Response to Reviewers' Comments

The authors wish to thank both reviewers for their thoughtful comments and useful discussions. Below are our point-by-point responses to each of the reviewers' comments.

Reviewer #1

Reviewer's comment:

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.

Authors' response:

We thank the referee for raising this important point. We agree that there are no direct measurements of abundance of surface defects as simple subdivision of the cubes in smaller parts can produce the same result. Observed BET [Brunauer, Emmett and Teller N_2-absorption technique (Brunauer et al., 1938)] surface enhancement only implies the presence of freshly introduced surface and edges by milling (i.e., new sentence in P23767 L4). But we believe that BET N_2-adsorption technique reflects the most direct measurement of bulk surface area per given mass (i.e., specific surface), and higher specific surface of milled hematite particles are related to the formation of freshly exposed surfaces and presumably also localized features (e.g., edges).

The statements in the following sections have now been rephrased to clarify this point:

P23761 L12 – "To assess the effect of surface milling, we used the Brunauer, Emmett and Teller (BET) N_2-absorption technique (Brunauer et al., 1938) and measured the bulk surface area per given mass (i.e., specific surface area, S_{BET}, $m^2\ g^{-1}$) of both cubic and milled hematite particles. The BET technique reflects the most direct measurement of bulk surface area that is analogous to the ratio of surface area per given mass. A higher specific surface area of the milled hematite particles is indicative of the freshly introduced surfaces and presumably also localized features (e.g., edges)."

P23765 L2 – "(g cm^{-3})" → "($M_{total,geo}$ in g cm^{-3})"

P23765 L3 – "($m^2\ g^{-1}$)" → "[i.e., $n_{s,BET} = N_{ice}/(M_{total,geo} \times S_{BET}) = N_{ice}/A_{total,BET}$]"

P23767 L3 – "BET surface areas" → "BET surface areas (S_{BET})"

P23767 L4 – For clarity, we have added the following sentence:

"Higher specific surface per unit mass of milled hematite particles are related to the increase of freshly exposed surface, edges and perhaps localized defects (e.g., cracks and steps)."

Reviewer's comment:
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.

Authors' response:
Changes in surface properties due to milling are inherently related. We did not test the influence of ONLY one characteristic while keeping other properties constant. We have now clarified the details in:

P23768 L25 to P23769 L6 – "The observed differences may be attributed to the role of various surface features as a result of milling, such as increased BET measured surface area, higher charge density associated with the presence of different functional groups on milled surface, increased active site densities due to newly exposed surface and edges or any combinations. It is noteworthy that we did not examine the influence of one characteristic individually while keeping the other surface properties constant. However, the importance of surface area increase seems not to be significant, as it can only be responsible for a factor of two higher n_s of the milled samples when compared to that of cubic particles, even though we observed an increase in n_s of about an order of magnitude (Fig. 3). Therefore, other surface properties that were altered as a result of milling are presumably responsible for the enhanced ice nucleation efficiency inferred by n_s. Nevertheless, milled hematite has the same crystal structure as cubic hematite and, thus, our data show that a simple mechanical modification can increase n_s by an order magnitude."

Reviewer's comment:
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?

Authors' response:
The expansion measurements were carried out from an initial AIDA gas T at −28 ˚C to the point homogeneous ice nucleation kicked in (T < -35.2 ˚C), but "droplet-freezing" was observed only at T range -35.2 < T < -33.5 C.

Reviewer's comment:
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?

Authors' response:
The WELAS detection limit ($< 0.1 \text{cm}^{-3}$) was needed to remove the outlier data due to fluctuation. In addition, we also attempted to start the expansion experiments form higher

AIDA gas temperature (as high as -19 ˚C), but we gained no evidence of droplet-freezing (with cubic hematite) at T > -33 ˚C beyond the detection limit of our WELAS-OPC.

Reviewer's comment:
Examining figure 3, I would have expected a wider temperature range for the milled hematite. At -34 C, ns for the milled particles is still greater than ns 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 ns, would be for a temperature of -25 or even higher. The data, as it is shown in Figure 3, spans only ~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.)

Authors' response:
Agree. For milled hematite, we would presumably expect to observe the immersion freezing at higher T if the expansion experiment was conducted at higher initial T. However, no experiment at higher start T was conducted for milled hematite.

