PRODUCTION OF ICE IN TROPOSPHERIC CLOUDS
A Review

by Will Cantrell and Andrew Heymsfield

Our understanding of how ice is created and multiplied in the troposphere has advanced considerably in the last decade, but major challenges still remain.

The majority of the ~10^{25} hydrometeors in Earth's atmosphere at any moment are liquid water, while the rest are ice. Though only a small percentage of the total condensed water in the troposphere, ice exerts an enormous influence on processes ranging from precipitation and cloud electrification to radiative transfer. To understand and ultimately predict these processes, we must understand the ways in which ice forms in the atmosphere.

To best appreciate our limited understanding of ice, compare it with the liquid phase. We can accurately calculate the initial number of cloud droplets if the number and chemical composition of the preexisting aerosol particles are known as a function of size. In contrast, the physical and chemical principles underlying ice nucleation are poorly understood. Until about 10 yr ago, freezing rates of the

pure liquid calculated from theory disagreed with those measured in the laboratory or inferred from field measurements, by orders of magnitude in some cases (Pruppacher 1995; Jeffery and Austin 1997). Now, despite nominal agreement between theory and measurements, disagreements between the theories persist. The case for freezing catalyzed by a foreign substance is worse. Neither a generally accepted theory nor a commonly agreed upon measurement technique exists.

Secondary mechanisms can enhance the concentration (both number and mass) of ice. Ample laboratory evidence has characterized one secondary ice initiation process that operates in a restricted temperature range and only in the presence of large particles undergoing riming, but the mechanism for the process is still uncertain. It is very probable that key secondary ice production processes have not been identified outside of this temperature range and without the presence of liquid water.

This review is intended as a supplement to, not a replacement of, earlier reviews on ice nucleation in the atmosphere (Vali 1985; Laaksonen et al. 1995; Vali 1996; Szyrmer and Zawadzki 1997; Martin 2000; DeMott 2002) and secondary production (Mossop 1985; Beard 1992). In most cases, work done prior to 1990 is discussed in more detail in the above-mentioned references. We start our review with a

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discussion of homogeneous nucleation, which leads naturally to an examination of the heterogeneous case. Next, we take up secondary production, then conclude with a critical look at the areas in which progress is most needed.

HOMOGENEOUS NUCLEATION. Liquid water in the troposphere frequently exists at temperatures well below the melting point of ice, which is a consequence of the energy barrier characterizing all first-order phase transitions. Because freezing is such a transition, ice in the atmosphere is always a consequence of nucleation, though the amount can be enhanced by secondary mechanisms (see later). If nucleation proceeds from a stochastic event in the pure liquid or solution, without catalysis from a foreign substance, the process is known to be homogeneous.

Classical nucleation theory postulates that the magnitude of the energy barrier between the supercooled, metastable liquid and the thermodynamically stable, crystalline phase can be calculated by assuming that a microscopic fragment of ice forms within the supercooled liquid. The resulting change in the free energy of the system is the sum of two terms: the contribution from the bulk, which is negative, and the contribution from the surface, which is positive. At some critical size, which is a function of how far below the melting point the liquid is cooled, the contribution from the bulk outweighs the surface term. That point defines the magnitude of the energy barrier to nucleation. The nucleation rate is then calculated from an Arrhenius-type expression (Pruppacher and Klett 1997, section 7.1),

$$J = J_0 \exp\left(\frac{-\Delta E}{kT}\right), \qquad (1)$$

where ΔE is the height of the barrier, k is Boltzmann's constant, T is the temperature, and the prefactor J_0 is proportional to the surface energy between the ice embryo and the supercooled liquid and the flux of molecules from the liquid to the growing embryo. (Note that J has units of s^{-1} cm^{-3}. The nucleation rate for the entire sample is dependent upon its volume.) This expression, along with the analytical form of ΔE, is especially attractive for experimentalists because it provides closed-form expressions against which data can be evaluated.

For many years, rates calculated from classical nucleation theory disagreed with measured nucleation rates, which were either inferred from field data or measured in the laboratory. [For a more detailed discussion, see section 3 of Pruppacher (1995).] Liquid

water droplets were detected in orographic wave clouds, which is as close to a controlled experiment as nature provides, at temperatures as low as –40°C (Sassen and Dodd 1988; Heymsfield and Miloshevich 1993). With the data available at the time, classical nucleation theory predicted that droplets of that size should have frozen before being cooled to such low temperatures. Laboratory studies also strongly suggested that the theory might need to be revised. Droplets with diameters on the order of 0.2 μm did not freeze until cooled to temperatures approaching –45°C (Hagen et al. 1981), while 5-μm droplets did not nucleate until temperatures dropped below –37°C (DeMott and Rogers 1990). Theory and experiment were clearly at odds, though it was unclear whether the underlying tenets of the theory were at fault, or whether inputs to it were simply inadequate.

