**Atmospheric
Chemistry
and Physics
Discussions**

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

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Welt et al. present a study of ice nucleation by kaolinite from the chemical supplier Fluka. They show that nucleation is time-dependent and there appears to be heterogeneity between the particles. The techniques used and analysis of data appear to be robust. However, discussion of previous literature is deficient.

My primary criticism is that Welti et al. have failed to place their results in the context of the existing literature and have miss-represented some previous work. In particular, Welti et al. need to take into account recent work from my research group. We have developed a microscope stage where droplets containing a controlled amount of solid material are cooled at a controlled rate or held at constant temperature. We have reported both the cooling rate dependence of freezing and freezing under isothermal conditions for kaolinite (Murray et al., 2011) and for a mixture of minerals which we

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argue is representative of atmospheric mineral dust (called nx-illite) (Broadley et al., 2012). Specific points relating to this issue and several other comments are set out below.

1) The previous studies of time dependence of nucleation by kaolinite (Murray et al., 2011) and nx-illite (Broadley et al., 2012) needs to be properly and prominently referred to in the introduction. There are very few studies of time dependence of ice nucleation in the literature and these should be discussed fully. Contrary to how the current article reads, Welti et al are not the first to study the time dependence of ice nucleation by kaolinite.

2) P12627 Ln 1-5. Murray et al. (2011) and Broadley et al. (2012) did not report 'the repeated exposure of the same sample to low temperatures'. Similarly, this was not a major feature of Koop's review article either. This needs to be corrected. In our work, an array of droplets containing a known amount of material was cooled down at a controlled rate or held at a constant temperature. The cooling rate was varied in these experiments.

3) Discussion and conclusions. The work of Murray et al. (2011) and Broadley et al. (2012) needs to be fully discussed and contrasted with the new data. Specific points of discussion include: 1) Murray et al.'s results fit very well with a stochastic model (we refer to this is a single component stochastic model, i.e. each particle of the same size has the same probability of catalysing freezing). Welti et al.'s data fit better to a model in which each particle has a different ice nucleating ability. Acknowledge this difference and discuss why there is a difference – most likely the difference in source of kaolinite powder. 2) In termso f the particle to particle variability Welti et al's kaolinite is perhaps more like Broadley et al's nx-illite, that is each particle has its own ice nucleating ability (we refer to this as a multiple component stochastic model). However, we found that we could not model our data using a classical theory based model and instead needed a much steeper temperature dependence of lnJ. 3) We found that for kaolinite the fraction frozen curve would shift by nearly 3 K on a change in cooling rate by a factor

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of 10. Welti et al. report a change of just 1 K on a change in time scale of a factor of 10. Broadley et al. report no significant change in freezing temperature on changing cooling rate by a factor of 10 for nx-illite. Acknowledge and discuss the difference.

4) Title: The title reads more like a review article or of a paper with more general conclusions. It needs to made clear that only kaolinite was used in these experiments. For example, I suggest 'Time dependence of immersion nucleation by kaolinite particles).

5) P12627 Ln 6-9. The Niedermeier et al paper cited here contains no experimental results, the authors may have intended to cite a different article by the same authors.

6) Section 2.1. Some discussion is required as to why kaolinite powder from a chemical company is atmospherically relevant and why material from the Clay Mineral Society was not used. The Sigma-Aldrich website gives no information as to its composition, impurities or processing or preparation. These are all key to justification of its atmospheric relevance; the concern is that this material is processed to make it a good material for synthetic chemists rather than a representative material for the atmosphere. If the authors have information, this should be provided in the paper. The Clay Mineral Society on the other hand state that they have not processed, acid washed or otherwise changed the samples they supply from their natural state. An additional advantage of the Clay Mineral Society samples is that a significant literature exists for these specific samples (See Murray et al. (2011).

7) P12638 ln 18. Vali does not parameterise ice nucleation data using an alpha-pdf model – revise.

