

## ***Interactive comment on “Heterogeneous freezing of water droplets containing kaolinite and montmorillonite particles” by B. J. Murray et al.***

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This comment is in response to both reviewer's (and also Hoose's) comments concerning our assumption that heterogeneous nucleation of ice on clay minerals is a stochastic process. This document is not intended to be a full response to all the reviewers' detailed comments. Our assumption that heterogeneous nucleation is stochastic is key to our interpretation of our nucleation data and also our proposed parameterisations. In this comment we report new data for ice nucleation by kaolinite.

As the reviewers point out, it has been clearly demonstrated that homogeneous nucleation of pure water droplets is stochastic. We feel that it is also sensible to assume that heterogeneous nucleation will depend on the surface area (rather than volume as in the case of homogeneous nucleation) as well as time (i.e. it is stochastic) The fact

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that application of this model to all our data for kaolinite with varying surface area of mineral dust inclusions and varying freezing temperatures results in a single straight line suggests that this model is valid for kaolinite. However, we are also aware that a more direct measure of the time dependence would be beneficial.

The reviewers suggest doing experiments at other (slower) cooling rates. The ideal way to examine the time dependence of nucleation is to perform isothermal experiments. However, in the past we did not have the capability to do an isothermal experiment since we were limited by mass transfer from supercooled liquid droplets to frozen droplets. The effect at slow cooling rates would be that supercooled droplets would disappear before freezing. In order to avoid mass transfer we needed to work at rapid (10 K min<sup>-1</sup>) cooling rates.

In the last few weeks we have managed to solve this problem by placing silicone oil over the droplets. This blocks mass transfer allowing us to work on much longer timescales. Tests at 10 K min<sup>-1</sup> demonstrated that the oil did not influence the freezing temperatures. We performed an experiment at 248 K in which droplets contained 0.23 wt% kaolinite. In this experiment droplets were cooled to 248 K and then held at this temperature for about 35 mins. We found the droplets nucleated to ice over the course of this time with some droplets remaining unfrozen at the end of the period.

According to the stochastic approach the number of liquid droplets containing solid particles should decay exponentially with time. A slope of a plot of  $\ln(n_{liq}/n)$  vs.  $t$  (where  $n_{liq}$  is the number of liquid droplets and  $n$  is the total number of droplets) should be linear with a slope of  $-JA$  (where  $J$  is the nucleation rate in units of  $\text{cm}^{-2} \text{s}^{-1}$  and  $A$  is the surface area per droplet). In Figure 1 we have plotted our data for  $\ln(n_{liq}/n)$  vs.  $t$  for droplets in the size range 10–20  $\mu\text{m}$  diameter. This plot is clearly linear showing that heterogeneous nucleation on kaolinite is time dependent and consistent with the stochastic assumption. The nucleation rate we obtain from the slope is on the order of 100  $\text{cm}^{-2} \text{s}^{-1}$ , which is in reasonable agreement with the parameterisation quoted in the discussion paper.

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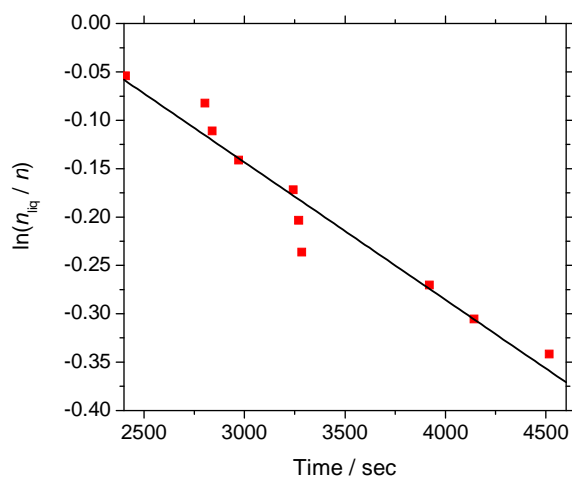
Vali, in his review, states that 'with nucleation on a foreign surface, stochasticity would result either from having a uniform surface or from having a very large number of identical sites uniformly distributed on the surface of even the smallest particles..... Neither is a realistic assumption.' We disagree with the statement that these scenarios are not realistic. Our data for kaolinite suggests that there is uniformity, in terms of ice nucleating probability, across all kaolinite particles. In experiments in which mixtures of minerals have been used (such as in Marcolli et al., 2007) individual particles may have distinct ice nucleating abilities because each particle is a distinct mineral (or mixture of minerals). Hence there is a wide spread in nucleation temperatures. Our data is important because it shows that we may be able to characterise each mineral type in terms of its ice nucleating properties (ideally in terms of a nucleation rate, as done here) and this information could be used to predict ice nucleation by natural dusts in conjunction with knowledge of the proportions of the various minerals.

We plan to repeat isothermal experiments for other temperatures for kaolinite and also for droplets contaminated by montmorillonite. We had initially planned to include this more recent work in a separate publication, but in light of the comments that have been made this data could be included in the present paper in order to support our assumption that nucleation of ice on kaolinite can be treated as being stochastic.

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**Fig. 1.** Figure 1. Results from an isothermal experiment at 248 K in which droplets were contaminated with 0.23 wt% kaolinite. This data is for droplets in the 10-20  $\mu\text{m}$  diameter size range.

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