

Interactive comment on “Enhanced ice nucleation efficiency of microcline immersed in dilute NH₃ and NH₄⁺-containing solutions” by Anand Kumar et al.

Anonymous Referee #3

Received and published: 8 March 2018

Review for "Enhanced ice nucleation efficiency of microcline immersed in dilute NH₃ and NH₄⁺-containing solutions" by Kumar et al., submitted to ACPD

The manuscript examines the ice nucleation ability of microcline, a feldspar mineral, and how this changes when microcline particles are immersed in different solutions. This is done by using a DSC (differential scanning calorimeter). It is a thorough study describing fundamental processes and gaining interesting results.

However, I have a concern when it comes to the methodology and how results can be directly related to the atmosphere. Comparing different data sets obtained with the herein used DSC with each other is fine, as long as the droplet size distributions in

C1

the different emulsions are the same. (The latter should be discussed more, and I elaborate on that below.) But details of the methodology influence the extent to which the obtained data can be used to derive atmospheric implications. Respective matters should be discussed in the text, which is mentioned below in more detail.

After these issues, together with some others listed below, will have been addressed, I can recommend the manuscript for publication in ACP.

Referring to the methodology and the relation to the atmosphere:

Some more information on the droplet size distributions in the emulsions would be good. The fact that not all droplets in the emulsions have the same size, and particularly that there likely are some large droplets with a high amount of material in them, will influence the extent to which the obtained data can be used to derive atmospheric implications.

In general, it is known that the ice nucleation ability of microcline particles depends on the minerals' surface area per droplet (Peckhaus et al., 2016, Harrison et al., 2016, Niedermeier et al., 2015). And the broadness of the peaks you obtain with DSC (e.g., Fig. 2) clearly shows that there is a broad distribution (of surface area per droplet) in your emulsions.

Broad droplet size distributions with few large droplets might explain why the onset temperature of heterogeneous freezing does not change much with microcline concentration (line 172-174): in all emulsions, there may have been a few large droplets with a comparably high microcline content (more precise: a high total microcline surface area per droplet), which were responsible for the onset of freezing. Interestingly, this temperature you report (~ 251 K) also is the temperature at which the strong increase in the freezing spectrum for microcline ("K-feldspar") in the paper by Atkinson et al. (2013) starts. The droplets with the highest content of microcline in your exper-

C2

iments likely are similar (in microcline surface area per droplet) to those examined by Atkinson et al. (2013).

I do take from your text that you yourself assume that there are multiple particles contained in single droplets, as you mention possible aggregation (line 288, lines 550-551). This is, however, only mentioned at these two occurrences, but might influence your results more broadly. This should be incorporated more wherever it could influence your results.

Has the DSC method been compared to single particle or freezing array methods before? If yes, this could simply be mentioned in the text, together with the results on how the different methods compare. In general, it would be good to know how large the droplets you looked at were on average, and how broad was their size distribution? And how broad was the particle size distribution? And how were the particles distributed to the droplets? Or, summarized in one parameter: how was the mineral surface area distributed to the droplets? Is anything known on that? If yes, please add this. If not, please at least mention this and discuss the implications. One implication is, that you cannot directly transfer your results to the atmosphere, where each droplet will always contain a single (comparably small) particle.

And last but not least: How reproducible are the distributions in the emulsions? And how reliably can the freezing spectra be evaluated (as e.g., those shown in Fig. 4)? And what is the uncertainty of the derived values?

Related to that are also the following two remarks:

line 345: You observe that F_{het} decreases during the first day after microcline was suspended in pure water, while T_{het} was preserved. Could a reason be that droplets are settling out? Again, it seems that the majority of your droplets might act different than the few ones that determine the freezing onset. And in this respect, if the different emulsions had different surface area distributions for the experiments in pure water and in dilute NH_3 and $(NH_4)_2SO_4$ solutions, this may also explain observed differences.

C3

Please discuss this shortly, too.

line 372: Here, too, different surface area distributions might influence F_{het} , similar to the point mentioned directly above.

As a bottom line of all of that said above (and besides for revisions in the text mentioned above), the direct translation of your results to the atmosphere, even with giving degrees of Kelvin by which the occurrence of freezing may be shifted, needs to be discussed more critically or may even be shortened. Your results on the influence on the surfaces and surface sites alone is already a valuable contribution.

