Reply to Community Comment by Gabor Vali

Vali: This work is a welcome addition to a rather sparse set of experiments in which freezing of a population of water drops is observed at fixed temperatures. This comment refers principally to that part of the paper. The constant cooling and repeat freezing data are of good quality and are well analyzed.

Response: We thank Vali for this lucid comment.

Vali: Experiments at fixed temperatures need to have large sample sizes in order to meaningfully determine the time dependence of freezing and to separate the influences of the distribution of different INPs in the individual samples (drops) from the stochastic time dependence of nucleation.

Response: We used many hundreds of drops to study each sample.

Reviewer: Previous constant-temperature experiments that can be used for the purpose are those by Vonnegut (1948; Vt48), Vali and Stansbury (1966; VS66), Vali (1994; V94), Vali (2008; V08), Wright and Petters (2013,WP13a) and Wright et al. (2013; WP13b). There is no quantitative comparison with these earlier works in acp-2021-830; this comment is aimed at remedying that and to critique what is reported in the paper.

Response: During the isothermal phase, Vali (1994) observed a doubling of the number of frozen drops after 10 mins (-18 degC, drops on aluminium foil). After 10 hrs, Wright and Petter (2013) saw an approximate quadrupling of the number of froze drops at constant temperature (-22 degC, 1% wt of ATD in each drop).

These results show stronger time-dependence than seen by our paper. After10 hrs we saw for our mineral-dust influenced sample, an increase by about 150%.

This underscores the importance of realism in choice of aerosol material if one wishes results to be representative of the real troposphere. Such previous studies were seemingly oriented more towards theoretical perspectives on ice nucleation, hence their idealized design.

Reviewer: In all the experiments to be examined, sets of sample drops were cooled from above 0_C to the test temperature Ts, held at that temperature for a period time and then cooled again until all sample drops were frozen. In Vt48, the sample was plunged to the test temperature in an uncontrolled way. In subsequent works the rate of cooling was controlled. The parameter best suited to discuss the results of the experiments is the rate of freezing, RT , originally given as Eq. 3 in V94, and defined as

R_T (t) = (1/Nuf) dNuf /dt (1)

where Nuf is the number (or fraction) of the sample that is not frozen at time t. This function is a more explicit representation of observations than the fraction frozen versus time curves, though some trends can also be seen qualitatively in those curves.

Freezing rates as functions of time are shown in Fig. 1 for four constant temperature data sets. Panel (a) shows the freezing rate extracted from Fig. 5 of Vt48 with data from experiments with 64 water drops on a treated metal plate. Values of R_T were derived by reading numbers off the published graph and then using Eq. 1. Panel (b) is derived from Fig. 4 of Pound (1952) which shows the percent of tin droplets remaining liquid as they are held in a dilatometer at various temperatures for up to 250 minutes. The dilatometer measures the change in volume associated with the solidification. The published graph of percent unfrozen was used to read off changes over various time intervals and then Eq. 1 applied substituting percent unfrozen for Nuf . This is not totally valid as the tin droplets were not uniform in size, but the focus here is on the temporal change of R_T which will be relatively insensitive to this simplification. Panel (c) is based on the same data as Fig. 3 in V94, but for only one temperature and not normalized to the rate of freezing at the moment cooling stopped. Panel (d) is based on data in WP13a shown in their Fig. 5. The original data were kindly provided by the authors. Freezing rates were calculated using Eq 1 again making the simplification that the dispersion of droplet sizes in the emulsion used in these experiments doesn't alter the points to be made here.

The four data sets shown in Fig, 1 derive from rather diverse methods and are based on limited sample sizes. Yet, there are common features worth noting:

