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Atmospheric Chemistry and Physics Discussions

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

V. Pinti et al.

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We thank Reviewer 2 for the helpful suggestions and comments. Below are detailed answers to each point (in italic).

General comments

Pinti et al. present an interesting experimental investigation into the ice nucleating abilityof a range of clay minerals. The emulsion-calorimetry technique has been usedin the past as has the bulk suspension test. Pinti et al. show significant differencesbetween samples with different compositions and also show that there are rare siteswhich catalyse freezing at high temperatures. There are a number of important conclusionsfrom this work and the topic area is certainly suitable for ACP. However, thereare some

issues which need to be addressed before publication.

Specific comments

Abstract:

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 characterization 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 byLohmann, Hoose, Diehl and co-workers who have based global modeling studies on such assumptions.

We shortened the abstract and grouped the freezing temperatures.We agree with the reviewer that it is an important conclusion that characterization of ice nucleation on the basis of threshold temperatures is inappropriate. Therefore we added a sentence to the abstract which states this.

Introduction:

1) P 3217, ln 4-5. Hoffer observed much lower freezing temperatures than this. This is misleading as written.

Hoffer (1961) reported freezing onsets of -13.5 C for montmorillonite. We state this value now explicitly in the introduction. We discuss his data in more detail in section 5.2.

2) P 3217, ln 9-10. Murray et al.'s montmorillonite freezing data was a lot higher in temperature than this.

Thank you for pointing this out. We corrected this.

3) P 3217, ln 11-12. I disagree that 'these recent measurements are not able to explainthe enhanced glaciations....'. These experiments simply explored a different temperatureregime, 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.

Measurements of mineral dust freezing in the immersion mode by Murray at al., (2010, 2011) and Lüönd et al., (2010)explored the whole temperature range where freezing was above their detection limits. However, the frozen fraction was below detection limit in the -10 to -20 C temperature range. Therefore we keep this sentence as it is.

Experimental.

1) P3218, ln 17. Units of resistivity are wrong. Need cm in there.

We corrected this.

2) The droplet size distribution used here is very small at a mode diameter of 1.9 um.What was the rational for working with droplets only a few times larger in diameter thanthe particles being examined? Also, a size distribution of the droplets should be show.Is it possible that there is a small mode of droplets which you cannot detect with theoptical microscope, since this must be pushing the capabilities of the microscope?

The size distribution of the droplets depends on two major factors: the steering process and the amount of surfactant (lanolin) with respect to mineral oil. Less surfactant leads to larger droplets but also to less stable emulsions. The amount of surfactant here chosen (i.e. 5wt%) is the minimum with which we could obtain stable emulsions.

We added the Figure 1b new to the manuscript showing the droplet size distribution of the emulsions.

Sometimes, we happen to have another (smaller) mode in the droplet size distribution which is not detectable with the microscope.Most of these smaller droplets do not contain any heterogeneous nucleus and appear as a small peak or shoulder below the typical homogeneous freezing temperatures. For example in Figure 5, panel a, the

MSTx-1b clay with a concentration of 0.1wt% shows a smaller peak at lower temperatures than the typical homogeneous peak, this indicates that we have an additional smaller mode in the droplet size distribution.

3) Some justification is needed for the use of particles sizes measured on the basis ofan aerosolised sample. Surely the size distribution of the aerosolised sample will differ from that of the bulk sample which is mixed with water.

The aggregation of mineral dust particles depends on the type of clay mineral, pH, and concentration. We discuss this in paragraph 5.3, (page 3233, and lines 3-16).Measuring the size distribution in suspension instead of aerosolized samples does therefore not necessarily lead to more representative results. We wanted to avoid aggregates as much as possible. Therefore, before each measurement, the suspensions were immersed in anultra soundingsystem (Badelin electronic KG, at 50-60 Hz) for approximately 10 minutes.

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 smallerprimary particles. SEM pictures in Broadley et al. and Welti et al., for example, clearlyshow aggregates.

Using the BET surface areas, we obtain the following primary particle diameters: KGa-2 (95 nm), KGa-1b(188 nm), K-SA (127 nm), Ill SE (21 nm), Ill NX (21 nm), M STX-1b (27 nm), M SWy-2 (70 nm), M K-10 (9 nm), M KSF (74 nm), Hoggar (48 nm). Comparing these numbers with the mode diameters given in Table 1, aggregation seems to be strongest for M K-10 and least for KGa-1b.

