Contact Nucleation Linked to "Evaporation Freezing"

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1. Introduction

Much of the water found in atmospheric clouds exists in a metastable, or supercooled state. Freezing of pure water drops occurs spontaneously if the temperature is low enough (homogeneous nucleation). Ice formation can, however, be catalysed by another substance (heterogeneous nucleation) in a small fraction of the cloud droplets, initiating freezing at higher temperatures. Ice particle populations develop in clouds through primary mechanisms including condensation, immersion, contact and deposition nucleation [Rogers and Yau, 1989], and secondary mechanisms including: (1) rime-splintering where copious ice particles are ejected during riming in clouds [Hallett and Mossop, 1974]; (2) ice particle fragmention during crystal-crystal collision [Vardiman, 1978]; and (3) ice crystal breakup during evaporation [Oraltay and Hallett, 1989]. Contact nucleation, defines the freezing of a supercooled cloud drop upon contact with an ice-forming nucleus (IN), traditionally from the outside of the drop [Pruppacher and Klett, 1997; Rogers and Yau, 1989]. This "Trockenkern" (dry particle) effect was first observed over 50 years ago [Rau, 1950]: a supercooled water drop freezes at a higher temperature if a dry particle makes contact with the surface than if it is first immersed in the water drop and then cooled.

Recently, we reported laboratory observations of increased freezing temperature when an IN is near the water-air interface compared to when it is in the bulk [Shaw et al., 2005]. Through an analysis based on classical nucleation theory it was determined that the increase in freezing temperature was due to a decrease in the free energy barrier for the formation of a critical IN and enhanced mobility of water molecules near the air-water interface. Here we describe additional experiments and data interpretation to explore the implications of "surface crystallization" for ice formation in atmospheric clouds. Specifically: (1) we challenge the existing hypothesised mechanisms for contact nucleation in light of the laboratory observations; (2) we present laboratory evidence for ice nucleation as a consequence of drop evaporation (evaporation freezing); and (3) we hypothesise that this more general picture of contact nucleation, based on our observations of heterogeneous surface crystallization, can result in evaporation freezing in atmospheric clouds.

2. Experimental Technique

We measured freezing temperatures under controlled laboratory conditions to investigate the phenomena of contact nucleation and evaporation freezing. The approach consists of cooling and freezing a single drop containing the same IN, many, many times to collect a statistical ensemble of freezing events. The IN of interest is placed in a small drop (~3-4 mm diameter) of ultra-pure water using a hypodermic syringe needle. We investigated water drops containing: (1) glass-rich volcanic ash particles with a bulk trachyandesitic composition (~400-650 μm diameter): volcanic ash represents an episodic component of the atmospheric IN load, and is broadly representative of silicate materials; and (2) soda glass microspheres (330±15 μm diameter).

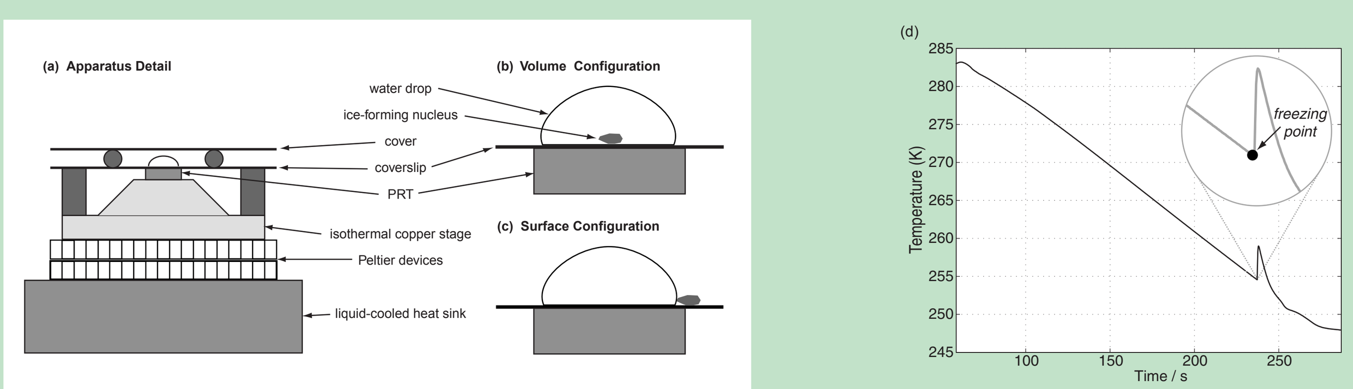


Figure 1. (a) Apparatus detail; (b) Volume configuration; (c) surface configuration; (d) example temperature curve from a cooling cycle.