Additionally, in our controlled AIDA experimental conditions (i.e., starting expansion cooling from -28 ˚C), we routinely found the full droplet activation (i.e., droplet number = aerosol number, assuming one drop forms per aerosol particle) at T $\leq$ -33.5 ˚C, which immediately exerted droplet freezing (i.e., Figure S1 and S2 - based on our depolarization-, water vapor- and optical measurements). Since our focus is on the immersion mode nucleation (droplet-freezing) of hematite particles and we assume that particles are individually immersed in droplets (Connolly et al., 2009), we need to set -33.5 ˚C as the lower bound for corrective evaluation of droplet-freezing. Further, we observed the contribution of deposition mode freezing at T > -33.5 ˚C, so the droplet-freezing was only dominant heterogeneous ice nucleation pathway for −35.2 ˚C < T < −33.5 ˚C. As stated in our text, the contribution of deposition mode freezing at T > -33.5 ˚C (t $\leq$ 120 seconds after initial cooling started, i.e., Figure S1 and S2) is excluded from our evaluation. This exclusion is valid because no saturation depletion was observed after full droplet formation until T < -35.2 ˚C, verifying that droplet-freezing was the dominant heterogeneous ice nucleation pathway for −35.2 ˚C < T < −33.5 ˚C.

Thus, n_s data for milled hematite particles at T > -33.5 ˚C cannot be presented. Now the following sentence has been rephrased to clarify this point:
P23769 L8 to 9 – "before the spontaneous formation of droplets" now reads, "before the full water droplet activation at -33.5 ˚C"

P23769 L16 – For further clarity, we have now added the following sentence:

"Thus, we evaluated the droplet-freezing efficiency of hematite particles within the limited temperature range of -35.2 ˚C < T <-33.5 ˚C."

Reviewer's comment:
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.

Authors' response:
Correct. Changes in surface properties are inherently related (i.e., P23768 L25).

Reviewer's comment:
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 Atotal,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 ns already accounts for that, ns = Nice / Aaerosol,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
- 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.

Authors' response:
This is a very good suggestion. We totally agree. What we observed is that a simple mechanical modification could OVERALL cause a ten-fold increase of n_s density. The importance of surface area enhancement seems not to be significant because factor 2 enhancement of surface area indeed does not lead to a factor of 10 increases in n_s. We now explicitly clarified these points in text:

P23768 L25 to P23769 L6 – "The observed differences may be attributed to the role of various surface features as a result of milling, such as increased BET measured surface area, higher charge density associated with the presence of different functional groups on milled surface, increased active site densities due to newly exposed surface and edges or any combinations. It is noteworthy that we did not examine the influence of one characteristic individually while keeping the other surface properties constant. However, the importance of surface area increase seems not to be significant, as it can only be responsible for a factor of two higher n_s of the milled samples when compared to that of cubic particles, even though we observed an increase in n_s of about an order of magnitude (Fig. 3). Therefore, other surface properties that were altered as a result of milling are presumably responsible for the enhanced ice nucleation efficiency inferred by n_s. Nevertheless, milled hematite has the same crystal structure as cubic hematite and, thus, our data show that a simple mechanical modification can increase n_s by an order magnitude."

Reviewer's comment:
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.

Authors' response:
Correct. We did not do intend to directly quantify abundance of defects per surface. As discussed above, observed BET surface enhancement only implies the effect of milling, introducing fresh edges and perhaps defects opening up additional surfaces (i.e., new sentence in P23767 L4).

Reviewer's comment:
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. 23766, which continues on the following page, is puzzling. How can the cubic hematite have a larger surface area (578.2 µm2 cm−3) than the milled hematite (143.0 µm2 cm−3). Please clarify this point. (The BET surface areas are more consistent with what I would expect from the unmilled and milled samples.)

Authors' response:
The BET "specific surface" is analogous to the ratio of the surface area per given mass as we rephrase in P23761 L12 (discussed above). These reported values (milled: 143.0 $\mu m^2\ cm^{-3}$ & cubic: 578.2 $\mu m^2\ cm^{-3}$) correspond to the APS measured total "surface concentrations" in the AIDA chamber. Note that the number concentrations of milled hematite (70.8 cm^{-3}) and cubic one (171.9 cm^{-3}) were different in two expansion experiments, though this difference had no influence on evaluating IN efficiency (n_s).

