

We thank Anonymous Referee #2 very much for his/her comments. Below are our point-by-point responses.

Reviewer's major comment [1]:

The developed parameterisation is not able to quantify immersion freezing ice nucleation activity in a microphysical manner. Eqs. (1) and (2) provide empirical relationships between the INP concentration detected with the CSU-CFDC, temperature and particle concentration larger 0.5 μm . These relationships might be limited to their experimental conditions, but not generally valid. This limitation should be reflected in the paper.

Authors' response:

This is a good point. We do state upfront, starting with the Abstract, that developing an empirical parameterization is a part of the study. We discuss reasons for and the potential utility of this approach in the Introduction. However, to make the nature of the parameterization clear, and to frame the specific limits of its use, we change the words “simple parametric” in the abstract to say “empirical”, and we now state in the paper the specific temperature range over which data were used. Additionally, we add statement that extrapolation outside of this regime cannot be expected to be reliable.

Thus, at the end of Section 3.1 we write: *“The parameterization developed herein is strictly valid where data were available, between 238 and 252 K, and use to warmer temperatures represents pure extrapolation.”*

At the end of Section 3 we write: *“While providing confidence that both parameterizations can thus be used to describe atmospheric ice nucleation by mineral dust particles specifically in the temperature ranges for which they were developed, we note that comparison to ice formation in atmospheric clouds has yet to be examined”.*

In the first paragraph of the Conclusions section we write: *“Use of the parameterization to warmer temperatures necessarily entails extrapolation of the present results.”*

Reviewer's major comment [2]:

An experimental demonstration that CFDC experiments running above water saturation or 105% RH_w respectively, approximates immersion freezing is missing. Mainly the unknown CCN active particle fraction is an issue. E.g. Welts et al., 2014 observed only 4% CCN active particle in their CFDC experiments covering a wide temperature range and RH_w up to 110%.

Authors' response:

We add more information and a new figure to the paper in response to this point, as discussed further below. We could not find information in Welts et al. (2014) to corroborate the last statement of the reviewer. Welts et al. (2014) show details of CCN active fractions of no more than 0.04 at 100% RH_w in their Fig. 6, and they then additionally interpret the ice nucleation signals above water saturation as representing other processes such as deposition and condensation freezing nucleation. No further attempt is made to discern or interpret ice nucleation at higher water supersaturations as immersion freezing, with the immersion freezing contribution being entirely defined by results from separate/previous experiments with a different experimental device. Low CCN activation at 100% RH_w is described to result from CCN activation delays in the case of mineral dusts at lower temperatures, at least ones that do not have associated soluble material. Nevertheless, they cautiously state, "An open question that remains is to what degree and at what saturation mainly insoluble dust particles will act as CCN at low temperatures." We take a different approach. While deposition and condensation freezing processes may be possible in the water supersaturated regime, in addition to immersion freezing, no direct resolution of the existence of multiple processes in single experiments has yet been demonstrated. Welts et al. (2014) compare different experiments (ZINC versus IMCA-ZINC) to derive the apparent non-immersion freezing contribution. This mimics such subtraction and calculation methods used in earlier studies that they reference. We assume that full CCN activation and growth must occur once an elevated RH_w is reached in the CFDC. We already point out that the expression and detection of CCN activation and freezing response in a CFDC-type instrument could depend on factors that are specific to a given device. It is our expectation that a CFDC should produce CCN activation in the same manner as a CCN instrument does, albeit with limitations imposed by delivery of the aerosol lamina, the variable supersaturation profile of a flow diffusion chamber, and other chemical kinetic factors. As evidence that CCN

