Immersion freezing of supercooled water drops containing glassy volcanic ash particles

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ARTICLE INFO

ABSTRACT

The freezing temperatures of hundreds of water drops with radii 20–50 μm containing known average concentrations of suspended, mostly micron- to submicron-sized, volcanic ash particles composed of SiO_2-rich glass were recorded using optical microscopy. As expected, the ash suppresses supercooling, and in contrast to earlier studies of much larger ash particles, the median freezing temperature clearly scales with the available ash surface area per drop. The heterogeneous nucleation rate coefficient per unit mass of ash (j_m) increases exponentially with decreasing temperature (T) (increasing supercooling) with a possible change in the slope of a plot of $\log j_m$ against T at $T = 245 \pm 1$ K. Although uncertainties in the ash surface area limit quantitative comparisons, we conclude that volcanic glass is a less effective ice-nucleating agent than feldspar crystals and more similar to other minerals previously studied.
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1. Introduction

Water droplets in clouds readily supercool to temperatures below 273 K and can reach temperatures as low as 235 K before ice crystals form [1]. Ice crystals affect the formation of clouds, their lifetime, radiative properties and precipitation [2]; consequently ice crystal formation has been studied both in the field and under controlled conditions in laboratory experiments for many years [3,4]. Recent reviews may be found in [2,5], and there has been considerable work since these appeared. The formation of ice crystals at temperatures significantly higher than 235 K can be initiated by particles in the atmosphere that act as ice nuclei. Since the 2010 eruption of the Icelandic volcano, Eyjafjallajökull, there has been renewed interest in volcanic ash and the role of these particles as ice nuclei [6,7]. Ice nucleation on volcanic ash affects radiative properties as well as ash aggregation and sedimentation e.g. [8,9], and consequently is important for understanding how volcanic eruptions affect climate and for predicting and detecting the location and concentration of ash clouds during eruptions.

Laboratory studies can provide important insight into the abilities of different particulates to reduce supercooling. Particular attention has been paid to ice nucleation in the immersion mode, whereby a solid material immersed in a drop of supercooled water induces ice formation by heterogeneous nucleation. Atkinson et al. [10] recently compared the freezing temperatures of droplets of diameter ∼10 μm containing suspensions of micron-sized mineral particles by optical microscopy, and showed that feldspars were significantly more effective at ice nucleation than the other minerals studied. Further recent work supports this conclusion [11–13]. Other workers have studied volcanic ash, either using optical microscopy (typically with much larger ash particles) [9,14] or cloud chambers [6,7]. Typically only the bulk chemical composition of the ash is reported in ice nucleation studies although volcanic ash may contain a variety of minerals as well as silicate glass fragments.

Here we use optical microscopy to study immersion mode ice nucleation by a sample of glassy volcanic ash from the Minoan eruption of Santorini, Greece. Since the individual ash particles are too small for us to image optically, we cannot discriminate between freezing where the ash particles are immersed in the bulk of the fluid (volume immersion freezing) and freezing where the ash particles accumulate preferentially at the drop surface (surface-initiated freezing, as investigated by Fornea et al. [14]).

Heterogeneous nucleation on solid particulate matter is expected to scale with the available surface area, assuming a fixed distribution of active sites [1]. Since determining the effective surface area of a dust or ash sample involves additional experimental uncertainties, we characterise the ice-nucleating behaviour of our ash sample in terms of the solid mass per drop. In general, the solid

mass per drop is not proportional to the effective surface area, because (for constant density) mass is proportional to volume rather than surface area. However, if the particles under test are sufficiently uniform, the effective surface area per drop will be proportional to the number of particles and therefore to the solid mass. We show experimentally that the particles comprising our sample are sufficiently uniform for the median freezing temperature T_m for an array of drops to be function of the mean mass m of ash per drop. We therefore determine the temperature (T)-dependent heterogeneous nucleation rate coefficient per unit mass (j_m) rather than per unit surface area. We demonstrate that the result does not change significantly when ash suspensions with different concentrations are used. We further show that the slope of a plot of $\log j_m$ against T provides a useful means of comparing ice-nucleating agents (materials that facilitate heterogeneous nucleation of ice) even when their specific surface area is uncertain.

2. Materials and methods

The ash studied was from a fine ash bed in the phreatomagmatic Phase 2 deposit of the Minoan eruption of Santorini, Greece [15]. It was collected on the caldera side of the Akrotiri Peninsula, east of the town of Akrotiri, about 7 km south of the eruption vent. Only the portion passing through a 22 μm sieve was used. An uncoated subsample was imaged by scanning electron microscopy (SEM) using an environmental SEM. Prior to imaging, the ash was suspended in ultrapure water, and a drop pipetted onto the SEM stub.