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

Suspensions are produced by vigorous stirring with a rotor-statorhomogeniser for 40 s at 7000 RPM. This information is given in section 2 (experimental setup).This proce-

dure can indeed breakup some aggregates.

Section 3.

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

We deletethis information for the clay mineralsbut add it for the Hoggar sample, since this could be an indicator for iron present in the sample.

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

We state this now for all clay minerals.

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

This means that the typical TOT structure of the clay is broken up.We added a sentence that states this now explicitly.

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

This is indeed the clay fraction; we state this now in the manuscript.We also added the percentage of quartz and diatomaceous hydrated amorphous silica fraction that Moreno et al. (2006) found.

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

We could not find any BET surface data for this clay in the literature.We think that for the use that we make of the BET surface area, this estimate is good enough. This is stated in the table capture, we also added it in the text.

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

MKSF is the montmorillonite which does not present the typical TOT structure of this clay mineral anymore because of the sulphuric acid treatment. We suspect that the material re-aggregates in an amorphous form which does not have the rigid crystalline structure.This results in a lower surface area.The typical cations which are between the layers are substituted with protons in case of a strong acid treatment.

Section 4.

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

We added to the table the impurities in the kaolinite samples from Clay Mineral Society.The table shows that the illite samples contain also other minerals (e.g. calcite, quartz and feldspar).

2) 'Best sites'. It is not clear to me that these sites should be associated with a particularmineral. 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 minorimpurity may dominate ice nucleation. Or maybe there is some effective biological icenucleating material incorporated with the dust. This caveat should be discussed.

We donotthinkthatthebestsitesareassociatedwithaparticularmineral. Weratherthinkthattheyareassociated with randomdefectsoralsoimpurities. Westatethisnowexplicitlyintherevisedmanuscript.

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

From Figure 8, i.e. bulk measurements, samples without lanolin also show both narrow and large ranges in freezing temperatures (see for example KGa-1b; Ill NX; Ill SE;

MSWy-2), indicating that this difference does not depend on the presence of lanolin, but on the sample itself. More experiments would be needed to find out whether the presence of lanolin influences the spread of freezing temperatures. The aim of Figure 7 is to show that the presence of lanolin is not responsible for the much lower freezing temperatures in the emulsion samples compared with the bulk samples.

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

We include the number of runs on each whisker plot in the revised manuscript. There is no correlation between the number of runs and the spread in freezing temperatures.

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

As stated by Vali, 2008: When all drops are dispensed from the same bulk sample, 'the distribution of particles among the drops is a chance process.' For our bulk samples this is the same: every suspension is prepared from the same dry sample, and every drop of each wt% is prepared from the same suspension, this means that every suspension has a chance to have a 'good' or even a "very good" IN. This may result, as in this case, in a suspension of 0.5wt% which has 'worse' IN than the one with 0.05wt%. In order to state that this difference is significant, a larger set of data is needed. On the other hand, we can overall observe a tendency of a lowering in median freezing temperatures with a lowering of suspension concentration.

In K-SA 0.5%, two of the three median freezing temperatures lie within the pure water box and can therefore not be attributed unambiguously to freezing by kaolinite particles. In case of the Hoggar 0.005 wt% sample, two of the three samples are well above the freezing range of pure water.

Discussion:

1) The contact angles used here are substantially larger than those derived in Murrayet

al. 2011. Why is this?

