

## ***Interactive comment on “Refreeze experiments of water droplets containing different types of ice nuclei interpreted by classical nucleation theory” by Lukas Kaufmann et al.***

**Anonymous Referee #1**

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The paper by Kaufmann et al. deals with heterogeneous ice nucleation in the immersion freezing mode, which is an important parameter for climate issues. A systematic investigation has been presented focusing on the question whether an ice nucleus triggers a stochastic or a deterministic nucleation process. This question is not new but can be considered as still unresolved. The authors have chosen four well-known ice nuclei, i.e. two mineral dust samples (from Hoggar Mountains and Arizona Test Dust), a plant extract (birch pollen washing water) and a long-chain alcohol (nonadecanol). They use two fitting parameters to receive a parametrization, the contact angle  $\theta$ , which is the interfacial energy and the dimensionless pre-factor  $\delta$ , which is the deviation of the nucleation rate. Furthermore, they calculate the sizes of the nucleation

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sites and the Spearman's rank correlation coefficient. The latter is determined from repeated freezing cycles and is used to discriminate between temperature and time dependence of heterogeneous ice nucleation, where temperature dependence counts for deterministic and time dependence for stochastic nucleation.

The paper is well-written and meets all criteria for a publication in ACP. However, there are a couple of revisions which should be carried out before publication:

Major Comments:

The concept of ice nucleation relies on the formation of stable hydrogen bonds and the formation of ice like structures which finally grow into a stable particle. In homogeneous ice nucleation only fluctuations and random structures impact this process and make it volume dependent. In heterogeneous ice nucleation the situation is more complicated since a substrate is catalyzing the phase transition. This substrate can be a macromolecule as well as a solid interface. The crucial point is that the rapid fluctuation of hydrogen bonds (life time 10ps) has to be stopped by interacting with the substrate. Up to now, nobody has ever observed morphology, structure and chemistry of an active nucleation site. All proof is of indirect nature. The authors should more carefully underline this fact at the beginning of the paper.

In general, I think that the samples are well-chosen, since they represent typical aerosol characteristics. However, the authors should compare only both dusts and both organic samples with each other – this demands a reorganization of some parts of the paper. From my point of view, it is highly questionable if a solid mineral surface and the surface of an organic and in water suspendable substance can exhibit comparable properties. The reason is that minerals offer steps, cracks and cavities at their surfaces which are active nucleation sites (see Kiselev A. et al (2016)), while the ice nucleation activity of organic macromolecules depends very much on their secondary, tertiary and/or quaternary structure. Folding and/or agglomeration of these rather large macromolecules can be very decisive and can change during repeated freezing cycles.

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One should expect that most nuclei (minerals and organics) exhibit several different nucleation sites. In order to make these sites of different activity visible, one could measure highly diluted samples, which typically show a flattening of the freezing curve with a steplike structure. Each step counts for one kind of nucleation site. Evaluating the median freezing temperature of each step would give an idea of the number and activity of these sites and one could test for changes of these parameters in repeated freezing cycles. This might even be more informative than the overall parameters  $\bar{A}_a$  and  $\bar{A}_c$ . To make it clearer, in how far can the authors assure that assigned singular or stochastic properties are not the product of changes of the particle or the nucleation site itself? This would not only change typical singular freezing characteristics but also the stochastic freezing, which would interfere the whole concept of the here presented evaluation.

#### Specific Comments:

##### Introduction

When introducing the concepts of stochastic and deterministic nucleation, these papers should be quoted: Vali G. & Stansbury E.J. (1966), Bigg E.K. (1953), Vali G. (1971).

##### Evaluation

When introducing the dust samples it should come clearer what the differences between both mineral compositions are. A table would be very helpful listing the different crystalline phases and impurities and giving the respective compositions in percentage. Another important parameter is particle sizes and alterations of these particles. Zolles et al. (2015) have applied milling in order to generate new and fresh nucleation sites. They have also considered aging and blocking of these sites. It would be interesting to know in how far this also applies for the here used samples in repeated freezing cycles.

When introducing birch pollen washing water it should be stated clearly that the molec-

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ular identity of the macromolecules is still unknown. Pummer et al. (2012) have assumed polysaccharides or glycoproteins. Augustin et al. (2013) have already pointed out that birch pollen washing water has at least two distinctive ice nuclei within their broad organic mixture. The group of Koop (Dreischmeier et al. (2014)) has shown in their cryo-DSC studies that there really are two distinctive nuclei and that the ratio between both is changing with concentration. It would be interesting to know if the ratio between both these sites is changing in repeated freezing cycles and if both sites show the same character. When evaluating these results, the authors have worked with the assumption that the washing water consists solely of 300 kDa macromolecules. This has been assumed for modelling reasons only. However, 300 kDa is only the upper limit according to Pummer et al. and nothing is known about the real size distribution. It would be interesting to know how strong variations of the size would impact the results.

##### Minor comments

Often the x-axes of comparing figures are not scaled in the same way and make comparison difficult, e.g. figure 10 and all figures of the Appendix A.

Page 18: Nucleation rates should always be given with the respective temperature in parenthesis.

Page 22: The give number of active molecules should be accompanied by the respective sample volume (e.g. ml-1).

Figure 2: The volume of the sample should be given, since the pure water line is at rather high temperature, which is only understandable in the context of the respective sample volume.

When working with oil-water emulsions in repeating freezing cycles, one should carefully check for the stability of these emulsions. Further information can also be gathered from Hauptmann et al. (2016).

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## References

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