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Ice nucleation and overseeding of ice in volcanic clouds

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[1] Water is the dominant component of volcanic gas emissions, and water phase transformations, including the formation of ice, can be significant in the dynamics of volcanic clouds. The effectiveness of volcanic ash particles as ice-forming nuclei (IN) is poorly understood and the sparse data that exist for volcanic ash IN have been interpreted in the context of meteorological, rather than volcanic clouds. In this study, single-particle freezing experiments were carried out to investigate the effect of ash particle composition and surface area on water drop freezing temperature. Measured freezing temperatures show only weak correlations with ash IN composition and surface area. Our measurements, together with a review of previous volcanic ash IN measurements, suggest that fine-ash particles (equivalent diameters between approximately 1 and 1000 μm) from the majority of volcanoes will exhibit an onset of freezing between $\sim$250–260 K. In the context of explosive eruptions where super-micron particles are plentiful, this result implies that volcanic clouds are IN-rich relative to meteorological clouds, which typically are IN-limited, and therefore should exhibit distinct microphysics. We can expect that such ''overseeded'' volcanic clouds will exhibit enhanced ice crystal concentrations and smaller average ice crystal size, relative to dynamically similar meteorological clouds, and that glaciation will tend to occur over a relatively narrow altitude range.

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1. Introduction

[2] Water is abundant in volcanic emissions (up to >99% by mole in volcanic gas emissions [*Symonds et al.*, 1994] and up to $\sim$8% by mass in pre-eruptive magma [*Plank et al.*, 2006]). However, the role of water phase changes in the dynamics and evolution of volcanic plumes and clouds is underappreciated, and is often not considered in models of volcanic plumes [e.g., *Sparks et al.*, 1997]. In this paper, we concentrate on the nature and importance of the ice formation process. This process is poorly understood because of our incomplete knowledge of ice nucleation in general, and ice nucleating properties of volcanic ash in particular. Evidence suggests, however, that ice nucleation in volcanic plumes and clouds affects dynamics [*Glaze et al.*, 1997; *Herzog et al.*, 1998; *Mastin*, 2007; *Woods*, 1993], radiative properties [e.g., *Robock*, 2004], particle aggregation and sedimentation processes [*Guo et al.*, 2004b] and sequestration of gaseous species [*Guo et al.*, 2004a; *Rose et al.*, 1995a; *Textor et al.*, 2003]. Moderate to large explosive eruptions also provide an important mechanism for transporting water to the stratosphere [*Glaze et al.*, 1997] and these fluxes depend in part on the microphysics in a rising plume.

[3] The objective of this paper is to provide constraints on the conditions under which ice would be expected to form from the liquid phase in volcanic clouds, and to consider the implications for volcanic cloud microphysics and dynamics. The conclusions reached here are based on data from two sources: (1) a review of previous volcanic ash freezing data, which has previously been interpreted primarily in the context of background IN effects on meteorological clouds, and (2) new experiments carried out to characterize the freezing temperature of volcanic ash. The role of two physical characteristics of ash particles that likely affect water freezing temperature were investigated: ash particle composition and ash particle surface area. Whereas most previous work has investigated ice nucleation initiated by bulk preparations of volcanic particulates (see section 3), the measurements presented here are based on a single-particle approach that allows particle composition and surface area to be investigated directly [*Durant and Shaw*, 2005; *Shaw et al.*, 2005]. Using these single-particle freezing data in conjunction with the previously published ash freezing data, we attempt to form a description of ice nucleation by volcanic ash that can be applied in models of volcanic cloud microphysics, dynamics, and chemistry, to include the effects of freezing.

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[4] The paper is organized as follows: general features of hydrometeor microphysics in volcanic clouds are discussed in section 2, with recognition that readers from the volcanological and atmospheric sciences communities potentially have rather different backgrounds, and therefore will benefit from differing levels of coverage in each area; past measurements of volcanic ash as ice nuclei are reviewed in section 3, with the aim of placing these data in the context of volcanic clouds as most of the original work was motivated by effects of ash on meteorological clouds; the new experiments are described in section 4, including detail on the experimental apparatus and techniques, and a summary of the main data features; and the implications of the new data, in addition to that of previous research on ice nucleation in volcanic clouds, is presented in section 5. The discussion further explores the microphysical consequences of abundant IN in volcanic clouds. The paper concludes with a brief summary of the main results and some comments on remaining puzzles and future work.

2. The Microphysics of Volcanic Clouds

2.1. Volcanic Clouds

[5] In this paper, we use the term volcanic cloud to describe a suspension of particles generated by explosive volcanic activity that are dispersed in the atmosphere. Volcanic clouds can be directly associated with an eruptive column or drift freely in the atmosphere. We avoid the term ''plume'', which refers to a volcanic cloud connected to a volcanic vent and could include the jet, convective and umbrella regions [*Sparks et al.*, 1997]. Cloud height is related to the magnitude of the eruption and determines the temperature of the cloud. Moderate to large explosive eruptions ($\sim$0.1–1.0 km^3 of erupted material) generate clouds that are dispersed within the troposphere at temperatures well below the melting point of ice. Cloud life time is defined as the time period over which the concentration of volcanic cloud particles falls below ambient background particle concentration, which may be on the order of at least one week.

[6] Volcanic clouds less than about one day in age nearly always contain abundant hydrometeors. Although not generally considered by volcanologists, this assertion is supported by both direct and indirect evidence. First, ice has been found in volcanic clouds by remote sensing [*Guo et al.*, 2004a, 2004b; *Rose et al.*, 1994, 2003] and by direct sampling [*Rose et al.*, 2006]. For example, *Rose et al.* [2004] investigated many recent volcanic clouds and in all cases, eruption columns that reached the tropopause contained ice in quantities comparable to ash for at least a few hours, irrespective of environmental conditions. Second, the existence of ice is demanded by the convective nature of volcanic clouds, which carry both magmatic water and entrained lower tropospheric water upward to a cooler atmosphere where ice nucleation is favored [*Textor et al.*, 2004]. Indeed, in many respects volcanic clouds are analogous to deep convective storms and their associated outflow, and this analogy has led to important advances in our understanding of plume dynamics, including the role of water and associated phase changes [*Herzog et al.*, 1998]. For example, as in meteorological clouds, hydrometeors in volcanic clouds form and evolve through a combination of interacting processes: activation of cloud condensation nuclei (pre-existing particles, often hydrophilic), water vapor condensation and evaporation, droplet coalescence and break-up, freezing and melting, aggregation, riming, and so forth. Of course, atmospheric and magmatic conditions vary from one eruption to another, so the relative role of water also varies: the amounts of entrained and externally derived water vapor can be quite large due to hydrospheric input, tropical atmospheric input or high magmatic water content, or limited due to low magmatic water content or by relatively dry atmospheric profiles, typical of high-latitude locations. The relative importance of water phase transitions for volcanic cloud dynamics are discussed in greater detail in the Appendix A.

2.2. Ice Nucleation

[7] Much of the liquid water in deep convective clouds exists in a metastable state, supercooled below the equilibrium freezing temperature. This is because the formation of an interface that separates a new phase (e.g., ice) from a parent phase (e.g., liquid water) has an associated energy barrier that inhibits nucleation, which is quantitatively analogous to an activation energy. Homogeneous nucleation describes the formation of a new phase involving only the pure water substance and requires supercooling to temperatures below -35°C or -40°C for atmospherically relevant drop sizes and lifetimes. Heterogeneous nucleation describes the nucleation of a new phase catalyzed by particulate material suspended in the atmosphere, such as desert dust, sea salt, volcanic ash and organic matter [e.g., *Young*, 1993]. These catalyst particles are known as ice-forming nuclei (IN), and when present, initiate freezing at significantly lower supersaturations and higher temperatures than in the case of homogeneous nucleation [*Pruppacher and Klett*, 1997, Ch. 9].

