ICE CRYSTAL BREEDING

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ABSTRACT. When ice crystals rapidly grow and aggregate in the Desert Research Institute (DRI) cloud chamber, they frequently produce new ice crystals without the presence of ice forming nuclei. Ammonium salts, initially present in the cloud water and later detected in the ice crystals, enhanced this phenomenon. The continual ice crystal production was observed at temperatures from -4C to -30C, although it occurred more frequently when the ice crystals were long needles or dendrites--highly non-spherical. Ice multiplication and secondary ice formation are commonly used in the meteorological literature to describe the phenomenon. The chemical literature (crystal growth) predates the meteorological literature and describes a similar process that occurs in systems of crystals growing in solution. The chemical literature calls the phenomenon crystal breeding. This paper describes the similarity between the systems and advances two postulated mechanisms, both of which are consistent with our observations of ice crystal breeding and other observations of crystal breeding in solution.

1. INTRODUCTION

In many ways, atmospheric ice crystal growth processes are analogous to processes which occur during crystallization of inorganic and organic chemical compounds from solution. There is no intrinsic reason why the nucleation and crystallization of water substance should be an exception to the way other substances nucleate and grow crystals. Thus, crystal formation and growth information derived from chemical research may be relevant to weather modification. For example, our previous work on rapid ice formation (Finnegan and Pitter, 1988a) drew upon crystallization concepts of spontaneous crystallization at high supersaturations.

The unfamiliarity of most weather modification researchers with crystallization literature has led to different nomenclatures in the two fields. Crystallization science studies need to be elucidated before they can be applied to weather modification. For example, during crystallization of some inorganic and organic compounds from solution, there may occur a sudden increase in the rate of formation of new crystallites (the smallest observable crystals). This occurs below the metastable limit (the supersaturation at which crystals spontaneously form and grow from the mother phase; also, in cloud physics, the supersaturation where homogeneous nucleation occurs), and requires the presence of some growing crystals to trigger this process. This phenomenon is called **crystal breeding** (Strickland-Constable, 1968). In the sugar industry, crystal breeding is called **false grain**, and has been known for over a century. This phenomenon is used by sugar boilers to induce and grow sugar crystals to a desired size (Van Hooke, 1961), and in industrial crystallizers to control the size and yield of the final product. Although this phenomenon is used commercially, it is poorly understood, mechanistically. Crystal breeding depends on a number of factors, including the presence of foreign impurities in addition to those factors mentioned above.

The growing crystals appear, in a sense, to catalyze the formation of new crystallites in solution. The presence of the catalyst speeds up a process of transformation of matter without itself being changed in the process; a catalyst neither initiates nor affects the equilibrium point of the process. In chemistry, processes include both chemical reactions and phase changes. Our emphasis here is that chemistry views phase change catalysis much differently than cloud physics views ice nucleation. To the chemist, a catalyst speeds up a process which is already occurring, but perhaps at a rate too slow to be apparent to an observer. In contrast, to the cloud physicist, an ice nucleant induces the formation of ice embryos: no embryos form in the absence of the nucleant, except under conditions of homogeneous nucleation.

If all formation of new crystals could be demonstrated to be either primary (heterogeneous) or homogeneous, then the chemical and cloud physical points of view of ice formation might be regarded as two views of the same thing: the chemists are studying the process, while the cloud physicists are studying the properties. This dichotomy has long been recognized (Williamson, 1851). However, observations of crystal breeding in crystallization science and of secondary ice formation in atmospheric clouds strain the dichotomy of the two points of view.

Secondary ice formation has been documented in clouds around the world and is suspected to be rather common. It is called a variety of names, including **ice multiplication** and **secondary ice nucleation**. Mossop (1985) summarizes observations of the phenomenon and investigations of various proposed mechanisms. However, the phenomenon is not yet completely understood, mechanistically. Our observations of this process under controlled conditions in the DRI cloud chamber indicate that this process is similar to, and perhaps identical to, crystal breeding in solution.