Once the drop is in place, the position of the IN can be manipulated so that it is either fully immersed within the drop (immersion freezing), or in contact with the surface (contact freezing). The position of the particle relative to the drop and the freezing events are observed directly using a microscope and digital camera. Temperature is decreased from 283 K to 248 K at a constant rate of 10 K min-1, and we detect a sudden increase in temperature from the enthalpy of freezing when ice nucleation occurs. The entire apparatus is housed in a chamber purged with filtered, dry air (frost point <208 K). The system is fully automated so that we can measure hundreds of freezing events involving a single IN.

2.1 Focus of experiments:

(1) **Contact nucleation:** independent experiments to investigate variation in freezing temperature with an IN (i) contacting the outside surface of a drop and (ii) the inside surface of a drop.

(2) **Evaporation freezing:** experiments to investigate variation in freezing temperature for an evaporating drop containing a single immersed IN. The drop is exposed to dry air in the chamber such that it evaporates during the course of several tens of cooling cycles.

3. Contact Nucleation

In our experiemnts, surface-initiated freezing occurred at a consistently higher temperature than volume-initiated freezing, with a difference typically of ~4 K (Figure 2).

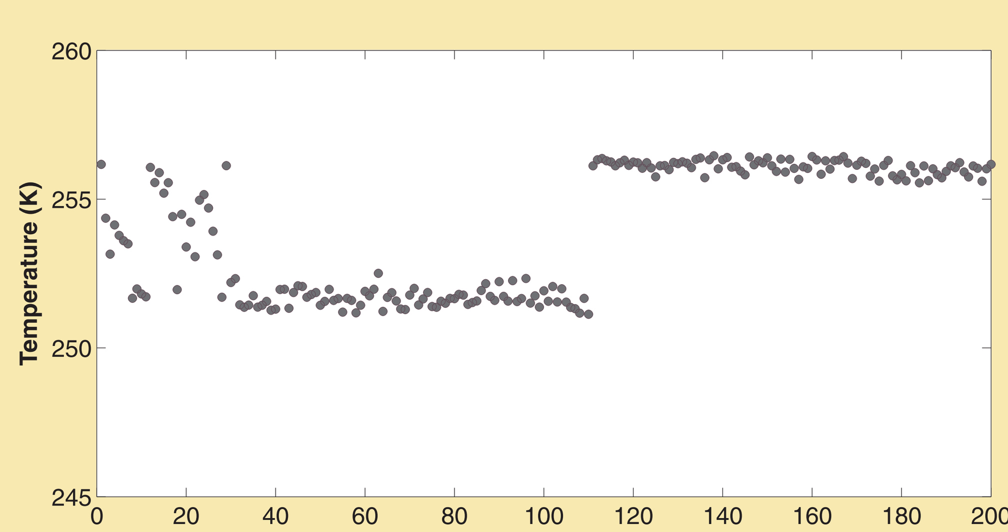


Figure 2. An example of variation in freezing temperature observed during one experiment. Fluctuating freezing temperatures in the initial ~30 experiments reflect transition between the two heterogeneous freezing modes. The first 30 freezing temperatures are sporadic due to initial movement of the IN: observations revealed that bubbles of air were exsolved after the initial freezing event and were excluded from the drop in subsequent cooling cycles. The presence and migration of air bubbles acts as a mechanism to physically move the IN inside the drop and it also implies many air-water interfaces are within the drop, resulting in the initial sporadic freezing temperatures. After cooling cycle 30 the IN is inside the drop, away from the surface. After cooling cycle 110 the IN moves and makes contact with the surface of the drop.

