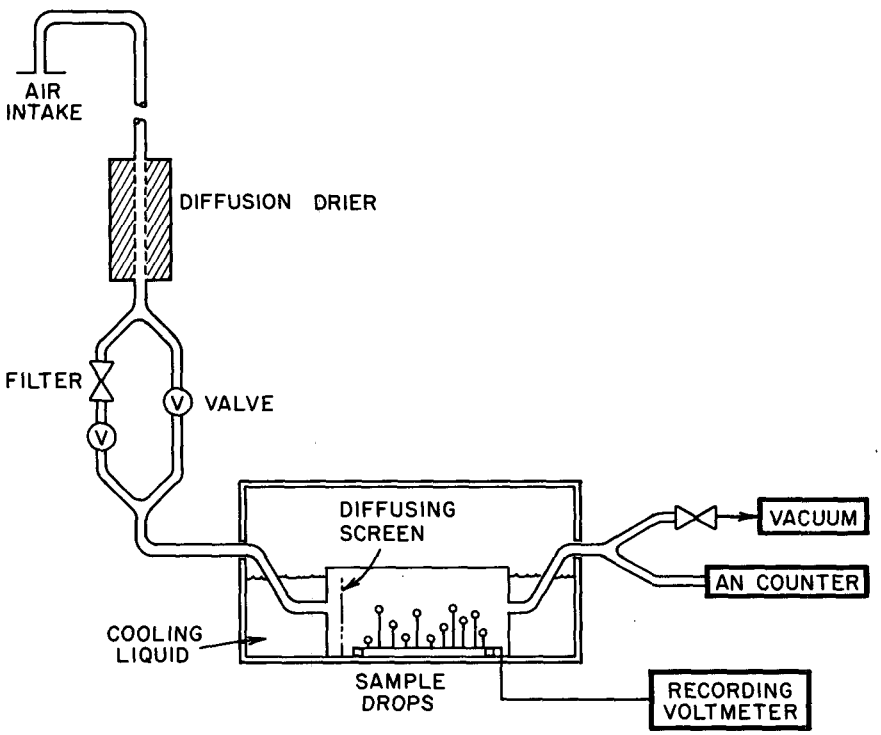

FIG. 1. Schematic of the sampling apparatus.

vent the thermocouple wire or contaminants on the wire from freezing the sample drops. A clear acrylic spray (Kleer Kote, Crown Industrial Products) was found to work well for this purpose. If the thermocouples became dirty, as evidenced by a large number of drops freezing without aerosol being admitted, they were recoated.

The sampling chamber was cooled to 0°C, then opened to place a drop of distilled water on each of 49 thermocouples. The drops were dispensed from a polypropylene syringe fitted to a device that used a stepping motor to produce uniform drops of 0.01 cm^3 volume (0.13-cm equivalent radius). The sampling chamber was closed, purged with filtered air for 15 minutes, and then cooled (without airflow) to a temperature 1° to 2°C colder than the desired sampling temperature. The chamber was held there for 1 h and then warmed to the sampling temperature. Drops that froze during the cooling and stabilization period, 2–4 h, were subtracted from the sampling population. When the test temperature was reached, sampling began by drawing air through the sampling chamber at 5 L min^{-1}. Outdoor aerosol samples were brought into the laboratory through an air intake approximately 15 m above the ground. Because of the long cooling time and stabilization period needed, it was impractical to sample at more than one temperature during a day. The sampling strategy adopted was to sample at one temperature for sequences of days during several weeks, and then do the same for another test temperature.

At the end of an experiment, the chamber was opened to confirm by visual count the recorded number of frozen drops. The degree of evaporation of the drops was not estimated during each drop-freezing experiment. Instead measurements made during the dye experiments (Deshler 1985), by recovering and weighing the sample drops at the end of an experiment, were used to estimate the degree of evaporation during the drop-freezing experiments. Humidities and sample times were similar for the two experiments. The drops were found to decrease in radius by about 8% during the course of an experiment. An average of the initial and estimated final radius was used for calculation of the collection kernel.