In the crystallization literature, crystal breeding is an interesting topic of research. Mason and Strickland-Constable (1966) point out that breeding may take place by several distinct mechanisms: initial breeding, needle breeding, and collision breeding. Initial breeding occurs when a dry crystal is added to a supersaturated solution, even at very low supersaturations. It occurs all at once, and is not repeated. It may be the result of small microcrystals on the surface of the parent crystal. If the parent crystal is pre-treated to dissolve any initial microcrystals, initial breeding can be eliminated.

Needle breeding is observed when crystals of $MgSO_4 \cdot 7H_2O$ (Epsom salts) are pre-treated then immersed in a solution of sufficiently high supersaturation. Apparently, small needles grow out of the ends of the crystal prism and are easily broken off if the solution is stirred. However, the yield due to needle breeding is low.

Collision breeding was briefly described by Mason and Strickland-Constable (1966) and investigated in more detail by Lal et al. (1969). They reported that the rate of formation of new crystallites induced by touching a mother crystal with a glass needle or rod was highly dependent on the amount of supersaturation. When the solution was stirred so that the mother crystal spun on the bottom of the beaker, high rates of crystallite formation were detected. Also, when the mother crystal touched the side of the beaker, new crystallites were formed. Identification of the mechanism responsible is complicated by several things. First, the stirring rate did not affect the rate of formation of crystallites. Second, although a minimum contact force was required for a glass needle or rod to create new crystallites, additional force did not yield additional crystallites. Third, the number of new crystallites formed was highly dependent on supersaturation. Thus, although the contact often produced fractures of the mother crystal surface, the new crystallites were probably not formed from shards of the mother crystal by breakage; their formation rate was strongly dependent on the supersaturation.

Wissing et al. (1986) studied the contact of a polyvinyl chloride rod with the basal plane of a polyhedral potassium dihydrogen phosphate (KDP) crystal and found that the minimum energy required to produce secondary crystallites was a function of the purity of the KDP used to grow the mother crystal. When the KDP contained more impurities (typically 10 ppm Fe^+), the minimum energy to produce crystallites was lower by a factor of two from the higher purity KDP mother crystal.

In cloud physics, studies of ice crystal nucleation and growth have usually been conducted with pure water. Although several studies have shown that low concentrations of organic vapors affect ice crystal habit or morphology (Vonnegut, 1948; Hallett and Mason, 1958; and Odencrantz, 1968), it has not been generally recognized that studies of ice crystal growth must also include consideration of the concentrations of various salts in the crystals. In the atmosphere, a variety of soluble ionic salts are present, including ammonium sulfate, ammonium carbonate, and sodium chloride, which have different effects on the growth of ice crystals from the vapor. In contrast, it is well-known in crystal growth research that the shapes of crystals depend in part on the impurities present in the system. For example, sodium chloride crystals grow as cubes from pure solutions, but as octahedrons from solutions with urea impurities.

Our research on the effects of dilute concentrations of soluble ionic salts in vapor-grown ice crystals has focused on ice crystal growth and interaction mechanisms (Finnegan and Pitter, 1988b). It was initially recognized that T-shaped aggregates could not be explained by conventional concepts of ice crystal interactions. Since electric forces due to external electric fields or net charges on the crystals could not be responsible for T-shaped crystals, the possibility of higher order charge distributions was examined. We found that a higher order charge distribution, represented by electric dipoles across each growing ice crystal interface, provided an appropriate charge distribution for enhancing the probability of T-shaped aggregate junctions, and that the electric potential difference across each growing ice crystal interface strongly resembled that described by Workman and Reynolds (1950) for ice growing in bulk supercooled water.

