

Reviewer comments in bold and authors' response in regular typeface.

This study is a laboratory experiment measuring the ice-nucleating properties of mineral dusts coated with SOA, as determined by 3 separate types of instruments, the PINC, CFDCs, and the AIDA cloud chamber. The experiments appear to be well designed and meticulously carried out, and the redundancy of multiple ice nucleation instruments, while not necessary, strengthens one's confidence in the results. There are some differences between the analyses of data from the separate instruments, and also the interpretation of these results in light of previous work which require further clarifications, as discussed below. Once resolved, this paper will make a good contribution to the literature.

The topic of deactivation of ice nucleation activity by coatings has been reported in a number of previous manuscripts. The main conclusion from this paper is that SOA-type coatings do not deactivate the INP activity of 2 types of representative mineral dusts. This is opposite to the previous conclusions of many papers that report that deactivation does occur. However, this study is specific to measurements in the mixed phase cloud regime.

The authors thank the reviewer for their comments

Major Comments:

1. The most interesting question in the manuscript is WHY does deactivation occur in some studies and not this one? My major comment is that this question warrants more attention and more organized discussion than is included in the current manuscript. References are made to other studies here and there throughout the text, but these are not summarized or reported in the context of all other studies making it difficult to draw any overarching conclusions. A systematic analysis or at least discussion of what does and does not lead to activation is needed.

This is a valid question. We have now extended the introduction to discuss deactivation ([see page 3 line 1 to page 4 line 14](#)) of INPs due to coatings. We discuss the differences in coating composition, aerosol substrate type and ice nucleation regime (deposition vs. immersion). Furthermore we discuss our results in this context in section 3.2 specifically [page 12 line 18-22](#), [page 13 line 3-13](#), and [page 14 line 30 to page 15 line 2](#).

To answer the reviewer's question: The distinction between this study and previous ones that have reported deactivation has been the mode of ice nucleation and the composition of coating. For a study where deactivation of dust particles was observed due to the same type of coating as used here (Möhler et al., 2008), the mode of ice nucleation was different (deposition mode) vs immersion mode in this work, as was the temperature regime.

Previous studies have observed a reduction in ice nucleation activity in the immersion mode but to a lesser degree than in deposition mode, unlike the conclusion we draw here. These studies used H₂SO₄ for coating which was capable of modifying and irreversibly changing the surface of the mineral dust particles used (Sullivan et al., 2010b) and producing new reaction products on the surface (Sihvonen et al., 2014). On the other hand, coatings of levoglucosan on kaolinite particles also showed no effect on the ice nucleation activities in the immersion mode (Tobo et al., 2012). As such, the fact that we observe no deactivation of the INPs in the immersion mode in this work, is in agreement with previously reported literature. Coatings can either react and chemically change the ice nucleating surface as has been observed with inorganic acid coatings, or block access of water vapour to active sites in deposition mode, which then become exposed with the

coating is solvated in the immersion mode. This has been observed for dust particles coated with HNO_3 (Sullivan et al., 2010a; Kulkarni et al., 2015) which did not impede immersion mode freezing, similar to our results here. This aspect is discussed in the revised manuscript on [page 14 line 2-17, page 14 line 30 to page 15 line 2](#).

A. A thorough discussion on the thicknesses of coating here compared to those in papers which did observe deactivation would greatly strengthen this paper. (Of course, such a discussion is dependent on availability of coating thickness (or aerosol mass/density W changes such as those obtainable with a particle mass analyzer (PAM)) observations.

We do not have PAM (or CPMA) measurements from the measurement period, however coating thicknesses were calculated using SOA yields and the surface area of aerosol in the chamber at the time of in-situ coating ([see section 2.1 page 7 line 28 to page 7 line 8](#)).

We have extended the discussion on coating thickness, and included new plots to demonstrate the lack of effect of coating thickness on the *INAS* densities (see Figure 6). The comparison of coating thickness in this work to that in the published literature is presented in section 3.2 specifically on [page 12 line 18-22, page 12 line 36 to page 13 lines 13](#).

The manuscript does conclude that no effect of coating thickness was observed over the range of 3-60 nm. However, it is possible that other studies were conducted on even thicker coatings. Is this known?