3.1 Contact nucleation mechanisms

(1) Partial solubility of the ice nucleus in water

Fletcher [1969] suggested that ice nucleation is initiated at active sites, locations on the surface on an IN where the ice phase preferentially appears. In the case of a partially-soluble solid dry IN, Fletcher [1970] suggested the difference between immersion and contact freezing temperatures is the result of dissolution of active sites at the surface of an immersed particle, thereby reducing its ice nucleating ability relative to a dry particle initiating ice in the contact mode with a pristine surface.

(2) Incomplete adsorption upon initial contact with water

Evans [1970] and Edwards et al. [1970] suggested that a surface layer of adsorbed water molecules determines the ice nucleating ability of an IN in the contact mode. During mechanical interaction between an IN and a water droplet, initial contact results in a disordered layer which is incompletely adsorbed. At this point, the energy barrier to form an ice-like structure is reduced. Ice nucleation can occur as long as the time required to form an ordered water film on the ice nucleus surface is far greater than the time required to form a critical ice germ in the disordered adsorbed layer. This timescale is on the order of the rotational period of a water molecule.

(3) Mechanical disturbance of the water-air interface

Fukuta [1975] provided a thermodynamic argument for movement of the liquid-air interface during IN-droplet collision. This idea invokes a transient high free energy condition that occurs as the ice nucleus-air-liquid boundary moves along the IN surface during interaction with the drop. The process forces complete wetting of the IN surface by the bulk water. The dissipation of the surface free energy from the air-liquid boundary temporarily increases the free energy of critical embryo formation, which enhances the ice nucleation rate.

3.2 Contact Nucleation Discussion

In our experiments the magnitude of the enhancement in freezing temperature is very similar to that typically observed in contact nucleation [Fukuta, 1975; Gokhale and Goold, 1968; Pitter and Pruppacher, 1973], but differs in that the IN is always in contact with the water drop - this is distinctly different from traditional observations of contact nucleation where a dry particle collides with a supercooled water drop. All of the previously proposed mechanisms are related in some way to the transient nature of contact between an IN and a supercooled water drop. There is no transient contact event during the experiments and normally no observable history in the freezing temperature. Therefore, the first and second mechanisms are rejected outright because the IN is already immersed in the droplet. Similarly, the third mechanism is unlikely because in our experiments there is no rapid movement or collision of the IN with a droplet. The enhancement in freezing temperature is observed regardless of whether the IN contacts the drop surface from the outside, or from within the bulk liquid. To distinguish from the traditional form of contact nucleation we refer to the latter as contact nucleation inside-out.

3.3 Generalised View of Contact Nucleation

(1) The formation of ice within a liquid water drop by heterogeneous nucleation occurs at higher temperatures if the IN is in contact with the surface of the drop, than if it is fully immersed within the bulk of the drop.

(2) The higher freezing temperatures occur regardless of whether this contact is from the outside-in, or the inside-out, and do not depend on any transient contact between the IN and the water drop.

(3) This finding contradicts three traditional mechanisms for contact nucleation based on transient effects.

The observations presented here and by Shaw et al. [2005] provide evidence that the notion of contact nucleation should be generalized, as illustrated in Figure 3:

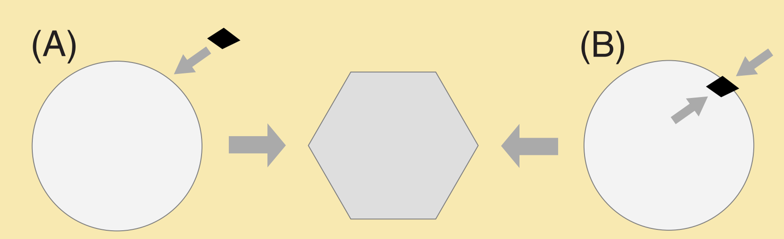


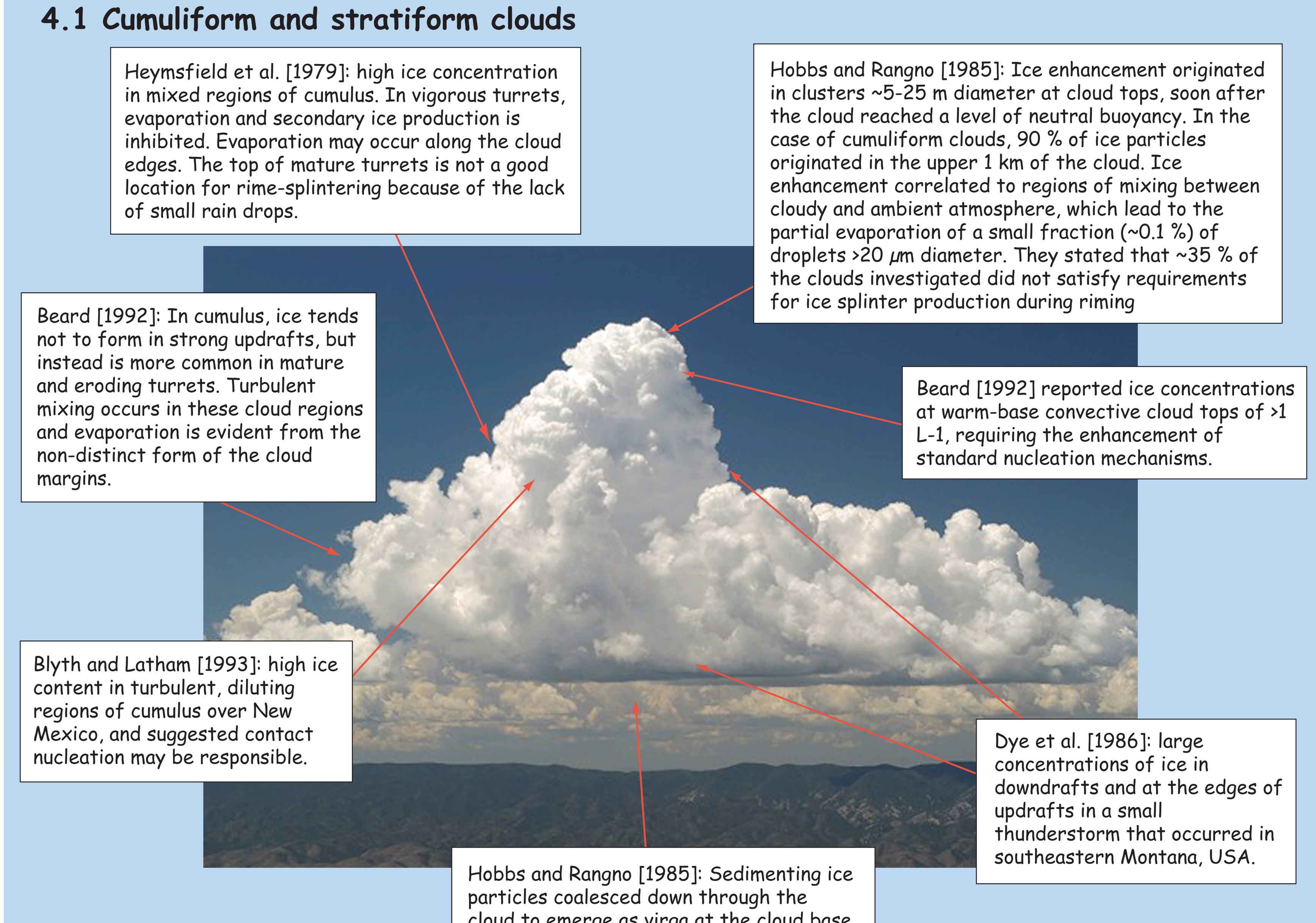
Figure 3. A schematic view of the standard view of contact nucleation (A), and the generalized view of contact nucleation (B), which includes contact nucleation "inside-out."

(2) We argue that the traditional form of contact nucleation is simply a manifestation of the enhanced nucleation rates due to surface crystallization. The enhancements appear to be related to variations in the thermodynamics and kinetics of the air-water interface, as discussed elsewhere [Shaw et al., 2005], but more work is needed to fully understand the detailed physics of surface crystallization.

