

Response to Zamin A. Kanji

The referee's comments are bolded and italicized while our comments are in plain text

***This manuscript discusses the deposition and immersion mode ice nucleation behavior of three volcanic ash samples as well as Kaolinite (KGa-1b) and Na/Ca Feldspar as references. The data presented is of timely interest to the readers of ACP, in particular the ice nucleation community. The methods used are sound and have been validated before in previous publications. The major conclusion is that not all volcanic ash samples have the same ice nucleation activity in immersion mode. In addition, Na/Ca Feldspar content was not found to be a good predictor of ice nucleation efficiency, rather it is proposed that the Silica (quartz) content would better explain the ice nucleation ranking behaviour of the ash samples in immersion freezing. The paper is written well and limitations are also discussed. I have suggested a few minor revisions, additions and have a few questions, all indicated directly in the manuscript. I recommend the paper to be published after the minor comments are addressed.***

The author's would first like to thank Dr. Kanji for his insightful comments that have improved the clarity of this manuscript

***Specific Comments:***

***Page 1387, line 21: You could consider using INP, this is not necessary but something to consider in case you have not***

While this is a valid suggestion that is prevalent in the ice nucleation literature, the authors prefer to use ice nuclei (IN) to ice-nucleating particles (INP) in order to differentiate between heterogeneous ice nuclei and particles that freeze homogeneously, as well as avoid confusion with the also-common "ice nucleation protein."

***Page 1388, line 18: What type of classification, mineralogy or emission mass, content?***

The authors agree that the phrase "similar classifications" is vague and perhaps inappropriate to use when comparing only two samples. Thus the text has been changed on Page 1388, line 18 to read "these results represent only two volcanoes."

***Page 1388, line 23: Maybe some more information on what this means, for the readership of the paper. It may be obvious to geologists/volcanologists but maybe not to cloud microphysicists and atmospheric scientist.***

The authors agree that this terminology may be unfamiliar to cloud microphysicists and atmospheric scientist who are the target audience for this paper. Thus, Page 1388, line 23 has now been changed to read "which are basaltic (45-52% SiO<sub>2</sub>), andesitic (56-59% SiO<sub>2</sub>), and rhyolitic ashes (63-75% SiO<sub>2</sub>) (Heiken, 1972), respectively."

***Page 1389, line 1: Would be nice to specify the type of Ka here. We know different batches have different IN activity in particular the samples from CMS are different from Fluka.***

Given this papers focus on linking mineralogy to ice nucleation efficiency, the authors agree that the type of kaolinite should be specified here. Thus, Page 1389, line 1 now reads “kaolinite (KGa-1b, Sihvonen et al, 2014).”

***Page 1389, lines 15-21: When was the sample conducted relative to the eruption? Date of samping?***

The authors agree that both the location and sampling date provide important insights into the results of the study. Thus, the paragraph start on page 1389, line 11 now reads:

“Volcanic ash was collected from three separate volcanic eruptions that produced three distinct types of ash. Volcan Fuego (14.4828° N, 90.8828° W) is an active stratovolcano that lies 16 km north of Antigua, Guatemala. The sub-Plinian eruption of October 14, 1974 produced ash fall that impacted an area of ~400 km<sup>2</sup>, and samples used here were collected by previous researchers immediately after eruption from a location 10 km from the vent. The Soufrière Hills volcano (16.7167° N, 62.1833° W) is an active stratovolcano located in Montserrat, an island in the Lesser Antilles island arc of the West Indies. The ongoing eruption, which began in 1995, produces cyclic dome-building and explosive activity, with samples used here resulting from an explosion in January of 2010; samples were collected immediately after deposition < 3 km from the vent. Finally, the Taupo caldera (38.8056° S, 175.9008° E) sits in the center of the North Island of New Zealand. Samples used here were collected from air fall deposits of the Oruanui ultra-Plinian eruption ~26 ka. The samples were excavated 39 km from the vent 25.4 ka after the eruption.”

***Page 1392, line 10: Were there conditions at which ice formed on the fused-silica disc? If so, what were the temp and RH conditions when you observed this? And could this have occurred else where on the stage not under the field of view of the microscope***

The authors agree that ice formation on the substrate could provide a significant artifact in the experiment and reporting the conditions at which this occurs is important. These results have been previously reported in Baustian et al., 2010. Thus the following line was added to Page 1392, line 10:

“We have previously reported the conditions under which a blank fused-silica disc initiates ice formation (Baustian et al., 2010). In that study, we found that the blank substrate nucleated ice at  $S_{ice}$  of 1.6 to 2.33 from ~235 to 215 K.”

***Page 1393, line 26: Can you distinguish if the ice formed before the contact or the contact occurred before the ice nucleation? See comment at Figure 3.***

The authors agree that care should be taken our immersion freezing analysis not to include contact freezing events. Such precautions were taken, and the text starting on Page 1393, line 26 has now been revised to read:

“Further, by recording 30 frame-per-second video, we could unambiguously determine if droplets coagulated or froze by contact freezing. In all experiments, no contact-freezing events occurred from the contact of two liquid drops. If two droplets coagulated, their coagulated droplet size was

considered. Unfrozen droplets, however, could be frozen by contact with growing ice particles; those contact-frozen droplets were disregarded in our analysis.”