This is a good point. The studies we compared our work to in the immersion mode, all have thinner coatings than the maximum reported in this work (60 nm). In particular for the studies that reported a partial or complete deactivation in the immersion mode freezing of dust particles due to coatings of H_2SO_4 (Sullivan et al., 2010b; Tobo et al., 2012; Augustin-Bauditz et al., 2014) looked at coating thicknesses between 1-15 nm. In particular Augustin-Bauditz et al. (2014) saw an influence on immersion mode activity with the thicker H_2SO_4 coating (15 nm) resulting in lower frozen fractions than feldspar with thinner H_2SO_4 coating (3 nm). Previous to this, Sullivan et al. (2010b) also found significant lowering of the *AF* in the immersion mode when coating thickness increased progressively from 1, 2.4 and 4.1 nm with the *AF* for the latter coating thickness being at the edge of the limit of quantification of the *AF*. On the other hand, studies that did not observe an effect of coating also do not report an effect of coating thickness. For example Kulkarni et al. (2014) report no effect of 1 and 40 nm thick H_2SO_4 coating on a variety of mineral dust particles in the immersion mode.

We note that the coatings discussed in the studies above are produced by transiting particles through heated vapour regions of the coating substance. As such thicker coatings are associated with higher processing temperature which could have an effect on the ice nucleation activity by enhancing reactions between the coating and the substrate particles. Sullivan et al. (2010b), showed that passing H_2SO_4 coated ATD particles through a 250 °C thermodenuder further reduces their ice nucleation activity compared to particles with the same coating thickness bypassing the thermodenuder.

We already discuss the coating thickness for the same type of SOA used here on illite and ATD particles from another study (Möhler et al., 2008) on [page 14 lines 28-30](#). We now expand on this

by discussing the effect of coating thickness as described above (see section 3.2, page 12 line 18-22, page 12 line 26 to page 13 lines 13).

B. The multiple measurements (PINC, CFDC, AIDA) are in general agreement, which suggests that the reported fractions frozen and ice nucleation active site densities are relatively accurate. It follows that the reasons that deactivation of INP efficiency was not observed is related to sample generation.

This could be true, however, other important considerations should be noted. The regime of ice nucleation (deposition vs. immersion), or the physical and chemical properties of the coating itself, how reactive it is or is not with the dust surfaces. Prompted by the reviewer comments, we have discussed this in the introduction of the revised manuscript (see page 3 line 1 to page 4 line 14). Furthermore, we have discussed and now elaborated in section 3.2 on the role of sample generation (page 13 line 20-22, page 14 line 7-11), coating type and ice nucleation regime (page 14 line 5 – 7, page 14 line 19 to page 15 line 2).

Are the substrate aerosols similar in size distributions to previous measurements? How does coating method compare to previous studies?

Size of particles used in this study are predominantly in the submicron size range similar to or overlapping the range (250 – 700 nm) of those reported in previous literature and the studies we compare to in the manuscript. The coating method used here conducted at room temperature and dry conditions, differs from other methods that use heating followed by condensation. The use of heat for coating is now discussed on page 13 lines 13-18.

C. It may well be that some aerosols are more receptive to coatings than others, for either chemical or physical reasons. Chemically, acidity will vary with atmospheric coating compositions. Also, the sticking coefficient on a Teflon aerosol (for example) would be much lower than dust (note that this would not explain why the dust doesn't deactivate). Physically, it is possibly that highly irregular shaped particles and/or highly porous particles may be more difficult to coat and therefore less likely to deactivate as INP.

We agree with the reviewer that we could have incomplete coatings of our particles. The difficulty in achieving complete coatings and thus the lack of deactivation observed is acknowledged on page 13 line 20 and page 14 line 7. Given our coating procedure of producing excess amounts of SOA as is evident from the nucleation mode of aerosol produced, we expect that the coatings should be complete, but cannot rule out the possibility of incomplete coatings. Additionally we clarify that difficulty in achieving complete coatings can arise from the use of natural dust samples, which are expected to exhibit porous features and irregular shapes (see page 13 lines 20-21).

D. Are there any other reports of coatings NOT activating mineral dust INP?

We believe by stating “..coatings NOT activating mineral dust INP” the reviewer means “coatings not deactivating mineral dust”? If that is the case, then we have referred to such studies extensively in the introduction (specifically page 3 line 1 to page 4 line 14), and we now discuss both circumstances of coatings impeding and not impeding ice nucleation in section 3.1 (page 11 lines 7-18). Furthermore, we discuss other instances of coatings not deactivating ice nucleating particles in comparison to our results in section 3.2 page 13 lines 3-18 and the reasons with regard to the mode of ice nucleation and potential surface modification of the INP on page 14 line 30 to page 15 line 2. There are numerous reports of H₂SO₄ coatings not (fully) deactivating mineral dust in

the immersion mode, or reactive uptake of HNO₃ not deactivating immersion freezing of mineral dust at all. However, these studies often found that the deposition mode was deactivated for the same processes/coated aerosol. This points to a key difference between how the deposition and immersion modes respond to coatings and particle processing for mineral dust particles, as we discuss on [page 3 line 1 to page 4 line 14](#), and in response to your question below.