The observational data of aggregate junctions (Finnegan and Pitter, 1988b) supported the postulate of electric multipoles in growing ice crystals, and prompted the investigation of the phenomenon in other ice crystal processes. As a result, the effect of included chemical ions on ice crystal morphology and symmetry (Pitter and Finnegan, 1989) was established and the effect of an electric multipole charge distribution on aerosol scavenging (Pitter and Zhang, 1990) was numerically determined. Therefore, on the basis of a broad spectrum of cloud microphysics and chemical phenomena which have been experimentally observed and numerically simulated, we suggest that the electric multipoles exist and are important in the evolution of ice crystals in atmospheric clouds.

During our cloud chamber studies of the effects of charge distributions in growing ice crystals upon microphysical and chemical processes, we obtained interesting results relevant to ice crystal breeding (ice multiplication). These findings are detailed below.

2. EXPERIMENTAL

The experiments were conducted in the Desert Research Institute's 6.7 m^3 cloud chamber, which is described in detail by Steele et al. (1980). The experiments were conducted at atmospheric pressure (850 mb) and constant temperature for each experimental run. The walls of the chamber were rinsed prior to the first experimental run of the day, thus forming a smooth ice glaze.

Cloud water was produced by an ultrasonic nebulizer. The cloud water consisted of distilled, deionized water or 10^{-4} normal solutions of sodium nitrate ($NaNO_3$), ammonium carbonate [$(NH_4)_2CO_3$], or ammonium sulfate [$(NH_4)_2SO_4$]. The air which drew the nebulized droplets into the chamber was filtered and passed through charcoal, removing any foreign aerosol particles and many organic vapors. The nebulizer was operated at room temperature and continuously introduced droplets into the cloud chamber. This

resulted in the formation of a region of transient supersaturation with respect to water within the chamber in the vicinity of the nebulizer inlet.

The cloud chamber liquid water content was measured by transmissivity of a 10.2 μm laser beam. Gertler and Steele (1981) demonstrated that this method is insensitive to the drop size distribution for drop sizes generated during cloud formation within the chamber.

Experiments were conducted at temperatures from -2 to -30C. Each experiment was conducted at a constant temperature; the air temperature was monitored and found to be within 0.2C during any run. Liquid water content at the beginning of the test varied between 1.5 and 3.0 g m^{-3}.

Ice was nucleated by expansion of moist compressed air. The ice crystals grew by vapor diffusion and fell out to the chamber floor.

3. OBSERVATIONS

Ice crystal breeding was detected during some, but not all, experimental runs. The determination of ice crystal breeding for each run was based on the length of the run, microscopic analysis of ice crystal morphology, and the attenuation noted by laser transmissometers. These observations and their relevance to ice crystal breeding are described below.

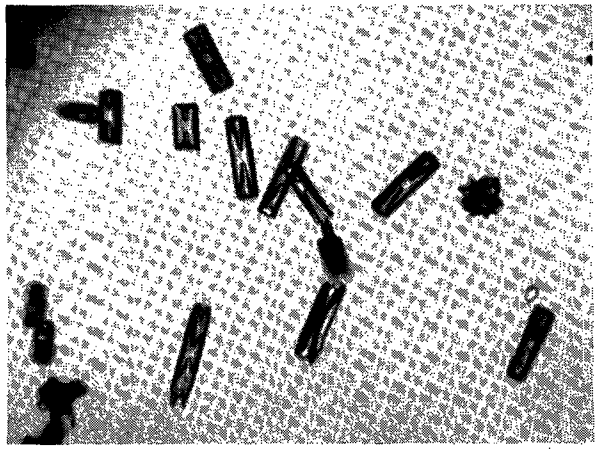

Figure 1. Narrow ice crystal size distribution with homogeneous morphology resulting from simultaneous ice formation by adiabatic expansion of moist air and subsequent growth at water saturation, with no ice crystal breeding. This run was conducted with sodium chloride solute in the cloud water at a chamber temperature of -6C.