Besides the regular sampling of outside air, tests were also conducted with a filter inserted in the inlet line to remove aerosol particles. A cartridge filter was used that reduced Aitken nucleus counts to 100–200 cm^{-3}, whereas typical counts during sampling were 10^3–10^5 cm^{-3}. Tests with filtered air were used to compare the freezing behavior of the sample drops in particle-free air with their behavior in the presence of natural aerosol and constituted a measure of the instrumental background.

To assess aerosol loss in the intake piping, aerosol concentrations were measured with an Aitken nucleus counter at the sampling intake and at the end of the sampling chamber. Average losses of 45% were observed; however, the fraction of aerosol loss is size dependent and is greater for the smaller aerosols. For particles > 0.01 μm, aerosol size distributions were measured using an electrostatic aerosol analyzer (Thermo Systems Inc., Model 3030). Losses of approximately 30% were observed for this size range.

To rule out the possibility of large losses of ice-nucleating particles of unknown sizes (and charges), the apparatus was operated without a diffusion dryer and with a short inlet line when the outside air was cold and dry enough for frost formation on the walls of the chamber to be negligible. With this setup aerosol losses were minimized. Three such tests were made and they yielded similar results to the regular tests. Hence, and in view of the approximately factor 2 uncertainty in the collection kernel, no corrections were made for aerosol losses. The reported concentration values are, when considering this factor alone, underestimates.

The possibility that transient supersaturations caused by the freezing of one droplet lead to increased freezing activity of nearby droplets (Gagin 1984) was examined by comparing the time between freezing events with the time required to flush the sampling chamber, approximately 3 min. At −15°C the shortest time interval between events was 20 min. At −18°C, 2 out of 39 freezing events occurred with a time interval of less than 3 min. The next shortest time was 6 min, and the average time interval was 94 min. Statistical tests show that even the shortest intervals cannot be considered to have come from a different population than the longer intervals. Thus, it appears that nuclei becoming activated in high supersaturation transients did not contaminate the results.

b. Measurements using silver iodide nuclei

As a test of the performance of the experimental apparatus, sampling was conducted using monodispersed silver iodide aerosol, with simultaneous measurements using the electrostatic precipitation technique of Vali (1974). These tests were especially useful since they could be done using ice nuclei of known sizes, and in concentrations high enough that the instrumental background was negligible. Since the fraction of silver iodide particles active as ice nuclei was not known a priori, these tests could not yield quantitative values of the collection efficiencies.

Ice nuclei were generated by atomizing a hydrosol of silver iodide. Uniformly sized particles were then extracted using an electrostatic classifier (Thermo-Systems Inc., Model 3077). The concentration of sized aerosol was measured using an Aitken particle counter, and was further diluted with filtered air to obtain reasonable concentrations for sampling of ice nuclei. The aerosol was then held in a mylar storage bag for the ice nucleus measurements.

Tests were conducted using aerosols of 0.03- and 0.045-μm radii since these sizes are suitable for mea-

surements by both techniques. In fact, limitations of the aerosol generation and size classification technique confined the tests to this narrow range of sizes, so that tests that might have illuminated differences in sensitivity of the two techniques were not possible. The results of the tests are shown in Fig. 2. The two techniques agree within about factors of 2. Aitken nucleus concentrations of the aerosol samples indicate that the fraction of particles active as ice nuclei was between 10^{-6} and 10^{-5}.

5. Measurements

a. Data collection

Sampling was conducted at three temperatures, −11°, −15°, and −18°C, of both outside air and filtered air. The outside, or unfiltered, air provides the set of natural aerosol (NA) samples, while the filtered air samples provide a measurement of the instrumental background, or control samples. The temperature variation about these target temperatures was ±1°C with the average temperature within 0.2°C of the target temperature. The range of relative humidities was 50% to 90% with an average of approximately 75% for all three temperatures. The majority of sampling was done at −15°C. At −11°C the freezing activity of NA was only slightly above the detection limit, while at −18°C the large number of drops frozen during the stabilization period reduced the sensitivity of the tests. The number of sample drops that froze during the stabilization period was less than 5% at −11°C, 5% to 10% at −15°C, and 10% to 50% at −18°C. Sampling times for NA were typically around 2 h, and ranged from 1.5 to 4 h. For the control samples times were typically 1 h, and ranged from 0.5 to 3 h.

