Review

Characterization of individual ice nuclei by the single droplet freezing method: a case study in the Asian dust outflow region

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This study investigates the ice nucleation characteristics of two samples of Asian dust collected from the west coast of Japan. Particles with diameters > 1.1 µm were deposited on a hydrophobic Si waver using an impactor. The ice nucleation ability of the collected particles was investigated in immersion freezing mode in a closed cell mounted onto a cold stage of an optical microscope. The ice nucleating particles (INPs) together with a number of inactive particles were characterized first with AFM and micro-Raman spectroscopy followed by SEM-EDX. For comparison several reference samples were investigated with the same methods. This study presents a new approach to characterize atmospheric INPs on an individual particle basis. It is a welcome complement to other combinations of methods used to characterize atmospheric INPs on a single particle basis. It shows once more how complex the composition of aged aerosol particles in the coarse mode is, rendering a clear classification of particles difficult. Nevertheless, the authors succeeded to identify physical and chemical characteristics that increase or decrease the ice nucleation ability of the particles. I recommend this paper for publication in ACP after revisions. Specifically, the experimental procedure needs to be explained in more detail. For the validation of the method, the reference samples need to be analyzed more quantitatively and compared more thoroughly with available literature. Moreover, more references need to be added to the introduction and the formulation of some sentences needs to be improved (see specific comments below).

Specific comments

Page 1, line 19: what is meant by “slower”? At lower temperature?

Page 2, line 9: reference to Murray et al. (2012) only is somewhat arbitrary. Add more references or “e.g.” in front of the reference to the Murray et al.review..

Page 2, line 21 – 22: This sentence needs to be reformulated.

Page 2, line 23: “sea salt and sulfates are often not considered as efficient ice nuclei.”: This is not generally true for sulfates. Ammonium sulfate is found to be ice nucleating at lower temperatures as is also stated later in the manuscript by referring to e.g. Abbatt et al. (2006). The sentence here needs to be corrected, e.g. by adding “under mixed phase conditions”.

Page 2, lines 30 – 31: This sentence needs to be improved.

Page 3, lines 1 – 3: this statement should be supported by more recent references.

Page 3, lines 3 – 5: this statement should be supported by a reference.

Page 3, line 12: which “above mentioned artifacts” are meant here? Please, be more explicit.

Page 3, line 20: more than just one reference should be given here to support this statement.

Page 3, lines 21 - 22: again, more than one reference should be given to support this statement.

Page 4, lines 25 – 28: Was the dew point kept constant at -6 to -3°C during cooling? Also, the degree of dilution of the particle should be estimated based on the size of the developing droplet. This is important to judge whether a freezing point depression as discussed later on in the manuscript is relevant at all.

Page 5, lines 26 – 27: This sentence needs to be improved.

Page 7, lines 11 – 16: Here, the freezing onset temperatures of the reference samples are compared with literature (Atkinson et al., 2013) and it is concluded that they are consistent. However, this comparison does not take the surface area present in the samples into account. The comparison needs to be based on the surface area present in the investigated reference sample of this study multiplied with published ice nucleating active sites (INAS) surface densities e.g. from Peckhaus et al. (2016) or Harrison et al. (2016) for feldspars. Moreover, It should be specified what frozen fraction was taken as the onset condition.

Page 7, line 18: The ATD and ADS samples should be discussed in more detail. How many particles were analyzed? Comparison of freezing temperatures with relevant literature is needed.

Page 7, line 19 – 21: the measurement procedure needs to be explained better. Was the same sample cooled repeatedly to investigate the ice nucleation activity of the 10,188 and 24,145 particles? If yes, what were the heating/drying conditions between the cooling cycles to remove the ice crystals?

Page 7, lines 22 – 23: Ice nucleation active fractions should also be given for the reference samples.

Page 7, line 24: specify “onset temperature” in terms of a frozen fraction.

Pages 9 – 10, Section 3.4: The elements C, N, O and Si could not be identified by SEM-EDX. The influence of this restriction should be discussed more explicitly. It should be analyzed whether based on the Raman spectra, some particles might be dominated by organics. In general, it might be helpful to combine the results of the Raman spectra and the SEM-EDX analysis already in the results section and not only in the discussion section. Also, do the compositions derived from the two techniques support each other or are they in some cases contradictory? At the end of this section, it is stated that the Raman peaks are “not necessarily representative of a major component of the particle”. This is certainly true for large samples. However, in case of particles with diameters < 5 µm, the laser spot penetrates the whole sample. This is supported by the presence of Raman peaks from the substrate present in the spectra. Moreover, in the method section, it is stated that Raman spectra were taken “each 750 nm step”. This should lead to a full coverage of the particles in the x- and y-directions.