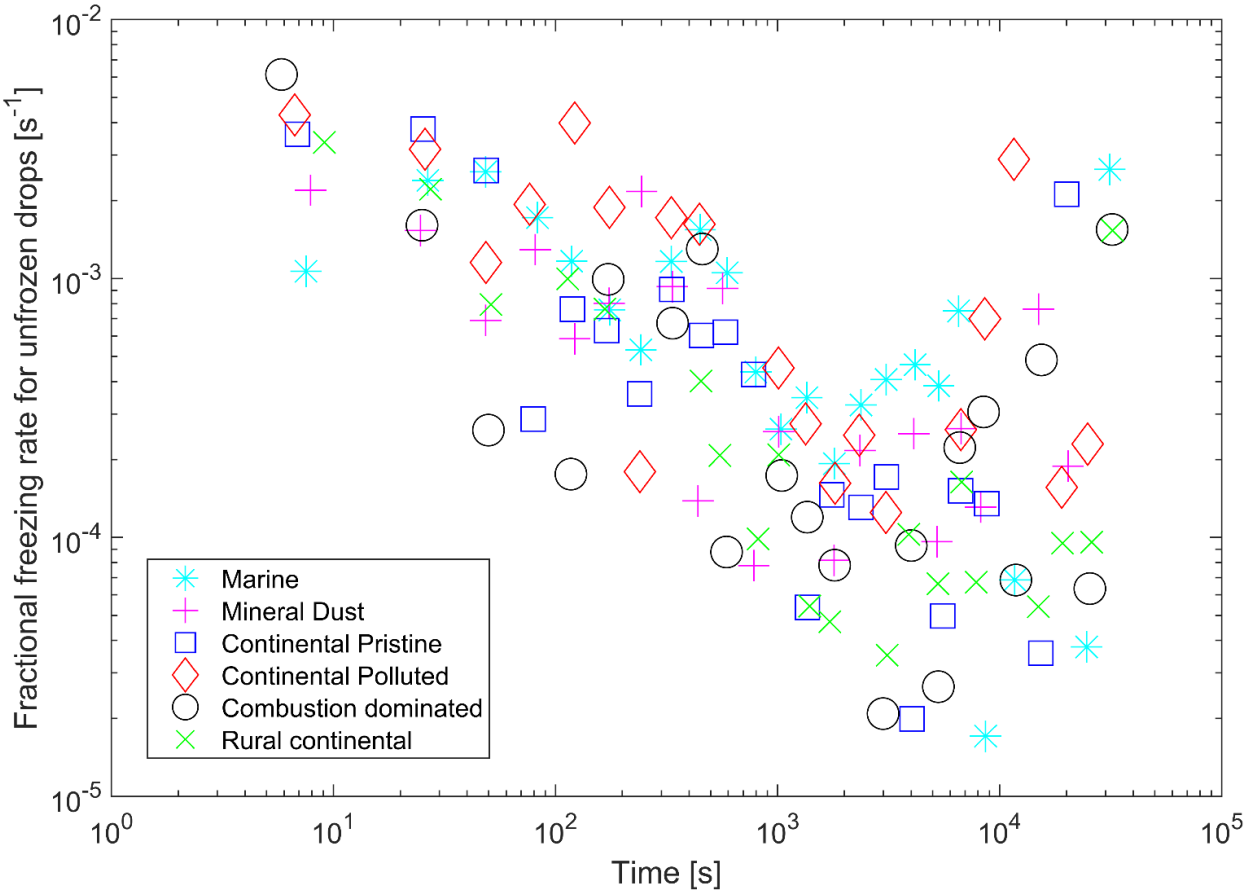
1. The freezing rate decreases with time in all cases. This is significant because it contradicts the prediction of a stochastic model of freezing of a population of drops assumed to have the same INP content. With that model the rate would remain constant while the temperature is constant.
2. The freezing rate is a function of temperature, as seen in panels (a) and (b) of Fig. 1. This is an expression of the general trend for INP numbers to increase with decreasing temperature.
3. The function best describing the time evolution of RT is not necessarily an exponential. A roughly exponential decrease was suggested in V94 from a limited data set and for a water sample that was shown in cooling experiments to have an exponential dependence of the INP concentration on temperature. The data shown in Fig. 1 is insufficient to judge to what extent power functions might be better in panels (a) and (d). There is no a priori reason to expect a simple algebraic relationship. Because of the lack of a quantitative theoretical explanation, any algebraic expression must be considered at this time a parameterization of the empirical data.

Results in Fig. 8 and Fig. 10 of acp-2021-830 support the first point in the list above but references to some "natural time scale" and to fast and slow nucleation are not explained. Point 2 is not tested with the current data as only one isothermal temperature was used for each sample.

Response: We agree with the three points.

We agree that the fractional change in the number of unfrozen drops is the important quantity, since it is related to the probability of any drop freezing per unit time. So we have included in the paper a new

Figure 11b to show this (R_T):



However, we think that some of the drops are irrelevant to the computation of R_T in an isothermal experiment, as they will never freeze at the isothermal temperature even at the longest conceivable times. So when we computer the number of unfrozen drops, we consider only those drops remaining that will freeze at the longest time (10 hrs). We reach the same conclusion that the fractional rate of change of the number of unfrozen drops falls somehow, perhaps by a power law.

Our paper observes the natural time-scale of ice nucleation, which is defined as the relaxation time in the exponential time factor (effectively the reciprocal of the fractional freezing rate).

It is reassuring to know from the Fig. 1 shown by Vali here that the time dilation of the freezing timescale during isothermal experiments (reducing fractional freezing rate) that we have seen is also present in the previously published studies.