SEM images such as Fig. 1 show ash particles with sizes ranging from 0.5 to 12 μm, with the most common appearing to have a radius of about 1 μm. However, grain size analyses carried out using a Mastersizer 2000 laser diffraction particle size analyser, assuming a particle refractive index of 1.52 and particle absorption index of 0.1, suggest that 85% of the particles within the solution were smaller than 1 μm. The light patches upon larger ash particles in SEM images (clearly seen on the large particle in Fig. 1a) are smaller ash particles apparently adhered to them. The particles are fragments of rhyolite glass, which based on glass analyses of other samples from the same eruption, are 73 wt% SiO_2, 14 wt% Al_2O_3, 5 wt% Na_2O, 3 wt% K_2O, 2 wt% FeO and 1.5 wt% CaO [15]. If there are crystals present in our sample then they are in trace quantities. The erupted magma did contain about 10 vol% crystals but these are not represented in the sample used in our experiments, which is of a finer grain size than the crystals.

Suspensions containing different weight concentrations of ash were produced and thoroughly mixed. An array of drops of radius in the range of some 10 μm was sprayed using a liquid atomizer (sold as a travel spray) onto a borosilicate glass cover slip, which had been coated with Dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride (DMOAP) to make it hydrophobic (the measured contact angle was $104 \pm 5°$). A drop of silicone oil was placed over the water drops with a pipette in order to prevent evaporation. The sample was then positioned on a Linkam THMS600 cold stage with a silver heating/cooling-block (see Supporting information). The cold stage was supplied with a controlled flow of nitrogen from a 25 L dewar. The sample was imaged using a Brunel IMX Zoom Stereomicroscope with LED variable lighting and a coarse and fine focus stand. The microscope has $40\times$ zoom and was fitted with a 1.3 MP digital camera.

Freezing was observed in the range 235–252 K. A cooling rate of $1\,K\,min^{-1}$ was used, pausing and keeping the temperature constant for one minute after each 1 K decrease. During each one-minute hold, a digital image of the sample was captured and the drop freezing temperatures were determined from the set of images (see Supporting information). Only drops with a radius in the 20–50 μm range were considered and they were analysed in bin sizes of 5 μm, with at least 10 drops in each bin and an average of 28 per bin. When drops freeze inwards following nucleation, pressure builds up as the water trapped inside the outer shell expands on freezing. This can cause the ice shell to crack and eject a spike of ice [16]. Any drops that were in contact with a spike were ignored, as the spike could have caused them to freeze by contact freezing.

3. Results

Fig. 2 shows the fraction of drops that freeze as a function of T in a given experiment. At each ash concentration, the data form a sigmoidal curve, as observed previously for a range of different mineral dusts [10,11,17]. The figure clearly shows that the ash suspensions freeze over a far greater range of temperatures than the ultrapure water. This large temperature range suggests that the ash particles incorporate sites with a considerable range of ice-nucleating abilities. Note that for the ultrapure water sample, the drops froze within a very small temperature range, close to the expected homogeneous freezing level, with less than 4% of the drops freezing at temperatures above 237 K.

Fig. 3a shows how the freezing behaviour, characterised by the median freezing temperature T_m, depends on the drop size as well as the concentration of ash in the sample. The freezing temperature for ultrapure water is independent of the drop size. Clearly, the presence of ash increases T_m, and therefore suppresses supercooling. This is consistent with the ash presenting sites at which heterogeneous ice nucleation is favoured. Within error, a drop of radius 20–25 μm from the suspension with the lowest ash concentration (0.024 wt%) has the same T_m as ultrapure water. This suggests that the probability of finding an ash particle within a typical drop of this size is very small.
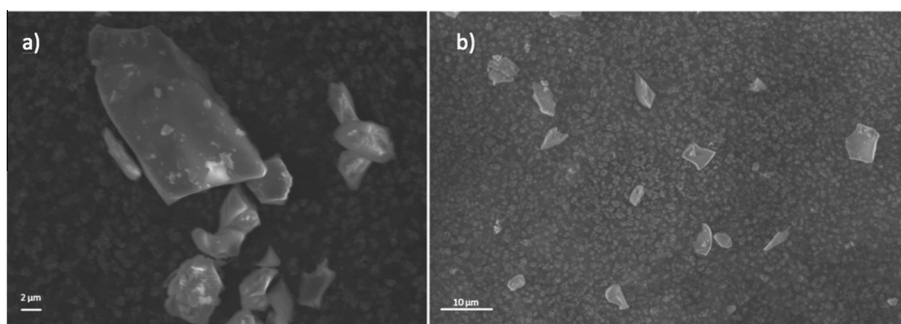

Fig. 1. Scanning electron microscopy images from the uncoated ash sample collected with a beam current of 0.6 nA and an accelerating voltage of 10 kV (a) or 7 kV (b).