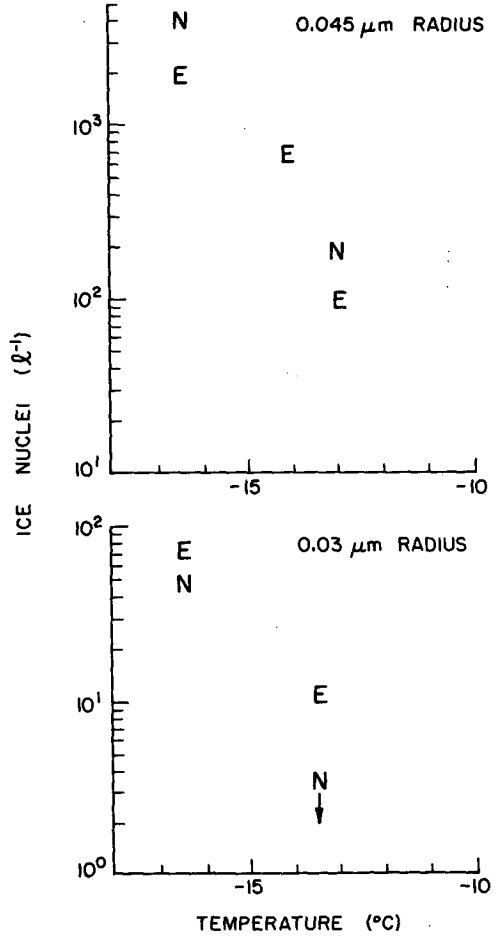

FIG. 2. Contact-freezing nucleus measurements with silver iodide aerosols of 0.03- and 0.045-μm radii, using two techniques (N: natural diffusion, E: electrostatic precipitation). The data point with the arrow represents an upper limit for that measurement (no drops were observed to freeze in that experiment).

Somewhat surprisingly, only a few freezing events were observed during any sampling period, indicating low concentrations of contact-freezing nuclei. The number of events ranged from zero to five; no freezing occurred in approximately half the experiments. The number of sample drops varied for each measurement due to fluctuations in the number of drops frozen during the stabilization period, and there were also some variations in the length of the experiments. To allow all measurements to be weighted equally, the data were normalized to a standard number of drops exposed for a set time. The standard was taken to be 90 drop-hours, that is, 45 sample drops exposed for 2 h, or 30 drops exposed for 3 h, etc., and was called a standard measurement unit (SMU). The result of each sampling period could then be represented as the fraction of drops frozen per SMU.

Natural (ambient) aerosols at Laramie, Wyoming, were sampled at intervals from November 1980 through February 1982. The small size of the town (population of 25 000), and the usually strong winds from the sparsely populated, mountainous West, justify the term natural aerosol, although the contribution of distant or local anthropogenic sources is not known. The majority of sampling was done in mid- to late afternoon. Sampling at night, in the early morning, and on weekends revealed no evident differences. Likewise, no trends were detected that could be correlated with changes in the weather.

The detection threshold for this measurement technique is approximately 0.6 L^{-1} for nuclei of 0.01-μm radius. This relatively high threshold and the frequent occurrence of concentrations below that limit rule out evaluations of day-to-day variability of nucleus concentrations. Hence, data are pooled into three sets according to temperature.

Data from all measurements are summarized in Table 1. The total sampling time and the average number of drops frozen per SMU at each temperature are listed. The data are displayed in Fig. 3 in the form of histograms of the number of freezing events per SMU. The

TABLE 1. Summary of measurements with control (CT) and natural aerosol (NA) samples. The measurements spanned the period from November 1980 to March 1982.

