

Interactive comment on “Surface charge-induced orientation of interfacial water suppresses heterogeneous ice nucleation on α -alumina (0001)” by Ahmed Abdelmonem et al.

Anonymous Referee #3

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The authors shed light on some of the underlying mechanisms of heterogeneous nucleation of ice, and for that reason alone I am in favor of publication. I have outlined a few points below which the authors may wish to consider.

One substantial improvement to the paper would be to note the water activity for the various solutions used. While the emphasis is on pH and the resulting charge at the surface, noting a_w would enable comparison with freezing point depressions as outlined in Koop et al. (2000). The statement on pg. 5, line 15 that the measured freezing temperature on Si wafers was the same for all pH solutions suggests that the water activity was very near 1 for all the solutions, but this should be confirmed.

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The principal conclusion that I draw from this paper is that surfaces can overtemplate water. This has been known for a long time. The authors cite Fletcher's paper from 1959, where he shows that increasing the order of water molecule's in a pre-critical embryo too much can actually decrease the probability of freezing. Fletcher showed that there is an appreciable entropic penalty for nucleation on the basal plane of silver iodide because it is polar. In contrast, the penalty for nucleation on a prism face is negligible. The prism face of silver iodide still acts as a template for the ice embryo, but the degree of alignment for the water dipoles is mitigated because ions of both signs are exposed. For this reason, I think the conclusion (page 9, lines 7-8) which reads "Apparently, charge-induced surface templating is detrimental for ice nucleation, regardless of the sign of the surface charge." should be softened. That statement may be true for this system, over this range of conditions, but I do not think it is appropriate to state it generally. (I concede that when taken together with the sentence just before that, this applies to corundum. Perhaps just add "on this surface" right after "ice nucleation" to reinforce the point.)

The conclusions in this paper suggest that for any pH other than 7, that the critical ice embryo forms in the second or third layer of molecules away from the surface. If the water molecules right at the surface are too tightly bound and/or constricted to allow them to adopt the ice lattice, doesn't that imply that other water molecules are the ones actually forming the embryo? It seems most likely that it would be water molecules that were affected by the ordering imposed by the surface, but were perhaps still free to rotate and/or translate enough to adopt the ice lattice. Is there any indication of this in the data? (To be clear, I am not asking for an exhaustive re-analysis of the data. I am simply curious as to whether a signature like this could be gleaned from this data.)

Pg. 2, lines 13-14: "The real influence of temperature and supersaturation on the interaction between water molecules and dust particle surface has not yet been explored." This is an overstatement. This has been extensively investigated. We don't have a

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definitive answer yet, but there are plenty of groups that have asked the question and contributed pieces to the puzzle.

References

Koop, T., Luo, B., Tsias, A., Peter, T., 2000. Water activity as the determinant for homogeneous ice nucleation in aqueous solutions. *Nature* **406**, 611–614. doi:10.1038/35020537

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