**Atmospheric
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Interactive comment on "Time dependence of immersion freezing" *by* A. Welti et al.

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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 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)

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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.

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 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 α–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.

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 nucle-

ation is approached, kinetic effects become more dominant.

Specific comments regarding the manuscript are listed in the following:

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 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.

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. 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.

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?

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 nm2 for active sites) and no evaluations are presented about the sensitivity of the results to these assumed values.

6. The degree of time dependence on nucleation in the α–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.

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 nm2, not 6 nm2 as in this work. What is the resulting numerical value for equation 8? How meaningful is it to extend the curve in Fig. 6 to 180° contact angle?

8. The last step in the active site model (section 4.2.3) refers to en 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?

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?

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 12623, 2012.