The duration of ice crystal formation in the chamber was documented both by the continued collection of ice crystals on microscope slides placed in the chamber and by visual observation, viewing the scintillations of a narrow beam of light directed though the chamber. In some cases, ice crystals were formed by nucleation from the adiabatic expansion and rapidly grew in the presence of liquid water drops, so that the crystals settled out within 10 minutes. In other cases, a continuous production of ice crystals was observed in the chamber for periods exceeding 15 minutes and occasionally over 60 minutes. Since ice crystals in the presence of a liquid cloud grow rapidly and quickly acquire significant fall speeds, the longer duration of ice in the chamber cannot be explained by the initial nucleation pulse: the ice germs created by adiabatic cooling of moist compressed air must either grow quickly, immediately after their formation, or they will evaporate. We used the duration of the experiment as an indicator for ice crystal breeding.

Uncoated glass slides were placed in the cloud chamber to collect ice crystals for microscopic analysis. Initially, the analyses were performed to determine the configuration of aggregate junctions (Finnegan and Pitter, 1988). However, it was noted that the presence of specific soluble ionic chemicals gave rise to ice crystals with characteristic shapes (Pitter and Finnegan, 1988), and we observed that the shorter experimental runs gave the most consistent ice crystal morphological results. When the ice crystals quickly fell out of the chamber, the microphotographs revealed a homogeneous crystal morphology and a narrow size distribution, as shown in Figure 1.

In the runs where ice crystals were produced for much longer periods of time, the size distribution was broad, the ice crystal morphology was not homogeneous throughout the crystal population, and the smaller crystals resembled the morphology of pure water, rather than the solute-containing crystal morphology typical of the larger crystals, as shown in Figure 2.

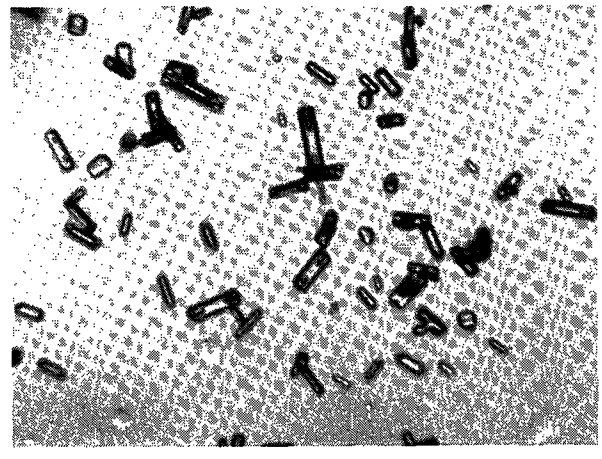

Figure 2. Broad size distribution resulting from ice crystal breeding. This run was conducted with ammonium sulfate in the cloud water at a chamber temperature of -6C.

A 10.2 μm CO_2 laser transmissometer was used to determine the liquid water content of the supercooled liquid water cloud, according to Gertler and Steele (1981), prior to ice nucleation. After nucleation, the transmissivity exhibited a short attenuation pulse, as the ice crystals which were initially nucleated grew through the size of maximum attenuation, approximately the size of the wavelength of the radiation. Petrushin (1983) demonstrated that randomly oriented nonspherical ice crystals, both plates and columns, have higher extinction coefficients at infrared wavelengths similar to their size. Ice crystals thus have maximum impact on the extinction of the CO_2 laser transmissometer beam when they are about 10 μm size.

When a short duration experimental run occurs, the transmissivity as detected by the laser beam follows the nucleation pulse with an asymptotic approach to the clear air value, indicating that almost all the liquid water is consumed by growing ice crystals, until the ice crystals begin to rapidly fall out. After crystal fallout acts to reduce the ice crystal concentration, the liquid water cloud reestablishes itself, and the transmissometer trace reflects this (Figure 3).