[8] Typically, only a small fraction of particles suspended in the atmosphere are capable of acting as IN, and the number of effective or ''active'' IN is dependent on temperature and water vapor pressure. Particles that act as IN are generally insoluble and larger than the Aitken size fraction of aerosol particles. The ice nucleating ability of a substance is determined in part by the strength, type and geometric arrangement (crystallographic structure) of chemical bonds at the surface, which assist the orientation of water molecules to assume an ice-like configuration, but currently, theory is not able to predict ice nucleating properties from first principles for realistic atmospheric particles [*Cantrell and Heymsfield*, 2005]. It is known, however, that ice can be formed through heterogeneous nucleation following several pathways [e.g., *Pruppacher and Klett*, 1997]: (1) contact nucleation occurs when an IN initiates freezing at the surface of a drop, at the highest temperatures; (2) immersion nucleation occurs when an IN is fully immersed and initiates freezing from within the volume of a drop, several degrees below the contact nucleation temperature; (3) deposition nucleation occurs when water vapor forms ice directly on the surface of a IN. The relative importance of these different modes remains an open question [*Cantrell and Heymsfield*, 2005].

[9] Measurements of the number of particles activated as IN in the atmosphere began in 1946 [*Shaefer*, 1952], and show that IN concentrations increase with decreasing tem-

perature or increasing ice supersaturation [e.g., *Fletcher*, 1962; *Meyers et al.*, 1992]. In the ambient troposphere, measured IN number concentrations range approximately from <0.01 to 100 L^{-1}. Typical cloud droplet number concentrations, however, are on the order of 10^5 L^{-1}, so the ratio of IN (and therefore of primary ice crystals) to cloud droplets is exceedingly small. The result is that mixed phase clouds are predominant in the approximate temperature range of $-10°C$ to $-30°C$. This is important because the saturation vapor pressure of water is greater than the saturation vapor pressure of ice, which in fact increases monotonically with decreasing temperature. The ice crystals that form on scarce IN therefore experience rapid growth and can subsequently trigger the precipitation formation process. The so-called "Bergeron-Findeisen-Wegener process" (or simply, Bergeron process) is one of two major pathways through which precipitation is formed in meteorological clouds, and is an important determinant of cloud lifetime, vertical fluxes of water and energy, and cloud radiative properties.

2.3. Formation of Hydrometeors and Ice Nucleation in Volcanic Clouds

[10] There is a lack of direct measurements of particle and IN concentrations inside volcanic clouds. Volcanic clouds have been sampled, however, within relatively dilute outflow regions after large particles have settled out and are found to contain an abundance of particulates that serve as both cloud condensation nuclei (CCN) and IN [e.g., *Hobbs et al.*, 1982, Appendix A]. Measured CCN concentrations in the 18 May 1980 Mount St. Helens volcanic cloud were 1000 cm^{-3} at 1% supersaturation at 13.6 km altitude, after much of the material had already fallen out [*Pruppacher and Klett*, 1997, p. 296]. Even in these dilute regions, particles in the $\sim$1 to several 10's μm range (mostly ash or mixtures of ash and water) have been observed to have number concentrations up to 100 or 1000 cm^{-3} [*Hobbs et al.*, 1982, 1991; *Stith et al.*, 1978].

[11] Methods for determining volcanic cloud ash mass loading and particle effective radius have been devised and applied to remote sensing measurements, which also allow estimation of the number concentration of particles in a given volcanic cloud. Some ambiguity associated with remote sensing measurements results from uncertainty in particle size distribution and shape. In one well-studied cloud produced from the 19 August 1992 eruption of Crater Peak, Alaska (observed at 1338 UT, $\sim$13 h after eruption), the estimated number density of volcanic particles with a mean radius of 1–4 μm was 26 cm^{-3}. As the size distribution of particles in the cloud was most probably lognormal, the actual number concentration is likely to be at least one order of magnitude larger [*Wen and Rose*, 1994]. Many other volcanic clouds have been studied with remote sensing [*Rose et al.*, 2000] and consistently have similar number density estimates (100–1000 cm^{-3}). Finally, studies of ash-precipitation deposits collected at the ground show that initial ash particle size distributions in volcanic clouds are lognormal and include significant concentrations of particles up to several hundreds of micrometers (e.g., A. J. Durant et al., Hydrometeor-enhanced tephra sedimentation: Constraints from the 18 May 1980 eruption of Mount St. Helens (USA), submitted to *Journal of Geophysical Research*, 2008). In summary, volcanic clouds are rich in particulate matter relative to meteorological clouds dominated by pure water. In the latter, concentrations of supermicrometer-sized particles are extremely low, but in volcanic clouds, especially in the convective region, such particles are abundant.

3. Measurements of Volcanic Ice Nuclei

[12] As stated in the introduction, one of the objectives of this study is to review the existing measurements of volcanogenic IN from the point of view of volcanic clouds rather than meteorological clouds. In all cases, experiments were carried out in the atmosphere and laboratory to determine the temperature at which appreciable ice crystals formed on a population of volcanogenic particles, of which some were activated as IN. The freezing temperatures reported are, therefore, "threshold" freezing temperatures, and IN concentrations would be expected to increase at temperatures colder than these thresholds. The historic measurements, together with the new measurements presented in section 4, are evaluated to ascertain the effectiveness of typical volcanogenic particles as IN and to begin to understand the nature of ice formation in volcanic clouds.

[13] There are conflicting views in the literature regarding the effectiveness of volcanic ash as IN, with some investigators concluding that volcanic emissions contain abundant IN [*Hobbs et al.*, 1971b; *Isono and Ikebe*, 1960; *Isono et al.*, 1959a, 1959b] and others who suggest the opposite [*Langer et al.*, 1974; *Price and Pales*, 1964; *Pueschel and Mendonca*, 1972; *Schnell and Delany*, 1976; *Schnell et al.*, 1982]. One difficulty with some of the latter studies relates to an inadequacy in the "membrane filter" measurement technique used, which biases measurements toward an underestimate of IN concentrations [*Hussain and Saunders*, 1984]. Primarily, however, it must be kept in mind that all of these investigators were focused on the role of volcanically produced IN in the context of the background atmosphere, rather than the volcanic clouds themselves. Thus when it is stated that volcanic ash is effective at nucleating ice, it is relative to other ambient particles, and it is implicitly assumed that the volcanic ash particles appear in low, background concentrations. It is the goal of the following subsections, therefore, to summarize the studies that characterize the freezing temperature of volcanic ash particles. These are then interpreted in section 5 together with the new experimental data presented here (described in section 4) to obtain a synthesis of volcanic IN properties.

3.1. Japanese Volcanoes

[14] *Isono and Komabayashi* [1954] determined a statistical correlation between high precipitation rates and enhanced concentrations of volcanic ash IN from eruptions of Japanese volcanoes. *Isono et al.* [1959a] measured atmospheric IN concentrations in Tokyo, Japan, using an optical cooling chamber between 1958–1959. During this time, several volcanoes including Asama, Aso, Mihara, Sakurajima and Suwanose were active and enhancement in IN concentrations were correlated with the passage of volcanic emissions from the eruptions. In their experiments, an air

sample was introduced into a chamber containing supercooled liquid water droplets at a predetermined temperature. The chamber was then cooled at a rate of 3 K min^{-1} and IN concentrations were determined at 260 K (−13°C), 258 K (−15°C) and 253 K (−20°C), using a counting technique based on visual determination of the number of ice crystals formed. Volcanogenic IN activity steadily intensified as temperature was decreased over the range of 258–253 K. In the experiments, maximum measured IN concentrations associated with the volcanic emissions reached 30–50 L^{-1} at 253 K; this would probably continue to intensify with supercooling to colder temperatures.

