

## ***Interactive comment on “Time dependence of immersion freezing” by A. Welti et al.***

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### **Response to the Comments of Gabor Vali (Referee 1)**

We would like to thank Gabor Vali for his helpful comments and suggestions. We reply to the individual comments below.

**General comment** *This contribution addresses an important question and brings together laboratory measurements and model calculations. It is an excellent idea to observe the time dependence of ice nucleation in a flow device and to do that with particles of known size and composition. There is also considerable previous work with the main instrument and that provides added confidence in the measurements.*

*Since the topic of this paper is subject to active debate in the literature, some*  
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*reflections on it seem to be warranted. The results obtained are quite convincing in showing that neither the stochastic nor the singular description of ice nucleation is consistent with the observed time dependence, and that a combination of the two is needed. This conclusion is the same as that of Vali and Stansbury (1966) and Vali (1994) and is also supported by the results of Marcolli et al. (2007), Niedermeier et al. (2010) and Hartmann et al. (2010), Murray et al. (2011), Broadley et al. (2012) among others. There seems to be little doubt any longer about the need to combine site specific influences (surface properties) with random (stochastic) time-dependent rate processes (kinetics) in order to describe heterogeneous ice nucleation. Views about the relative weights of these two factors are more varied because the two contributions are difficult to separate experimentally. In this paper the authors state that their results cannot resolve “... whether single active sites or the surface structure of the entire IN are responsible for immersion freezing ...”. In the former case, the nucleation rate could be different for each site, whereas in the latter case a single nucleation rate function would suffice to characterize nucleation probability.*

This is true for an individual IN. To represent an ensemble of particles one nucleation rate function would not be enough as also the  $\alpha$ -pdf model which is addressed by "...the surface structure of the entire IN..." attributes an individual nucleation rates coefficient to each single particle. By the statement we intended to stress that it is not conclusive if differences between individual particles or the variation between active sites are responsible for the deviation of the measurement data from the classical stochastic description. This is equivalent to saying: it is not clear how big an active site is i.e. if the whole particle surface acts as an "active site" or only tiny, highly preferable spots on the particle surface. Given our understanding of the ice germ formation, it is likely the latter.

*In Vali (2008) I presented evidence for specific site characteristics to be the primary factor in determining the temperature at which nucleation can be expected but with*

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*random fluctuations adding time-dependent variations. From repeated freezing of large numbers of samples I deduced that the nucleation rate (probability of nucleation per unit time) for given sites rises four orders of magnitude within about 2-3° C. This is still far from a quantitative determination of the nucleation rate as a function of temperature and of site characteristics and at this point has no independent confirmation. The  $\alpha$ -pdf and active site models are formulations of a scenario in which different parts of the (mineral) surface provide for different probability of nucleation. These formulations represent that variation with changes in the contact angle within the framework of classical (thermodynamic-kinetic) nucleation theory. Thus, the variations of nucleation rate with temperature associated with changes in contact angle refer to differences in site characteristics. The nucleation rate in these models is that deduced from CNT which usually yields much steeper variations in magnitude with temperature. No numerical values are provided in this paper for the rate function.*

We did not find such a steep dependence of the nucleation rate from temperature in the experimental data. The best fit using the stochastic model however would be in agreement with a four order of magnitude increase in the nucleation rate within 2-3° C. Figure 1 shows the individual nucleation rates derived for the individual data points together with the apparent nucleation rates from the different models. Nucleation rates of experimental data for 400 and 800 nm kaolinite particles with residence times between 1.1 s and 21.4 s are shown as symbols. As an example, nucleation rates calculated from the models are shown for 1 s and 20 s nucleation time and the range spanned by these two lines is shown against a blue background for 800 nm and red for 400 nm respectively. Nucleation rates for the singular and semi-singular models were calculated indirectly by first deriving the frozen fraction as predicted by the models and using the obtained frozen fraction as input in the stochastic formulation of nucleation rates given by  $J_{\text{het}} = -\frac{\ln(1-FF)}{A \cdot t}$ . The physical meaning of deriving nucleation rates from a singular and the semi-singular models is however debatable. From our point of

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view the concept of nucleation rates only holds for the purely stochastic case. Therefore we did not show nucleation rates in the discussion paper. We will add the figure as a supplement for the interested reader.

*An additional point should be born in mind when comparing different sets of observations of time dependence. The relative importance of surface sites and of kinetic effects can be expected to vary with temperature. As the temperature of homogeneous nucleation is approached, kinetic effects become more dominant.*

This is an important point. We draw this conclusion in Sec. 6.1. line 15 ff. by arguing that with the change of the apparent, median contact angle with temperature. To make the argumentation more comprehensive we added: "The increase in the apparent median contact angle can be interpreted as evidence for an increase in the importance of the nucleation kinetics to ice formation as the temperature of homogeneous freezing is approached. Surface features lowering the contact angle of an ice embryo to the substrate on the other hand become increasingly important towards higher temperatures."

