

Response to Anonymous Referee #3

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

The present work extends the knowledge on depositional and immersion mode freezing of ice on volcanic ash samples. Three selected ash samples have been chosen to study IN formation by Raman micro-spectroscopy. These samples cover the range of basaltic, andesitic and rhyolitic ash. While all three samples exhibit a similar behavior during depositional freezing, the authors claim varying behaviour during immersion mode freezing, which might be related to differences in the mineralogy of crystalline material. In contrast to previous studies, their results indicate, that a 'simple' parameterization of the immersion mode freezing for volcanic ashes is not legal. After a brief and straightforward introduction, a detailed experimental section is following. The results of their study are presented according to IN properties in the depositional and immersion mode. The paper concludes with a discussion on atmospheric implications. The paper is well written and could be interesting to the readership of Atmospheric Chemistry and Physics. However, the paper lacks of experimental details and interpretation of data obtained from Raman spectroscopy. Further, the significance of the results has to be discussed related to the limited dataset. Therefore, publication in ACP can only be considered after addressing the following major remarks in detail.

The author's would first like to thank anonymous referee #3 for his/her insightful comments that have improved the clarity of this manuscript

Major issues:

**) The title of the paper includes ". . . using Raman spectroscopy" – however, only Raman spectra related to depositional freezing are shown in figure 1. The authors claim, that their study is the first immersion mode freezing study, therefore it is absolutely important to discuss and display details of Raman spectra obtained during the immersion mode experiments in detail. Even experimental details have to be discussed like influence of laser power on heating of the droplets and disturbing the measurements and results. Further, for confocal Raman microscopy, height of the z-resolution must be discussed related to the sample size and height. How reliable are results from a single spot measurement of 20 to 70 μm droplets (see fig. 3)? A discussion about the legitimacy of Raman micro-spectroscopy for immersion mode measurements is absolutely necessary. For a reader, the experimental work appears in that way, that only the optical part of the microscope was used for obtaining the dataset, but not the Raman spectrometer.*

The authors thank the referee for making the valid point that we do not show any Raman spectra for the immersion freezing experiments. Unfortunately, this is because Raman spectroscopy was not utilized during immersion freezing experiments. This was largely because Raman spectra of water droplets containing volcanic ash or minerals were dominated by the -OH stretch due to liquid water. The authors agree that including the phrase "using Raman Spectroscopy" in the title may be misleading. Thus, the authors have removed the phrase "using Raman Spectroscopy" from the title.

****) The authors claim that up to now only two datasets have been used to suggest one characteristic ice nucleation efficiency. They extended the dataset from two to five ash samples. There is no statistical confidence within this interpretation. How can the authors reliably conclude that immersion mode freezing is dependent on the composition of the ash by this limited dataset?***

The authors agree that the immersion freezing of volcanic ash may not be entirely dependent on the composition of the ash. Thus, the following sentence has been added Page 1401, line 8:

“It is important to note that the above discussion interprets immersion freezing only from a chemical mechanism standpoint.”

****) How was sampling of the volcanic ashes done? Were the samples collected from the nearby ash fall around the volcanos? How long were the ashes exposed to environmental conditions after the eruptions of the related volcanos? Are particles which settle close to the volcano comparable with fly-ash which is able to cover a distance of several hundreds of kilometres? Is there a general independence of the chemical composition, environmental aging from the size and the difference in exposure (atmosphere, soil, . . .)?***

The authors agree that the volcanic ash sampling details were not sufficiently detailed. 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 km², 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.”

The authors also acknowledge that there may not be a general independence of chemical composition and due to distances from the vent or environmental aging; unfortunately, such questions probe complex chemical mechanisms that are beyond the scope of this work. To highlight this we have added the following sentence to Page 1390, line 7:

“Chemical differences due to collection distances from the vent or environmental aging were not explicitly taken into account in this study.”

General minor issues:

****) Raman spectra in figure 1 (and others): These Raman spectra are displayed like they were measured in the anti-Stokes mode. Are these anti-Stokes spectra or are the spectra displayed in***

an unusual way for Stokes-Raman spectra. Further, assignment of the Raman excitations would improve the quality of the figure and assist a detailed understanding of the work.

While the authors agree that the Raman spectra are displayed as if they were measured in the anti-Stokes mode, we have traditionally presented the Raman spectra from our Raman microscope in this orientation. This decision was made to accommodate readers in the fields of atmospheric chemistry and physics who, the authors assume, are generally more familiar with infrared spectroscopy. To clarify this, we have altered Page 1391, line 5 to now read “Stokes-mode Raman spectra.”

****) Sampling: Indication of the geo-coordinates of the volcanos and the sampling site as well as the distance from the sampling site to the craters would be helpful.***

See comments above about sampling.