To calculate ΔE in Eq. (1), density, viscosity, specific heat, latent heat, and surface tension of water, all as a function of temperature, must be known. Until very recently, values for these quantities for temperatures below the melting point were extrapolated from data acquired above 0°C. Pruppacher (1995) proposed that water exhibits anomalous behavior near –45°C and extrapolated the properties that were needed to calculate the nucleation rate to lower temperatures based on that assumption. He also incorporated new data on the cooperative nature of hydrogen bonding into the model. However, the assumption of a singularity at –45°C was called into question almost as soon as it was published. By condensing water in a supersonic expansion, Bartell and Huang (1994) produced droplets of approximately 3-nm diameter, then probed them using electron diffraction. They found liquid water down to –70°C—a clear refutation of the singularity at –45°C.

Jeffery and Austin (1997) took a different approach to revising the data that were needed as input to classical nucleation theory, partially motivated by the studies showing that water probably did not possess the hypothesized critical point. They formulated an analytic equation of state for water (Jeffery and Austin 1999), which they used to calculate the density and enthalpy of fusion, which were then used to derive the surface energy. These parameters were used to calculate ΔE in the expression for the homogeneous nucleation rate.

Figure 1 is a plot of both Pruppacher's and Jeffery and Austin's (1997) calculated nucleation rates for temperatures of tropospheric interest, along with data from several laboratories. All of the data are from experiments in which the drops are suspended in air, excluding the possibility of artifacts from sub-

strates or emulsions. The calculated nucleation rates are in reasonable agreement with the data for temperatures greater than –38°C. At the lower temperatures, Pruppacher's calculation underpredicts the measurements by as much as two orders of magnitude, but at the moment, it seems that current theories and their representations in models are adequate to predict homogeneous nucleation rates for water droplets in the atmosphere.[1]

Homogeneous nucleation from nearly pure water droplets does occur in the atmosphere, for example, in the updrafts of cumulus clouds (Heymsfield et al. 2005; Rosenfeld and Woodley 2000). Though those droplets most likely form upon soluble aerosol particles, the droplets grow to a size such that the resulting solution is so dilute as to be nearly pure water. Homogeneous nucleation from smaller droplets, which is more likely the case in cirrus, implies more concentrated solutions. Just as the presence of a solute depresses the melting point of ice, it also depresses the freezing point of the liquid. One approach to calculating the nucleation rates for solutions is to utilize expressions for homogeneous nucleation of the pure liquid, but with a modified temperature of the form

$$T^* = T + \lambda \delta T, \qquad (2)$$

where δT is the melting point depression and λ is a numerical factor that relates the freezing point depression to δT (Sassen and Dodd 1988; Rasmussen 1982).

Koop et al. (2000) have postulated that the nucleation rate in an aqueous solution is independent of the nature of the solute and depends only upon the water activity. Many laboratory and field studies lend credence to that supposition. For instance, Möhler et al. (2003) measured the freezing rate of sulfuric acid droplets in the Aerosol Interactions and Dynamics in
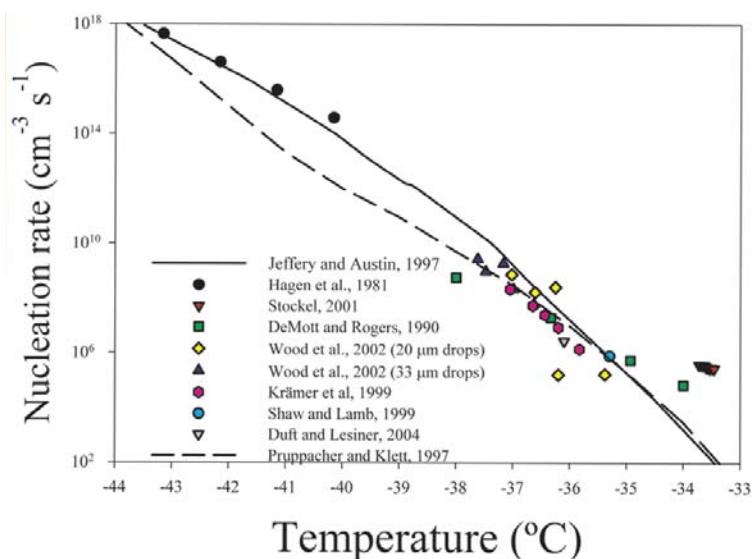
FIG. 1. Calculated nucleation rates using data from several experiments. All of the data taken from experiments are from suspended or freely falling droplets.