3.2. Continental North American Volcanoes

[15] *Schnell and Delany* [1976] directly sampled gas-rich volcanic clouds generated from eruptions of Augustine volcano, Alaska, by aircraft between January and February 1976. Samples were collected on membrane filters and later processed in a thermal diffusion chamber to determine IN concentrations. Measured volcanic cloud IN concentrations were not elevated above typical background levels and in some cases were lower, which was attributed to IN deactivation by gaseous components in the cloud. The volcano at the time of sampling was passively degassing, so it is unlikely that the cloud contained a high concentration of silicate particles that could act as IN. *Radke et al.* [1976] carried out airborne sampling to determine IN concentrations in SO_2-rich emissions from Mount Baker, Washington, between March and June 1975. Using the membrane filter technique, they determined that IN concentrations were low; again, this was probably related to the lack of silicate particles in the volcanic cloud or inadequacies with the measurement technique.

3.3. Hawaiian Volcanoes

[16] IN concentration measurements were carried out routinely at the NOAA Mauna Loa Observatory (MLO) beginning in the 1950s [*Bigg*, 1978; *Fullerton and Garcia*, 1978]. IN measured on the Big Island originated from: (1) remote continental or oceanic sources, followed by transport to the islands above the trade wind inversion [e.g., *Isono et al.*, 1971]; (2) a local oceanic source below the trade wind inversion; and (3) local subaerial island sources with particulates generated by volcanic activity, agriculture and urban areas [e.g., *Hobbs et al.*, 1971a; *Isono et al.*, 1971; *Schnell*, 1982]. *Hobbs et al.* [1971a, 1971b] suggested that "ice nucleus storms" detected at MLO correlated to eruptions of Kilauea volcano along the East Rift Zone. In both cases, eruptive activity was characterized by large lava fountains up to 220 m high which generated a large amount of silicate particulates. Measured ice nuclei concentrations increased by a factor of three or more relative to background levels during the eruptions. *Langer et al.* [1974] made IN measurements at MLO following an eruption of Kilauea on 14 August 1971, where activity was characterized by lava fountaining and effusion of large volumes of magma. Emissions from the eruption were advected to the measurement site and enhanced IN counts during the night, and during daytime in response to diurnal wind patterns. Additionally, IN deactivation was observed in a gas-rich volcanic cloud from Halemaumau crater in Kilauea caldera.

3.4. Laboratory Measurements of Volcanic Ice Nuclei Activity

[17] In some of the earliest laboratory experiments, *Schulz* [1948] reported a freezing temperature of 260 K initiated by powdered trachyte. *Schaefer* [1946, 1949] used a cold cloud chamber in the General Electric Research Laboratory to investigate the ice nucleating ability of various substances including volcanic ash. A supersaturated environment was created inside a refrigerated chamber to promote the growth of a cloud of supercooled liquid water droplets. Fine particles of a variety of substances were then added to the cloud to induce ice crystal formation. The phase of the cloud particles was inferred from the scattering pattern of a beam of light passed through the dispersion; any ice crystals that formed would scintillate. The temperature of the chamber was varied to identify the temperature at which ice first formed for each of the substances investigated. *Schaefer* [1949] observed freezing temperatures for volcanic ash from Crater Lake, Oregon, and Paricutin, Mexico: ice formed at "threshold" temperatures of 256 K and 251 K respectively (also referenced by *Mason* [1971]). Threshold freezing temperature in these studies describes the temperature at which ice was first observed to form.

[18] *Isono and Komabayashi* [1954], *Isono* [1955], *Isono et al.* [1959a] and *Isono and Ikebe* [1960] carried out experiments using the optical cooling chamber described previously to investigate the ice nucleating ability of various powdered substances, including volcanic ash. *Isono* [1955] found that ash from an eruption of Mount Asama became active at temperatures between 258–260 K. *Isono et al.* [1959a] introduced powdered ash samples (particles ~1–10 μm diameter) into a cooling chamber filled with "supercooled fog" at a range of temperatures. IN concentrations were again determined using an optical counting technique. In some cases, volcanic ash nucleated ice at temperatures as warm as 265 K, but generally for all the ash compositions investigated, the "threshold freezing temperature" (in this case the temperature at which 1/20,000 of the total particles in a sample are active IN) was 260–261 K. *Isono and Ikebe* [1960] carried out further experiments using the same approach and investigated volcanic ash from eruptions of 8 Japanese volcanoes, which nucleated ice between 250.0–265.5 K.

[19] *Mason and Maybank* [1958] tested the freezing temperature of a variety of natural substances in an enclosed cooled glass chamber. A supercooled water cloud was generated in the chamber at a specific temperature by evaporating water from a gauze using an electric bulb. Samples were powdered using a pestle and mortar then introduced into the chamber. Ice crystals that formed were captured on a supercooled film of a water-detergent mixture; on contact with the film, ice crystals would rapidly grow to a size large enough to be visually identified. The number of crystals appearing as a function of time was used to infer ice crystal number concentrations. They specified a "threshold" freezing temperature of 261 K for a sample of volcanic ash from an unspecified eruption of Mount Etna, Sicily.

[20] *Tanaka* [1980] investigated ice nucleation initiated by ash erupted from Mt. Usu on 13–14 August 1977 as a function of temperature and water vapor saturation, using a diffusion chamber filter-based technique. Soluble com-

pounds were removed from the samples prior to analysis through dialysis. The threshold freezing temperature at saturation was ~260.5 K. *Schnell et al.* [1982] combined several techniques to investigate the ice nucleating ability of particles in the volcanic clouds generated by the eruptions of Mount St. Helens in 1980. In their experiments, ash was suspended at specified ash mass loadings in a Mylar-coated tent, from which samples were extracted for analysis. Results using the "drop-freezing" technique [*Schnell and Vali*, 1976; *Vali*, 1971] indicated ash from the 18 May 1980 eruption of Mount St. Helens became active at 265 K ($\approx 10^2$ IN g^{-1} ash), with most IN activity observed at 257 K ($\approx 2 \times 10^2$ IN g^{-1} ash), or below. Results from the "membrane filter" technique indicated that "threshold" IN activity occurred at 263 K, and ≈1 IN L^{-1} was present at 259 K with an ash loading of 3000 μg m^{-3}. They concluded that ash generated during the Mount St. Helens eruptions in 1980 was a relatively ineffective catalyst for ice nucleation at temperatures above 257 K.

4. Experiments and Results

[21] In order to provide further insight into the process of ice formation in volcanic clouds, we performed a series of single-particle ice nucleation experiments. Our objective was to understand the role of two physical properties that classical nucleation theory predicts would be controlling parameters: ash particle composition and surface area. In our experiments, volcanic ash of two limiting compositions was used as IN: (1) silica-rich trachyandesitic to ryhodacitic ash from the 12–15 August 1992 eruption of Cerro Hudson, Chile; and (2) silica-poor basaltic reticulite erupted during the 1969–1974 Mauna Ulu eruption of Kilauea, Hawaii. The ash particles were collected at the ground following transport and deposition from the eruption column, and the reticulite was crushed in the laboratory to generate ash-size (<1000 μm) particles; particles typically had a long axis measuring ~500 μm. Finally, size-calibrated borosilicate glass microspheres were used in order to extend the range of surface area that could be investigated in the freezing-temperature versus surface-area experiments.

