Ice Nucleation by Volcanic Ash: Influence of Composition and Morphology

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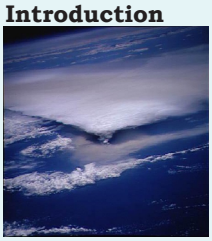
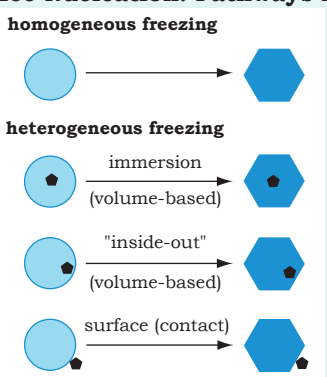
Introduction



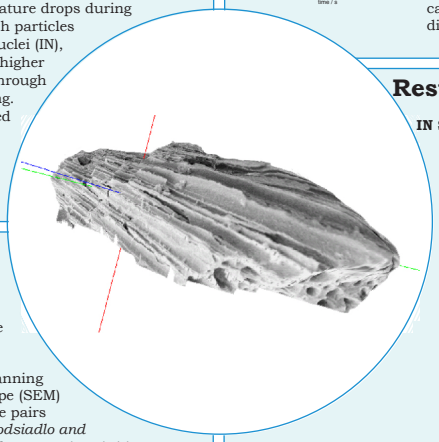
Large explosive volcanic eruptions (>VEI=4) produce plumes that inject large amounts of aerosols into the stratosphere every 2 years [*Textor et al.*, 2003], with a significant eruption into the stratosphere every 5.5 years [*Grainger and Highwood*, 2003]. Ice forms a significant component of volcanic clouds and has been observed in several recent eruption clouds (e.g., 1994 eruption of Rabaul (picture right) [*Rose et al.*, 1995]).

Ice can conceal the characteristic spectral absorbance features of ash, making satellite detection challenging. Furthermore, plume dynamics and cloud processes (such as radiative properties and lifetime) are sensitive to the manner in which liquid water is converted to ice and, therefore, to the ice nucleating properties of volcanogenic particles. Volcanic and cirriform clouds occupy a similar vertical range in the atmosphere, so insight gained from study of cirrus clouds has direct application to volcanic analogues. Understanding of ice nucleation in cirrus clouds is largely based on simple, "classical" theory [e.g., *Pruppacher and Klett*, 1997, Ch. 9], and empirical observations [e.g., *Demott*, 2002]. Here we report on laboratory measurements of heterogeneous ice nucleation on volcanogenic particles of varying composition and morphology. We are specifically interested how composition and surface area of ash particles acting as IN affects cloud drop freezing temperature. We ran 2 series of experiments investigating the ice nucleating ability of basaltic ash from Kilauea (Hawaii), and trachyandesite / rhyodacite ash from the 1991 eruption of Cerro Hudson (Chile). This approach is particularly suited to investigate the statistical nature of heterogeneous freezing of cloud drops.

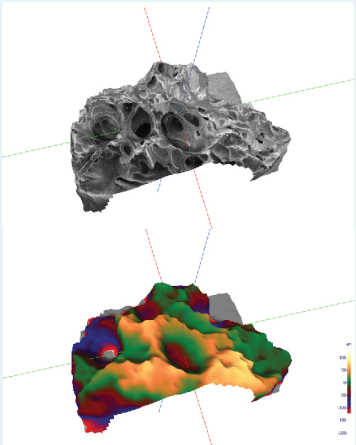
Ice Nucleation: Pathways from Water to Ice



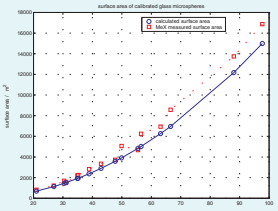
Homogeneous nucleation of cloud ice is possible under certain conditions, but this requires vapor supersaturations of several hundred percent. In a volcanic plume, high number concentration of particles (relative to background atmospheric concentration) act as cloud condensation nuclei (CCN) and initiate drop formation at lower vapor supersaturations: For this reason, drops in volcanic plumes probably contain at least one ash particle. Temperature drops during plume ascent and ash particles in drops act as ice nuclei (IN), initiating freezing at higher temperatures than through homogeneous freezing. Drop freezing initiated by IN is called heterogeneous ice nucleation, which is the focus of our experiments.



Surface Area from SEM Stereoscopy



Above: *DEM (upper) and accompanying 3-D surface elevation map (lower) of an ash particle investigated in the experiments.*



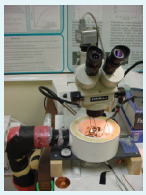
Above: *Plot showing MeX measured surface area against calculated surface area of NIST calibrated silica microspheres (blue); MeX-derived surface area is consistently greater than the calculated area which may represent slight irregularities in the surface of the microspheres (courtesy of O. P. Mills, MTU).*

Quantative 3-D analysis of morphology, shape and surface topography of microparticles is possible using scanning electron microscope (SEM) stereoscopic image pairs [*Hudson*, 1973; *Podsiadlo and Stachowiak*, 1997]. We employed this technique to characterize the surface area of individual ash particles investigated in the ice nucleation experiments.