the Atmosphere (AIDA) 84-m³ chamber designed to mimic the temperatures and pressures of the atmosphere from the lower troposphere. The freezing rate of the droplets agreed with Koop et al.'s (2000) parameterization within the error of the measurement (see also Haag et al. 2003.) Cziczo et al.'s (2004) analysis of the residual aerosol particles from individual ice crystals in anvils of Florida cumulonimbus clouds during the Cirrus Regional Study of Tropical Anvils and Cirrus Layers (CRYSTAL)–Florida Area Cirrus Experiment (FACE) showed a preference for sea salt to be incorporated into ice crystals rather than left as interstitial aerosol. They attributed that to the fact that sea salt is present in the larger particles and is hygroscopic. Thus, it would form large, dilute drops, which would freeze preferentially, in agreement with Koop et al.'s model. In contrast, at temperatures less than –38°C, where homogeneous freezing dominates, Seifert et al. (2003a) found that residuals from ice crystals collected in the Southern Hemisphere during the Interaction of Chemistry and Aerosols (INCA) project did not show a pronounced tendency to be larger particles. The particles were not volatile when exposed to a temperature of 250°C, so they could not have been water mixed with either sulfuric or nitric acid—the most commonly assumed composition of aerosol particles in the clean, free troposphere (Seifert et al. 2003b). The authors of the study speculate that the nonvolatile residuals could have been small sea salt particles or insoluble particles that acquired a liquid coating that froze homogeneously. In either case, knowledge of size-segregated aerosol composi-

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[1] Pruppacher's (1995) hypothesized singularity at –45°C precludes applying his model to the measured point at –70°C (Bartell and Huang 1994). Jeffery and Austin's (1997) model overpredicts the nucleation rate at that point by approximately two orders of magnitude. This point is not included in Fig. 1 because such low temperatures are not important for nucleation of pure (or nearly pure) water droplets in the atmosphere and water droplets of such a small size are not found in the troposphere in any case.

tion may be necessary to adequately implement Koop et al.'s model (Seifert et al. 2003a), a conclusion that is echoed by Cziczo et al. (2004).

The spread in empirically determined values of λ in Eq. (2) contradicts the claim that freezing in solution is independent of the solute (DeMott 2002). In particular, Cziczo and Abbott (2001) noted that the spread in freezing temperatures of solutions of ammoniated compounds is outside the bounds that can be explained by experimental error or the different sensitivities of the techniques that are used to measured nucleation rates or temperatures. They concluded that either the measurements using infrared spectroscopy and a thermal gradient diffusion chamber are erroneous, or the assumption that surface tension and the diffusion activation energy are independent of solute is in error.

Despite its conceptual simplicity and success in predicting homogeneous nucleation rates in size and temperature ranges that are applicable to the atmosphere, classical nucleation theory is built upon assumptions that may prove to limit its usefulness. In what might be termed the classic version of classical nucleation theory, the microscopic fragment that initiates nucleation forms in the bulk liquid. As Eq. (1) shows, the nucleation rate should be proportional to the total volume of the liquid, irrespective of how it is dispersed. Djikaev et al. (2002) (see also Tabazadeh et al. 2003) have suggested that nucleation may be favored at surfaces, not in the bulk, under the condition that at least one facet of the crystal is only partially wetted by the liquid. The ice–water system does meet this condition (Elbaum et al. 1993). However, in experiments on droplets of 49- and 19-μm diameter, Duft and Leisner (2004) concluded that the freezing probability scaled with volume, not surface area. They estimated that surface nucleation would only become important for droplets smaller than 1 μm in diameter.

The idea that the embryo that initiates freezing has the same properties as the bulk crystal is at the core of classical nucleation theory. Under that assumption, freezing must be a transition from the liquid to hexagonal ice with no intermediate stage. Theory and experiments show the possibility of an intermediate stage (Oxtoby 2003). For instance, nanometer-sized droplets, freezing at –70°C, have a cubic, not hexagonal, structure (Bartell and Huang 1994; Huang and Bartell 1995). Previous studies using different techniques showed similar results (Mayer and Hallbrucker 1987; Keyser and Leu 1993). Evidence for cubic ice in the atmosphere includes photographs of a 28° halo (Riikonen et al 2000) and

sampled crystals that had an unmistakable cubic morphology (Goodman et al. 1989). Like supercooled water, the cubic form of ice is not a stable phase (Eisenberg and Kauzmann 1969), which may have consequences for ice in the atmosphere. If supercooled water droplets nucleate as cubic ice, the cloud would equilibrate at a higher relative humidity than would a cloud of hexagonal crystals, because the vapor pressure over the metastable phase will always be higher than that over the stable one. Because hexagonal ice has a lower vapor pressure, crystals that do convert from the cubic to hexagonal form will grow at the expense of those crystals that do not, becoming larger with greater fall velocities as a result. Cold clouds may dehydrate via this mechanism (Murphy 2003).

HETEROGENEOUS NUCLEATION. Homogeneous nucleation of ice is important mainly in the upper troposphere, where temperatures are consistently lower than –33°C.[2] Freezing at higher temperatures, at least on the time scales and volumes of water found in the atmosphere, occurs via catalysis by a foreign body, known as heterogeneous nucleation.