Page 10 – 12, Section 4.1: This section needs to be improved. The assignment of clay minerals is solely based on a fluorescence signal in the Raman spectra. However, fluorescence is also often taken as an indication for the presence of biological aerosol particles (e.g. Twohy et al., 2016). How can a biological origin of the fluorescence signal be excluded?

Page 11. lines 5 – 6: An Al-K-(Ca+Na) ternary plot is not a typical way to discriminate K-feldspars from Na/Ca-feldspars. For this purpose a K-Na-Ca plot is usually used.

Page 11, lines 6 – 7: Why should clay minerals and mica appear in the middle of an Al-K-(Ca+Na) ternary plot? The clay mineral kaolinite contains only Al but no K nor Ca/Na. It should appear therefore at the Al corner. The clay mineral illite contains Al and K but no Ca/Na. It should therefore appear on the Al-K line. The same with the common mica muscovite: it contains Al and K but no Ca/Na.

Page 11, line 8: How was the presence of mica inferred?

Page 11, lines 17 – 19: Only one study is cited although the sentence starts with "Previous studies". Either give reference to at least one more study or change to "A previous study".

Page 11, line 23: improve formulation, e.g. reformulate: “most IN particles active above -30°C.”

Page 11, lines 23 – 26: The discussion of the origin of the fluorescence signal needs to be improved.

Page 12, lines 7 – 8: It should be stated here, that this number has a low bias because contributions from organics are missed in SEM-EDX. An estimate of the contributions of organics based on the Raman spectra might be added.

Page 12,. line 23: “at any event” seems a too strong conclusion considering that aged sea salt particles + inclusions were also found as a small fraction in the IN active particle fraction.

Page 13, line 30 – 31: “Therefore, the liquefied $Ca(NO_3)_2$ coating is expected to show strong molar depression of freezing point, which could explain their weak IN ability”. This argumentation is only valid in the case of concentrated solutions. Its validity in the present case depends on the degree of dilution of the soluble material in the droplet. The dilution should be estimated to test the validity of this argumentation.

Page 14. Line 31: Can the OH peaks be associated with either alcohol or carboxy functionalities?

Page 15, lines 25 – 26: improve this sentence. You might split it: “…mainland Japan. Further upstream…”

Page 16, line 2: why exactly 3.27±1.80 particles/cm^3? Please explain.

Page 16, line 8: how far away is NOTOGRO from the sampling location?

Page 16, lines 20 – 27: this paragraph reads like a conclusion and might be deleted here and merged with the conclusion section.

Page 17, line 5: the text in the bracket needs to be formulated better. Is it meant that mineral components such as clay minerals have defects in their crystal structure and contain impurities?

Page 28, Fig. 3 and page, 35, Fig. 10: the line along which the transect of the particle was scanned should be indicated. The length bar of 0.5 µm given on top of the AFM images does not seem to correspond with the length axis given at the bottom in some images. Please check.

Page 30, Fig. 5: what sulfates are meant here if not ammonium sulfate or calcium sulfate?

Technical comments:

Page 3, line 9: “residues” instead of “residue”.

Page 8, line 31: Sobanska et al. (2012) is missing from the reference list.

Page 14, line 4: “nucleus” instead of “nuclei”

Page 26: figure caption: “supersaturation” instead of “super saturation”.

Page 27, Figure 2: the axis numbers are too small to be readable.

Page 28, Fig. 3 and page, 35, Fig. 10: The label “BCC” in the Raman spectra should read “BBC”.

References:

Harrison, A. D., Whale, T. F., Carpenter, M. A., Holden, M. A., Neve, L., O’Sullivan, D., Vergara Temprado, J., and Murray, B. J.: Not all feldspars are equal: a survey of ice nucleating properties across the feldspar group of minerals, Atmos. Chem. Phys., 16, 10927–10940, doi:10.5194/acp-16-10927-2016, 2016.

Peckhaus, A., Kiselev, A., Hiron, T., Ebert, M., and Leisner, T.: A comparative study of K-rich and Na/Ca-rich feldspar ice-nucleating particles in a nanoliter droplet freezing assay, Atmos. Chem. Phys., 16, 11477–11496, doi:10.5194/acp-16-11477-2016, 2016.

Twohy, C. H., McMeeking, G. R., DeMott, P. J., McCluskey, C. S., Hill, T. C. J., Burrows, S. M., Kulkarni, G. R., Tanarhte, M., Kafle, D. N., and Toohey, D. W.: Abundance of fluorescent biological aerosol particles at temperatures conducive to the formation of mixed-phase and cirrus clouds, Atmos. Chem. Phys., 16, 8205–8225, doi:10.5194/acp-16-8205-2016, 2016.