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Interactive comment on "Influence of surface morphology on the immersion mode ice nucleation efficiency of hematite articles" *by* N. Hiranuma et al.

Anonymous Referee #1

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I support publication of the paper. The role that defects play in heterogeneous nucleation is an important topic, and this will be an important addition to the literature. There are, however, a few places where I believe that the authors have over-stated their case.

The title of the paper suggests that it is a change in the morphology of the particles which drives the changes in the efficiency of those particles in the immersion mode. In the body of the paper, reference is made to more abundant "steps and cracks" in the milled hematite particles (see e.g. pg 23768, line 28; pg. 23770, line 11), but that is never quantified. How do you know that the cracks and steps are more abundant? The particle size distributions do show that there are smaller particles present when the hematite is milled, but that does not prove that there are more cracks and steps in those smaller particles.

The paper presents convincing evidence that electrical effects play a role in immersion mode heterogeneous nucleation; there's also evidence that breaking the original hematite particles led to the change in the electric fields, but the argument linking that to specific morphological changes is missing. This is the major point the authors should address.

Temperature range. Section 2.2 indicates that tests were run in the temperature range -28 to -39 C, yet results are presented only for the range -35.2 $<$ T $<$ -33.5 C. Why are results for only 15% of the range included?

I notice there is a statement on page 23769 (lines 15-16) which indicates that time intervals in which the crystal concentration was below the WELAS limit were excluded. Does that explain this? Is hematite only active once $T < -33.5$ C?

Examining figure 3, I would have expected a wider temperature range for the milled hematite. At -34 C, n_s for the milled particles is still greater than n_s for unmilled particles at -35 C. Why not show the data for the milled hematite down to the detection limit, which, judging from the slope of n_s, would be for a temperature of -25 or even higher.

The data, as it is shown in Figure 3, spans only $\sim$ 1.5 C. That's quite a small range of temperatures. I understand that -35 C is about as cold as you can go without significant interference from homogeneous freezing. It seems reasonable to me that the lower limit, set by the detection limit of ice in the chamber, is only 1.5 C higher than that for the unmilled hematite. However, as stated above, the data suggests that the milled hematite should be above the detection limit for a much wider range of temperatures than is shown in the figure. If you have the data, show it, even if the only comparison you can make with the milled hematite is that unmilled particles were below the detection limit. (That, in and of itself, is a significant finding in my opinion.)

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Morphology vs. electrical effects. As noted above, I think the authors have presented convincing evidence that electrical effects play a role in immersion mode ice nucleation and that milling led to those electrical effects. The authors have not presented evidence that morphology, specifically steps and cracks, played a significant role. Steps, cracks and other defects are not quantified.

The surface areas are quantified, but a larger surface area doesn't necessarily mean more defects. As the authors point out, the smaller particle sizes for the milled hematite will result in larger surface areas. That said, the last sentence on pg. 23776, which continues on the following page, is puzzling. How can the cubic hematite have a larger surface area (578.2 μm^2 cm^{-3}) than the milled hematite (143.0 μm^2 cm^{-3}). Please clarify this point. (The BET surface areas are more consistent with what I would expect from the unmilled and milled samples.)

On page 23768, lines 6-8, the authors state "To conclude, a distinct difference in the surface chemical properties of milled and cubic hematite was found and ice might have nucleated at the deprotonated active sites on the surface of milled hematite particles." That statement undercuts the argument that it is the morphology that is driving the changes.

On page 23768, lines 25-28, the authors state "The observed differences may be attributed to the role of various surface features, such as BET measured surface area (a factor of two higher $A_{total,BET}$ of milled samples than that of cubic ones), highly chargeable components on milled surface, and active sites (cracks and steps)." I don't think you can attribute the difference in the activity of the milled and unmilled samples to the difference in surface areas because n_s already accounts for that, $n_s = \frac{N_{ice}}{A_{aerosol,total}}$. The authors state in the next sentence that the difference in the surface area seems to not play a significant role anyway. I think the argument is as follows:

- The number of active sites for the milled hematite increased by more than the a simple increase in the surface area (geometric or BET) would predict

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- Therefore, the milling introduced some other factor, which led to an increase in the number of active sites over and above what a simple increase in surface area would have produced.

If this is, indeed, the argument, I think it could be presented more clearly in the paper.

Minor points.

It isn't clear to me what the modeling results add to the paper. I am not suggesting that they be removed, but perhaps the authors could elaborate on this point. On page 23770, they state "We also note that the model application in this study only demonstrates the effect of using different INAS densities for a given aerosol population on the ice crystal number concentration." Didn't the AIDA results show that? The simulation shows that ice crystal number was, on average, about an order of magnitude higher when the simulation was run with the milled hematite case. This is what you would expect from the experiments. Given the very limited temperature range of the experiments, I don't see what the simulation adds to our understanding.

Pg. 23759, reference to Pruppacher and Klett, 1997: That's a 954 page book. Please, at least reference a chapter. A page or page range would be even better.

Pg. 23760, line 7: "helps" should be "help".

Pg. 23763, lines 15,16: "At droplet- or ice-activation in the AIDA, quick response in intensities can be observed." This is an awkward sentence. Do you mean that a quick response in the intensities is observed?

Pg. 23764, line 1: "ADIA" should be "AIDA"

Pg. 23769, line 10: "...minor contributions of deposition mode ice crystals (up to 27% ..." 27% is not minor. Perhaps, simply replace "minor" with "the".

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