***Page 1394, line 21: What are the silica contents different in Table 1 and 2?***

The authors acknowledge that the difference between silica content and quartz content was not sufficiently explained in the discussion paper. The silica content of the ash is determined from elemental analyses, most commonly as X-ray fluorescence, and will include Si contributions from the melt glass, minerals, and lithic materials in the ash. Quartz is a pure, crystalline form of SiO<sub>2</sub>, and its content is determined from X-ray diffraction. To clarify this in the text, we have added the following sentences to Page 1390, line 1:

“It is important to note that silica content of the ash is determined from elemental analyses, most commonly as X-ray fluorescence, and will include Si contributions from the melt glass, minerals, and lithic materials in the ash; this is not to be confused with quartz, which can be one mineral component of the ash composed is pure, crystalline SiO<sub>2</sub>.”

***Page 1398, line 5: Why not calculate nucleation rates if you really would like to take time dependence into account? And compare nucleation rates to one another?***

While the authors agree that calculating nucleation rates and comparing those nucleation rates to previous studies would indeed be taking time dependence into account, the focus of this exercise was to validate our immersion freezing setups with a material and framework (i.e., the singular approximation) used by both continuous flow and cold stage instruments. Finally, while an in-depth discussion of the time-dependence of heterogeneous ice nucleation would be an interesting area to explore, to fully analyze it is beyond the capabilities of this data set.

***Page 1411: Why is the silica content here different from that in Table 1?***

See comments above about silica content.

***Page 1412: There is an appearance of a small peak in the ground and nebulized sample. What is this attributed to and shouldn't it be addressed.***

The authors agree that there is a small peak near 663 cm<sup>-1</sup> that is present in the ground and the ground/nebulized samples, but not present in the unground samples. Since volcanic ash is a complex mixture of volcanic glass, minerals, and possibly lithic material, peak identification is outside of the scope of this manuscript. We do, however, postulate that this peak emerges due to better homogeneity of the ground samples. To highlight this, another vertical dashed line has been added to Figure 1 and the following passages have been altered in the manuscript to read:

Page 1391, line 20: “An example set of these spectra for Soufrière Hills ash is shown in Fig. 1. It can be seen that the main ash signatures at 507 cm<sup>-1</sup>, 408 cm<sup>-1</sup>, and 281 cm<sup>-1</sup> in the Raman spectra are not significantly altered between the unground, ground, and aggregated particles, indicating that any major chemical alteration due to ash processing was not detected for these samples. A small peak at 663 cm<sup>-1</sup>, however, does appear in the ground and ground/nebulized and dried ash; we attribute this peak this better homogeneity of minor components within the ground samples as compared to the unground samples.”

Page 1412: “A set of example Raman spectra of unground, ground, and ground/nebulized Soufrière Hills volcanic ash. As shown, the main peaks at  $507\text{ cm}^{-1}$ ,  $408\text{ cm}^{-1}$ , and  $281\text{ cm}^{-1}$  (vertical dashed lines) are minimally affected by mechanical grinding and wet generation, suggesting that bulk chemical alteration does not occur. A small peak at  $663\text{ cm}^{-1}$ , however, does appear in the ground samples, possibly due to better homogeneity of minor components when compared to unground samples.”

***Page 1414: Is it possible to provide a more magnified version of this figure, where the lack of structure and appearance of a structure in the frozen droplets is more evident. It is not super clear in these figures. Although if one observed closely, the bottom figure does have a few crystals with protrusions that would imply ice formation.***

Unfortunately, video recordings of the experiments were taken at 20x magnification in order to view a statistically significant number of particles within the image frame. Magnifying the images would not increase the level of detail within the image.

***Page 1414: If the droplets continue to coagulate even after you have stopped depositing the particles on the stage and during the cooling process, this needs to be made clear. It is also evident from the images that in the liquid phase there are more droplets than in the image where ice is present. So is this only due to the bergeron-findeisen process or could it be from contact nucleation with the small droplets diffusing to the large ones as pointed out in the image.***

See comments above about droplet coagulation and contact freezing.

***Page 1415: Kelvin here, but degrees C in the next plot, then you switch back to Kelvin. Why? Can you just chose one and stick to it?***

The authors agree that switching between the two temperature scales is confusing; however to better compare figures to previous work in the literature, we have kept all frozen fraction curves in the Celsius scale and all  $n_s$  and  $S_{ice}$  plots in the Kelvin scale.

***Page 1419: Are these data points that cover homogeneous nucleation, if so, you may consider removing them from this plot. To me it looks like these drops based on plots from Figure 7, froze homogeneously, then I think that there is no need to plot them on an  $n_s$  curve, since the surface area should not matter for their freezing. This is also implicit by the steep slope. You may want to comment about the lack of temperature dependence or the different temperature dependence here for these data point.***

The authors agree that the points below  $\sim 238\text{ K}$  may be due to homogeneous freezing as indicated by their steep slope in Figure 8 and their coincidence with the homogeneous freezing curve in Figure 7. Thus, the temperature range on Figure 8 has been altered to truncate at  $238\text{ K}$ .

### ***Minor Changes***

The word “for” has been added to Page 1387, line 4.

“Further” has been changed to “furthermore” on Page 1387, line 11.

The word “ice” has been deleted Page 1387, line 13.

The reference Hoyle et al., 2011 ACP has been added to Page 1388, line 4.

The phrase “in modifying the composition of the aerosolized ash” has been added to Page 1389, line 24.

The phrase “droplet size” has been added to Page 1393, line 22, so that it now reads “and 65-165  $\mu\text{m}$  (droplets size, lateral diameter).”

The last sentence on Page 1393 has been changed for clarity. It now reads “The temperature error of 0.5 K for all droplets was determined by repeated homogeneous freezing experiments of ultra-pure water.”

The phrase “in the temperature range investigated” has been added to Page 1395, line 9.

The “Hiranuma et al., 2014a” reference on Page 1398, line 14 has been changed to “Hiranuma et al., 2015.” This has also been changed in the reference section.