4. Evaporation Freezing

Motivation: Observations are abundant of enhanced ice formation in regions where cloud droplets are evaporating in cumuliform, stratiform, and wave clouds that cannot be explained by invoking the standard heterogeneous nucleation mechanisms [Ansmann et al., 2005; Baker and Lawson, 2005; Beard, 1992; Cooper, 1995; Cotton and Field, 2002; Field et al., 2001; Rangno and Hobbs, 1991]. In these cases, ice concentrations of 1-10 L^{-1} are often present in regions where evaporation is occurring.

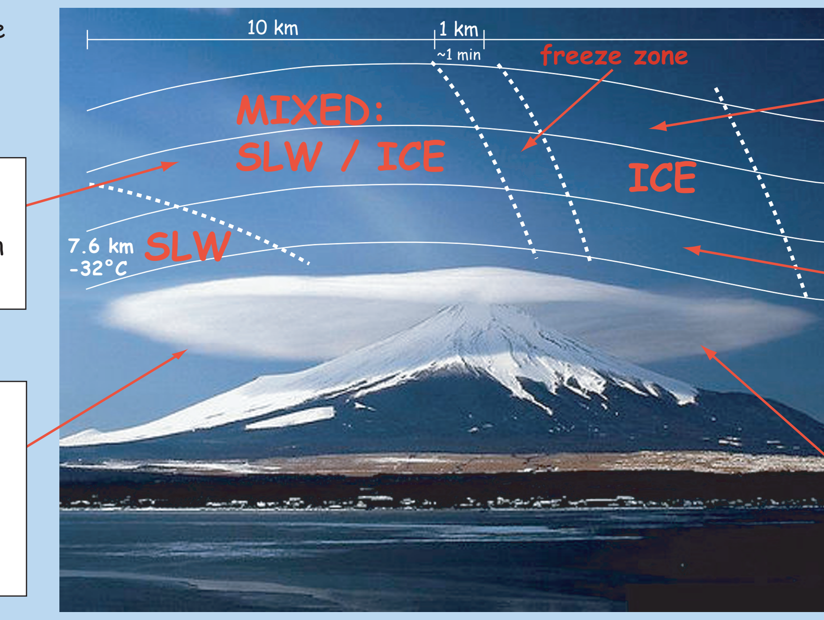
4.1 Cumuliform and stratiform clouds



4.2 Wave clouds

Ice enhancement has been observed in wave clouds in regions characterised by evaporation (Figure 4). In the conceptual model of a wave cloud generated over a mountain top, air is forced up and experiences a steady expansion and a decrease in temperature that results in cloud droplet formation. Once over the peak, the air descends and temperature and pressure increase, causing the cloud to dissipate. Flow is generally isentropic: mixing along isentropes is suppressed and horizontal gradients of scalar atmospheric properties are small.

Figure 4. Idealised wave cloud with observations from Cooper [1995].



Primary ice nucleation could not account for glaciation in the cases mentioned before, except as a trigger for secondary ice formation. Beard [1992] proposed that an evaporation nucleation mechanism may explain the enhanced ice particle concentrations.

4.3 Ice Nucleation during Drop Evaporation

In the second series of experiments, we investigated the possible role of contact nucleation from the inside-out on freezing temperature during drop evaporation.