activation ensues well ahead of 110% RH_w and prior to the point that we infer maximum ice activation in the CSU CFDC (i.e., it is occurring already at 105%, but the full expression is not seen until higher RH_w), we now provide references and a new figure (Fig. B1) shown below. We also note that previous studies suggest no impedance of water uptake and homogeneous freezing in the CFDC, when the instrument is operated to provide sufficient growth times at low temperatures (DeMott et al., 2009; Koehler et al., 2009; Richardson, 2009; Richardson et al., 2010). Those studies already suggest up to 70% of aerosols of varied hygroscopic properties achieving appropriate water uptake to freeze as nearly dilute cloud droplets at -40°C , or as more concentrated solution droplets at lower temperatures. The Koehler et al. study is notable for demonstrating the varied RH_w for which full freezing ensues in dependence on the water uptake properties of particles. We add here results of two more RH_w scans from the ICIS-2007 studies conducted for desert dust particles at a slightly warmer temperature for which there was only very little freezing observed and for which RH_w was raised to much higher values. These experiments were not otherwise used for the parameterization development in the paper. The new figure and caption are here:

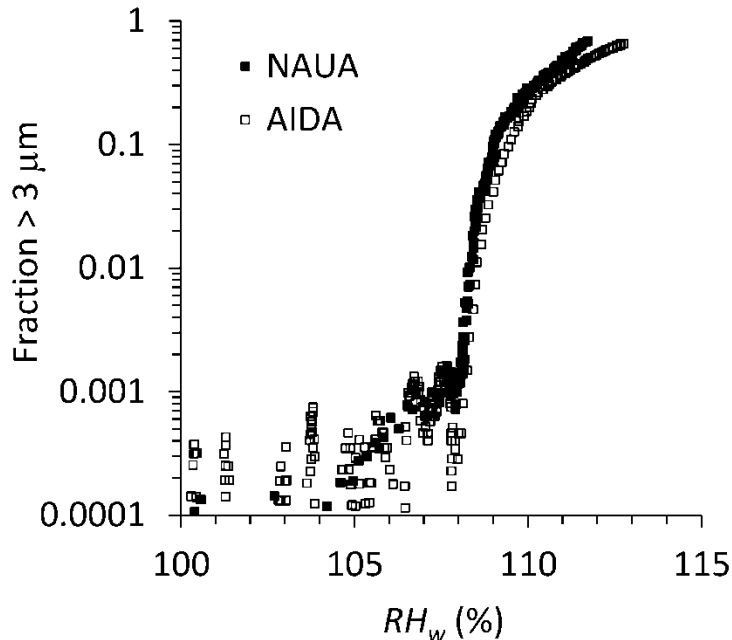


Figure B1. As in Fig. 2, raw 1 Hz CFDC data from an ICIS-2007 experiment on the fraction of total aerosol concentrations (measured by a CPC) appearing at OPC sizes above $3 \mu\text{m}$ during RH_w scanning for two experiments at -21°C when processing particles from a dust sample that

had been collected following a dust storm in Israel (Kanji et al., 2011). The data termed NAUA was sampled following dispersion into a 4 m³ aerosol chamber, with concentrations of approximately 5000 cm⁻³ present at the time of sampling. The data termed AIDA was sampled directly from the AIDA expansion chamber prior to a cloud expansion, when the total particle concentrations were approximately 100 cm⁻³. Water droplet breakthrough of the CFDC evaporation region occurs at ~108% in each case and progressively more activated cloud droplets survive through the evaporation region as RH_w is increased further.

Elevation of RH_w well beyond the point of water droplet breakthrough at ~108% RH_w in Fig. B1 shows that the fractions persisting at water droplet sizes following the evaporation section of the CFDC increase up to 0.8 at higher supersaturations. Absent removal of the evaporation section (i.e., maintenance of supersaturation to the bottom of the instrument) to demonstrate the existence of water droplets in the growth section of the CFDC, not possible in this particular study, these data strongly support that unimpeded immersion freezing on fully activated water droplets should be observable in the CFDC at a point prior to the breakthrough RH_w. For this reason, we believe that our interpretation of experimental results is plausible, with the Welts et al. study providing a contrasting viewpoint.