Reviewer's comment:
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.

Authors' response:
Agree. But, as discussed in above (i.e., P23768 L25 to P23769 L6), the n_s difference is originally caused by the modification of morphology due to milling. It is therefore the morphology is responsible for enhanced IN efficiency.

P 23768 L 6 – The statements have now been rephrased to clarify this point:

"To conclude, a distinct difference in the surface chemical properties of milled and cubic hematite particles was found and ice might have nucleated at the active sites, which may coincide with higher charge density on milled hematite particles."

Minor points.
1.Reviewer's comment:
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.

Authors' response:
The model study was motivated by the experimental result to check the response of the model to the change in ice nucleation efficiency. In specific, apart from ice nucleation, our modeling simulation considers complex ice microphysical processes such as vapor deposition, sublimation, melting, sedimentation, self-collection, auto-conversion, accretion and riming, which were not examined in AIDA experiments. Our model also incorporates with temporal evolution of mass and number densities of 4 hydrometeor classes [i.e., cloud droplets, ice crystals, raindrops and snow (the last two are non-advective classes)]. Our results show that even though the ice nucleation rate differs only in a small temperature range for the two types of dust particles, it has an important impact on the simulated ice number and mass concentrations from 200 hPa to 700 hPa. We have emphasized these points in the following sections:

P23770 L25 – We have now added the following sentences:
"Apart from ice nucleation, our model simulations consider complex ice microphysical processes as well as temporal evolution of mass and number densities of four hydrometeor classes (i.e., cloud droplets, ice crystals, raindrops and snow). Our results show that even though the ice nucleation efficiency differs only in a small temperature range for the two types of hematite particles, it has an important impact on the simulated ice number and mass concentrations from 200 hPa to 700 hPa. Hence, the response of the model to the change in ice nucleation efficiency was successfully demonstrated."

P23769 L18 to 19 – The text now reads:
"Figure 4 shows the simulated time evaluation of ice crystal number concentration and ice water content. Likewise, the simulated monthly mean vertical profiles over the same region are shown in Figure 5."

P23770 L17 – "not shown" → "Figure 4B and 5B"