The most commonly used approach to heterogeneous freezing is an extension of the classical theory of homogeneous nucleation. The nucleation rate, shown in Eq. (1) still applies, but the magnitude of the energy barrier between the supercooled liquid and the crystal is lower because of the influence of a substrate. In Kurt Vonnegut's novel, *Cat's Cradle*, Dr. Asa Breed explains the process using the analogy of a stack of cannonballs. The cannonballs on the lowest level "teach" the ones in subsequent layers where they should be in order to form a stable structure. Heterogeneous nucleation of ice is envisioned as such a process, where a substrate forms a template onto which water molecules adsorb in a configuration close enough to the crystalline structure of ice that the energy barrier between phases is substantially reduced.[3]

Recent work on the heterogeneous nucleation of ice in the atmosphere is motivated by evidence, primarily from modeling studies, that heterogeneous freezing may significantly impact the radiative properties, both in the visible and infrared, of cirrus clouds. For instance, in a study of thin wave clouds

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[2] An exception to this would be ice fog, which is found in the high latitudes in both hemispheres.

[3] Kurt Vonnegut's brother, Bernard, was one of the first scientists in the United States, along with David Turnbull and Vincent Schaefer, to research the subject of heterogeneous nucleation of ice on a physicochemical level.

over New Mexico, DeMott et al. (1998) concluded that heterogeneous processes initiated ice formation before that of homogeneous freezing alone, and caused the ice crystal spectrum to be significantly broadened to larger sizes. The implication is that ice crystals formed via ice nuclei would quickly grow to larger sizes and possibly be the first to precipitate from the cloud because they have a "head start."

The leading candidates for heterogeneous nucleators to date are mineral dust and emissions from aircraft, primarily soot. Mineral dust is frequently lofted from both the Sahara and Gobi Deserts and is transported great distances. During CRYSTAL–FACE, DeMott et al. (2003b) reported ice nuclei concentrations of 1 cm^{-3} at –36.5°C and 123% relative humidity with respect to ice through a layer 2 km deep during a time period when lidar data, air parcel backtrajectories, and surface sampling confirmed the presence of dust from Northern Africa over the region. The authors asserted that such concentrations are 100 times greater than median concentrations encountered in "normal" conditions (Rogers et al. 1998). Sassen et al. (2003) implicated dust in glaciating a moderately supercooled (–5.2° to –8.3°C) altocumulus cloud. In a ground-based study that utilized a single particle mass spectrometer downstream of an ice nucleus counter, DeMott et al. (2003a) found that heterogeneous ice nucleators were dominated by mineral dust and/or fly ash and metallic particles. They noted that particles classified as mineral dust and/or fly ash were generally unmixed with other species; sulfate and/or organic material were detected with the particles only 25% of the time.

Interest in cirrus clouds motivated several laboratory studies as well. Zuberi et al. (2002) extended many previous studies of heterogeneous nucleation by investigating two common atmospheric constituents—kaolinite and montmorillonite—immersed in an ammonium sulfate solution in the temperature range from –34° to –75°C. They found that the freezing temperatures of 10–55-μm-diameter droplets with dust immersed in them were 10°C higher than those of droplets with the same concentration of ammonium sulfate but no dust. The authors did not report a difference in the efficiency of kaolinite over montmorillonite, but did note that dust was more effective when the weight percentage of ammonium sulfate in the solution exceeded 27. Earlier work from the same group showed that heterogeneous nucleation by solid ammonium sulfate or letovicite could be very important in the upper troposphere (Zuberi et al. 2001). Hung et al. (2003) opted to study hematite and corundum aerosol particles in an ammonium sulfate

solution in the temperature range from –56.6° to –40.9°C. They showed that the presence of the mineral inclusion shifts the apparent freezing temperature upward by as much as 6°C. They also inverted their data to report surface area–normalized nucleation rates (i.e., number of nucleation events normalized by the surface area of the mineral immersed in the droplet) ranging from 100 to 10^6 cm^{-2} s^{-1}, with the values depending on temperature, the size of the mineral particle in the aqueous droplet, and the mole fraction of ammonium sulfate in the solution.

Prompted by the possibility that soot from aircraft exhaust might act as ice nuclei in the upper troposphere, DeMott et al. (1999) investigated the ice-forming activity of black carbon particles, both as formed and then as treated with sulfuric acid. The untreated black carbon particles acted as either deposition or absorption nuclei at all temperatures below –42°C. The activation characteristics of particles that had been treated with a monolayer of sulfuric acid were not significantly different from the untreated particles. Particles that had the equivalent of multiple layers of acid initiated ice formation as well as the untreated particles for temperatures above –53°C and better than the untreated particles for temperatures lower than that threshold.

The surface character of soot particles can have a significant impact on its ice-nucleating efficiency. If the surface contains chemical groups capable of forming hydrogen bonds with water molecules, the soot's ice-forming potential could be increased. Particles generated using a method known to enhance the concentration of OH and carbonyl groups were three orders of magnitude more efficient as ice nuclei at –20°C than those generated using a method that produced particles that were virtually free of OH and carbonyl groups on the surface (Gorbunov et al. 2001). The surface characteristics of soot are not the only conflating factor. The morphology also presents a challenge. Quasi-elastic neutron-scattering studies of water on kerosene soot showed that water in a liquidlike state exists in pores of particles down to –73°C (Suzanne et al. 2003).