Aerosol	Time period (mo/yr)	Temperature (°C)	Number of measurements	Sampling time (hours)	Average sample drops per SMU*	Number of SMUs	Drops frozen per SMU
CT	9/81–1/82	−11	15	14.5	45.4	7.3	0.14
NA	11/80–1/82	−11	36	80.2	45.4	40.5	0.22
CT	12/80–2/82	−15	44	59.2	41.8	27.5	0.22
NA	11/80–2/82	−15	69	173.2	41.3	79.5	0.74
CT	9/81–3/82	−18	27	43.1	34.4	16.5	0.30
NA	9/81–3/82	−18	25	75.1	33.5	28.0	1.40

* SMU: standard measurement unit

smooth curves drawn in Fig. 3 are Poisson distributions fitted to the data for use in the statistical tests described in the Appendix. The −15° and −18°C data are compared to Poisson distributions. The Poisson distribution would be strictly applicable to measurements from identical sources; in this case, changes in ice nucleus concentrations between sampling runs add to the variability.

Due to the small number of experiments and the small number of freezing events per experiment, a careful evaluation is necessary of the significance of the difference between NA samples and controls. The question to be examined is whether the results for NA and control samples are subsets of different populations: one due to nuclei in the air and the other due to random freezing of the sample drops. Three different statistical procedures, described in the Appendix, test the null hypothesis that the freezing events observed in control runs could arise by random draw from the parent population consisting of the combination of NA and control runs. The results of the three tests are consistent in indicating that the NA measurements at −15° and −18°C reflect characteristics of the air sampled, while at −11°C the NA samples and the control are not sufficiently different.

b. Concentrations of contact-freezing nuclei

Concentrations of contact-freezing nuclei were calculated for each sample period from the number of drops that froze, the number of sample drops, the time of sampling, and the temperature and humidity in the sampling chamber, using Eqs. (1) and (2). Calculations were done for several assumed aerosol radii. The sample drop diameter was taken to be an average of the initial and estimated final value (after partial evaporation).

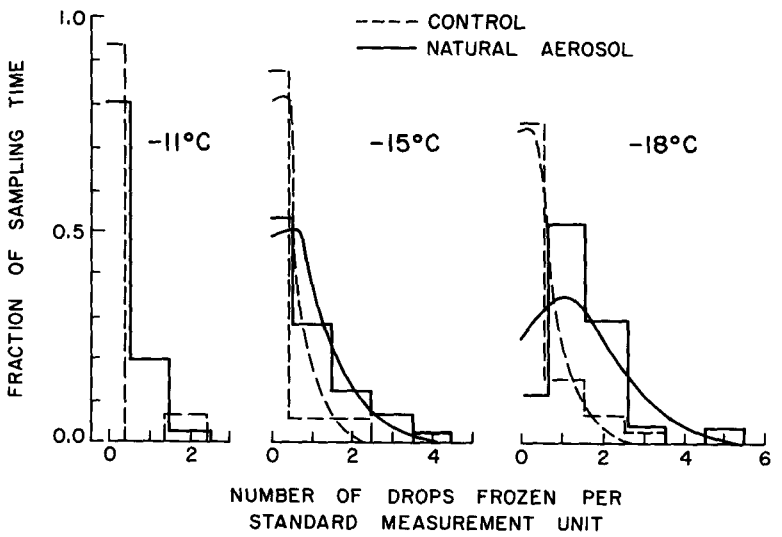

FIG. 3. Frequency distributions of the number of freezing events per standard measurement unit (SMU) for the NA (solid line) and the control (dashed line) samples at −11°, −15°, and −18°C. The bin widths are 1 freezing event per SMU. Poisson distributions are shown for the −15° and −18°C measurements based on the means of these measurements.

The average and standard deviation of the nucleus concentrations obtained for control runs and for NA samples are shown in Table 2 for several assumed aerosol radii. Also shown for −15° and −18°C, at the bottom of Table 2, are the average and standard deviation obtained by subtracting from each NA measurement the mean of the control measurements.

The actual frequency distributions of concentrations are given in Fig. 4 for an assumed aerosol radius of 0.01 μm. Scales are also included for 0.005- and 0.05-μm radii, making the size conversion using the average value of the relative humidity for all experiments.

