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

**A. Welti et al.**

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Received and published: 23 August 2012

### **Response to the Comments of Ben Murray**

We thank Dr. Murray for his extensive and stimulating comments.

**General comment** *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,*

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*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 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.*

The focus of the current work was to present time dependence immersion freezing measurements for two sets of size selected singly immersed particles at a number of different residence times. This is the only study of its kind with this technique. We therefore did not compare to previous literature that used significantly different methods and in cases where more than one particle and different sizes could be immersed in the droplet. However, we agree with Dr. Murray, that there is some value to putting the current work into context of previous literature given that the conclusions from our work, have some overlap with previously published studies. We have enhanced and corrected the acknowledgment of previous studies from your research group.

### Specific comments

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.*



We now incorporate the two mentioned studies as they provide examples how time-dependence might be masked by a broad size distribution and also show the importance of the temperature where an aerosol species becomes an efficient IN on the balance of the singular and the stochastic contribution to ice nucleation.

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.*

The citations have been revised.

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 catalyzing 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 terms of 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  $\ln J$ . 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 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.*

We now discuss the work of Murray et al. (2011) and Broadley et al. (2012) in more detail, but we have added a caveat to this comparison since we are discussing techniques where polydisperse and multiple particles in one droplet are being compared to the current technique where size selected, singly immersed particles were studied. And as has been shown by Pinti et al. (2012) there are few, more efficient IN in an ensemble which might bias such a comparison. From the fact that the experimental procedure, the dust species and the analysis of the measurements are different it seems improbable to us to reconcile the results.

- 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).*

Prompted by Dr Murrays suggestion we revised the title to: Time Dependence of Immersion Freezing: An Experimental Study on Size Selected 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.*

We refer to figure 1 in the cited paper which contains an extended dataset of measurements shown in a previous paper of the author in comparison to a new dataset obtained at a different residence time.

- 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*

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*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)).*

The reason why we used kaolinite from Fluka is that it was used in many previous ice nucleation studies (see Hoose and Möhler (2012)). It has also been used for immersion freezing experiments with the same experiment (Lüönd et al., 2010), therefore the temperature range where ice formation can be expected was known to be within 10 K of the homogeneous freezing temperature. This was important to be able to detect time dependence within the limited residence times achievable with the IMCA/ZINC experimental setup.

7. *P12638 In 18. Vali does not parameterize ice nucleation data using an alpha-pdf model – revise.*

The study of Vali, 2008 was cited as a reference for the term "modified singular models". The term is replaced with "modified stochastic models" and the citation removed.

8. *P12642 In 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 al. is for adsorption onto silver iodide not kaolinite. Also, wa-*

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*ter 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 does not mean a spherical assumption is better than a gas adsorption measurement when determining surface area.*

We partly agree with Dr Murray and removed the statement about the larger size of water molecules compared to nitrogen. However the partly hydrophobic property of kaolinite as reported by Yin and Miller (2012) suggests that water molecules that form an ice germ might not have access to the same surface area as nitrogen. Therefore we preferred to use the geometric surface areas which are a factor of 3 to 6 lower than the BET surface areas for 400 and 800 nm respectively. We did not intend to convey that one assumption is better than the other. The relevant changes have been made to the discussion.

- 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 Möhler (Hoose and Möhler, 2012). This should either be discussed fully or removed.*

The assumption of spherical particles represents a lower limit. This is stated clearly on page 12642 line 4-6: "...results for size selected particles are likely to represent a lower limit of the surface area of the particles used in this study."

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

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We replaced the citation.

11. *P12646, In 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.*

We added: "This is in agreement with the findings of Niedermeier 2011 and Broadley 2012."

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.*

The conference proceedings was admittedly a somewhat unsatisfactory reference. We replaced the statement by: "Midlevel clouds which cover about 25% of the globe (Sassen and Wang, 2012) consist to 61.8% of mixed-phase clouds containing liquid droplets and ice crystals, with the highest occurrence in mid-latitudes and over the polar oceans (Zhang et al., 2010). This infers that in average mixed-phase clouds cover about 15.5% of the globe."

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 reference.*

If there are unimmersed aerosol particles present, contact freezing is a possible ice nucleation mechanism. We reformulated the sentence and added Lohmann and Diehl (2006) as a reference. In light of the very recent publication by Bunker et al. (2012) reporting that hundreds of collisions were needed to initiate ice nucleation, we mention that if the number of collisions is small, ice formation by contact freezing might not to be significant compared to the immersion mechanism.

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