As noted above, most investigators targeted particulates as the primary heterogeneous ice nucleators in the atmosphere. One alternative that is receiving increasing attention is films of high-molecular-weight organic compounds on droplets. Such compounds are emitted to the atmosphere, especially in regions that are influenced by biomass burning (Elias et al. 1999). Some of the best heterogeneous ice nucleators yet discovered are long-chain alcohols and testosterone, both of which catalyze the phase transition at a

supercooling of only 1°C (Popovitz-Biro et al. 1994; Fukuta and Mason 1963),[4] though there is evidence that organic material associated with pollutants may significantly depress the homogeneous freezing temperature in some cases (DeMott et al. 2003b). Because they are amphiphilic, long-chain alcohols self-assemble at the air–water interface, forming a two-dimensional crystal with a unit cell that can be represented as a distorted hexagonal cell, which differs from the lattice of the basal plane of ice with a mismatch of only 0.4% (Popovitz-Biro et al. 1994). Lead iodide also has a mismatch of only 0.4%, but catalyzes the freezing transition at a temperature of −6°C (Bryant et al. 1959), so the lattice match between the alcohol and ice cannot be the only explanation for the high characteristic freezing temperature.

Using the alcohol monolayers, Seeley and Seidler (2001) investigated a phenomenon unique to heterogeneous nucleation. Preactivation, also known as the memory effect, is explained as an increase in the effective freezing temperature after the ice nucleator has catalyzed the phase transition once or has been cooled below −40°C (Pruppacher and Klett 1997, 337–338). The effect is lost if the temperature of the system exceeds some threshold, which is typically close to the melting temperature. Though the initial explanations appealed to remnants of ice in cracks, crevices, or other small cavities where ice might persist, further work showed that it was due to an ordered, icelike layer of water molecules on the substrate, which is stable at temperatures well above the melting point (Evans 1967; Roberts and Hallett 1968; Edwards et al. 1970; Edwards and Evans 1971). Though Seeley and Seidler's (2001) work showed that the long-chain alcohols did exhibit preactivation, their findings differed from previous studies in an important way. The characteristic freezing temperature changed only after the alcohol film was exposed to an elevated temperature. The important point is that ice formation, or cooling below the melting point of ice, was not required before the alcohols acted as effective ice nucleators, which implies that the ordered layer induced by the alcohols was already present at room temperature.

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[4] A wide variety of organic compounds were tested for their ice-nucleating ability in the 1960s. Much of the research was driven by the desire to find effective substances with which to seed clouds, though as Fukuta (1966) noted, "Such studies of organic nuclei are important . . . because of the light that can be shed on the fundamental mechanism of heterogeneous ice nucleation" (see Fukuta and Mason 1963; Langer et al. 1963; Parungo and Lodge 1965, 1967).

Rosinski (1991) and Rosinski and Morgan (1991) documented another type of conditioning that led to an ice-nucleating ability where none had been apparent before. They conditioned particles in the following cycle. First, particles were exposed to supersaturated water vapor at a temperature below 0°C, then the resulting droplets (no ice crystals formed) were evaporated. Finally, the particles were exposed to water vapor that was supersaturated with respect to ice, but subsaturated with respect to liquid water (variable temperatures, down to −20°C). When subjected to that conditioning, a fraction of the particles formed ice crystals by deposition from the vapor phase. None of the samples exhibited ice formation from the vapor phase in the absence of such conditioning. In contrast, the authors also documented deactivation of ice nuclei. Ice crystals that had formed by the freezing of droplets, which had condensed on cloud condensation nuclei (by definition), sometimes lost their ice-nucleating ability after the ice was sublimed away. In other cases, the ice-forming activity persisted through several condensation–freezing–evaporation cycles. The chemical composition of the specific substances (or mixtures) are unknown. Rosinski (1991) also documented the freezing of solution droplets as they evaporated. That mechanism was invoked in a model study of a wave cloud when other modes of nucleation failed to explain both the peak ice number concentration and ice water content (Cotton and Field 2002).

Contact nucleation is another vexing issue in ice nucleation in the atmosphere. It is defined as the freezing of a droplet initiated by contact with an aerosol particle. Many substances have different freezing thresholds when they act as contact nuclei, as opposed to when they act as deposition, condensation, or immersion nuclei, indicating that the freezing mechanism is different for the different modes. Several investigators have put forward conjectures on the mechanism of contact nucleation, all of which depend on the contact nucleus impinging upon the droplet's surface from air (Pruppacher and Klett 1997, 338–341).

Figure 2 is an example of a recent, serendipitous manifestation of contact nucleation. The experiment, which employed a device similar to the one described in Seeley and Seidler (2001), probed the freezing characteristics of volcanic ash. Droplets of water (millimeters in diameter) with a single particle of ash (~100 μm diameter) were immersed in silicon oil, then cycled through hundreds of freezing events. The freezing temperature in each cycle was detected from the increase in temperature due to the release of latent heat upon the phase transition (Mi et al. 2004).