6. Comparisons with other measurements

To provide some indication of the significance of these measurements, they are compared with other ice nucleus measurements from the same area, and with ice crystal concentrations in nearby clouds. While the different data come from different time periods, the comparison serves to indicate that systematic differences among the various ice nucleus and ice crystal concentrations are no larger than the range of variability of the measurements.

Results from four different sets of measurements of ice nuclei are shown with large letter symbols (N, E, F, and D) in Fig. 5. The results of the measurements discussed here are shown for assumed aerosol radii between 0.005 and 0.05 μm. Other measurements of contact-freezing nuclei are from Vali (1974) and Cooper (1980). The former were obtained by electrostatic precipitation of aerosol onto supercooled drops, while the latter were obtained by the settling of drops on filter samples. Data on deposition nuclei are from the filter measurements of Huffman (1973), for water saturation. All of these ice nucleus measurements were made at or near Laramie, Wyoming. For reference, Fletcher's curve for the average temperature dependence of ice nuclei is shown (Fletcher 1962).

The individual points plotted in Fig. 5 show ice crystal concentrations in stable orographic clouds, for which primary ice formation was shown to be the dominant process (Cooper and Vali 1981). The clouds formed in wintertime over Elk Mountain, about 80 km northwest of Laramie. Ice crystal concentrations were measured from an aircraft with an imaging probe (Particle Measuring Systems 2D-C probe; Knollenberg 1970). Data are shown for 141 cloud passes upwind of the mountain summit, from 23 days during the winter seasons of 1975–1979. For each pass, the geometric mean of ice crystal concentrations and the arithmetic mean temperature are given. The geometric mean is appropriate for representing ice crystal concentrations, since the distribution of concentrations fits a lognormal distribution. The temperatures of the clouds ranged from −8°C to −25°C and the ice crystal concentrations from 0.02 to 70 L^{-1}. These data are from Vali et al. (1982), and are a subset of the data given in Cooper (1986).

It appears from Fig. 5 that the results of the present measurements, N, are comparable to the other measurements of contact-freezing nuclei (E, F), and to the centroid of the observed ice crystal concentrations, provided particle radii of 0.005 μm (or somewhat larger) are assumed. The concentrations of deposition nuclei are lower by an order of magnitude.

If the three different contact-freezing nucleus measurements had indeed come from the same sample, the comparison could be interpreted as an indication that these nuclei are near 0.01-μm radius. The values for N corresponding to such a size (intermediate between those shown) would agree best with the values from F, and would be consistent with being higher than the values from E (due to diminished collection efficiency in the precipitator for those sizes). However, with the limitations of the current data, the deduced nucleus size is merely suggestive; in fact, it cannot be ruled out that the relatively good agreement between the different techniques is fortuitous, nor that it is due to comparable concentrations of contact-freezing nuclei

TABLE 2. Average and standard deviation of contact-freezing nucleus concentrations (L^{-1}) derived from observations at −11°, −15°, and −18°C for the control (CT) and natural aerosol (NA) samples. The bottom two rows represent the nucleus concentrations at −15° and −18°C after correction for the control.

		Radius (μm)							
		0.005		0.01		0.05		0.10	
Aerosol	Temperature (°C)	Ave	σ	Ave	σ	Ave	σ	Ave	σ
CT	−11	0.4	1.0	0.9	2.3	2.6	7.0	3.3	8.8
NA	−11	0.3	0.7	0.7	1.7	2.6	6.8	3.4	9.0
CT	−15	0.5	1.2	1.1	2.8	3.6	9.5	4.5	12.0
NA	−15	0.9	1.3	2.2	3.2	7.9	15.0	11.0	27.0
CT	−18	0.6	1.2	1.6	2.9	5.5	9.5	7.0	12.0
NA	−18	1.8	1.5	4.4	3.7	16.0	13.0	21.0	18.0
Corrected	−15	0.7	1.2	1.7	2.8	6.4	13.8	9.9	25.5
NA	−18	1.3	1.3	3.1	3.3	11.6	11.8	15.6	16.3