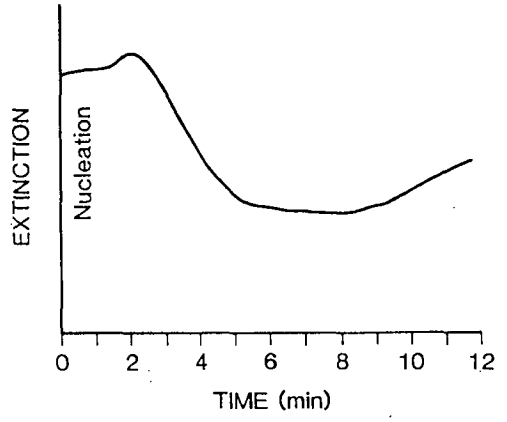

Figure 3. The attenuation of a 10.2 μm laser beam in the cloud chamber during a run without ice crystal breeding, showing the nucleation pulse and the decay in the cloud water content with time during crystal growth.

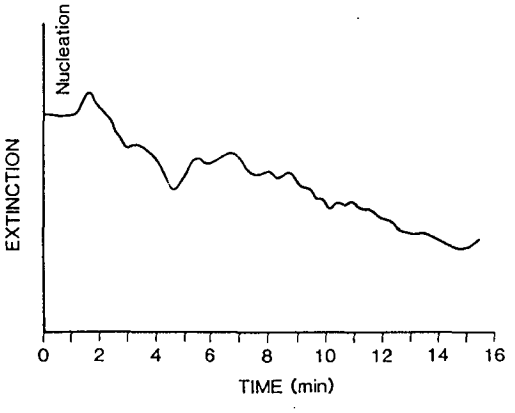

Figure 4. The attenuation of a 10.2 μm laser transmissometer beam in the cloud chamber during a run with ice crystal breeding, showing multiple spikes in the attenuation due to the continual formation of new ice crystals during the run.

In longer duration runs, there are several distinct pulses in the transmissometer trace (Figure 4). Superimposed on the asymptotic rise of the transmissivity of the laser beam are numerous short pulses of higher attenuation indicative of newly formed ice crystals growing through the 10μm size range. The timing of the pulses and the occurrences of small ice crystals on glass slides is consistent: small ice crystals, attributed to the ice crystal breeding process, appeared on glass slides after the attenuation pulses were observed.

The cloud chamber uses a low-power HeNe laser of 0.55μm wavelength for aiming the CO_2 laser transmissometer. On a few occasions, we investigated the simultaneous behavior of the transmissivity at both wavelengths. Figure 5 shows typical results. Both transmissivities diminished with the initial nucleation pulse (the 0.55 μm wavelength laser about 20 seconds before the 10.2μm wavelength laser). Subsequently, the HeNe laser detected pulses in attenuation slightly before they were detected by the CO_2 laser, indicating that the attenuation pulses were due to small, recently formed ice crystals growing through the sizes comparable to the wavelengths of the two lasers.

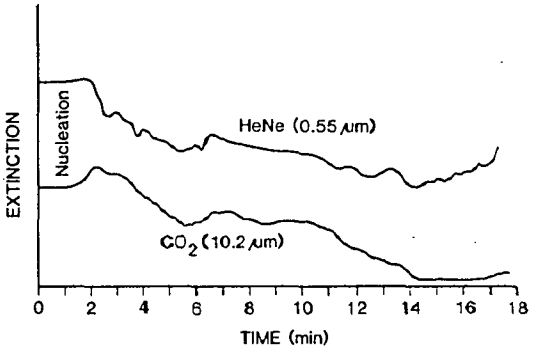

Figure 5. The attenuations of two laser transmissometer beams, 0.55 and 10.2μm wavelength, during a run with ice crystal breeding.

The experimental runs were conducted under a variety of conditions of initial liquid water content and amount of adiabatic expansion used to nucleate the ice, so the initial ice crystal and water droplet concentrations varied from one run to the next. In runs where no aggregation was detected on the microscope slides, the numbers of ice crystals on the slides were also low, causing us to surmise that the ice crystal concentrations in the chamber were probably too low for significant aggregation to occur.