In Figure 11, we calculate the freezing temperatures as a function of contact angles from Classical Nucleation Theory (CNT) using the parameterization of ice nucleation from Zobrist et al. (2007). Murray et al. (2011) calculate the contact angle from the Arrhenius formulation of the nucleation rate assuming a constant pre-exponential factor A_{het} *in their Eq. (12). The value of the pre-exponential factor that Murray et al. require in order to fit to the nucleation rates shown in their Figure 7 is approximately* 10^{10} *cm*^{2}*/s,while it is* 10^{21} *cm*^{2}*/s at 236 K in the Zobrist et al. (2007) parameterization.*

In terms of CNT, such a different pre-exponential factor implies either a very different value for the number of water molecules at the nucleus/water interface, which is the well known $n_s = 10^{15}$ *cm*$^{-2}$*in the Zobrist et al. parameterization (calculated from the surface coverage of single water molecules) or a very different value for the diffusivity. For the diffusivity, the Zobrist et al. parameterization uses the Vogel-Fulcher-Tammann equation with the diffusivity function of liquid and supercooled water given by Smith and Kay (1999), which includes the fitting parameter E = 892 K. To realize the pre-exponential factor of Murray et al. in terms of CNT, either* n_s *needs to be much lower, namely* 10^4 *cm*$^{-2}$*, or E needs to be much larger, namely* $2.4 \cdot 10^3 K$.

The Zobrist et al. parameterization is based on CNT of homogeneous ice nucleation and from this the heterogeneous formulation is derived, having as a single free parameter the contact angle. Conversely, Murray et al. use an empirical procedure, allowing the prefactor to vary, but without providing a justification for this approach.Both approaches might have their justification: Zobrist's, because it is based on the foundation of CNT; Murray's because an 11 orders of magnitude smaller surface coverage might actually be related to having rare active sites instead a homogeneous surface. This is an interesting explanation, which should be further explored. However, it is important to note that the contact angle values given by Murray et al. cannot be used together with the parameterization of Zobrist et al.

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

The singularhypothesis assumesthatfreezing occursimmediately once a threshold temperature is reached and that freezing occurs at different types of sites or impurities with different freezing temperatures. With our reference to the singular hypothesis we wanted torefer to the first aspect, not the second one. Since in literature both aspects are usually taken together, we agree to remove our reference to the singular hypothesis in this context.

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

We agree with the reviewer and, for this reason,we specifically stated one sentence ahead in the text (page 3229, line 13-15):

'However, given the experimental uncertainties represented by the error bars, there is no direct conflict between the almost concentration-independent constant experimental

and CNT.'

4) Relying on a surface area for the Hoggar sample from a measurement of a samplefrom a different location is difficult to justify. I'm sure ETH has a commercial BETinstrument. If not, I'm sure a colleague somewhere around the world could arrange tohave this measurement made. I strongly suggest this is done.

We measured now the BET surface area of the Hoggar sample and obtained a value of 46.3 m^2*/g, which is indeed close to the value that wequoted from literature (49.7* m^2*/g) for another Saharan dust sample. We list now our value in table 1 and updatedFigure*

11 accordingly.

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

We now compare the run-to-run temperature changes that Vali presents in his Table 1 with our values. This comparison is now included in the revised manuscript.

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

In Figure 11, we present our data as a function of BET surface area and for an onset freezing temperature that corresponds approximately to 1% of the droplets freezing. It is therefore difficult to directly implement the literature data into the figure. Moreover, this figure is already quite crowded and it would become almostunreadable if we added even more data.For these reasons, we would like to keep it as is.

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

We state that the agreement is good for MSWy-2, not forclay minerals in general and not forK-SA(page 3233, line 22).

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

The probability to contain an IN increases with droplet size.The smallest droplets are therefore on average empty while the larger droplets are filled. The DSC instrument is sensitive to the volume of water that freezesatacertain temperature. Freezingof a large dropletttherefore givesrisetoa largerheat flow than freezing of a small droplet. To take this into account, we calculate in the third columnofTable 3theheterogeneoussignalfrom theprobability ofoccupationasafunctionofdropletsize. Comparison of columns

2and3shows thatalthough there are only 0.09particles per droplet on average, a fraction of 0.55 of the volume of water should freeze heterogeneously. The measured volume fraction of 0.26 of water freezing heterogeneously is therefore even too low.We state this now more clearly in the text.

Technical comments:

1) P3220, ln 3. Full stop missing. 2) P3220, ln23. Insert ‘the’ before ‘Clay’.

Added

3) Table 1:What are the units of the StDev?

What we have in this table is the geometric standard deviation, i.e. without units, we added geometric now in the table.

References:

Smith RS, and BD Kay. 1999. "The Existence of Supercooled Liquid Water at 150 K." Nature 398:788-791.

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