The first thing to note is that the freezing temperature is remarkably stable for a given configuration of the ash–droplet system. The mean freezing temperature when the ash intersects the surface of the droplet is –21.5°C, with a standard deviation of 0.1. The standard deviation increases when the particle is completely immersed in the water, but is still only 0.3. The most intriguing aspect of the data shown in Fig. 2 is the abrupt drop in freezing temperature when the ash particle no longer intersects the surface of the droplet. The behavior is not limited to a single set of experiments or a single ash particle. It has been observed in every experiment in which the particle intersected the surface of the droplet. The temperature shift cannot be a consequence of the act of impingement upon the surface of the water droplet because it persists as long as the ash particle intersects the surface of the droplet. The causes underlying this inside-out contact nucleation are currently unknown, though an extension of Djikaev et al.'s (2002) theory of nucleation induced at the surface of pure water may be applicable.

There are a variety of other mechanisms that have been proposed for heterogeneous (used here in the broadest sense) nucleation. Ion tracks, produced by cosmic rays, might initiate freezing in haze droplets in the upper troposphere to stratosphere. This hypothesis is advanced as one possible mechanism to explain correlations between climatically relevant parameters and the flux of cosmic rays through Earth's atmosphere (Tinsley and Heelis 1993). Seeley et al. (2001) exposed a microliter drop of pure water to a 0.2 μCi Pb[210] source (an α particle producer) for 225 freezing cycles, then contrasted the statistics of the freezing events with those obtained when the source was not present. Based on that comparison, the authors concluded that the ionizing radiation did not affect the nucleation rate.

SECONDARY PRODUCTION. Though all ice in the atmosphere is the consequence of a nucleation event, the concentration of ice in many cumulus and stratus clouds, where initial ice production is predominantly by heterogeneous nucleation, frequently exceeds the concentration of ice nuclei by orders of magnitude. This implies a secondary production mechanism.

Production of splinters during riming, known as the Hallett–Mossop process (Hallett and Mossop 1974; Mossop and Hallett 1974; Mossop 1976), is the most commonly invoked mechanism. Figure 3 is a graphical illustration of two of the most important variables in the riming–splintering process—the
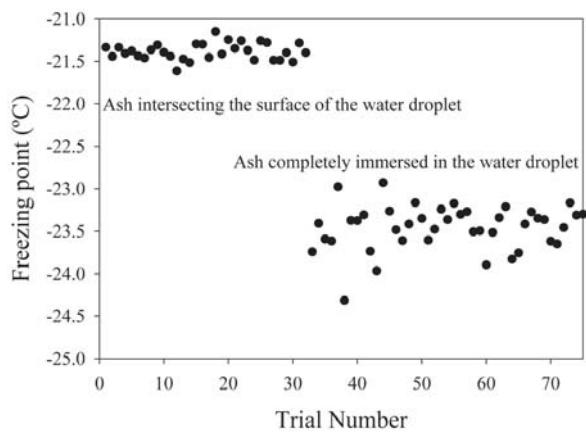
FIG. 2. Freezing temperature, as a function of trial number, of a water droplet with a single particle of volcanic ash in it. The freezing temperature is 2°C lower when the ash is completely immersed in the drop. This is a manifestation of a form of contact nucleation, though it is not consistent with the conventional mechanisms (see text for discussion). [Data courtesy of R. Shaw, Department of Physics, Michigan Technological University.]
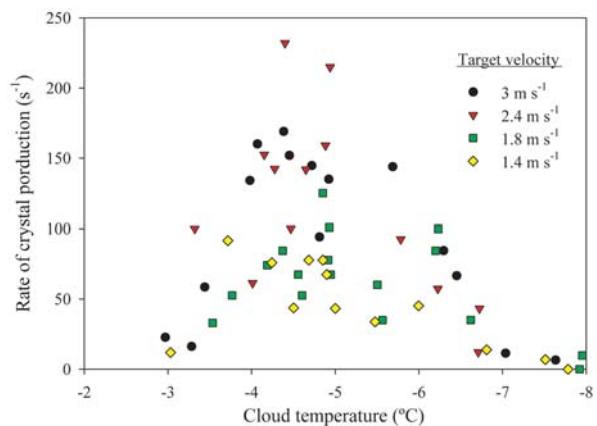
FIG. 3. Rate of crystal production from a riming, rotating rod in a cloud chamber. [Adapted from Mossop 1976.]

temperature of the cloud of supercooled water and the speed at which the graupel particle falls through it. In those experiments splinters formed only when the air temperature was lower than –3°C, but was higher than –8°C, and the number of crystals produced increased with the speed of the collecting graupel. Saunders and Hosseini (2001) extended the range of velocities shown in Fig. 3 and showed that ice production passes through a maximum at a speed of 6 m s^{-1}, which is hypothesized to be a consequence of a trade-off between an increased capture efficiency for small drops and the spreading of droplets as they hit the surface of the graupel. The rate at which sec-

OUTSTANDING PROBLEMS

Homogeneous nucleation

- What role do collective fluctuations in water play?
  Do water molecules make the transition from liquid to nascent crystal one by one or in groups? The hydrogen bonding network does become increasingly cooperative with decreasing temperature (Hare and Sorensen 1990; Rice and Sceats 1981), but X-ray scattering data showed that the correlation lengths of density fluctuations in water are virtually independent of temperature (Xie et al. 1993). However, those same experiments showed that the number of water molecules incorporated into clusters increased as the temperature decreased.
- What is the structure of the ice embryo and where does it form?
  Classical nucleation theory assumes that the ice embryo forms in the bulk liquid and has the structure of the bulk crystal. Both assumptions have been challenged (Djikaev et al. 2002; Oxtoby 2003).
- Is freezing only a function of the water activity?
  Koop et al.'s (2000) conjecture holds for a wide variety of substances. Ammoniated compounds seem to be an exception. Is this a peculiarity of ammonia or does it indicate a flaw in the model?

