Evaporation freezing by contact nucleation inside-out

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[1] Ice formation in atmospheric clouds is crucial to our understanding of precipitation and cloud radiative properties. In recent work it was shown that heterogeneous ice nucleation rates can be strongly enhanced by a form of surface crystallization (Shaw et al., 2005). Here we present new laboratory data and consider the implications for contact nucleation and its relevance to ice nucleation in atmospheric clouds. Our observations contradict three leading hypotheses for contact nucleation and suggest, instead, that the notion of contact nucleation should be generalized to include surface crystallization from particles contacting a supercooled drop from the inside out, as well as from the outside in. Our findings lead to the hypothesis that the freezing temperature of an evaporating drop will suddenly become higher once the drop surface contacts an immersed ice nucleus. This mechanism for evaporation freezing is therefore a plausible explanation for the abundant observations of high ice concentrations associated with cloud dilution and droplet evaporation. **Citation:** Durant, A. J., and R. A. Shaw (2005), Evaporation freezing by contact nucleation inside-out, *Geophys. Res. Lett.*, *32*, L20814, doi:10.1029/2005GL024175.

1. Introduction

[2] Much of the water found in atmospheric clouds exists in a metastable, or supercooled state. Understanding how ice forms in these clouds is a major challenge in cloud physics [*Beard*, 1992; *Vali*, 1996; *Pruppacher and Klett*, 1997, sections 2.2 and 9.2; *Lamb*, 1999]. Freezing of pure water drops occurs spontaneously if temperature is low enough (homogeneous nucleation). However, ice formation can be catalyzed by another substance (heterogeneous nucleation) in a small fraction of the cloud droplets, initiating freezing at higher temperatures. Contact nucleation, an important but poorly understood heterogeneous nucleation pathway, defines the freezing of a supercooled cloud drop upon contact with an ice-forming nucleus (IN), traditionally from the outside of the drop [*Rogers and Yau*, 1989, Figure 9.1; *Pruppacher and Klett*, 1997, p. 309]. 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. The phenomenon has been studied extensively since, yet the mechanism for the unusual effectiveness of contact nucleation remains unknown [*Pruppacher and Klett*, 1997, pp. 339–341].

[3] Furthermore, the relative role of contact nucleation in ice formation in atmospheric clouds is not clear. For example, observations are abundant of enhanced ice formation in regions where cloud droplets are evaporating in cumuliform, stratiform, and wave clouds [*Hobbs and Rangno*, 1985; *Cooper*, 1986; *Beard*, 1992; *Rangno and Hobbs*, 1994; *Cooper* 1995; *Field et al.*, 2001; *Cotton and Field*, 2002; *Ansmann et al.*, 2005; *Baker and Lawson*, 2005], and it has been speculated that contact nucleation may be responsible for this "evaporation freezing." The results are difficult to interpret because of the turbulent nature of some of these clouds, and the lack of understanding of the detailed ice formation processes. Heretofore, no ice nucleation mechanism has provided a satisfactory explanation for what apparently is evaporation freezing [*Beard*, 1992].

[4] 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. In this letter 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 hypothesized 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 hypothesize 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

[5] We have measured freezing temperatures under controlled laboratory conditions to investigate the phenomena of contact nucleation and evaporation freezing. Although details of the experimental system have been presented elsewhere [*Shaw et al.*, 2005], we briefly describe the method with attention given to aspects relevant to the data presented here. 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. 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

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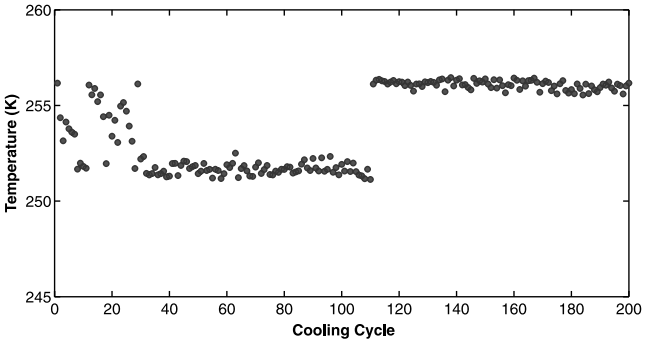

Figure 1. Example of sudden shifts in freezing temperature due to changes in the position of the IN within the droplet. The first 30 freezing temperatures are sporadic due to initial movement of the IN (see text for details). After cooling cycle 30 the IN is inside the drop, away from the surface. After cooling cycle 110 the IN moves and makes contact with the surface of the drop.

microspheres (330 μm diameter). The nature of the setup requires that the particles are much larger than typical IN found in the atmosphere, but we have consistently observed that the increase in freezing temperature due to surface crystallization is independent of the size of the IN or of the water droplet (within the investigated size ranges). To be clear, the freezing temperature depends on IN characteristics such as composition and surface area, but the difference in freezing temperatures for immersion and contact modes is roughly constant.