In the revised manuscript, the last sentence of Section 2.1 now states, *“Additional experimental support for the fact that nearly complete CCN activation and growth of mineral dust particles occurs in the CSU CFDC at RH_w between 105 and about 110% RH_w is given in Appendix B, Fig. B2. We may contrast our assumptions and approach in this regard to that of Welts et al. (2014), who used separate experiments to define immersion freezing fractions and then applied calculation and subtraction methods to interpret and attribute additional INP fractions freezing as contributions from a condensation freezing process at RH_w > 100%.”*

In Appendix B, as part of the discussion of the high RH_w offset for complete immersion, we write: *“Despite these concerns, evidence clearly exists for high CCN active fractions ultimately occurring in the CSU CFDC instrument for RH_w values close to the values used to define the maximum immersion freezing INP concentrations in these studies. Figure B1 shows two additional experiments from the ICIS-2007 studies where RH_w was raised to higher values to examine full droplet breakthrough, indicating CCN fractions up to 0.8. Similar freezing curves*

occurring for homogeneous freezing of solution droplets have also been previously demonstrated for the CSU CFDC instruments (DeMott et al., 2009; Koehler et al., 2009; Richardson, 2009; Richardson et al., 2010), indicating no special limitation on freezing high fractions of particles in these instruments. These results support the validity of the assumption that immersion freezing activity is assessed with the CFDC instrument in the present study.”

Reviewer’s major comment [3]:

Comparing to the AIDA expansion chamber with an uncertainty in the CCN active particle fraction of +/-30% (Niemand et al., 2012) seems not optimal. A comparison to immersion freezing experiments ensuring particles are immersed in droplets (IMCA, coldstage, EDB, DSC) would be interesting.

Authors’ response:

Nearly every method to induce and observe immersion freezing entails some non-ideality or experimental issues. We do not possess an IMCA, and we promote in this study that we do not necessarily require one to effectively observe immersion freezing. Furthermore, we consider that the most straightforward natural simulation of immersion freezing must be for a volume of air undergoing expansion that is not in close contact with walls, or subjected to strong thermal gradients, electric fields and so forth. Hence, a larger expansion chamber like AIDA has long been envisioned as a standard for ice nucleation studies. We do not consider the AIDA uncertainty in droplet active fraction of +/-30% at low aerosol concentrations to be particularly limiting, and during restricted periods as shown in our very typical example of experiments used in this study (Fig. 3), variability is often less than that. Description of experiments comparing the CFDC instrument to a classical immersion freezing device for other various dusts are in preparation for separate publication at this time.

In Section 2.2, we amend the discussion as: *“Full activation of aerosol into cloud droplets is achieved in AIDA ($\pm 30\%$ maximum deviation, as noted by Niemand et al., 2012) and ice active fraction...”*

Reviewer's major comment [4]:

Another option would be a characterisation following the homogeneous freezing curve to determine the fraction of CCN active particles. From the discussion in Appendix B it appears that this is not feasible due to the lower temperature in the evaporation region. Is that the case?

Authors' response:

The reviewer interprets correctly that the CFDC instrument used in this study contains an evaporation section in which the temperature of the air decreases as droplets are evaporated away. This is not the most ideal for examining the homogeneous freezing response of an aerosol population, but since the RH_w decreases at the same time as temperature in this region, there may be little impact. This type of CFDC and a version of the CSU CFDC design for which the wall temperatures were not altered to induce evaporation in the lower portion of the instrument have been used in studies of homogeneous freezing (DeMott et al., 2009; Koehler et al., 2009; Richardson, 2009; Richardson et al., 2010), and these show the ability to detect homogeneous freezing of CCN nearly ideally. We add this information with additional information on CCN activation (next comment) into the revised manuscript.

Repeated our response above, in Appendix B, where much of this discussion already appears, we write: *“Similar freezing curves occurring for homogeneous freezing of solution droplets have also been previously demonstrated for the CSU CFDC instruments (DeMott et al., 2009; Koehler et al., 2009; Richardson, 2009; Richardson et al., 2010), indicating no special limitation on freezing high fractions of particles in these instruments. These results support the validity of the assumption that immersion freezing activity is assessed with the CFDC instrument in the present study.”*

Reviewer's major comment [5]:

Has the active fraction in the breakthrough regime been observed to reach 100%?