[22] After collecting the freezing measurements, the surface area of volcanic ash particles used as IN was measured using Scanning Electron Microscope (SEM) stereogrammetry. This technique allows particle surface characteristics to be quantified based on a digital elevation model (DEM) generated from a stereo-pair of secondary electron images [e.g., *Podsiadlo and Stachowiak*, 1997]. Although our measurements were not able to directly resolve what might be active site features, we were able to constrain micron-scale surface area. Particles investigated in the laboratory freezing experiments were carefully retrieved, dried and mounted on aluminum SEM sample holders. Using a sputter coater, an electrically conductive gold layer was applied to the sample to a thickness of ~20 nm. To optimize image quality, a low accelerating voltage (20 kV) was used to preserve textural features [*Yañez and Barbosa*, 2003], which act as points of reference during the stereo image-pair reconstruction. The separation angle used to generate the stereo image pairs was 6°, achieved by tilting the stage −3° and +3° degrees relative to horizontal. DEM generation and quantitative surface analysis was carried out using Alicona Imaging MeX software. The surface analysis feature of the software is based on ISO (International Organization for Standardization) document 4287, which details a standardized quantitative procedure to describe the surface texture of materials. As the SEM stereology technique only images one side of the specimen, DEM-measured surface areas were doubled to provide an estimate for the total surface area of a given particle. Measurements from the stereology technique showed good agreement against calculated surface area for NIST size-calibrated microspheres with diameter between ~20–330 μm (see *Durant* [2007] for details). The total surface area of IN in the experiments was calculated by multiplying the number of microspheres (diameter 331 ± 15 μm) in a given drop by the surface area of a perfect sphere ($A = 4\pi r^2$). One advantage of using size-calibrated microspheres is that composition and surface morphology are well-constrained and remain constant between experiments, allowing only the effects of IN surface area on freezing temperature to be investigated.

[23] To determine the probability of freezing, we measured the freezing temperature of a single drop containing a single IN many times to obtain a statistical ensemble of nucleation temperatures. An advantage of using the same IN repeatedly is that composition, morphology, and surface area remain constant through each experiment, which enables statistics to be built up for a single drop. The apparatus and experimental details are described elsewhere [*Durant and Shaw*, 2005; *Shaw et al.*, 2005], but we review the general approach here. At the base of the sample stage, a liquid-cooled isothermal heat sink (maintained at T ≈ 255 K) removes thermal energy from the system. Two thermoelectric Peltier devices are mounted on the heat sink, and one acts as a heater and the other as a cooler. A cone-shaped copper block rests on top of the Peltier devices, which focuses a temperature gradient to a platinum resistance thermometer (PRT). At the top of the stage, a silanized microscope coverslip (thickness ~0.6 mm) rests on the PRT (silanization is a treatment process that involves silanes to create a hydrophobic surface). During the experiment, a drop (typically ~30 μL) of ultrapure water (distilled, deionized, filtered, and UV irradiated) was placed on the coverslip directly over the PRT, and covered. The experiments were observed and recorded using a microscope equipped with a digital camera unit. The entire system was housed in an isothermal chamber, and purged with dry filtered air (frost point less than 208 K) at a rate of ~2 L/min.

[24] The experimental approach consists of a heating cycle followed by a cooling cycle: temperature was raised to T ≈ 283 K and then lowered at a constant rate of 10 ± 0.1 K min^{-1} using Proportional-Integral-Differential (PID) control to a minimum T ≈ 248 K. This temperature range adequately encompassed all freezing temperatures involving ash particle IN compositions investigated in the experiments. Additionally, the upper limit was sufficiently high to eliminate IN "pre-activation" [e.g., *Young*, 1993, pp. 100–102]. To the possibility of nucleation by the apparatus, the freezing temperature of the silanized cover slip was first tested with a drop of pure water for the first cycle: if the cover slip was sufficiently silanized, the freezing temperature was ≤248 K. Volcanic ash IN used in the experiments were rinsed with distilled water, then were introduced into the drop using a

Table 1. Mean and Standard Deviation of Experiment Freezing Temperatures Averaged by Compositional Group

IN Type	Surface Area, μm^2	Freezing T, K	σ, K	Minimum, K	Maximum, K
Single Particle Experiments					
Volcanic ash (basalt)		254.1	2.1	250.7	257.1
Volcanic ash (trachyandesite)		252.6	2.0	248.7	256.6
Volcanic ash (all compositions)	$2.3 \times 10^5 - 2.9 \times 10^6$	253.1	2.1	248.7	257.1
Microspheres (borosilicate glass)	$1.7 \times 10^6 - 3.4 \times 10^7$	252.6	3.4	249.1	259.2
Bulk Particle Suspension Experiments					
Volcanic ash (andesite; crater peak)		257.5	0.5		
Volcanic ash (rhyolite; Ogallala)		259.5	0.7		
Volcanic ash (rhyolite; Oruanui)		257.6	0.2		

hypodermic syringe needle: it was possible to position the IN on the surface or inside the volume of the drop during the experiment. Drop freezing was detected from the latent heat of fusion released, which produces a sharp peak in the cooling curve. At the end of the experiment, the freezing temperature of the cover slip was again tested to ensure it was $\leq$248 K.

[25] Data for each experiment consists of a series of freezing temperatures for a given water drop and IN. Average freezing temperature and standard deviation were calculated for each experiment; results for each compositional group (basaltic ash, tranchyandesitic ash, borosilicate glass NIST-sized microspheres) and IN surface area ranges are presented in Table 1. Qualitatively, the bulk SiO_2 content of IN investigated in the experiments increases from basaltic ash ($\sim$45–52% bulk SiO_2), to trachyandesitic ash ($\sim$52–63% bulk SiO_2), to borosilicate glass microspheres ($\sim$100% bulk SiO_2). The results indicate that basaltic ash freezes at slightly higher ($\sim$1.5 K) temperatures, but the range of freezing temperatures for a given composition is approximately a factor of 5 greater than that difference. This suggests that typical limiting compositions for volcanic ash yield similar ranges of freezing temperature, and implications of this are discussed in section 5. Figure 1 shows freezing temperatures plotted as a function of total IN surface area, which was varied over 2 orders of

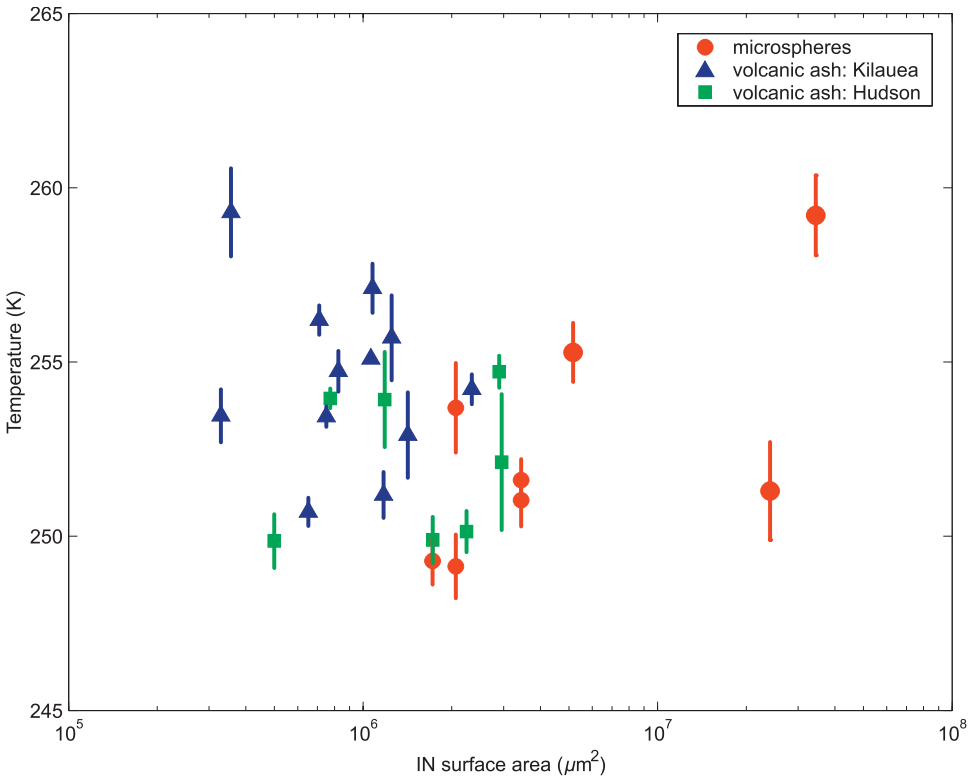

Figure 1. Freezing temperature as a function of IN surface area. Blue triangles (Mauna Ulu, Hawaii; basaltic ash) and green squares (Cerro Hudson, Chile; trachyandesitic ash) are mean freezing temperatures and standard deviation of experiments using volcanic ash particles as IN. Surface area (A) of ash particle IN was determined using SEM stereogrammetry for single particles. Red circles are freezing data for size-calibrated borosilicate glass microspheres and surface area in this case was calculated for a population of N particles using the relationship: $A = 4N\pi r^2$.

magnitude in the experiments. As can be seen, there is considerable scatter. The data for ash particles taken alone do appear to show a subtle trend, but it is not significant given the measurement uncertainty.