[6] The IN of interest is placed in a small drop (~3–4 mm diameter) of ultra-pure water using a hypodermic syringe needle. The drop is positioned over a platinum resistance thermometer (PRT) covered with a thin (~0.6 mm) microscope coverslip, which is silanized to create a hydrophobic surface. The PRT rests on an isothermal copper stage in contact with a liquid-cooled heat sink, with the temperature controlled by a thermoelectric (Peltier) cooler/heater. 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). Temperature is decreased from 283 K to 248 K at a constant rate of 10 K min^{-1}, and we detect the sudden increase in temperature resulting 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 position of the particle relative to the drop and the freezing events are observed directly using a microscope and digital camera. (A movie showing an example of a single freezing event can be downloaded from online supporting material[1] for this article.) The system is fully automated so that we can measure hundreds of freezing events involving a single IN. Because the same IN is used repeatedly during the experiments, ambiguity due to variations in composition, surface area, and morphology are avoided.

[7] We investigated both immersion and contact ice nucleation. In the case of contact nucleation, we carried out independent experiments with the IN at the outside and inside surface of the drop. We also investigated variation in freezing temperature for an evaporating drop containing a single IN. In this scenario, the drop is exposed to the dry air in the chamber such that it evaporates during the course of several tens of cooling cycles (normally the drop is enclosed by a small glass cover to minimize evaporation).

3. Results and Implications for Contact Nucleation

[8] In our experiments the heterogeneous freezing mode can be changed by moving the IN from the interior of the drop to make contact with the surface, or visa versa. Figure 1 shows an example of variation in freezing temperature observed during one experiment: surface-initiated freezing occurred at a consistently higher temperature than volume-initiated freezing, with a difference typically of ~4 K. Fluctuating freezing temperatures in the initial ~30 experiments reflects transition between the two heterogeneous freezing modes. 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.

[9] The magnitude of the enhancement in freezing temperature is very similar to that typically observed in contact nucleation [*Gokhale and Goold*, 1968; *Pitter and Pruppacher*, 1973; *Fukuta*, 1975]. We emphasize, however, that the conditions here are distinctly different from those in traditional observations of contact nucleation, where a dry particle collides with a supercooled water drop. Instead, in our experiments the nucleus is always in contact with the water drop. 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.

[10] The enhancement in nucleation rate for contact nucleation relative to that for immersion nucleation has been hypothesized to occur in at least three ways [see *Pruppacher and Klett*, 1997, pp. 339–341]. Briefly they are: (1) partial solubility of the IN in water [*Fletcher*, 1970; *Guenadiev*, 1970]; (2) incomplete adsorption upon initial contact with water [*Evans*, 1970]; (3) mechanical disturbance of the water-air interface upon contact [*Fukuta*, 1975]. All of the proposed mechanisms are related in some way to the transient nature of a contact between a dry IN and a supercooled water drop. In our study, however, we observe that in most instances the freezing temperature of an IN is a statistically stationary random variable over hundreds of cycles, with the mean depending solely on the location of the nucleus relative to the 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 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 (we cannot rule out, however, that small

[1] Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2005GL024175.

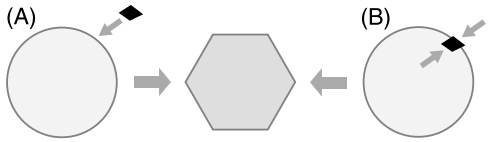

Figure 2. A schematic view of the standard view of contact nucleation (A), and the generalized view of contact nucleation (B), which includes contact nucleation "inside-out."

vibrations from the cooling unit, or even motion due to Brownian diffusion could cause sufficient relative motion between the IN and the water drop, although this seems implausible).

[11] We believe 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 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.

[12] An additional hypothesis for the enhancement of contact nucleation relative to deposition nucleation applies to ice embryos being created in the vapor [*Cooper*, 1974], rather than in supercooled water as in our experiments. The basis of this hypothesis, however, relies on differences in the free energies of the air-water-IN system versus the water-IN system and perhaps could be extended to immersion vs. contact nucleation [e.g., *Djikaev et al.*, 2002].