E. Might deactivation of heterogeneous nucleation occur only for certain ice nucleation mechanisms not explored here? That too, would be interesting. For example, Sullivan (2010) observed very different effects of coating for super and subsaturated conditions, as mentioned on page. 3.

This is true, the RH regime investigated can result in different effects of coating. Sullivan et al. (2010a); Sullivan et al. (2010b) observed a stronger deactivation of mineral dust in the deposition mode versus the immersion mode for H₂SO₄ coatings, and for reactive uptake of HNO₃ vapor, only the deposition mode was impeded, but immersion mode ice nucleation was not affected. Furthermore, in the water subsaturated regime (deposition mode) for the same type of SOA used here, Möhler et al. (2008) reported a suppression of ice nucleation for illite and ATD coated particles. We already discuss this in section 3.2 ([page 14 line 5-7 and line 19 to page 15 line 2](#)) but now further clarify the comparison of the ice nucleation regimes (subsaturated vs. supersaturated).

The Sullivan immersion freezing results do show deactivation, which is different than the results here. How do the temperatures of the 2 studies compare?

The temperature regime is similar, but the coating substance is different. In the subsaturated regime, complete deactivation is observed for both H₂SO₄ and HNO₃, however, in the saturated regime (immersion freezing), partial deactivation is only observed for H₂SO₄ and no deactivation for HNO₃ coated dust. We already discuss this in the manuscript on [page 3 lines 5 to 21](#) and also now include this in discussing our results in section 3.1 ([specifically page 11 lines 7-15](#)). The somewhat different strength of the response to H₂SO₄ versus HNO₃ processing may be due to the heated vapour source used for H₂SO₄ coatings, and/or different chemical reaction pathways with the mineral components accessible to HNO₃ versus H₂SO₄, as well as different solubilities of HNO₃ vs. H₂SO₄ reaction products.

The manuscript currently takes a broad brush on activation vs. deactivation (pg. 3 ln 15..." the effects of inorganic acid and organic coatings on a variety of mineral dust particles" are all reported in one lump statement. It would be interesting to more carefully consider how variations in substrate aerosol result in more/less deactivation and also how differences in coating compositions lead to different results.

The sentence being referred to by the reviewer (page 3 line 15 in original manuscript) is now on [page 3 line 1 onwards](#) in the revised manuscript) We expand on the discussion of inorganic ([page 3 lines 1 to page 4 line 13](#)) and organic coatings ([page 5 lines 4-19](#)). Not only do we discuss the effects of the coating composition on suppressing ice nucleation but we also include in our discussion: enhanced ice nucleation due to chemical treatments and the effects of the aerosol substrate and ice nucleation regime (deposition vs. immersion).

2. Pg 4 ln 28 Why does the CFDC require such a high supersaturation (105%) to simulate immersion freezing?

There are a number of reasons for this. First, the need to be well above $RH_w = 100\%$, to ensure all the aerosol particles activate into droplets in the short (~ 5 second) residence time of particles in the CFDCs. Second, the reported RH_w of 105% is only true for a defined narrow aerosol lamina within the chamber outside which the RH should be lower. Aerosol particles are drawn into the chamber sandwiched between two particle-free sheath flows in order to constrain the aerosol to the narrow lamina. However, due to non-ideal flow conditions, the aerosol layer can have a width that may extend beyond the defined region of the set point RH and can result in being exposed to a variation of up to $\pm 1-3\%$ RH_w from the set point conditions (depending on the temperature applied and the ratio of aerosol to sheath flows used). Third, if the sample width increases even more or particles escape from this defined layer which has been reported to occur (DeMott et al., 2015; Garimella et al., 2017), the sample could be exposed to even lower RH_w than the set point RH_w . As such operating at $RH_w=100\%$ would mean a fraction of particles may not be exposed to water saturated conditions, and thus exaggerating the RH_w to 105% ensures all particles are exposed to supersaturated conditions favourable for forming cloud droplets and thus freezing by immersion. We refer to this aspect on [page 5 line 22-26](#), [page 10, line 9-25](#).

Also, for reference, the PINC operating supersaturation should be reported at the same point in the text.