We divided the runs into two groups, depending on the dissolved salts in the cloud water. The deionized water and the solution of sodium nitrate have low freezing potentials (Workman and Reynolds, 1950), whereas solutions of ammonium carbonate and ammonium sulfate have high freezing potentials of 60 to 100 volts.

4. RESULTS

Table 1 presents the results of 87 experimental runs at chamber temperatures between -4 and -30C. The deionized water and sodium nitrate solutions were used in 53 experimental runs; 39 in which aggregation was noted, and yielded evidence of ice crystal breeding in 28 of the runs, or 72 percent of those with aggregation. At -13 to -20C, ice crystal breeding was observed each time aggregation occurred; the lowest percentages (of breeding when aggregation was observed) were found at -9 to -12C and below -20C.

The ammonium sulfate and ammonium carbonate solutions were used in 60 experimental runs (48 in which aggregation was noted) and produced evidence for ice crystal breeding in 45 of the runs, or 94 percent of those with aggregation. Ice crystal breeding was observed in 100 percent of the cases

where aggregation was detected at -13C and below (19 cases), and in 18 of 19 cases (95 percent) where aggregation was detected between -4 and -8C. The lowest percentage of breeding occurred between -9 and -12C, where 80 percent of the cases with aggregation yielded evidence of ice crystal breeding.

Table 1. Results of investigations of ice crystal breeding in the DRI cloud chamber.

Sodium Nitrate Solution

Temperature Range (C)	Number of Experiments	Ice Crystal Breeding	Percent
-4 to -8	20	14	70
-9 to -12	7	4	57
-13 to -20	7	7	100
-21 to -30	5	3	60
	39	28	72

Ammonium Sulfate or Ammonium Carbonate Solutions

Temperature Range (C)	Number of Experiments	Ice Crystal Breeding	Percent
-4 to -8	19	18	95
-9 to -12	10	8	80
-13 to -20	8	8	100
-21 to -30	11	11	100
	48	45	94

5. DISCUSSION

The present results indicate that ice crystal breeding occurs under conditions of aggregating, rapidly growing ice crystals, at all temperatures between -4 and -30C. The results also indicate that ammonium salts, which exhibit strong freezing potentials, promote ice crystal breeding when contained in growing ice crystals.

Our ice crystal aggregation studies (Finnegan and Pitter, 1988b) found that soluble ionic salts present in the cloud water and incorporated into the growing ice crystals (most likely by droplet freezing on contact with the ice embryos formed by rapid adiabatic expansion) affected the junction orientations of the initial ice crystal aggregates. The results, though limited, also indicated that the salts moderated the rate of aggregation. We postulated that the differential incorporation of chemical ions during growth creates freezing potentials similar to those observed by Workman and Reynolds (1950) for bulk freezing.

Additionally, studies of single ice crystals grown under identical vapor and temperature conditions in the cloud chamber have revealed that the salts incorporated into the growing ice crystals affect their detailed shapes (Pitter and Finnegan, 1990). Preliminary data consistently shows that the more elaborate dendritic shapes of ice crystals are associated with solutions which, in bulk freezing, yield higher magnitudes of freezing potentials.

Thus, we have postulated that growing ice crystals acquire an internal charge distribution corresponding approximately to that of an electric dipole across each growing ice interface. The magnitude of the charge separation depends on the rate of growth and the soluble salts present on the surface of the growing crystal. Certain ions, particularly ammonium and the halides, are incorporated into the ice phase more readily than other ions, such as sulfate and nitrate. Workman and Reynolds found that ammonium salts, such as ammonium sulfate and ammonium carbonate had freezing potentials of 60 volts or more, while deionized water and sodium nitrate solutions yielded freezing potentials of less than 10 volts. Since Workman and Reynolds investigated bulk freezing, and configured their experiments to obtain the maximum magnitudes of freezing potentials, we interpret their results to indicate that deionized water and sodium nitrate solutions produce very weak electric multipoles in growing ice crystals, while ammonium carbonate or sulfate solutions produce stronger electric multipoles.