4. Ice Nucleation During Drop Evaporation

[13] We also carried out experiments to investigate the possible role of contact nucleation from the inside-out on the freezing temperature during drop evaporation. 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. Figure 3 shows data for an evaporating drop containing soda glass microspheres (in this instance several microspheres were used to increase the total IN surface area, but the result is valid for single particles as well). 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 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].

[14] These laboratory results can be compared with observations of evaporation freezing in wave clouds, where the evolution of cloud droplet and ice particle concentrations are measured along approximately-Lagrangian trajectories. In one common scenario, supercooled cloud droplets form on the upwind side of the wave and a rapid onset of cloud glaciation is observed in the downwind region where cloud droplets are evaporating, at temperatures too high ($T > -35^{\circ}C$) for homogeneous nucleation to dominate [*Cooper*, 1995; *Field et al.*, 2001; *Baker and Lawson*, 2005]. No known mechanism for ice nucleation has provided an explanation for what apparently is evaporation freezing [*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."

[15] The results illustrated by Figure 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 of the wave, the droplets evaporate and eventually their freezing temperatures increase suddenly by ~3 to 4 K as the retreating droplet surface makes contact with the insoluble particle. We note that the total temperature variation in a wave cloud is often within this range [*Cotton and Field*, 2002; *Baker and Lawson*, 2005], 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 ~0.1% of the cloud droplets would need to experience this form of freezing [*Cooper*, 1995].

[16] Given the unique symmetry of a wave cloud we must consider why contact freezing does not occur on the upwind side when supercooled drops are first activated on IN. During a single drop's trajectory through a wave cloud, the IN, which is initially at the center of the drop, will migrate away from the center by Brownian diffusion: using Stokes-Einstein diffusion with an observed transit time of $t \approx 150$ s at a temperature of 248 K [*Cotton and Field*, 2002, Figure 7], IN with radii of 100 nm and 1 μm will diffuse inside a droplet over distances of approximately 10 μm and 3 μm, respectively. As a result, contact between the air-water interface and an immersed IN will occur well before complete drop evaporation, and therefore at a lower

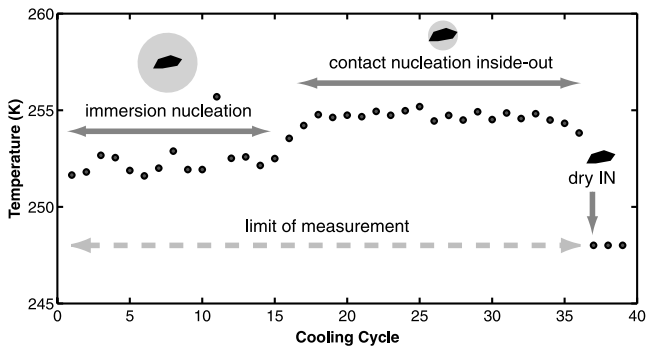

Figure 3. Example of a series of freezing events occurring as a single drop evaporates. A shift in freezing mode occurred after cooling cycle 15. The drop completely evaporated by cooling cycle 36. The temperatures measured after cycle 36 are the minimum temperature of each cooling cycle (no freezing event).

temperature. Clearly this line of reasoning must be challenged with further experiments; it is somewhat academic, however, because in convective clouds the temperature at drop activation will likely be different than that during drop evaporation.

5. Conclusions

[17] Through simple experiments, we have observed that 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 (the underlying thermodynamics and kinetics are discussed elsewhere [*Shaw et al.*, 2005]). 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.

[18] This finding contradicts three traditional mechanisms for contact nucleation based on transient effects. We are thus brought to a more general picture of contact nucleation as a manifestation of surface crystallization (see Figure 2). The generalized view of contact nucleation leads naturally to the hypothesis that evaporating droplets will eventually favor contact freezing when the droplet surface reaches the surface of an insoluble IN. Laboratory tests confirm that this does occur, thereby providing a mechanism for evaporation freezing. It is plausible, therefore, that sudden ice formation in evaporating wave clouds is due to contact nucleation from the inside out.

[19] Methods for testing this in future field experiments are being developed. Its possible role in explaining high rates of cloud glaciation in regions where clouds are mixing will be more challenging to determine, but modern instrumentation and facilities offer new opportunities. If active in these clouds, the mechanism has major implications for our understanding of ice formation and its links to precipitation formation and radiative properties of the atmosphere. We further 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 et al.*, 2003; *Rose et al.*, 1995].

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