5. Discussion

5.1. Freezing as a Function of IN Composition and Surface Area

[26] In our experiments, mean freezing temperature changes by approximately 1.5 K between the two silicate compositional groups tested, with freezing temperature decreasing as a function of bulk silica content. The effect is very weak, even after considering the historical data for which the composition can be determined. The data suggest that other physical properties such as surface morphology, defects, or impurities, all of which may act as ''active sites,'' play as much or more of a role in determining the freezing temperature of a given ash particle. In the case of the microspheres, morphology was better constrained (almost perfect spheres). In future experiments, IN composition should be geochemically characterized, for example, using SEM-EDS to unequivocally ascertain any temperature dependence related to IN composition. It appears likely, however, that any temperature dependence will be slight, and in real volcanic clouds, other uncertainties will make a purely composition-based dependence of questionable utility. Similar conclusions can be reached regarding the surface area dependence of freezing temperature: IN surface area does not appear to have a dominant effect on freezing temperature relative to other factors, at least within the range of surface areas studied here. The surface areas studied in our experiments are representative of the largest particles expected to be present in volcanic clouds with significant concentrations (see discussion in section 2). Past experiments have shown evidence for a freezing-temperature dependence on IN size, but for much smaller particles (<0.08 to <0.15 μm) [*DeMott*, 1990]. On the basis of this evidence, it seems likely that there is, in fact, a freezing temperature dependence when the surface area is varied by many orders of magnitude. However, the freezing data in the large-particle size range of our experiments suggest that the effect is weak.

[27] Our visual observations of the IN-drop geometry suggest that much of the variability within the total freezing temperature range of the experiments ($\sim$250–261 K) is a result of freezing associated with the different heterogeneous nucleation modes, i.e., immersion versus contact nucleation (from the inside-out [*Durant and Shaw*, 2005]). During the experiments, IN within the drops had a tendency to shift between making contact with the drop surface and being fully immersed within the drop volume [*Durant and Shaw*, 2005; *Shaw et al.*, 2005]. For any given particle, the contact mode has a freezing temperature $\sim$4–5 K higher than the immersion mode. Thus the mode of nucleation is yet another aspect of the problem that likely contributes as much, or more, to the variability in freezing temperature as IN composition and surface area.

[28] In Figure 2, we compare some of the historical data reviewed in section 3 to the measurements collected in this study. The mean and standard deviation of freezing temperatures for all volcanic ash in our experiments is shown, as well as the total range of freezing temperatures (shaded region). The spread of the historical data is similar to that observed in our experiments, but it is important to recognize differences in the experimental techniques that necessitate care in comparing freezing temperatures directly. The unique aspect of the current study is that freezing of water drops was carried out using individual IN instead of analyzing systems containing large numbers of particles, as in most earlier studies. For example, in many of the previous studies, powdered ash was introduced into a preexisting cloud of supercooled water droplets, or IN were collected in bulk on filter samples and later exposed to water vapor supersaturated with respect to ice. Most of the historical measurements of freezing temperature, therefore, are ''threshold'' temperatures, not average temperatures, so it is reasonable to compare the upper limit of our observed range (shaded region) with these historical IN activation data. For closer comparison to the historical measurements, and also to test several additional ash compositions, we froze bulk suspensions of ash. Specifically, this simple experiment consisted of freezing a water droplet of approximately 6 mm in diameter ten times, with the droplet containing thousands of ash particles. The results for three ash samples consisting primarily of rhyolite (Ogallala, Atitlan, and Oruanui) and one ash sample consisting primarily of andesite (Crater Peak) are displayed in Figure 2. The freezing temperatures are higher, as expected, because bulk freezing experiments measure a threshold temperature (the freezing temperature of the most effective IN in the sample). With this understanding of freezing temperature thresholds in mind, the agreement among the various measurements of volcanic IN is quite compelling.

[29] Finally, we note that the temperatures reported here are for pure water and clean ash. Volcanic gases such as SO_2 and HCl dissolve in liquid water and ash particle surfaces may have adsorbed soluble salts or gases, all of which can alter the ice nucleating properties. Soluble components could play a complex role: for example, they may tend to favor particles acting as immersion, rather than deposition IN. The primary effect of adsorbed or dissolved substances most probably will be to depress the mean freezing temperature, but not necessarily alter the variance. However, this is dependent on the rate at which gases diffuse into liquid water. In the following discussion, we will refer to the temperature range observed in our experiments, but similar arguments can be made even if the range is shifted to lower temperatures due to solute effects. Clearly the details of gas-particle interactions and their consequences for volcanic IN are in need of further study.

[30] To conclude this section, we synthesize the data shown in Figure 2 in the following way: The historical data, as well as the data from our laboratory, suggest that volcanic ash particles initiate freezing in a relatively narrow temperature range of approximately 250 to 260 K (or perhaps up to 265 K). Note that we use the word ''initiate'' because in a volcanic cloud there is a continuous size distribution of particles that may extend down to submicrometer-sized particles, which have not been studied here and which likely have lower freezing temperatures. The super-micrometer-sized ash particles, however, are abundant and it is likely that these are the most effective IN. The high temperature end of the range represents the threshold