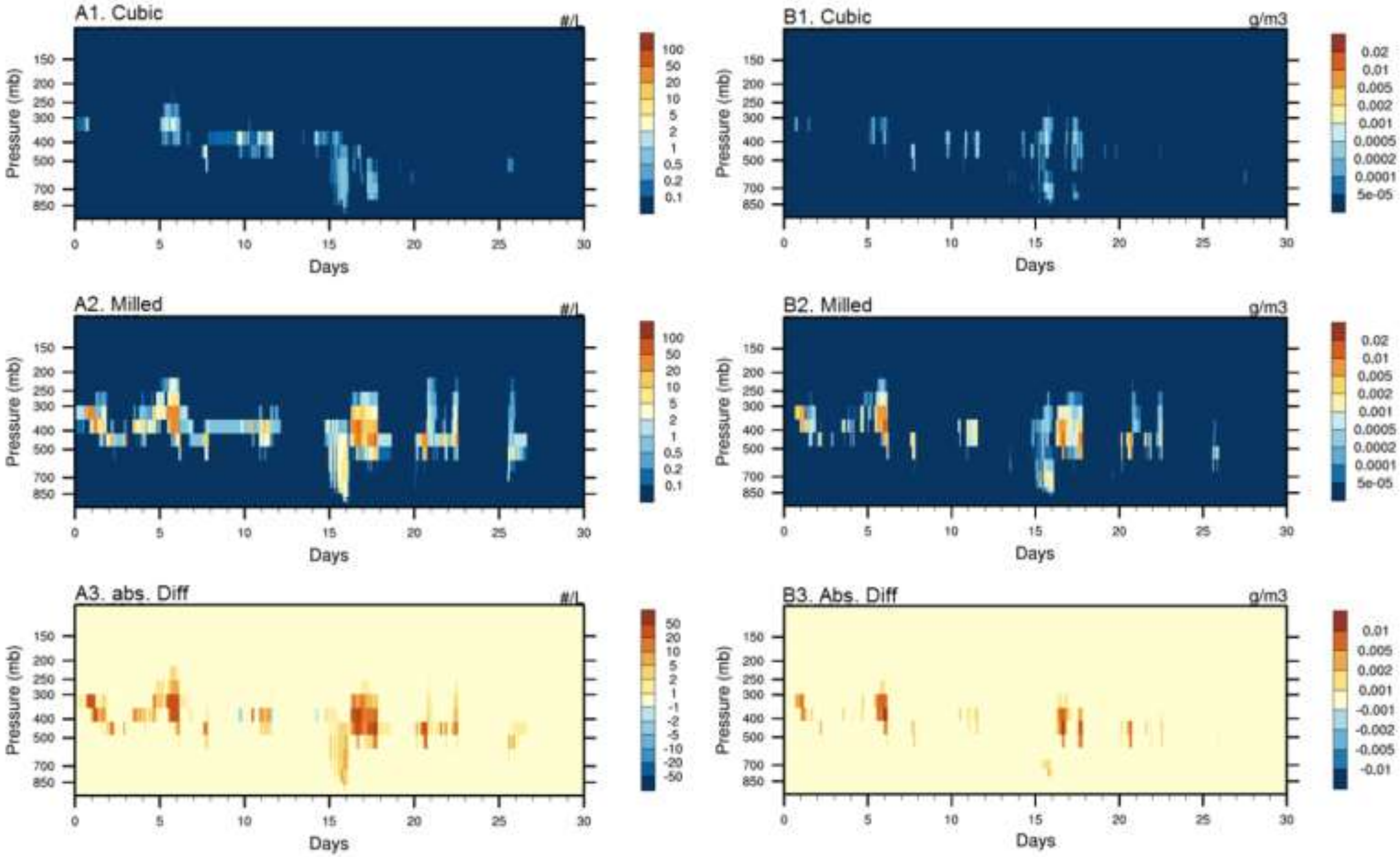

Figure 4. Simulated time evolution of (A) ice crystal number concentration (color-scaled in L^{-1}) and (B) mass mixing ratio of cloud ice (color-scaled in g m^{-3}) over the ARM-SGP site in April 2010. Top panel shows the result of simulation with cubic hematite particles and middle panel shows that of the milled hematite particles. Bottom panel shows the absolute difference between these two simulations.