General comments:

line 51ff: Below, you discuss that deposition ice nucleation was questioned by Marcolli (2014), and similarly, for condensation freezing, you should also include that Vali et al. (2015) says: "Whether condensation freezing on a microscopic scale, if it occurs, is truly different from deposition nucleation, or distinct from immersion freezing, is not fully established." This is also related to line 442, where you use "condensation freezing", which, however, following the definition by Vali et al. (2015) given in your introduction does certainly not take place in your DSC measurements. But you used these measurements to make up your scenarios. Please be consistent!

line 276-278: Is it really so improbable that the (100) surface is exposed? - After all, you milled your samples, and the number density of active sites in microcline is "only" $\sim 1000000 \text{ cm}^{-3}$ at 251 K in Atkinson et al. (2013). This site density would need to be compared to the expected number of cracks and defaults that may occur during milling, before this statement you make here can be made. BTW: this is again a point where it would be good to know the exact distributions of droplet sizes and of particles in the droplets.

The whole chapter 4.5: This chapter made a somewhat unfinished impression on me.

C4

How do the results here fit in line with what you described earlier? And as you only did the experiments at a single (and always different) pH for each of the solutions, a difference between the effect of the dissolved substance versus the pH cannot be obtained. This should also be mentioned in the text (e.g., connected to what you write in line 381). Also, in the end of Chapter 4.5, you cite a number of studies, however, without putting them in context to your results, so while reading this part of your text, I got confused. Similarly, when later reading the part on aging in the conclusions (line 501 ff) I was astounded as this did not reflect what I took from this chapter. Please revise these parts of the text.

line 410: You state that “Saharan dust particles undergo little chemical processing during long-range transport across the Atlantic unless they become incorporated in cloud droplets”. However, dust particles are CCN in the atmosphere (Karydis et al., 2011), so I wonder if you want to say that dust particles do not act as CCN, or that they do not become incorporated in cloud droplets because Saharan air masses are so dry that clouds do not form? Please clarify, and make clear that dust particles are CCN.

line 435: (Again:) Your method prohibits to make statements about single particles - and, strictly speaking, also about atmospheric onset temperatures, as a single (and then likely smaller) particle in the atmosphere will only activate ice at lower temperature. I know that I mentioned this before. But again, I urge you to state this clearly.

line 505: Let me ask you a question: Have you ever observed ice crystals outside of clouds in the mixed phase cloud temperature range (unless they fall out from a cloud)? What you suggest here might suggest that this could be observed. Based on the fact that your method rather is a bulk method and not one for single particles, I (again) suggest you are careful in drawing conclusions for processes going on in the atmosphere.

Technical corrections:

C5

line 45: The abbreviation “IN” is used but has only been defined in the abstract. I’d define it again on the first appearance in the text.

line 72: You say “the particle”, but in this context, it is not clear, which particle you mean.

line 115: Replace “the” with “a”, as this is where the setup is first introduced. Also, DSC was defined in abstract, but I’d define it again in main text upon its first appearance, ideally together with a citation where it is described in detail.

line 115: Upon reading this the first time, I wished for more information on the microcline when it was first mentioned here, particularly as you give all the detailed information about all the chemicals here, too. Now I know that this is given in 2.4. – maybe you could swap the chapters, so that 2.4 comes first, or you could at least mention here that there is more on the microcline sample later.

line 120: Again, this is the first time that emulsions are mentioned, so delete “the”.

line 155: Delete the “,” following “Microcline”.

line 179-180: There is something wrong with this sentence, please correct. Looks like a copy/paste error to me.

line 275: Kiselev et al. was published online 2016, and I have a version downloaded 2017 that says “cite as ..., 2016” - please check which year is correct.

line 298: I’d prefer “suggest” to “conclude”. BTW: In line 296, you say that “excess solute strength hampers the IN efficiency”. Do you have any idea, why that would be? If you could add a sentence on that here, I’d appreciate it.

line 310: Please add at or above which water activity you are referring to, here, in this sentence, as data all agree quite well in the lower concentration range.

Literature: Atkinson, J. D., B. J. Murray, M. T. Woodhouse, T. F. Whale, K. J. Baustian, K. S. Carslaw, S. Dobbie, D. O’Sullivan, and T. L. Malkin (2013), The importance of

C6

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C7

Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2018-46>, 2018.

C8