**Atmospheric
Chemistry
and Physics
Discussions**

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

C. Hoose

corinna.hoose@kit.edu

Corinna Hoose (corinna.hoose@kit.edu), Ottmar Möhler, Karl-Heinz Naumann

With great interest have we noticed and read the paper by Benjamin Murray and his team about heterogeneous freezing experiments with kaolinite and montmorillonite mineral particles immersed in water at variable mass fraction and thus variable particle surface area per water volume. Some of the issues touched in this article have raised our attention and, in our opinion, deserve further discussion.

- We agree that fundamental lab work on heterogeneous ice nucleation is needed for both pure mineral particles and more natural mixtures of mineral particles

C2261

originating from major source areas. Experiments with more homogeneous particle samples of single minerals, may be more appropriate to shed light on the basic understanding of heterogeneous ice nucleation mechanisms and on the most important parameters controlling the ice nucleation rate. However, in order to translate those results into parameterizations for ice nucleation in atmospheric models, one still needs to know the relative abundance of respective minerals in the complex mixture of atmospheric dust particles. Experiments with mineral dust samples from desert source regions may be more appropriate to provide a link between fundamental lab work and atmospheric applications. In addition, artificially milled samples, as used here, might provide more active (rougher) surfaces than atmospheric dust (Möhler et al., 2006).

- Specific surface area of the samples (Table 1). The values given in Table 1, mostly determined by BET, are for dry samples. In particular for montmorillonite, which easily takes up large amounts of water and has inner cavities (Karaboni et al., 1996), these values might not be valid for particles immersed in water.

- Information on the size distribution of the mineral particles and an estimate of the number of immersed particles per droplet (and their statistical distribution) would be helpful to interpret the data. Assuming monodisperse, spherical particles, back-of-the envelope calculations yield montmorillonite number concentrations of > 1000/droplet, even for the lowest investigated wt%. This might give a clue on the peculiar behaviour of montmorillonite: If there is always a large number of particles in the droplets, and if they are sufficiently efficient at initiating freezing, freezing is always initiated immediately (saturation effect). On the other hand, for the lowest kaolinite concentration, estimated particle number concentrations per droplet are so small that it seems likely that many droplets did not contain any mineral particle at all. Such empty droplets would logically fall on the homogeneous freezing line. It should be mentioned whether it was technically possible to detect empty droplets and whether or not they were included in the data analysis.

C2262

- Cooling rate dependence. All experiments are conducted with a fast cooling rate of 10K/min, which in the uppermost range of atmospherically relevant cooling rates. As classical nucleation theory is applied to the data, extrapolation to other cooling rates yields a strong dependence of the fraction of frozen droplets at a certain temperature on the cooling rate (Fig. 8). However, this is not supported by the experiment itself. We suggest that experiments with variable cooling rates need to be conducted to confirm or disprove this behaviour.

- Although the kaolinite data are fitted well by classical nucleation theory, this is not a prove that a different model (e. g. a singular model with a certain surface density of active sites, as in Connolly et al. (2009)), would not fit the data equally well.

- Murray et al. provide a nice and clear direct proof of the surface area dependence of immersion freezing, but it should be noted that it is common knowledge in the community that the previously observed volume-dependence for freezing of suspensions is not due to the water volume, but to the fact that larger droplets contained more dust particles. The surface area dependence for immersion freezing has been experimentally demonstrated and discussed in previous publications by e. g. Zuberi et al. (2002); Hung et al. (2003); Archuleta et al. (2005); Marcolli et al. (2007).

- Note also that several parameterizations, also used in global and smaller-scale models, which are based on classical theory, include surface-area and time dependence (Liu and Penner, 2005; Khvorostyanov and Curry, 2005; Hoose et al., 2010). Pruppacher and Klett (1997) is cited as a reference for volume-dependent freezing; however, Pruppacher and Klett (1997) also amply discuss classical nucleation theory with surface area-dependent freezing rates.

- The total number of droplets examined should be given.

C2263

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C2265