8) P12642 ln 5-12. I strongly disagree with the statement that 'Due to the larger size of water molecules and the partly hydrophobic property of the mineral dust surface, the area where water can adsorb on a particle can be expected to be smaller than the surface occupied by nitrogen molecules'. Atomic Force Microscopy measurements of surface area of kaolinite agree very well with those obtained by N2 isotherms which contradicts this statement (Bickmore et al., 2002). The reference supplied by Welti et

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al. is for adsorption onto silver iodide not kaolinite. Also, water is not often used in adsorption measurements because it is a polar molecule and its adsorption will therefore depend on the polarity of the surface (Gregg and Sing, 1982). In fact, Zettlemoyer et al (referenced by Welti et al.) suggest that silver iodide is hydrophobic and water adsorbs at steps. This might give a clue to the mechanism of nucleation, but it doesn't mean a spherical assumption is better than a gas adsorption measurement when determining surface area.

9) The fact is that Welti et al. is forced to make an assumption that the particles are spherical, which undoubtedly underestimates the surface area. This is a disadvantage of working with the system they have constructed. This is not in itself a problem, but it is necessary to state the assumption clearly and state this is a lower limit to surface area. Do not go down the alternative route of attempting to discredit other experiments (especially on the basis of poorly researched claims) in order to make your chosen approach seem better. There is some discussion of surface area measurements in the new review of Hoose and Mohler (Hoose and Möhler, 2012). This should either be discussed fully or removed.

10) P12645, ln 10. Crosier et al. would be a better citation here (Crosier et al., 2011).

11) P12646, ln 12-16. The dependence of droplet freezing on time described here sound very much like the experimental results presented by Broadley (2012) and also the model results of Niedemeier et al. (Niedermeier et al., 2011). They show a rapid decrease in liquid droplets initially followed by very slow change. This should be referred to.

12) P12625. Ln 2. Is there a full reference for the claim that 15% of the globe is covered in mixed phase clouds. A conference abstract (Wang) is unsatisfactory for such a prominent statement.

13) P12625. Ln 12. There will be unimmersed aerosol present in a mixed phase cloud, so why can't you get contact freezing? The revised version of this sentence needs a

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reference.

References

Bickmore, B. R., Nagy, K. L., Sandlin, P. E., and Crater, T. S.: Quantifying surface areas of clays by atomic force microscopy, Amer. Mineralogist, 87, 780-783, 2002. Broadley, S. L., Murray, B. J., Herbert, R. J., Atkinson, J. D., Dobbie, S., Malkin, T. L., Condliffe, E., and Neve, L.: Immersion mode heterogeneous ice nucleation by an illite rich powder representative of atmospheric mineral dust, Atmos. Chem. Phys., 12, 287-307, 10.5194/acp-12-287-2012, 2012.

Crosier, J., Bower, K. N., Choularton, T. W., Westbrook, C. D., Connolly, P. J., Cui, Z. Q., Crawford, I. P., Capes, G. L., Coe, H., Dorsey, J. R., Williams, P. I., Illingworth, A. J., Gallagher, M. W., and Blyth, A. M.: Observations of ice multiplication in a weakly convective cell embedded in supercooled mid-level stratus, Atmos. Chem. Phys., 11, 257-273, 10.5194/acp-11-257-2011, 2011.

Gregg, S. L., and Sing, K. S. W.: Adsorption surface area and porosity, Academic Press, London, 1982.

Hoose, C., and Möhler, O.: Heterogeneous ice nucleation on atmospheric aerosols: A review of results from laboratory experiments, Atmos. Chem. Phys. Discuss., 12, 12531-12621, 10.5194/acpd-12-12531-2012, 2012.

Murray, B. J., Broadley, S. L., Wilson, T. W., Atkinson, J. D., and Wills, R. H.: Heterogeneous freezing of water droplets containing kaolinite particles, Atmospheric Chemistry and Physics, 11, 4191-4207, 10.5194/acp-11-4191-2011, 2011.

Niedermeier, D., Shaw, R. A., Hartmann, S., Wex, H., Clauss, T., Voigtländer, J., and Stratmann, F.: Heterogeneous ice nucleation: Exploring the transition from stochastic to singular freezing behavior, Atmos. Chem. Phys., 11, 8767-8775, 10.5194/acp-11-8767-2011, 2011.

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