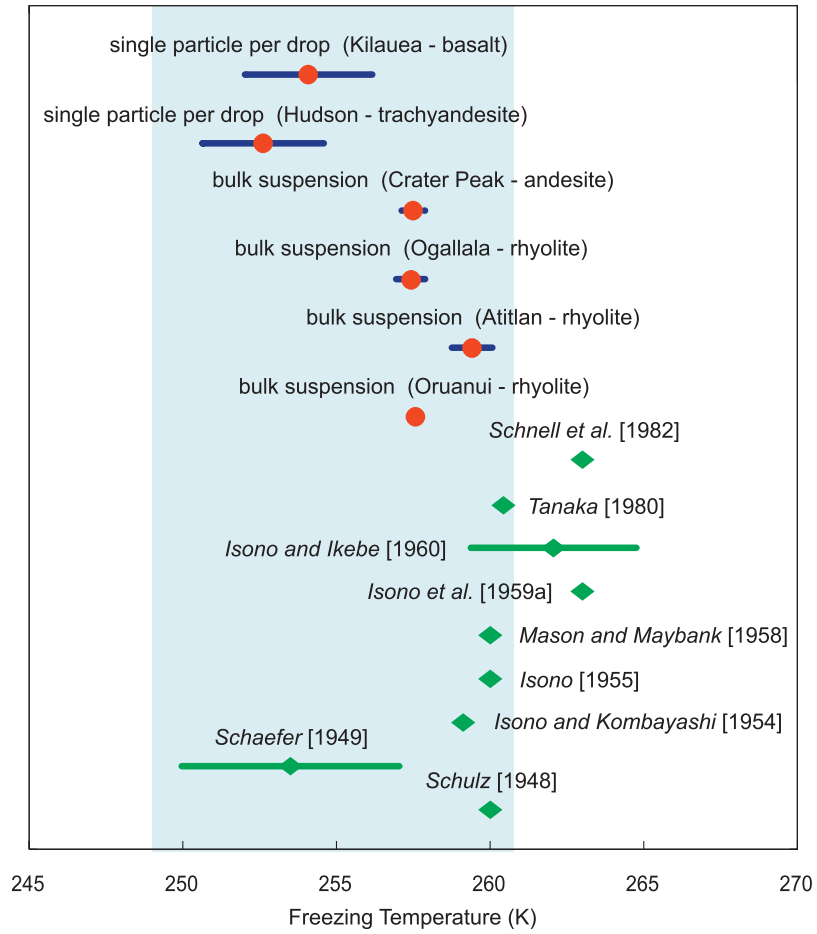

Figure 2. Experimental freezing data for both volcanic ash compositions investigated in the current study (single particle per drop and bulk suspension, red circle) compared to historical freezing data from the literature (green diamonds): single particle per drop, basaltic (254.1 K σ = 2.1) and trachyandesitic ash (252.6 K σ = 2.0); bulk ash suspension, Oruanui, New Zealand, 40 ka eruption (257.6 K σ = 0.2), Atitlan, Guatemala, 84 ka eruption (259.5 K σ = 0.7), Ogallala, Nebraska, erupted 11 Ma (257.5 K σ = 0.5), Crater Peak, Alaska, 1992 eruption (257.5 K σ = 0.4); *Schulz* [1948], trachyte (260 K); *Shaefer* [1949], ash from Crater Lake, USA, and Paricutin, Mexico (253.5 K σ = 3.5); *Isono and Komabayashi* [1954], ash from Mount Asama, Japan (259.5 K); *Isono* [1955], Mt. Asama, Japan (260 K); *Mason and Maybank* [1958], Mt. Etna, Italy (261 K); *Isono et al.* [1959a], ash (fall) from various Japanese volcanoes (263 K); *Isono and Ikebe* [1960], includes volcanic ash freezing data for 8 Japanese volcanoes (262.1 K σ = 2.7); *Tanaka* [1980], ash from Mount Usu, Japan, 13–14 August 1977 eruption (260.5 K); *Schnell* [1982], Mount St. Helens, Washington, 18 May 1980 eruption (263 K).

temperature at which these IN start to become active, and in the single particle measurements, all ash particles become activated by ~250 K. This temperature range is remarkably robust to changes in ash composition and size, including the reviewed historical ash measurements, and therefore provides an empirical basis for simplifying our representation of ice nucleation in models of volcanic clouds. We now consider possible microphysical consequences of these results for freezing temperatures of super-micrometer-sized ash particles. Further discussion of the relevance of these measurements to volcanic cloud energetics are discussed in the Appendix A.

5.2. Microphysical Consequences of Abundant Volcanic Cloud IN

[31] It is clear from airborne measurements within volcanic clouds [*Hobbs et al.*, 1982, 1991; *Stith et al.*, 1978] that fine ash (1–1000 μm) number concentrations can reach hundreds per cubic centimeter, and remote sensing measurements, although less direct, confirm such numbers [*Guo et al.*, 2004b; *Rose et al.*, 2001; *Schneider et al.*, 1999]. Particle number concentrations in a rising volcanic cloud, where less dilution has occurred, are likely to be even higher, and this has important implications for the ice formation process. As has been pointed out, typical water clouds are IN-limited, such that in supercooled regions, relatively few droplets freeze to form ice. Consider, for example, the classic IN parameterization by *Fletcher* [1962] which gives the number of IN per liter as a function of supercooling ΔT: $n_{IN} = A \exp(B\Delta T)$, with $A = 10^{-5}$ L^{-1}, $B = 0.6$°C^{-1} [*Pruppacher and Klett*, 1997, section 9.2]. For $T = -20$°C this results in only $n_{IN} \approx 2$L^{-1}, which may be compared to typical cloud droplet number concentrations on the order of 10^5 L^{-1}. More recent laboratory work by

Meyers et al. [1992] has led to the parameterization $n_{IN} = \exp(A + B \times s_i)$, with $A = -0.639$, $B = 0.1296$, and s_i being the ice supersaturation. Assuming a cloud saturated with respect to liquid water at $T = -20°C$, we obtain $n_{IN} \approx 7\ L^{-1}$.

[32] We note that analogous parameterizations have been borrowed for use in models of volcanic cloud microphysics [*Herzog et al.*, 1998; *Textor et al*., 2006]. Volcanic plumes and clouds, in contrast, likely contain number concentrations of fine ash comparable to the number concentrations of water droplets in meteorological clouds. That is, 10^4 to 10^5 times greater than the typical background concentration of ice nucleating particles active at $-20°C$, and possibly even higher in relatively undiluted plumes. Our laboratory measurements, taken together with the previous measurements reviewed here (which cover a range of different ash compositions and particle sizes), suggest that large volcanic ash particles become active as IN within a 10°C temperature range centered at $-20°C$. As moderate to high magnitude eruptive clouds typically reach altitudes where $T < -20°C$, our measurements imply that the majority of fine-ash (super-micrometer-sized) particles act as IN within that temperature range. Clearly the volcanic cloud is in a fundamentally different ice nucleation regime than most meteorological clouds: meteorological clouds are IN-poor and volcanic clouds are likely to be IN-rich.

[33] What are the implications of this different regime for ice nucleation in IN-rich volcanic clouds? In meteorological clouds that are IN-poor, the formation of a relatively small number of ice crystals in the presence of an overwhelming number of supercooled liquid droplets leads to the rapid, favored growth of those ice crystals via the Bergeron process. This is one of two primary ways by which hydrometeor suspensions can become unstable and produce precipitation (the other being the "warm rain" coalescence process). It must be noted, however, that a necessary condition for the Bergeron process is that "the number density of ice particles must be much smaller than that of the liquid droplets" [*Korolev*, 2007]. In an IN-rich environment, it is likely that the Bergeron process will be suppressed because a large fraction of volcanic cloud droplets can be expected to form ice due to their contact with ash IN. This, in turn, will tend to stabilize the cloud by removing the mechanism for favored growth of a relative minority of particles: rather, the cloud will consist of large numbers of small ice crystals in the presence of little or no supercooled liquid water.

[34] There is a close analogy to this concept from the early days of cloud physics, when cloud seeding was a major research focus. In Mason's classic text the concept is described concisely: "'Overseeding' with massive doses of nuclei will result in large concentrations of crystals that will be unable to grow sufficiently large to fall out and reach the ground. Such an operation may therefore retard or prevent the development of precipitation and, in particular, suppress the growth of large, damaging hailstones" [*Mason*, 1971, p. 369]. *Rogers and Yau* [1989, p. 244] state that the number of IN necessary to glaciate an entire cloud "is excessive and much beyond the capability of any seeding system in current use," but of course, IN concentrations in volcanic clouds are in a different category than artificial seeding technologies (e.g., aircraft-mounted flares).