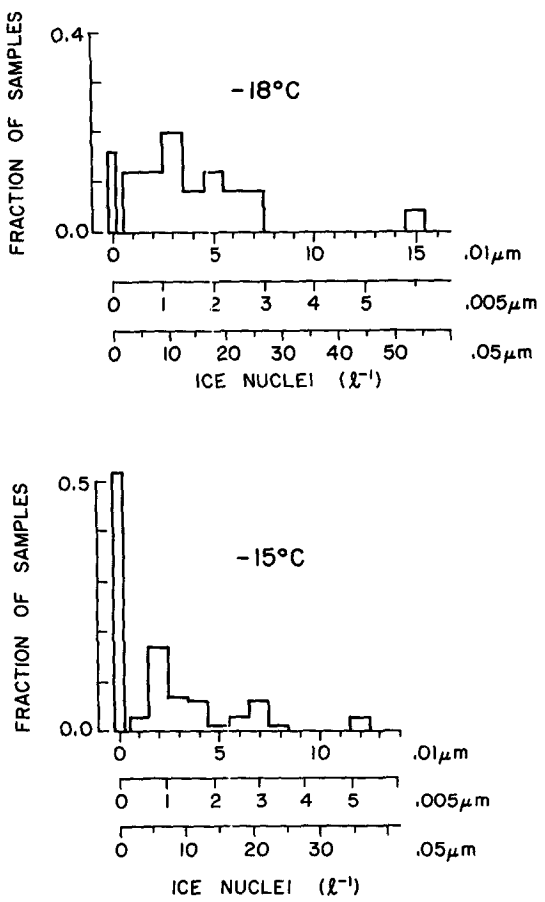

FIG. 4. Frequency distributions for the nucleus concentrations observed at −15° and −18°C. The histograms are exact for the 0.01-μm assumed particle size, but the scale changes are approximate for 0.005- and 0.05-μm particles.

in the different size ranges to which the various techniques are most sensitive.

The rough agreement between contact-freezing nucleus and ice crystal concentrations may be taken as indicative of a causal relationship, but such a deduction is not fully warranted. Even beyond the differences in the time and location of the measurements, the time available in the clouds for contact-freezing nuclei to become active (to be collected by cloud droplets) would have to be accounted for in a more rigorous comparison. The collection rate by droplets would, of course, depend on the sizes of the nuclei. With the data now available, the agreement does not provide conclusive evidence. More weight can be given perhaps to the agreement in the form of the temperature dependence of the nucleus and crystal concentrations.

7. Summary and conclusions

Atmospheric concentrations of contact-freezing nuclei were measured, relying on diffusion to transfer aerosol particles to supercooled sampling drops suspended in a chamber. The rate at which drops froze was used to calculate contact-freezing nucleus concentrations on the basis of a verified theoretical expression for the collection kernel of the sampling drops. In the absence of independent size determinations, concentrations were deduced for a range of assumed sizes.

In the configuration used, the minimum detection threshold of the instrument was approximately 0.6 L^{-1} (for 0.01-μm radius particles). Stabilization of the sampling environment required several hours before measurements, so the frequency of observations was restricted to 1–2 per day. In total, approximately 80, 173, and 75 h of sampling were conducted at temperatures of −11°, −15°, and −18°C, respectively. The observed freezing rates of drops at −15° and −18°C were significantly above those found in control experiments, but those at −11°C were not. Average concentrations from these measurements, for an assumed aerosol radius of 0.01 μm, are 1.7 L^{-1} at −15°C and 3.1 L^{-1} at −18°C.

Perhaps the primary conclusion to be drawn from these measurements is that high concentrations of small contact-freezing nuclei, which have been suggested by some researchers, were not observed in our tests. The diffusive-capture technique is specially sensitive to submicron ice nuclei, yet large concentrations were never measured. Even the highest values observed in this series of measurements are within the ranges of previous measurements. Thus, for conditions for which our tests were representative, one can put to rest the notion that previous measurements of atmospheric contact-freezing nuclei suffered seriously from not being sensitive to aerosol particles of smaller sizes.

