

## ***Interactive comment on “Ice nucleation efficiency of clay minerals in the immersion mode” by V. Pinti et al.***

**Anonymous Referee #2**

Received and published: 26 March 2012

### General comments

Pinti et al. present an interesting experimental investigation into the ice nucleating ability of a range of clay minerals. The emulsion-calorimetry technique has been used in the past as has the bulk suspension test. Pinti et al. show significant differences between samples with different compositions and also show that there are rare sites which catalyse freezing at high temperatures. There are a number of important conclusions from this work and the topic area is certainly suitable for ACP. However, there are some issues which need to be addressed before publication.

### Specific comments

Abstract:

C909

In general, the abstract is too long and technical in nature. It fails to get the key conclusions across in a succinct way and instead is a complex list of freezing temperatures. For example, an important conclusion in my opinion is that the characterisation of ice nucleation on the basis of threshold temperatures is inappropriate. For example, Pinti et al. refer to older work from Pitter and Pruppacher and state that these experiments should not be used to define ice nucleation by all particles of the material under investigation. This has important implications for studies by Lohmann, Hoose, Diehl and co-workers who have based global modelling studies on such assumptions.

Introduction:

- 1) P 3217, In 4-5. Hoffer observed much lower freezing temperatures than this. This is misleading as written.
- 2) P 3217, In 9-10. Murray et al.'s montmorillonite freezing data was a lot higher in temperature than this.
- 3) P 3217, In 11-12. I disagree that 'these recent measurements are not able to explain the enhanced glaciations....'. These experiments simply explored a different temperature regime, they do not rule out freezing by mineral dust in the -10 to -20 C range – the way this is stated in the paper is misleading.

Experimental.

- 1) P3218, In 17. Units of resistivity are wrong. Need cm in there.
- 2) The droplet size distribution used here is very small at a mode diameter of 1.9  $\mu\text{m}$ . What was the rationale for working with droplets only a few times larger in diameter than the particles being examined? Also, a size distribution of the droplets should be shown. Is it possible that there is a small mode of droplets which you cannot detect with the optical microscope, since this must be pushing the capabilities of the microscope?
- 3) Some justification is needed for the use of particles sizes measured on the basis of an aerosolised sample. Surely the size distribution of the aerosolised sample will differ

C910

from that of the bulk sample which is mixed with water.

4) I would like to see some estimate of primary particle size based on the BET measurements. I suspect the particles measured by SMPS are aggregates of much smaller primary particles. SEM pictures in Broadley et al. and Welti et al., for example, clearly show aggregates.

5) How are the suspensions produced? Does this process break up any/all aggregates?

Section 3.

1) Is the color of the samples really relevant? What does this tell us?

2) P3221, ln 18. All clay minerals belong to the silicate and phyllosilicate group, so it is a little odd to state this only for montmorillonite.

3) What does delaminated mean? Please define and discuss.

4) The Hoggar dust sample: are the given proportions of the total mass or just the clay fraction. I'm guessing the former since no natural samples are purely clay. How much quartz etc is in the sample?

5) III SE: has a different size distribution and composition (and likely doesn't match the supplier details as with III NX), use of the same BET surface area as III NX needs some justification or can a more appropriate surface area be used?

6) M KSF: It is counter-intuitive for completely delaminated clay to have a lower surface area than other intact clays. Why is this?

Section 4.

1) P 3224, ln 25-26. The table doesn't show that illite is less uniform. No impurities are listed for kaolinite, but they are reported by the Clay Mineral Soc.

2) 'Best sites'. It is not clear to me that these sites should be associated with a particular

C911

mineral. By their very nature they are very rare and could therefore be some impurity. Cziczo's work on ice nucleation by lead inclusions, for example, shows some minor impurity may dominate ice nucleation. Or maybe there is some effective biological ice nucleating material incorporated with the dust. This caveat should be discussed.

3) Fig 7 and p 3227, ln 7-8. Visual inspection of this plot seems to clearly show that the presence of lanoline impacts freezing! This is potentially a very important consideration when interpreting emulsion experiments and cannot be dismissed in the way it has. This must be discussed.

4) PG3226:17. How many runs for each sample? Might this easily be included into figure 8? Is there a correlation between the number of runs and the range of the whiskers?

5) Pg 3228, ln11-14. (fig 10) Why is 0.5% significantly worse than 0.05%? Why is Hoggar 0.005% considered significant but K-SA 0.5% (fig 9) isn't?

Discussion:

1) The contact angles used here are substantially larger than those derived in Murray et al. 2011. Why is this?

2) P3229:10-12. There is a serious error here. A number of authors including Niedermeier et al. (2011) define the singular description in terms of ice nucleation sites per unit surface area. Hence the probability of freezing varies with surface area within the droplets.

3) P 3229, ln 6-8. 'In contrast, the heterogeneous freezing peaks...' Given the uncertainty quoted in the plot I'm not sure you can make this claim. Over the temperature range the expected freezing temperature for a constant contact angle is comparable to the variability or error in freezing temperature.

4) Relying on a surface area for the Hoggar sample from a measurement of a sample from a different location is difficult to justify. I'm sure ETH has a commercial BET

C912

instrument. If not, I'm sure a colleague somewhere around the world could arrange to have this measurement made. I strongly suggest this is done.

5) P 3230, ln 1. What is the standard deviation on the variability in freezing temperature in the bulk experiments. This would be useful for comparison with Fig 2a of Vali (Atmos. Chem. Phys., 8, 5017–5031, 2008).

6) Discussion on p 3231 on the literature data could be facilitated by inclusion of the literature data in Figure 11.

7) P3233. In 2024. I disagree that the agreement is good. Looking at the table there are some very significant discrepancies. e.g. K-SA 0.5 wt%

8) Table 3: Looking at the first line. If there are 0.09 particles per drop, then  $\sim 0.1$  of the droplets will contain a particle. But this doesn't tie in with the 0.26 which froze heterogeneously. This needs to be corrected or clarified.

Technical comments:

1) P3220, ln 3. Full stop missing. 2) P3220, ln23. Insert 'the' before 'Clay'. 3) Table 1: What are the units of the StDev?

---

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 3213, 2012.