Authors' response:

As noted already, we have confirmed active fractions approaching 100%, although usually up to 20% less. Full confirmation of such activation at a specific RH_w above 100% would require use of a detection method that could differentiate liquid and ice particles. This has not yet been

achieved for our instrument, and therefore we now qualify that full CCN activation is by the inference of other experimental evidence, such as the RH_w scans shown in the new figure.

Reviewer's major comment [6]:

According on Fig.2 it seems that only 4% of the particles are CCN active. Is that the case?

Authors' response:

No, this is not the case based on our experience in performing many RH_w scans with the CSU CFDC, including the additional ones now shown from the same experimental period as some of the laboratory studies used for analyses in this paper. The case shown in Fig. 2 was terminated prior to realizing full water droplet breakthrough of the evaporation section, as full definition of that breakthrough signal was not sought in most experiments. Rather, it was simply recognized and then the experiments were terminated. We used the case in Fig. 2 as the experimental example due to its use in the study as one of the Saharan dust experiments. As a future recommendation, based on both reviewer comments, we now amend statements in our Conclusions as, *“Nevertheless, these results have implications for the design and operation of any CFDC-type ice nucleation instrument, suggesting careful characterization of ice nucleation response to RH_w for any particular device and different INP types that compose natural populations. In particular, scanning up to and beyond the RH_w for droplet breakthrough to establish CCN activation (e.g., Fig. B1) is recommended. This will more clearly define the upper RH_w limit for assessing ice active fraction versus temperature uniformly for any INP type being tested and CFDC instrument type being used.”*

Reviewer's detailed comment [1]:

17368, line 19 and Fig. 3: What is the RH_w for CCN activity setting in AIDA and how long does it take to form a cloud once this RH_w is reached?

Authors' response:

As in the atmosphere, there are no highly accurate measures of RH_w inside a cloudy volume of air. With a water vapor concentration accuracy of 3-5% using the AIDA tunable diode laser

hygrometer (Fahey et al., 2014), the CCN activation RH_w cannot be accurately measured or validated in AIDA. The matter of most relevance is what proportion of particles are put into liquid drops at the point of cloud activation that are then further cooled. We suggest that this proportion is essentially 1, with the stated 30% uncertainty. Based on Fig. 3, which is a common example for the present studies, full activation, as measured by cloud particle counters, is achieved in less than 15 s. No special addition to the text is made, except to note that in the figure caption for Fig. 3 that the data points are at 5 s intervals.

Reviewer's detailed comment [2]:

17370: One particular feature of Eq. (2) is that it predicts the fraction of particles (which are larger than $0.5\mu\text{m}$) initiating ice formation to increase with increasing $n_a > 0.5\mu\text{m}$ at a given temperature. Accordingly fractions above 1 can result for high $n_a > 0.5\mu\text{m}$ and low temperatures. Does this indicate that the parameterisation is only valid for a specific range of particle concentration or activation of smaller particles? Where does the choice of $a > 0.5\mu\text{m}$ originate from?

Authors' response:

One must be careful not to confuse a parameterization that simply relates INP number concentration to the number concentration of particles of diameter $> 0.5 \mu\text{m}$ with the population of aerosols of all sizes that are available to serve as INP. Hence, active fractions > 1 with reference to $0.5 \mu\text{m}$ particles are allowed, the occurrence of which is fully consistent with the fact that $0.5 \mu\text{m}$ is the observed mode size of for natural INP over the course of a number of studies. Smaller INP do exist. The use of this INP reference size, motivated by the observed mode size of natural INP and natural dust particles, and historic studies noting the relation between INP concentration and the concentration of all aerosol particles exceeding a certain size, is discussed in detail in DeMott et al. (2010). Practically, active fractions exceeding 1 in comparison to $n_a > 0.5 \mu\text{m}$ are restricted to very low temperatures, as it is the case that INP concentrations equivalent to only a few to ~ 10 percent of $n_a > 0.5 \mu\text{m}$ are typically active for natural dust particles at -30°C . However, the parameterization shown in this paper should be

restricted for use in the mixed-phase cloud regime at temperatures warmer than homogeneous freezing occurs. We try to clarify this point now.