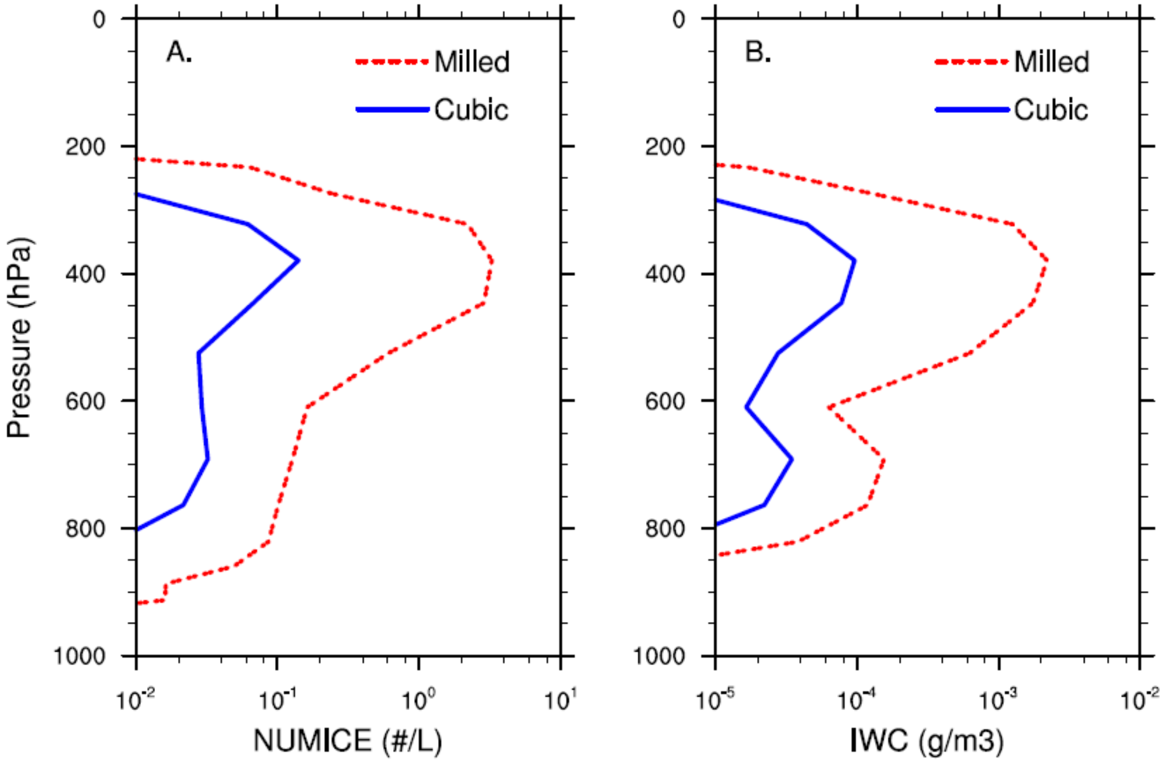

Figure 5. Simulated monthly mean vertical profile of (A) ice crystal number concentration (L^{-1}) and (B) ice water content ($g\ m^{-3}$) over the ARM-SGP site in April 2010.

2. Reviewer’s comment:
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.

Authors’ response:
Chapter number and relevant page numbers have now been added.

P23759 L6 – “Pruppacher and Klett, 1997” → “Chapter 9 of Pruppacher and Klett, 1997”

P23776 L1 – “Pruppacher, H.R....“ → “Pruppacher, H.R. and Klett, J.D.: Microphysics of Clouds and Precipitation, Atmospheric and Oceanographic Sciences Library, Kluwer Academic Publishers, Dordrecht, The Netherlands, 309-360, 1997.”

3. Reviewer’s comment:
Pg. 23760, line 7: ”helps” should be ”help”.

Authors’ response:
Corrected.

4. Reviewer’s comment:
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?

Authors’ response:
Yes. Thank you. Now the sentence reads:
“At droplet- or ice-activation in the AIDA, a quick response in the intensities is observed.”

5. Reviewer’s comment:
Pg. 23764, line 1: ”ADIA” should be ”AIDA”

Authors’ response:
Corrected.

6. Reviewer’s comment:
Pg. 23769, line 10: ”...minor contributions of deposition mode ice crystals (up to 27%...” 27% is not minor. Perhaps, simply replace ”minor” with ”the”.

Authors’ response:
We agreed and the sentence has now been rephrased:
“…, the contributions…”

Reviewer #2

Reviewer's comment:

1. The aerosol surface areas are measured in the AIDA chamber by APS only. APS instruments can have problems measuring surface areas for small particles. Are the authors confident that there is not significant aerosol surface area, at small particle sizes, present in the milled particle experiments that is not being captured by the APS? Were SMPS measurements also performed?

Authors' response:

Yes. SMPS measurements were simultaneously carried out during APS measurements prior to each expansion experiment. Beyond the lower bounds of APS size limit (0.24 µm and 0.26 µm for cubic and milled, respectively), negligible contribution of SMPS counts to total surface areas were measured (<2.3%). Thus, SMPS measurements were neglected.

Reviewer's comment:

2. Just a small amount of chemical contamination could significantly affect the results. How did the authors confirm that chemical contamination of the milled samples did not occur when milling was conducted? For example, did any material from the bronze beads become attached to the hematite particles? Could the EDX results (mentioned in the Abstract) be explicitly described in more detail in the paper? What limit of detection do they have? How strong is the belief that the hematite particles are of the same composition milled and unmilled?

Authors' response:

We conducted EDX measurements to identify the elemental composition of individual particles in both hematite subsets (over 80 particles). To minimize background noise, we employed high magnifications and looked over 100 nm x 100 nm area per particle. EDX measurements did not indicate any statistically significant difference of particle compositions. For clarity, we now report our statistical confidence limit in the relevant sentence.

P23766 L21 – "identical" has now been rephrased to "statistically similar at the 90% confidence limit"

Reviewer's comment:

3. Although it is likely that surfaces of the milled particles are roughly at a microscopic level, there is no direct evidence in the paper to support this. Very high spatial resolution electron microscope images of these scratches/pits/edges would have made the paper much stronger.