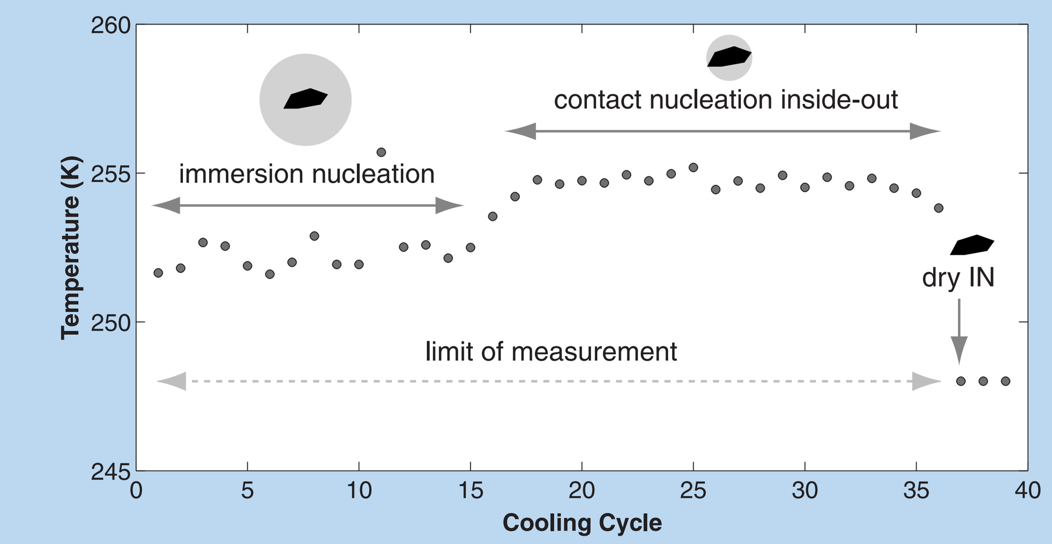


Figure 3. Example of a series of freezing events during drop evaporation. Initially, the IN remained fully immersed in the drop, and freezing occurred through immersion nucleation at ~252 K. As the drop evaporated and the surface made full contact with the IN, freezing occurred at a higher temperature of ~255 K. The drop completely evaporated by cooling cycle 36. The temperatures measured after cycle 36 are the minimum temperature of each cooling cycle (no freezing event). The gradual transition between immersion and contact freezing temperatures is likely related to the amount of IN surface in contact with the air-water interface [Djikaev et al., 2002].

4.4 Evaporation Nucleation Discussion

These experimental results can be compared with observations of evaporation freezing in wave clouds where no known mechanisms provide an explanation for the associated ice enhancement [Beard, 1992]. For example, detailed modelling of microphysical processes could not reproduce measured characteristics of one isolated wave cloud based on standard heterogeneous nucleation mechanisms (i.e. contact, deposition, condensation, immersion) [Cotton and Field, 2002]. Cotton and Field [2002] concluded "the key… appears to lie in most ice nucleation occurring very rapidly at a critical time coincident with evaporation of the liquid droplets in the downdraught of the lee wave."

We hypothesize that as a supercooled water drop evaporates, its surface (the air-water interface) will eventually come into contact with any immersed, insoluble IN, thereby increasing the freezing temperature. The results illustrated by Fig. 3 suggest a plausible mechanism for the observations of sudden glaciation of wave clouds in regions where cloud drops are evaporating. In this case, some fraction of the droplets that form on the leading edge of the cloud do so on insoluble aerosol particles. Once entering the downdraft, the droplets evaporate and the freezing point increases suddenly by ~3-4 K as the shrinking droplet surface makes contact with the insoluble particle. The total temperature variation in a wave cloud is often within this range [Baker and Lawson, 2005; Cotton and Field, 2002], so the shift due to contact nucleation from the inside-out is significant in this context. Furthermore, to match observed ice concentrations in one wave cloud, only 0.2 % of the cloud droplets would need to experience this form of freezing [Cooper, 1995]. Hobbs and Rangno [1985] reported that ice enhancement in cumulus occurred in regions of mixing between cloudy and ambient atmosphere, which lead to the partial evaporation of ~0.1 % of droplets >20 μm diameter.

4.5 Evaporation Nucleation Mechanism

(1) Experiments confirm that evaporating droplets will freeze in contact mode when the droplet surface reaches the surface of an immersed insoluble IN. This provides a mechanism for evaporation freezing and it is plausible that sudden ice formation in evaporating wave clouds is due to contact nucleation from the inside-out.

(2) We speculate that evaporation freezing would be especially sensitive to sources of large insoluble aerosols, such as desert dust or volcanic ash, with the resulting possibilities for interactions with other components of the Earth system [Ansmann et al., 2005; DeMott, 2003; Rose et al., 1995].

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