“The parameterization developed herein is strictly valid where data were available, between 238 and 252 K, and use to warmer temperatures represents pure extrapolation.”

Reviewer’s detailed comment [3]:

17382 line 13-15: Looking at Fig. 1 the evaporation region is at -35C for an experiment at -30C and 105% RH_w. But the droplets seem to only be cooled down by 3 and not by 5 C, why?

Authors’ response:

This is due to the kinetics of heat and mass transfer. Given more time in the evaporation region, full cooling would be achieved. Temperature in the aerosol lamina relaxes in time toward the cold wall temperature.

Reviewer’s detailed comment [4]:

17383 line 15-17: The statement that the RH_w dependence can be ignored should be supported by more discussion. Fig.2 shows that not all particles are activated at 105% and that the activated fraction is increasing with increasing RH_w. These results show a RH dependence and thus contradict the above statement. Doesn’t Fig.2 also disprove the Petters et al (2009) assumption on p. 17367/17368 that the nucleation mode observed at 105% RH_w is immersion freezing? It seems necessary to reconcile these apparently contradicting results.

Authors’ response:

What appears needed is for us to more clearly articulate this discussion. The RH_w dependence shown in Fig. 2 is the real expression seen in raw CFDC data. However, it’s source for physical reasons that relate entirely to the instrument and particle response within it is the reason for ignoring specific attribution of INP concentrations to specific RH_w values during the asymptotic

increase of INP concentration with RH_w , and in attributing full immersion freezing activity instead to the maximum value achieved prior to water droplet breakthrough. Petters et al. (2009) promote the use this high RH_w value as reference, not 105% RH_w . The 105% value is a value that is almost always practically achievable in any ambient sampling scenario with a CFDC. For example, one would not want to flirt with entering the droplet breakthrough regime if they are collecting ice crystals from activated INP onto an impactor for inspection of INP composition. That would contaminate the sample with droplet residues. Furthermore, the breakthrough RH_w values depend somewhat on temperature (Richardson, 2009). Hence, these higher RH_w values are simply avoided in practical sampling, although this might motivate one to alter the CFDC design in the future for access to RH_w values that are not usually deemed of relevance (yet they are, at least for quantifying immersion freezing – that is the point). In a laboratory setting we are able to assess the full activation behavior with experimental RH_w up to the point of drop breakthrough, and we use that information here to gain better quantification of immersion freezing of mineral dust particles. We are literally calibrating the values obtained at 105% for these types of INP and we are saying that there is a correction necessary.

For this reason, we now emphasize “*calibration*” instead of “*correction*” in relating immersion freezing observed at 105% to that at an RH_w deemed to represent full CCN activation. In the abstract we modify statements to read, “Measurements made with the Colorado State University (CSU) continuous flow diffusion chamber (CFDC) when processing mineral dust aerosols at a nominal 105% relative humidity with respect to water (RH_w) *are taken as a measure of the immersion freezing nucleation activity of particles.*” In Section 2.1, prior to referencing more detailed discussion of Appendix B on why we believe that freezing at 105% is not the full expression of immersion freezing, we modify a statement to read, “Finally, a reference condition was placed on the processing RH_w *deemed representative of immersion freezing nucleation.*” And in discussing Fig. 2, we now write, “*This result suggests that unresolved factors are limiting the full expression/observation of immersion freezing nucleation in the CFDC until relatively high water supersaturation.*” Changes related to CCN activation in the CFDC have already been mentioned above.

Reviewer's detailed comment [5]:

Fig.2: As pointed out before the active fraction is increasing with increasing RH_w . This is either a disagreement to an immersion mode mechanism taking place or an indication of incomplete CCN activation of the particle population.