A stereoscopic pair of SEM images consists of two images of the same particle taken at different angles at the same magnification. SEM images are captured from different angles by tilting the sample relative to the electron beam. All images also share a common working distance between the sample stage and final lens. In this case, we used a working distance of 39 mm and imaged particles 3° in each direction relative to the sample stage, giving a total tilt angle of 6°; low angles of 5-10° are typically used to image irregular particles with high surface relief. Particle surface elevation is calculated from the disparity between locations of the same surface points in each image. An algorithm can be employed to calculate surface elevations over the whole particle from analysis of the stereo-pair images, producing a map of elevations at specific points. The elevation map is completed by interpolating between points to form a 3-D digital elevation model (DEM).

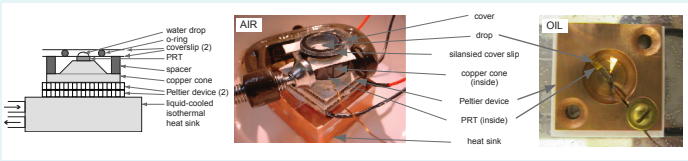
In this study, we used MeX software from Alicona Imaging to generate DEMs from SEM images for visualization of particle topography. We then used a module in the software to measure particle surface area from the DEM created by the program. As the particles were observed from directly above, we only have surface area information for one half of the particle. Therefore, we simply doubled our measurements to give a close approximation for total surface area. The method was tested using NIST-calibrated silica microspheres.

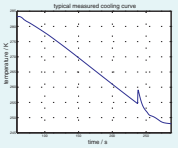
Experiment Design



The experimental approach is to measure the freezing temperature of drops containing ice nuclei (IN) many times to obtain a statistical ensemble of nucleation temperatures. This approach is desirable as it investigates the same IN repeatedly, avoiding complication through variation in composition, morphology, and surface area. A single ash particle was placed inside, or on the surface of a small water drop (typically ~30 μL) of ultrapure water (distilled, deionized, filtered, and UV irradiated), which was then immersed in oil and positioned on a platinum resistance thermometer (PRT). In a later series of experiments, we developed components to measure the freezing temperature of the drop in air (see below for schematic).

In the case of the air experiments, it is possible to move a particle in and out of the drop during the experiment, and to position it on the surface or inside the volume of the drop. The nucleating temperature of the silanised cover slip can be tested by putting a drop of pure water on the sensor for the first cycle: if the cover slip is sufficiently silanised, the freezing T should be less than 250 K (usually about 249 K). The IN is then introduced into the drop and the experiment run. At the end of the experiment, the freezing temperature of the cover slip is again tested.



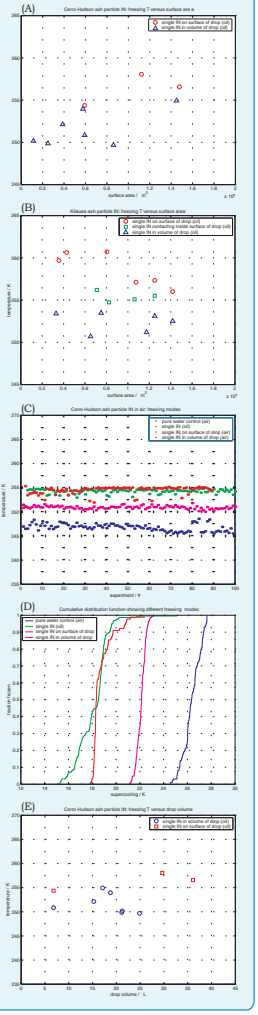


The Peltier devices control cooling rate - we used a rate of 10 K/min. The entire system is housed in an isothermal chamber. Temperature is decreased linearly with time, with active PID control to within better than 0.1 K. When the water drop freezes we can observe the enthalpy of freezing directly by detecting sudden 'spikes' in the cooling curves (figure left [also see *Seeley et al.*, 1999]). The system is fully automated so that we can measure hundreds of freezing events on a single IN in the same drop. The freezing event can be observed and recorded using a microscope equipped with a digital camera unit.

Results and Conclusions

IN Surface Area and Composition

Freezing temperature is plotted against IN surface area (as determined by SEM stereoscopy) in A (Cerro Hudson IN) and B (Kilauea IN), with distinction between both volume-based and surface freezing modes. The data do not illustrate a clear trend. However, the Hudson data may be suggestive of a slight positive correlation between freezing temperature and IN surface area. Overall, the range of freezing temperatures for the more mafic Kilauea ash was about 2 K higher than the Hudson ash. However, it is not possible to ascertain if composition (versus for example morphology) is the causal parameter; more experiments are required.



Freezing Modes

Plot to right shows freezing temperatures for a single IN in both the air and oil apparatus (A); heterogeneous freezing temperatures were higher than a pure water control. At least 2 different freezing modes can be distinguished depending on if the particle is nucleating ice at the drop surface, or inside the drop volume. Compared to the volume-based freezing rate, the surface-based nucleation rate is consistently higher which results in a higher freezing temperature; the difference between these two modes is typically ~4 K.

The cumulative distribution function (CDF) of freezing temperatures for the same particle is plotted in (D). The shape reflects the distribution of freezing events expected as a function of time, and the gradient of the curve indicates how much the data deviates from the mode. The general form of the CDF for both heterogeneous freezing modes in air is similar, suggesting the mechanism in each is not fundamentally different. There is also remarkable similarity between experiments carried out in air, and those in oil.

Drop Volume

Plot (E) shows freezing temperature as a function of drop volume. Experiments investigating surface-based and volume-based nucleation are plotted separately. There appears to be no relationship between drop volume and freezing temperatures. Therefore, heterogeneous drop freezing temperature is independent of drop volume.

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