Ice crystal multiplication in clouds, of the type found in our cloud chamber studies, is conceivably another manifestation of crystal breeding. Further, we postulate two possible mechanisms by which crystal breeding is accomplished. The first involves the action of the locally high electric field, in the immediate vicinity of the interacting, growing crystals. This intense, non-uniform, time-dependent field may act to orient water vapor molecules and cause them to cluster in response to intense electrostatic forces, thereby processing the airflow between the two ice crystals in the last moment before aggregation to create ice germs. If the ice germs survive and grow by vapor diffusion or by collision with existing water droplets, they will initially form pure water ice crystals. This would be consistent with our findings of the newer (smaller) ice crystals to have the morphological characteristics of pure water crystals.

A second postulated ice crystal breeding mechanism should also be considered. This mechanism is derived from a concept of how ice grows by diffusion. It has been demonstrated (Pitter, 1981) that ice crystal vapor diffusion growth is not deposition growth, but rather is condensation of vapor onto the crystal surface, followed by surface flow of the quasi-liquid layer to the growing edges, where the water molecules finally get incorporated into the ice crystal lattice. Other inorganic crystals have been found to grow by this mechanism (Van Hooke, 1961). When we consider the increasing intensity of the electric fields in the vicinity of the two interacting ice crystals just prior to collision, it is conceivable that the strong, inhomogeneous electric fields may act to accelerate water molecule clusters that have become associated on and with the ice crystal surface (i.e., have condensed, but are still mobile), causing them to accelerate so rapidly that they are propelled off the ice crystal at the growing edge. This could result in the formation of large numbers of very small, deforming droplets in an electric field, which then freeze and grow to detectable size. This mechanism is also consistent with the observations, in that the sodium nitrate solutions, which have much lower freezing potentials, also have lower frequencies of ice crystal breeding than the ammonium salt solution cases.

The implications of these experiments is that ice crystal breeding may be relevant in the design of winter orographic cloud seeding programs for snowfall augmentation.

6. CONCLUSIONS

The experimental results presented in this article support a new concept of ice crystal breeding that is mechanistically different than previously postulated mechanisms for this process. We have shown that ice crystal breeding is possible at all temperatures investigated between -4 and -30C, with maxima at temperatures where ice is most highly nonspherical. The morphology of the newly-formed crystals during ice crystal breeding resembles that of pure water ice crystals for the experimental temperature, causing us to reject crystal breakup as a mechanism of multiplication in the cases investigated. Rather, we postulate two possible ways in which ice multiplication may occur. Additional work needs to be performed to determine exactly how pure water ice crystals form during ice aggregation.

The experimental results are analogous to those in the chemical literature on crystal growth, which describes crystal breeding as the increased rate of formation of new crystals during crystal aggregation at sufficiently great supersaturations. We therefore conclude that we have detected ice crystal breeding.

We have found that ice crystal breeding may occur when ice crystals, in the presence of supercooled liquid water, are aggregating. Additionally, the solutes present in the growing ice crystals affect the percentage of time that breeding is detected in the DRI cloud chamber. We have not yet determined why ice crystal breeding is a go or no go situation in any specific experimental run.

Glaciogenic snowfall enhancement operations in wintertime orographic storms utilize supercooled liquid water as a primary seeding criterion. Therefore, the cloud seeding may result in ice crystal breeding as the ice crystals formed on generated aerosols grow and begin to aggregate. It is conceivable that the use of an appropriate inorganic solute in the generator formulation may enhance the ice crystal breeding and thereby multiply the effectivity of some seeding operations.

7. ACKNOWLEDGEMENTS

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