Authors' response:

We believe that we have described evidence that this ensues due to requiring RH_w in excess of that presumed necessary for full CCN activation of the particle population, kinetics of droplet growth, non-uniformity of exposure of all particles to exactly the same RH_w , and so forth. It is difficult to know how to further emphasize this point.

Reviewer's detailed comment [6]: Fig.3: Why does the scale of the number fraction go up to 3? At what RH_w is complete CCN activation at -30 C detected in AIDA? Please consider adding a third panel showing the RH_w , RH_i conditions prevailing during the experiment.

Authors' response:

The scale goes to 3 so that the maximum values around 1 are clearly visible. This shows that CCN activation is nearly complete in the volume of the AIDA cloud. Plots including RH_w are already shown in Niemand et al. (2012) and in other papers from the AIDA group, so we choose not to add a panel with that measurement here. What we consider most relevant are the facts that full CCN activation occurs, followed by ice formation as the parcel cools. If the reviewer is seeking to somehow point out differences in the ice nucleation signal response in the AIDA expansion chamber versus the CFDC, we can only note that one should not expect to see the exact same behavior in simulated cloud parcels as seen in a CFDC. See our earlier responses on this topic, and the extended discussion of the RH_w response in the manuscript.

Reviewer's detailed comment [7]:

Fig.5: A red line for high- blue for low temperature would be more intuitive. Some dashed lines are not reproduced. Please also add error bars (in both directions).

Authors' response:

We have altered the color scheme as requested. Dashed lines have been improved in the new figure version. Error bars are now added to data points. Representative error bars, representing standard prediction error are added now on the parameterization lines (see response to Reviewer 1).

Reviewer's detailed comment [8]:

Fig. 6: I would expect D10 to be a straight line in this figure. Why isn't it, i.e. where does the scatter come from? Please add in the caption that $cf = 1$ was used.

Authors' response:

Thanks for this comment. D10 points vary slightly from a straight line due to use of the actual temperatures of observations, which are allowed to vary slightly (within 1°C) from the reference processing temperatures used for comparison, as stated in the methods discussion. We note this now and add the $cf = 1$ qualifier in the figure caption. This figure is now Figure 7.

Reviewer's detailed comment [9]:

Fig. 7: RH_{max} is instrument specific and therefore an arbitrary condition to compare to. The active fraction would increase further for higher RH_w as can be seen e.g. in Welti et al, 2009. Isn't the correction factor an indication that the mechanism looked at is different from immersion freezing?

Authors' response:

RH_{max} is not arbitrary if justified within a certain range for a specific CFDC type instrument. For the CSU CFDC, further increase may occur, but we contend that we are reaching a plateau by 109% RH_w . This is consistent with the additional evidence and figure we now provide (see response to major comment #2) that shows that a high proportion of particles are clearly within droplets before this high value is achieved in the CSU CFDC. The reviewer is correct that this is a function of the particular instrument, and a matter for each investigator to explore and quantify. Given evidence that CCN activation is achieved at values below 109% RH_w in the CSU CFDC

for the dust particles sampled, we cannot justify that we are observing a different mechanism of ice formation than immersion freezing at that point. On the otherPlease note that Fig. 7 will now be Fig. 8.

Reviewer’s detailed comment [10]:

Fig. 10: Should the RH_w range be 105 +/-3% as stated in the text?

Authors’ response:

We will clarify in the figure caption that the calculated lamina RH_w was held within the stated range of 0.5%. This simply says that good control on the target RH_w was maintained. We now provide more accurate discussion of the RH_w uncertainty in the methods section of the paper on the basis of temperature-dependent information provided in Richardson (2009).

We state in Section 2.1, “An additional consideration in selecting this value *is that RH_w uncertainty, as estimated and extrapolated from Richardson (2009), is $\pm 1.6, 2$ and 2.4 % at $-20, -25,$ and -30°C , respectively (Hiranuma et al., 2014).”*

Reviewer’s detailed comment [11]:

Fig. A1: b) The scale “Fraction of particles observed” should end at 1.

Authors’ response:

We prefer a scale which allows resolution of the values reaching their full value of 1.

References:

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