Heterogeneous nucleation

- What are the most important properties of the heterogeneous nucleator?
  Lattice match between ice and substrate is sometimes a good indicator of how effectively a substance will promote ice nucleation, but it is not predictive. The presence of defects in the substrate, the type of bond that the adsorbing water molecules form with the substrate, and the type of atoms exposed on the substrate all affect heterogeneous nucleation. The relative importance of these factors is unknown.
- What is the mechanism underlying contact nucleation?
  None of the mechanisms put forward to explain contact nucleation explain the data shown in Fig. 2.
- What is the mechanism underlying evaporation nucleation, and is it important in the atmosphere (e.g., on the trailing edge of wave clouds)?
  Rosinski (1991) documented ice nucleation in solution droplets as they evaporated. Does this happen at a critical solute concentration? Is it more important for some solutes than others?
- What role do organic compounds play in ice nucleation?
  Some organic compounds are very effective ice nucleators. There is evidence that organic compounds inhibit ice nucleation. What is their role in the atmosphere? What is the variation with time and space?

Secondary production

- Are there secondary production mechanisms that operate in the presence of liquid water other than riming–splintering?
  The Hallett–Mossop process does not explain some documented cases of secondary production. Is there another process operating, or is the Hallett–Mossop process not sufficiently understood?
- Are there significant secondary production mechanisms that do not require the presence of liquid water?
  Crystals (especially dendrites) will break up in certain conditions, but not in sufficient numbers to produce rapid ice multiplication. Are there other mechanisms that have not been identified?
- How are ice particle size distributions maintained?
  Size distributions of ice particles consistently show more small particles than large ones (Heymsfield and Platt 1984). This implies that either small particles are continually being created or that they are prevented from growing. What mechanism(s) sustains the small mode?

ondary particles are produced is also sensitive to the surface temperature of the graupel particle and the size distribution of the supercooled water droplets (Pruppacher and Klett 1997, 355–360).

In many instances, the Hallett–Mossop process is consistent with the concentration of ice measured in cumulus clouds. For instance, Hogan et al. (2002) observed small ice crystals at concentrations up to 1000 l^{-1} in embedded convection in a frontal system off the coast of the United Kingdom. At the temperature at that level in the cloud (–6°C), homogeneous nucleation is virtually impossible and the authors argued that typical heterogeneous ice nuclei concentrations were from three to five orders of magnitude lower than the measured ice concentration. The peak in the concentration of ice was above a region believed to contain riming particles in the Hallett–Mossop temperature range. Calculations showed that splinter particles thrown off in that region could grow to a size detectable in the time required to loft them to the higher level. Those considerations, along with the narrow spatial extent of the enhanced concentrations of ice, led Hogan et al. to conclude that the Hallett–Mossop process was responsible. A model-

ing case study of that system also concluded that the enhancement in ice crystal concentration over that due to primary nucleation was consistent with the Hallett–Mossop process (Phillips et al. 2003).

Studies of ice production in cumulus clouds in New Mexico led to essentially the same conclusion (Ovtchinnikov et al. 2000). The modeling study, based on data reported by Blyth and Latham (1993) and Blyth et al. (1997), showed that two distinct phases of ice production occurred in the cloud. Heterogeneous nucleation was first, producing concentrations on the order of 1 l^{-1}. The authors attributed the second phase to the Hallett–Mossop process. The field studies showed that ice was most frequently observed in downdrafts, a result that the model ascribed to the time required for small, newly nucleated crystals to grow to a size that was detectable by typical instrumentation on research aircraft. By the time the crystals were large enough to be detected, they advected from updrafts into downdrafts along the edges of the cloud. According to Ovtchinnikov et al., a fraction of those crystals were entrained into the primary updraft and initiated the Hallett–Mossop process. The authors note that in regions of high liquid water content, the ice particle concentration may increase by a factor of 10 on the time scale of a few minutes.

In a synthesis of data from frontal clouds, maritime convective clouds, and continental convective clouds, Bower et al. (1996) concluded that in most instances, ice concentrations could be reconciled with either primary production or the Hallett–Mossop riming–splintering mechanism. The authors noted that in some cases, ice was found in concentrations greater than could be explained by primary nucleation, and at temperatures outside the range applicable for riming–splintering. Mason (1998) suggested that in the cases where Bower et al. found appreciable ice concentrations in frontal clouds in the temperature range of –15°C that slope convection had advected splinters that originated in the Hallett–Mossop zone. He pointed out the presence of liquid water between the –12° and –15°C levels, which would provide an ample reservoir of water vapor, enabling small crystals to grow to an observable size during transport from the lower levels of the cloud.