## Specific comments

1. *First and foremost, it is important for proper appreciation of this work that the temperature range of the reported measurements be made more evident to the reader. While that information is stated in the Abstract and in Section 2.2, it is absent from the Discussion and from the Conclusions. The fact that the observations reported in the paper were carried out within ten degrees of the homogeneous freezing temperature of water is important because it means that the results refer to a rather inactive heterogeneous ice nucleating sample compared to others described in the literature and that the range of temperatures covered is much colder than a large part of the troposphere. By not placing any emphasis on the temperatures of observations, the authors imply that the results may have*

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*general validity for all heterogeneous ice nucleation. This assumption is far from obvious. Most significantly for the main argument of the paper, the balance of influence on embryo formation between kinetic factors and the interaction with the nucleus surface shift toward the latter by large factors at lesser supercooling. The authors should be clear about this issue in their paper and appropriately constrain their conclusions.*

The temperature regime of the measurements presented here are now repeated in the discussion as well as in the conclusion section to emphasize the range of validity of the results. However we note that for mineral dust particulates the most active immersion freezing temperature range has been reported to be between 235-245 K e.g. Pinti et al. (2012), Hoose and Möhler (2012) and references therein.

- 2. The experiments here reported go beyond the initial operating mode of the ZINC and of the ice crystal detector IODE, so some questions arise about the performance of the apparatus. Flow conditions in the ZINC instrument were shown by Stetzer et al. 2008 to require delicate tuning. Were those conditions adequately defined and tested for the whole range of flow rates employed? Similarly, is the detection efficiency for ice crystals known to be the same for all the different transit times? Any variation in this efficiency as a function of ice crystal size would transfer directly into the time dependence measured as the principal objective of this paper and alter the results.*

3-dimensional fluid dynamic simulations (Ansis, Fluent) of the whole IMCA/ZINC experimental setup have been conducted to investigate the effect of changing the flow rate. The simulations indicate only minor divergence of the flow field (at 10l/min) due to the operation of the chamber in the range of flows used for this measurements (5-19 l/min). Figure 2 shows the conditions within the experiment derived from such a fluent simulation at 10 l/min where most of the measurements where conducted. Previous measurements by Lüönd et al. (2010) which where

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conducted at 5 l/min flow rate also lend confidence that the ZINC experiment can be used for flows ranging from 5-19 l/min. IODE has been tested to reliably detect particles larger than approx.  $2\ \mu\text{m}$ . The droplets and ice crystals in this experiment were larger than  $5\ \mu\text{m}$ . The different flow conditions and resulting change in residence time of particles in the detection volume is taken into account in the analysis software which uses a wavelet peak detection algorithm.

3. *Page 12629, line 12 states that “... the mineral particles act as CCN ...”. This, and the earlier description of the experimental setup, indicate that each mineral particle is assumed to form a droplet and conversely that each droplet contains one mineral particle. A clearer statement of this assumption would be useful if that is the basis of the analyses. If it is not, there is more to explain. Even more useful would be some proof for what is the empirical fact. Is the number of droplets formed equal the number of particles emerging from the DMA? If only ice particles can be detected, a run at below the homogeneous freezing temperature could provide the information needed. A related issue is the possibility of coagulation of particles in the upstream flow before condensation, either upstream or after the DMA. As is well known, aggregates have a different surface area to mobility relationship than individual particles.*

As can be seen in Figure 2 in the discussion paper the kaolinite particles are exposed to 120% relative humidity with respect to water at 300 K what should lead to reliable CCN activation. Therefore we based the analysis on the assumption that all particles activate as CCN. We state this more clearly in section 2.1. Coagulation of kaolinite particles can not be excluded is however unlikely after the DMA as the size selected particles all have like charges and the used concentrations (300 cc) are not high enough to yield any significant coagulation rates.

4. *The caption to Fig. 2 refers only to the droplet as size as a calculated value. Aren't all the plots derived from model calculations?*

The temperature,  $RH_w$  and residence time as a function of position in the chamber have been derived from a Fluent simulation of the experiment. We now specify this in the figure caption.

5. *The model formulations are given as equations but very few of the numerical values used in the calculations are presented. For each model, one set of values were used for critical parameters (e.g.  $6 \text{ nm}^2$  for active sites) and no evaluations are presented about the sensitivity of the results to these assumed values.*

We did not conduct a sensitivity study. The numerical values used were the same as in Lüönd et al. (2010) and references therein as has been explicitly indicated in section 4.2.3. In addition we also provide a justification for the use of  $6 \text{ nm}^2$  as a critical parameter.

6. *The degree of time dependence on nucleation in the  $\alpha$ -pdf and active site models depends on the rate of rise of  $J$  with decreasing temperature. Thus, it would be very useful for readers to see what that function looks like with the numerical values assumed in this work.*

See Figure 1 in this response.

7. *How were the “fit parameters” in the active site model determined? Marcolli (2007) is cited as a source but the active site there is assumed to be  $10 \text{ nm}^2$ , not  $6 \text{ nm}^2$  as in this work.*

See response to comment 5. The fit parameters in the active site model determine the surface density of active sites with a certain contact angle given by the function reported in Marcolli et al. (2007). The size of active sites changes the number of active sites per particle. The assumption of  $6 \text{ nm}^2$  active sites corresponds to the critical ice embryo size at 239 K (Lüönd et al., 2010).