Authors' response:

Agree – high resolution microscopy images can be used for qualitative spot analysis. But overall defects in bulk population cannot be qualitatively characterized with a snapshot picture of few particles. For our n_s application, we believe that the increase in N_2 adsorption-based specific surface area of milled hematite particles is more direct indicative of the presence of newly exposed surface and edges (as a result of milling) over bulk quantities. Thus, we believe making this type of measurement is beyond the scope of our study. The following sentence has been rephrased to provide additional insight:

P23768 L25 to P23769 L6 – "The observed differences may be attributed to the role of various surface features as a result of milling, such as increased BET measured surface area, higher charge density associated with the presence of different functional groups on milled surface, increased active site densities due to newly exposed surface and edges or any combinations. It is noteworthy that we did not examine the influence of one characteristic individually while keeping the other surface properties constant. However, the importance of surface area increase seems not to be significant, as it can only be responsible for a factor of two higher n_s of the milled samples when compared to that of cubic particles, even though we observed an increase in n_s of about an order of magnitude (Fig. 3). Therefore, other surface properties that were altered as a result of milling are presumably responsible for the enhanced ice nucleation efficiency inferred by n_s. Nevertheless, milled hematite has the same crystal structure as cubic hematite and, thus, our data show that a simple mechanical modification can increase n_s by an order magnitude."

Reviewer's comment:
4. I don't see strong justification for including the atmospheric modeling. It does not present major surprises, given the laboratory results that feed it.

Authors' response:
Please see our response to minor comment 1 from reviewer 1 above.

Reviewer's comment:
5. Page 23761, line 8. What is meant by "aged"?

Authors' response:
Following the method described in Sugimoto and Sakata (1992), $Fe(OH)_3$ solution was kept in 100 ˚C oven dryer for 8 days and "aged" for the flux growth of hematite prior to freeze-drying process.

Additional authors' note to reviewers and editor

Authors' note:

1. In our modeling simulation, we assume the ice nucleation can happen only when cloud droplets exist. In the previous simulation, we used the predicted droplet number as a limit. However, after a closer check, we found that the simulated minimum droplet number concentration was always higher than the threshold value, so using the droplet number as a limit was not feasible. Therefore, in the new simulation, we now use the mass mixing ratio of cloud liquid (~10^{-8} kg-cloud liquid/kg-air) as a limit.

P23765 L27 – After "…mixed phase clouds.", we have now added the following statement to clarify the limit:
"We also limited the droplet-freezing in our simulations below the mass mixing ratio of cloud liquid of 10^{-8} kg-cloud liquid/kg-air."

Authors' note:

2. Though an evidence of surface active sites on macroscopic surface where ice preferentially and repeatedly form is presented in Fig. 4 of Anderson and Hallett, Journal of the Atmospheric Sciences, 33, 822-, 1976, there are no direct measurements of ice nucleation on an ice nucleating particle-surface. Concerning this issue, we have now added the following sentence:

P23764 L24 – After "...Niemand et al., 2012).", the next sentence reads:
"One caveat is that a uniform distribution of active sites over the given particle surface area is assumed, since there has been no direct measurement of ice nucleation at a particular site on the particle surface."

Authors' note:

3. In Acknowledgement, we have added the following statement:
P23773 L9 – "We also wish to thank P. Alpert and D. Knopf for useful discussions."

Authors' note:

4. In Acknowledgement, the statement of "The service charges…Association." has now been carefully rephrased as "We acknowledge support by Deutsche Forschungsgemeinschaft and Open Access Publishing Fund of Karlsruhe Institute of Technology."

Authors' note:

5. For clarity and additional insight, we have rephrased the following texts:
P23770 L12 – "cracks and steps" → "edges, cracks and steps"

P23760 L1 – "defects" → "irregularities"

Supplemental Material L54 to L56 – "was quantitatively minor and did not" → "was too small to"

Supplemental Material L63 – "at" → "initiated around"

Typo

Title: “articles” → “particles”

Supplement title: “Hematite” → “Hematite Particles”

Supplemental Material L29 – “Hematite” → “Hematite Particles”

Supplemental Material L36 – “addition” → “adding”

Table S1 caption: “miled” → “milled”