[35] The question of how many IN are required to "overseed" a cloud, thereby completely glaciating it and shutting down the Bergeron process, was dealt with directly and clearly by *Rokicki and Young* [1978], and the essential results are summarized in Young's later text [*Young*, 1993, Sec. 11.2.1 (ii)]: "If natural ice crystal concentrations are relatively low, increasing the concentration of ice crystals can increase the precipitation rate by converting a larger fraction of the cloud water to precipitation particles. As the concentration of ice crystals is increased, competition for the available liquid water increases, reducing the ultimate sizes of the ice particles. If this is carried to the extreme, the resulting ice particles will be too small to be able to fall to the ground before subliming (or melting and evaporating) completely. Thus for a given cloud, there must be some optimal ice crystal concentration that will maximize the amount of precipitation from the cloud." Using a detailed cloud model, *Rokicki and Young* [1978] concluded that ice crystal concentrations above 1000 L^{-1} (1 cm^{-3}) cause the precipitation-formation time to diverge rapidly. Interestingly, this agrees with the earlier, more empirical conclusion of *Mason*, that there is a critical seeding level of approximately 1 cm^{-3} in order to suppress precipitation [*Mason*, 1971, p. 397]. Actual ash concentrations in Plinian eruption columns and volcanic clouds exceed this threshold by at least one, and possibly up to three, orders of magnitude, placing volcanic clouds in the unique microphysical category of strongly overseeded for ice nucleation.

[36] One competing process is supersaturation that results from rapid ascent [e.g., *Phillips et al.*, 2007]. The Bergeron process only weakens after water supersaturation becomes negative and all supercooled cloud-liquid evaporates away. In the case of a volcanic plume, high vertical velocities presumably require large numbers of ice crystal concentrations to attain this condition. Order of magnitude estimates carried out for cumulonimbus clouds [*Knollenberg et al.*, 1993; *Phillips et al.*, 2005] suggest that for vertical velocities of 10 to 20 m s^{-1}, concentrations of "a few per cubic centimeter" or greater are sufficient to hold the quasi-steady state supersaturation [*Rogers and Yau*, 1989, p. 110] below water saturation. One implication is that production of ice crystals above this threshold via heterogeneous freezing will tend to suppress further heterogeneous freezing because of the reduced efficacy of freezing methods that depend on the presence of liquid water (immersion and contact) and the weakening of deposition nucleation with decreasing ice supersaturation [e.g., *DeMott et al.*, 1999; *Field et al.*, 2006]. The quasi-steady state supersaturation for an idealized, monodisperse population of crystals, is proportional to w/n, where w is the updraft speed and n is the number density, so the critical number density determined by *Phillips et al.* [2005] can be simply scaled to match the updraft speed of interest. Even for the strongest updrafts observed in volcanic clouds, this critical number density would not be expected to exceed tens of particles per cubic centimeter, and it therefore is plausible that the "self-quenching" of nucleation will occur as a consequence of overseeding.

[37] The volcanic IN abundance and overseeding question also has linkages to aerosol indirect effects. For example, there is an observed trend of larger numbers of small ice crystals in regions with higher boundary layer

aerosol concentrations [*Sherwood*, 2002b]. In a study of "smoking rain clouds" over the Amazon basin during massive burning episodes, there was an observed shift of precipitation development to larger heights under smoky conditions [*Andreae et al.*, 2004]. More aerosols tended to suppress precipitation, but also lead to dynamically more vigorous and more violent storms: it was not clear whether the total precipitation changed as a result of smoke ingestion. On a global scale, the combined microphysical and dynamical effects of the ice indirect effect are complex, in part because most studies have centered on globally averaged optical properties [*Lohmann*, 2002], rather than the local microphysical effects of interest here.

[38] The existence of IN-rich volcanic clouds should also have implications for the ability of Plinian eruption columns to inject water, ash, and other gases and particulates into the upper troposphere and lower stratosphere. For example, *Sherwood* [2002a] showed that increasing stratospheric water vapor can be directly related to ice crystal size: more numerous, smaller ice crystals are lofted higher, settle out more slowly, and evaporate more quickly than larger less numerous crystals. This raises the possibility that ice microphysics in volcanic clouds are an important factor affecting injection of water vapor and other trace gases into the stratosphere, which have long-lived, global consequences. The chemical effect is made more compelling when one considers the larger uptake rates of various trace gases for liquid water relative to ice. Conversion of liquid water to the ice phase results in a lower chlorine uptake capacity [*Tabazadeh and Turco*, 1993], for example, and this may be consistent with serendipitous measurements made in the ice-rich Hekla volcanic cloud that suggest chlorine removal was suppressed in the rising plume [*Rose et al.*, 2006].

6. Summary and Conclusions

[39] Freezing experiments were carried out with water drops containing basaltic and trachyandesitic volcanic ash particles acting as IN. The combined mean freezing temperature for all volcanic ash compositions tested is 253.1 K (σ = 2.1). These data are in reasonable agreement with historical measurements of freezing initiated by volcanic ash, when differences in measurement techniques are accounted for. The experiments taken together support an approximate freezing range of 250 to 260 K, over which the majority of fine ash particles (super-micrometer) in the presence of water will induce freezing (neglecting solute effects).

[40] Combining the volcanic ash data and data from experiments with borosilicate glass microspheres, drop freezing temperature was investigated over approximately two orders of magnitude of IN surface area (2.3×10^5 – 3.4×10^7 μm^2), but no clear correlation was identified. The observed variability is apparently dominated not only by morphological and compositional variability from particle to particle, but also by competing heterogeneous freezing modes (immersion and "inside-out" nucleation), which is evident from the spread of freezing temperatures observed for individual IN particles. A surface area dependence likely would be observed if a larger range of particles sizes were studied, and this will be the subject of subsequent research. For now, however, we have focused on particles relevant to the fine ash (super-micron) mode that is observed in volcanic ash size distributions.

[41] A further implication of this work is that volcanic clouds are likely in a distinct ice-microphysical parameter range compared to analogous meteorological clouds. According to our observations, large ash particles act as IN within an approximately 10 K temperature range. Volcanic clouds with high fine-ash number concentrations therefore have plentiful IN and are capable of efficient conversion of liquid water to ice. We speculate that this "overseeding" will tend to suppress the traditional ice-driven precipitation process (Bergeron-Findeisen-Wegener) and stabilize the cloud by increasing particle residence times: ice crystal number concentrations may be enhanced, ice crystal size may be small, and hydrometeor-enhanced sedimentation may be suppressed as a consequence. Additionally, trace gas depletion rates may be altered due to a dearth of supercooled water, with possible implications for injection of these gases into the upper troposphere and stratosphere.

[42] Future work includes extending experiments to focus on specific heterogeneous nucleation modes, such as contact, immersion, and deposition freezing. Additionally, the IN should be geochemically characterized using a technique such as SEM-EDS to obtain a more accurate measure of the effect of composition on freezing temperature. The surface area dependence of freezing temperature should be extended to investigate a larger sample size over a greater range of IN diameter to reveal any significant trend. This should include investigation of ash particle sizes down to 1 μm in order to evaluate the role of these particles, which are present in high concentrations even in aged volcanic clouds after coarse ash particles have been removed through precipitation or settling.

[43] Finally, we conclude that IN parameterizations developed for meteorological clouds are inadequate for models of volcanic plumes and clouds. Our hope is that this work can help provide a basis for revised parameterizations for IN concentrations appropriate to volcanic clouds. The results presented here suggest that the following simplification is reasonable: if there is sufficient water, ice formation will be initiated on super-micrometer-sized ash particles within the approximate temperature range 250–260 K, largely independent of ash composition or ash surface area. The abundance of these particles is extremely high in most eruptions, and can be estimated from remote sensing measurements, measurements of ash deposits, and airborne measurements. With this empirical input for IN concentrations and freezing temperatures, numerical models can be used to investigate the detailed microphysical and dynamical effects of the overseeded-IN regime that is expected to be a distinguishing characteristic of volcanic clouds.