The most puzzling observations of ice concentrations in clouds is presented in a series of papers spanning nearly 10 yr by Hobbs and Rangno (1985, 1990) and Rangno and Hobbs (1991, 1994). In flights over the Pacific Northwest, over both ocean and continent, they documented numerous instances of ice concentrations exceeding those that could be explained by

primary nucleation. In many cases, the authors concluded that the Hallett–Mossop riming–splintering process could not have produced ice concentrations of the magnitude that they observed in the time available. They give a concise outline of their rationale in Hobbs and Rangno (1998). Their three most salient points are that the clouds glaciated much faster than the Hallett–Mossop theory could explain, the crystal habits observed were often not compatible with the temperature range in which the Hallett–Mossop mechanism operates, and high concentrations of small ice particles appeared concurrently with frozen drizzle drops, not afterward as would be expected if the smaller crystals were a product of riming–splintering. The authors concluded the final paper in the series (Rangno and Hobbs 1994) with a summary of their findings. They admitted that the mechanism for the high concentrations of ice they report was perplexing, closing "In summary, the origin of ice in cumuliform clouds remains a mystery. However, the database we have presented here and elsewhere should be adequate for developing and testing proposed mechanisms."

Spurred in part by Hobbs and Rangno's results, investigators put forward a variety of mechanisms other than that of Hallett–Mossop. Mechanical fracture, particularly of dendritic crystals, is one of the primary suspects. Oraltay and Hallett (1989) examined evaporating dendritic, columnar, and plate crystals in the millimeter-sized range and reported that fracture occurred only for dendrites. A 5-mm crystal produced 10–30 pieces, with the number depending on both the relative humidity and temperature. Bacon et al. (1998) studied evaporating 100–200-μm frost particles in an electrodynamic trap in the temperature range range from –2° to –30°C and found that breakup rates were independent of relative humidity. The authors observed no fracture for pristine columns or plates or for any crystals during growth from the vapor phase. Though mechanical fracture will enhance ice concentrations in some clouds, it appears insufficient to explain the magnitude of the increase in ice over the time scale summarized in Rangno and Hobbs (1994).

CONCLUSIONS. From the preceding review, we draw two conclusions. The first is that we have made significant progress in several areas, most notably homogeneous nucleation and, to a lesser extent, the secondary production of ice. The second conclusion we draw is that though there have been advances made in identifying important sources of ice nuclei (e.g., desert dust), progress in heterogeneous nucleation is

desperately needed. Hardly a paper dealing with the subject can be found that does not mention the lack of a unifying, theoretical framework. The following three examples should serve to make the point.

- "Definitive laboratory and atmospheric benchmark data are needed to improve the treatment of heterogeneous nucleation processes" (Lin et al. 2002).
- "Parameterizing heterogeneous freezing is much more difficult than it is for homogeneous freezing because the factors controlling heterogeneous processes are not well known, both experimentally and theoretically" (Kärcher and Lohmann 2003).
- "It seems that such a theoretical framework is necessary to separate the important factors for ice-nucleation activity from the unimportant ones, to distinguish effects altering the degree of nucleation ability, and also to develop adequate ice nuclei measurement techniques. On the other hand, well-designed laboratory experiments and field observations provide basic information for the theoretical approach to the nucleation process. A systematic, step-by-step approach in both the theory and detection technique appears to be urgently needed" (Szyrmer and Zawadzki 1997).

It is true that laboratory and field experiments have yielded important clues as to the form that a theory of heterogeneous nucleation might take, but data are needed in key areas. There is still room for experiments designed to probe specific mechanisms of heterogeneous nucleation. Such experiments are fundamental, with consequences far beyond atmospheric science. For instance, it is clear by now that a lattice match between a substrate and ice is suggestive, but not a quantitative predictor of its ice-nucleating efficiency. Other mechanisms need to be investigated in a way that eliminates confounding factors such as defects. The high-molecular weight organic compounds discussed above are one promising avenue in this respect, as are freshly cleaved, single-crystal substrates like BaF_2. Surface-sensitive techniques like atomic force microscopy and non-linear spectroscopy (e.g., sum frequency and second harmonic generation) also offer promise as tools to investigate the mechanics of how water hurdles the energy barrier between the supercooled liquid and stable crystal. These mechanistic investigations will aid in the interpretation of data from 1) laboratory experiments, which simulate conditions experienced by aerosol particles in the atmosphere [e.g., from the AIDA chamber (Möhler et al. 2003)], and 2) from field campaigns, which collect a wide array of data, constraining the mechanisms that might be responsible for freezing [e.g., flights during the Interaction of Aerosol and Cold Clouds (INTACC) campaign (Cotton and Field (2002)].

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