*What is the resulting numerical value for equation 8? How meaningful is it to extend the curve in Fig. 6 to  $180^\circ$  contact angle?*

The resulting surface density of active sites as a function of contact angle is shown in Fig. 6. We now refer to this figure in the text. The contact angles in the active sites model range up to  $180^\circ$  to take into account all possible efficiencies of active sites.  $180^\circ$  is the most common contact angle i.e. only a fraction of the particle surface contributes to immersion freezing in this model. This is important to account for, for the size dependence of immersion freezing and the variation from particle to particle.

8. *The last step in the active site model (section 4.2.3) refers to an ensemble of particles. If all droplets are identical (same size particle, one particle per drop) what is meant by the summation in equation 10 and what are the numerical values used?*

We randomly attribute active sites of a certain contact angle to each particle. Therefore each particle carries a different set of contact angles. The frozen fraction of an ensemble of droplets containing individually varying particles is then calculated as the sum of the individual freezing probability of each droplet divided by the total number of droplets in an ensemble. We used  $N_{tot} = 1000$  droplets for our model. We now state this more clearly in the text below equation 10.

9. *The calculations for cloud glaciation are presented in a very compressed way. How does the frozen fraction in a cloud keep increasing even after ten minutes when the curves shown for the model results in Fig. 7 level out after about ten seconds? Is it because of the inclusion of the Bergeron process and the evaporation of cloud droplets increases the frozen fraction not additional ice formation?*

The evaporation of droplets is not taken into account. The increase in the frozen fraction flattens out in the semi-singular models due to the differences from particle to particle. Some particles with a high contact angle, will freeze given sufficient time. The importance of the stochastic contribution to the nucleation process becomes most evident there and could explain the observation of long last-

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ing ice precipitating clouds. Please note the logarithmic time axis.

10. *It is difficult to judge the generality of the results obtained without quantitative comparisons to other published results. The title of the paper lays claim to a broad treatment of the topic while in reality the work is presented in isolation. It is also difficult to determine to what extent the properties of the mineral used for the tests enter into the model calculations; it would be useful if the authors made this clear since it appears that most of the assumptions about contact angles could equally well apply to other materials.*

We adapted the title to: "Time Dependence of Immersion Freezing: An Experimental Study on Size Selected Kaolinite Particles". The contact angles presented here are only valid for the kaolinite sample used. The main motivation for this study was to directly measure the importance of time on the immersion freezing process, the basic underlying physics. The second goal was to test if any physical representation of the immersion freezing mechanism was capable of reproducing the measurement. We claim general validity of this work in two aspects: we were able to observe a time dependence and neither a pure stochastic nor singular description is appropriate description but there is a dependency on temperature and the particle property (in this study size, which can be fairly well controlled) as to how important the kinetics or the interaction with the particle surface is.

### Technical corrections

None.

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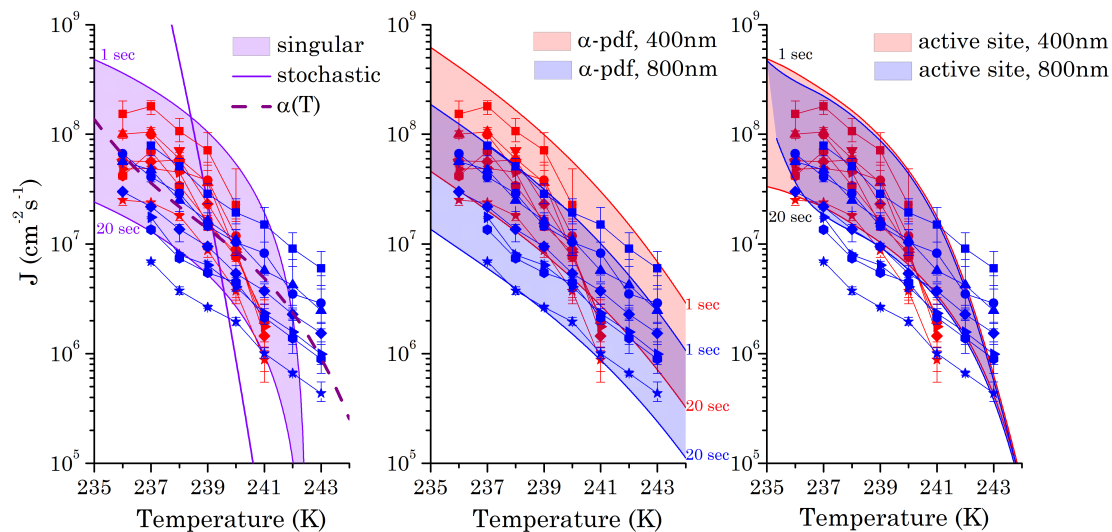
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**Fig. 1.** Nucleation rates of experimental data in comparison to nucleation rates calculated from the different models for 1 s and 20 s nucleation time.

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