If one could somehow ensure that each drop had the same INP composition and size and only one INP per drop, would one then see the stochastic hypothesis hold true with constancy of R_T ?

Response: Regarding point 3, acp-2021-830 employs nested equations requiring three parameters (_Nice;1, Ci and _) to describe the fraction of drops frozen as a function of time. It is unclear what physical model is there to justify this approach.

Response: What we write is that "*the limited literature of observations show that the unfrozen fraction is often seen to decay exponentially with time (Bigg 1953ab, Vali 1994, PK97; Knopf et al. 2020). Consequently, from our isothermal measurements (Fig. 11), the time dependency effects were inferred by fitting the observations with this empirical isothermal formulation*:

$$N_{ice}(t^*) = N_{ice,0} + \Delta N_{ice,\infty}\left(1 - e^{-\frac{t^*}{\tau}}\right) \qquad (1)$$

".

This justification of our isothermal formulation (Eq (1)) suffices for the present paper. We follow an empirical approach, so there is no need to justify it with any model of underlying physics.

Response: It also may be noted that the overall trend in Fig. 10, neglecting differences among samples, appears to be a power function similar to two of the panels in Fig. 1. It does confuse matters somewhat, that those examples were obtained for polidisperse drop populations.

Incidentally, the large range of three orders of magnitude in RT in Fig. 10 is somewhat surprising given what is seen in Fig. 8.

Response: What is shown in Figure 11a (previously Fig. 10) is evidence of time dilation of the natural time-scale of the observed freezing (the time-scale is the reciprocal of the fractional freezing rate). That may be seen in Fig. 9 (previously Fig. 8) if it is appreciated that the time axis is plotted logarithmically.

Reviewer: In general terms, the results in acp-2021-830 confirm that time is less important than temperature in heterogeneous freezing nucleation. The important issue is how to explain this (secondary) time dependence and to what extent the new data support earlier conclusions. At this point only a qualitative evaluation seems possible but at that level the current results are compatible with the three points listed above. It is less clear to what extent the authors agree with this interpretation of their data, since their analyses are not well explained.

Response: As found by Knopf et al. (2020), the evolution with time of the fractional rate of freezing observed in drop freezing experiments is governed by variability among drops of the amount of IN material per drop. So it might be apt for the nucleation community to transition towards more realism of lab experiments, with perhaps isothermal observations of aerosol suspended in air that is somehow humidified so that there is only one INP per droplet (E.g. at the AIDA cloud chamber).

Reviewer: Briefly, the three points listed above summarize aspects of the view of heterogeneous freezing nucleation developed in VS66, V94 and WP2013b. In these 5 papers the freezing rate RT is

shown to be determined by two processes, one related to the stochastic time dependence of embryo growth, the other to the random distribution of INPs of different character in the sample drops. The first process leads to the site nucleation rate function with the characteristic temperature that anchors that function.

The allocation of INPs of different characteristic temperatures in the sample drops is described by the nucleus spectrum. The analyses given in ACP-2021-830 may be based on similar thoughts to those summarized in the preceding paragraph. If a closer agreement between the new data and those in earlier publication could be shown that would be a welcome reinforcement of the VS66/V94/WP2013b formulation. This is a crucial point to be clear about, as the interpretation of experiments as well as any effort to construct models of ice nucleation in complex systems like clouds or plants depend on this understanding.

Response: We have heeded the reviewer's suggestion to relate the present results to those from V94 and WP2013. We now include a paragraph with comparison in the concluding section.

Reviewer: The scheme presented in the paper for incorporating time dependence in cloud models follows the temperature shift approach suggested in V94 but without accounting for the rate of cooling. Regrettably, no comparison is offered with the TDFR parcel model of Vali and Snider (2015).

Response: We looked at the TDFR model of Vali and Snider (2015). Their Eq (6) connotes a natural time-scale of the freezing (1/q) that is constant with time. We get a drastic steady increase with time of this time-scale. Thus, if we were to somehow apply the TDFR model to our observations we would see a discrepancy at long times presumably.

Reviewer: In all, the excellent device described in acp-2021-830 can certainly yield important inputs to studies of immersion freezing.

Results in Section 3.1 show this; the presentation there suffers somewhat from the lack of quantitative error analyses. Only one test temperature in the isothermal experiments (Section 3.2) is a limitation but what data has been generated already is valuable and deserves a clearer presentation and more thoughtful analyses. The value of the parameterization in 3.2.2 could be evaluated by comparison with other, possibly simpler, solutions to the problem. Hopefully, these shortcomings will be corrected in a revised version of the paper and it will become clearer to what extent the results reinforce, or demand re-consideration, of earlier results.

Response: We thank the reviewer for the encouragement.