The sentence being referred to by the reviewer ([now page 5 line 25](#)) in the introduction section, is citing/discussing work from a previous publication and not describing the operation RH conditions in this work. The latter has now been added to the methods section for both PINC ([section 2.2, page 8 lines 4-7](#)) and CSU-CFDC ([section 2.3 page 8 line 28](#)). The sampling conditions are also discussed at the beginning of the results section on [page 10 lines 9-25](#). Lastly, the operating supersaturation of PINC and CSU-CFDC is also labelled in the figures where the data is introduced for *INAS* and *AF* (Figures 4 – 8).

Later, it is reported that the PINC's droplet survival region is at 107% ss and higher. Was 107% the ss chosen for immersion measurements?

No, the evaluation RH for the results presented here was $RH_w=105\%$, the same as the CSU-CFDC. This has now been clarified at the end of [section 2.2 page 8 lines 4-7](#).

Further, I am confused about this survival statement- if droplets only survive at 107% and wetter, then how is all the Figure 6 and Figure 7 PINC data (at 105%) obtained?

The droplet survival relative humidity defines the point at which water droplets that form in PINC and don't freeze survive the evaporation region at the end of the chamber and thus also get sampled by the detector (OPC). In the OPC, ice crystals are distinguished from unactivated aerosol particles only by size. I.e. all particles entering PINC have $d < 0.7 \mu\text{m}$ (see section 2.2). If the particles nucleate ice, these grow to larger than $3 \mu\text{m}$. As such only by detecting the number of particles in the size bins larger than $3 \mu\text{m}$, one can assess the total number of ice crystals (hence INP) without interference from unfrozen droplets. If the chamber (PINC) is operated at $RH_w \geq 107\%$, the water drops that survive would also be sampled by the OPC and have overlapping sizes with those of the ice crystals, and thus we would no longer be able to trust the OPC signal to indicate only ice. This means that $RH_w = 107\%$ is the maximum operable RH for the temperature regime presented here ($< 253 \text{ K}$). This condition does not exclude the possibility of water droplets forming inside the growth region of PINC, but it just ensures that water drops are not sampled at the exit of PINC

since we are interested only in the ice crystals at the exit of PINC. We have discussed this (and added some clarifications in the revised manuscript) on [page 8 line 1-11](#).

3. Figure 8 and text page 13: The text says there is only one outlier below the 1:1 region on the figure. I see at least 2 outliers, one PINC and one CFDC.

Indeed, there is only one outlier that does not overlap with the 1:1 line in Figure 8. The confusion for the reader may arise from the fact that we specifically refer to the region where $INAS_{(coated)} > 10^{10}$ sites m^{-2} . i.e. specifically on the y -axis. To clarify this, we now specify “ y -axis” in addition to the previously stated “ $INAS_{(coated)} > 10^{10}$ sites m^{-2} ” ([see page 15 line 15](#)).

4. pg 15. The conclusion that “observations of scatter between the 3 INP chambers can be attributed to differences in the evaluation of immersion...” appears to have been added as an afterthought. This is an important point and should be made and elaborated on earlier in the text.

We agree with the reviewer, and the evaluation of immersion freezing for CFDCs compared to other devices has been addressed and elaborated upon before the conclusions, for example at the end of the introduction section ([page 5 lines 22-28](#)) and in Section 3.0 ([page 10 lines 16-25](#)). Furthermore, we have extensively discussed the scatter between the data of the three chambers in section 3.3 ([see page 15 line 15 to page 16 line 2](#)).

Minor Comments

1. page 1 line 30. The last sentence in the abstract is grammatically incorrect. Revise.

We agree, the sentence was clunky, and have now revised it also based on Rev. 1 comments ([page 1 line 30-32](#)).

2. page 4, ln 17. “There are no other studies in the MPC regime” I had to look back to find MPC defined. It should be written out. Also, since this statement is so central to the paper, the regime should be specified here, add “...that is, over the temperature range of, and above water supersaturation range of ...”(these values are currently provided later in the manuscript.)

Since MPC is used at so many instances (> 10) in the paper, we keep the acronym in this sentence, however we do clarify with temperature and relative humidity values how we define the MPC regime ([see page 5 line 16 and line 21](#)).

2. page 15, ln 7, there is a misplaced phrase, (with T in C). Please revise sentence.

This is now corrected ([page 17 line 19](#)).

3. page 16, ln 6, “We note..” This is a run-on sentence that needs to be revised.

We have now revised this sentence extensively as it was also critiqued by Reviewer 1 ([page 18 lines 21-23](#)).

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