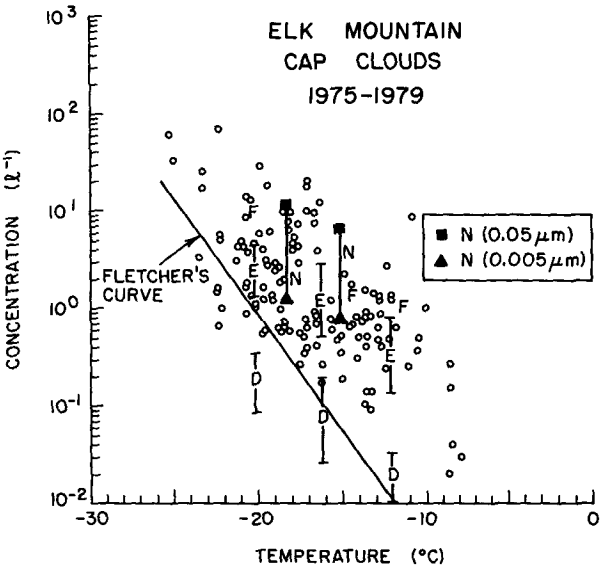

FIG. 5. Nucleus concentrations for contact-freezing (N: natural diffusion, E: electrostatic precipitation, F: filters) and for deposition (D), and ice crystal concentrations in stable winter clouds.

Differences between the concentrations of contact-freezing nuclei presented in this paper and those determined by Vali (1974) and by Cooper (1980) are within the variability of the measurements and the uncertainties associated with the unknown sizes of the nuclei. The concentrations of deposition ice nuclei in the same area are lower by an order of magnitude. In shallow orographic clouds, in which contact freezing was shown to be possibly responsible for the origins of ice crystals, the concentrations of crystals and of contact-freezing nuclei are of comparable magnitudes.

The degree of generality of the results reported here is not known. The similarity of the results to other measurements from the same area shows that the current data did not originate from unusual conditions. Furthermore, these data are similar in magnitude and in temperature dependence (roughly 8°C per factor 10 change in concentration) to other ice nucleus measurements taken at different locations and by different techniques (cf. Vali 1985a), underscoring the relatively small variability of nucleus concentrations in comparison with the large variability of ice crystal concentrations in clouds. Evidence to support this statement is now available only for temperatures colder than −15°C. Ice nucleus measurements at warmer temperatures, and with the mode of nucleation identified, remain to be obtained. From the point of view of precipitation evolution in clouds, that aspect of the problem appears to be crucial to resolve.

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APPENDIX

Statistical Tests

Three statistical tests were made to gauge the significance of the differences between measurements with natural (ambient) aerosols (NA) and with filtered air (control samples). The latter are considered as the instrumental background. The null hypothesis is that the freezing events observed in control runs could arise by random draw from the parent population consisting of the observations for NA and control experiments.

The first test is based on the central limit theorem, supposing sample means to be distributed normally about the population mean, a condition expected to be satisfied for sufficiently large sample sizes. For the sample sizes available here the test has limited validity. For the number of drops frozen per SMU (cf. Table 1), the t statistic is 0.53 at −11°C, 4.1 at −15°C, and 6.1 at −18°C. Comparing these values with the t distribution indicates that for the −11°C data the null hypothesis cannot be rejected, while at −15° and −18°C there is less than a 0.03% and 0.001% chance of obtaining the control by a random draw from the parent population. Hence, the results for NA samples are indicated to be significantly different from the control at these two temperatures.

The second test assumes that the parent population is Poisson distributed with an expected mean of μ. This is a better assumption for these data. The control SMUs are considered as a subset from this population. The probability of observing N_f or fewer freezing events in R_f control SMUs is then calculated from a Poisson distribution of mean n, where $n = R_f\mu$ is the average number of freezing events expected for a sample of R_f SMUs from the population. This probability is given by

$$P = \sum_{i=0}^{N_f} \frac{e^{-n}n^i}{i!},$$

which yield $P(-11°C) = 55\%$, $P(-15°C) = 0.25\%$, and $P(-18°C) = 0.09\%$. This test supports the first, indicating that the null hypothesis can be rejected for the measurements at −15° and −18°C.