Appendix A: Water, Freezing, and Volcanic Cloud Energetics

[44] Magmatic water is an obvious source for water in volcanic clouds [*Wade et al.*, 2006], but it can also be contributed from external sources including oceans, groundwater, fluvial and lacustrine environments [e.g., *Koyaguchi and Woods*, 1996; *Rose et al.*, 1995a], and entrained tropospheric air [e.g., *Glaze et al.*, 1997]. The proportion

Table A1. Intensive Energies of Volcanic Clouds

Process	Intensive Energy	Parameter Estimates	Energy Estimate
Vent kinetic energy	$v^2/2$	$v \sim 200$ m s^{-1}	2×10^4J kg^{-1}
Ash cooling	$C\Delta T$	$C \sim 1000$ J kg^{-1} K^{-1} $\Delta T \sim 800$ K	8×10^5J kg^{-1}
Condensation	L_v	$T = 10$°C	2×10^6J kg^{-1}
Freezing	L_f	$T = -15$°C	3×10^5J kg^{-1}

of externally derived water is dependent on the magnitude and style of eruption, and the latitude of the volcano. Despite this complexity, models have been developed that include the effect of water phase changes on volcanic cloud dynamics [e.g., *Glaze et al.*, 1993; *Herzog et al.*, 1998; *Mastin*, 2007; *Woods*, 1993]. In situ measurements of water and particle concentrations in volcanic clouds (including data on CCN and IN) are scarce due to the hazards posed to aircraft-based sampling. *Hobbs et al.* [1982] made airborne measurements of particles and gases in the emissions from the 1980–1981 eruptions of Mount St. Helens along the periphery of the cloud, between altitudes of 2.4–3.8 km MSL at distances up to ~450 km from the volcano. For the paroxysmal eruption of 18 May 1980, water vapor and particle flux (0.008–66 μm diameter) was 5×10^5 kg s^{-1} and 6×10^4 kg s^{-1} respectively; this represents a ratio 8.3:1 of water to fine ash. Number concentrations of particles >2 μm in the 18 May 1980 eruption emissions were up to 20,000 times greater than in the ambient atmosphere. It is clear from these observations that there are abundant fine particles and CCN in volcanic clouds, and as temperature falls, some proportion will become activated as IN. This is in contrast to meteorological clouds, which typically have limiting IN concentrations. In this context we proceed to consider, in turn, the role of ice formation in the energetics of volcanic clouds, and some specific effects of the unique microphysical properties of volcanic clouds.

[45] It is illuminating to compare the energetics of several processes occurring in a typical Plinian eruption column, with the goal of evaluating the relative magnitude of energy released during the freezing process. Initially we generalize by considering an intensive energy (per kilogram of ash or water) associated with the gas thrust zone (vent kinetic energy), cooling of pyroclasts (focusing on fine ash), condensation of water, and freezing of water. The intensive energy of the gas thrust zone is $v^2/2$, where v is the vent velocity; for cooling of ash it is $C\Delta T$, where C is the specific heat capacity of ash, and ΔT is the difference between the initial ash temperature and the final cloud temperature; for condensation of water it is simply L_v, the enthalpy of vaporization; and for freezing of water it is L_f, the enthalpy of fusion. Relative values are given in Table A1 for reasonable estimates of the various parameters. The intensive energy associated with cooling of pyroclasts, which is known to be an important source of buoyancy in Plinian eruption clouds, is of the same order of magnitude as the energy released upon freezing of liquid water. Actual energies depend on the mass fluxes of pyroclasts and water, and it is difficult to determine the relative proportions in a volcanic cloud with any certainty.

[46] Water can compose up to ~8 wt.% of ejected magma [*Plank et al.*, 2006], and in this limiting case, it has been concluded that "the exsolved volatile contents of magmas are too small to have a significant influence on column behavior" [*Sparks et al.*, 1997, p. 106]. It should be acknowledged, however, that several environmental factors can influence this markedly: (1) the relative masses of water vapor and pyroclasts change dramatically with height due to rapid fallout of ballistic pyroclasts; (2) entrainment of ambient air with a high concentration of water vapor is more likely for low-altitude and low-latitude volcanoes, or in eruptions where pyroclastic flows are important [*Dartevelle et al.*, 2002]; and (3) there could be non-volcanic sources of water from the hydrosphere in the volcanic cloud [e.g., *Rose et al.*, 1995a].

[47] The opposite limit is to consider relative ash and water masses measured in volcanic clouds, after significant entrainment and fallout have taken place. Hobbs and colleagues have reported airborne measurements of peak water vapor and particle fluxes from the Mount Augustine 1976–77 eruptions [*Stith et al.*, 1978], the Mount St. Helens 1980–81 eruptions [*Hobbs et al.*, 1982], and the Mount Redoubt 1990 eruptions [*Hobbs et al.*, 1991]. In all three cases, the fluxes (in units of mass per unit time) of water vapor and fine ash particulates to the atmosphere are quite similar in magnitude (Table A2). These fluxes, combined with the intensive energies from Table A1 allow calculation of the power of the various processes, which are summarized in Table A2. In addition, the estimated powers resulting from ash cooling and water freezing are comparable: for example, in the Augustine measurements, water freezing is slightly less important, and in the St. Helens measurements, water freezing is slightly more important than ash cooling.

[48] In the context of these calculations we consider, briefly, the implications of the IN measurements summarized in section 5 for column dynamics. If we assume the volcanic cloud rises purely by convection (which is more applicable to the higher levels of the plume, i.e., the convective region [*Sparks et al.*, 1997]) and ignore the effects of mixing with ambient atmosphere and heat contributed by tephra, then the

Table A2. Estimated Powers Resulting From Ash Cooling and Water Condensation and Freezing, Based on Measurements of Ash Particle and Water Fluxes at the Edges of Volcanic Clouds[a]

Volcano	Particle Flux, kg s^{-1}	Water Flux, kg s^{-1}	Ash Cooling Power, W	Condensation Power, W	Freezing Power, W	Ref.
St. Augustine (1976–1977)	6×10^5	1×10^5	5×10^{11}	2×10^{11}	3×10^{10}	a
Mount St. Helens (1980–1981)	6×10^4	5×10^5	5×10^{10}	1×10^{12}	2×10^{11}	b
Mount Redoubt (1990)	1×10^4	9×10^3	8×10^9	2×10^{10}	3×10^9	c

[a]References are: (a) *Stith et al.* [1978]; (b) *Hobbs et al.* [1982]; (c) *Hobbs et al.* [1991].

change in cloud temperature as a function of height in the troposphere may be approximated by the pseudoadiabatic lapse rate ($\sim$6 K km^{-1}). The approximate temperature range for substantial glaciation resulting from volcanic IN, based on the discussion in section 5 is 250–260 K. On the basis of the pseudoadiabatic lapse rate and experimental freezing temperatures, freezing of all hydrometeors would be predicted to occur over a narrow height interval of $\sim$1.7 km. For moderate to large explosive eruptions that reach the tropopause (e.g., VEI $\approx$ 3–4), typical average rise rates are of the order 10–50 ms^{-1} (e.g., Mount St. Helens [*Harris et al.* [1981], Crater Peak [*Rose et al.*, 1995b], and Hekla [*Lacasse et al.*, 2004] eruptions all are in this range), resulting in glaciation times of roughly 0.5 to 3 min. Assuming the majority of water in the cloud freezes there will be an associated increase in buoyancy within a relatively short time. A dramatic illustration of this effect comes from early cloud seeding experiments in which cloud tops of seeded clouds were increased by several kilometers compared to unseeded clouds, due to the extra buoyancy generated by ice formation (both due to the latent heat of fusion and the overall reduction in vapor pressure at a given temperature, which implies more water in the condensed state) [*Tribus*, 1970].

[49] More detailed discussions are beyond the scope of this paper, but these scaling estimates provide a sense of the relative importance of the ice formation problem to the energetics of volcanic clouds, especially when one considers that the effects may be relatively localized. As is true in meteorological clouds, the dynamics of an eruption column and the resulting volcanic cloud will be influenced by both the condensation and eventual freezing of water. It is therefore important to consider the details of the freezing process, including the temperature range at which most freezing is expected to take place, and the eventual size distribution of ice particles, which is largely determined by the nucleation process.

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