The third test is the nonparametric Mann–Whitney rank test. For this test the dataset had to be reorganized because of the preponderance of ties (zeroes) in the data organized as the number of freezing events per SMU. The data were recompiled as the number of SMUs between freezing events. The advantage of organizing the data in this way is that each freezing event leads to a unique data point. The disadvantage is that zeros do not get counted individually but are summed into a large number of SMUs between freezing events. Figure A1 summarizes the data compiled in this way. Frequency distributions for NA and the control runs are shown for each test temperature. The number of SMUs between freezing events is grouped into bins of 0.5 SMUs, or 45 drop-hours. A Poisson distribution fitted to the mean for the NA samples is also shown for −15° and −18°C. A Poisson distribution is not expected to apply strictly to the NA samples due to the inhomogeneity of the NA samples, as discussed previously. For the control tests, the distribution to be expected depends on the mechanism which gives rise to the freezing events. For nuclei suspended in the water, and for a constant supercooling, an exponentially decaying rate should be expected (Vali and Stansbury 1966), but the initial overcooling of these samples, and the long exposure time, are certain to alter that pattern.

The nonparametric rank test assumes that the populations from which the samples are drawn have the same shape and tests to see if the populations differ in location. A rank is assigned to each data point in the parent population. The test statistic S consists of the sum of the ranks of the data points in the control set. For many repeats, S is expected to be normally dis-

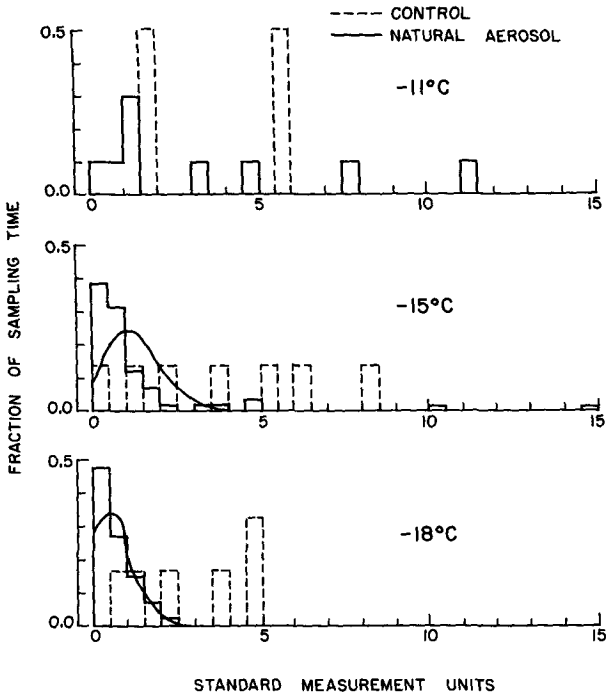

FIG. A1. Frequency distributions of SMUs as a function of the SMUs between freezing events for the NA (solid line) and the control (dashed line) samples. The bin widths are 0.5 SMU. Poisson distributions are shown for the −15° and −18°C NA samples. The mean and standard deviation of the NA samples are: $\mu(-11°C) = 3.6 \pm 2.9$, $\mu(-15°C) = 1.4 \pm 2.4$, and $\mu(-18°C) = 0.7 \pm 0.6$. For the control samples they are: $\mu(-11°C) = 4.0 \pm 4.1$, $\mu(-15°C) = 4.0 \pm 3.0$, and $\mu(-18°C) = 2.7 \pm 1.7$.

tributed about the mean $\langle S \rangle$ if there was no difference between the sample and the population. The excursion of S from $\langle S \rangle$ is then an indication of the difference between the control sample set and the population. The standard normal variable $Z = (S - \langle S \rangle)/\sigma$ can be used to estimate the probability of obtaining a particular value of S from a normal distribution about $\langle S \rangle$. Here, σ is the expected uncertainty in $\langle S \rangle$.

The rank test was applied only for the −15° and −18°C data. The results are $Z(-15°C) = 2.46$ and $Z(-18°C) = 3.07$. This indicates that there is less than a 2% and 0.1% chance that the control samples would be obtained by a random draw from a population with the characteristics of the combined results for the control and NA sampling runs at −15° and −18°C.

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