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Atmospheric
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Interactive comment on “Repeatability and randomness in heterogeneous freezing nucleation” *by* G. Vali

G. Vali

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Responses to Anonymous Referee #1:

Many thanks for the reviewer’s positive comments, his support of the argument I make in the manuscript, and for pointing out possible improvements in the presentation. The final version of the paper will reflect more fully my responses to the suggestions; I present here, briefly, answers to specific points.

More information about the size distribution of the ice nuclei would be important for interpreting the results in terms of substrate characteristics, such as site density or bulk properties. That was not the goal of this work and thus no effort was made to identify either the chemical composition or detailed physical state of the nucleating agent. This is different from studies that utilize some pure substance to initiate ice. For

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this research, the important factor was to work with a sample that allowed simultaneous observations at a large range of temperatures. In addition, the soil sample is one of some atmospheric relevance as well. However, with a complex sample like that, even in principle it is not feasible to determine the size distribution of the particles that carry the nuclei, since those particles that carry nucleating sites represent a small fraction of the total amount of particulate in the sample. As a very rough indication, it may be mentioned that the drops with the soil suspension had no particles of visible size in them, and that the total number of soil particles per drop was $>$10ˆ8.

The reviewer questions the need for focusing on the SN (single nucleus) subset. His remark is correct - the conclusions are well supported by the full set of data without this step. Such a limited impact of separating the SN subset is associated with the high dilution of the material in the sample, and the large spread of freezing temperatures discussed in the preceding paragraph. However, the concept of the SN subset is important for this type of study, since the results of repeated freezing test would be confounded by the possibility that each observed event is actually due to a different particle or nucleating site. Without narrowing the analysis on the SN subset, the doubt would be difficult to dispel; its use makes the results more definitive, with still sufficient sample sizes not to decrease the statistical significance of the conclusions. As for the derivation of the equation used: it comes from the Poisson distribution.

The reviewer is correct in pointing out that the derived nucleation rates cannot be quantitatively compared with the rates of homogeneous nucleation and that the actual magnitudes calculated here are relative to the volume of the drops. For this reason, only the shape and range of variation of the nucleation rate is discussed, and the point is made that the rate refers to a specific nucleus of given characteristic temperature.

Responses to Anonymous Referee #2:

The comments of this reviewer are much appreciated and most suggestions will be incorporated in the revised paper. Brief responses to some of the points raised are given here. Equation 3 on page 4067 is derived from the Poisson distribution. Steps of derivation will be included in the revised paper.

The reference that includes some detail on the characterization of the soil sample used is: "Ice nucleation relevant to formation of hail", McGill University, Stormy Weather Group Sci. Rep., MW-58, 62 pp." But, see the response to reviewer #1 on this point.

Page 4070, line 20: The SN subset was identified based on the first run in the sequence. The question points to a simplification in the sense that a slightly different set of drops would qualify for the SN designation in each run. However, the near-constancy of freezing temperatures makes this simplification of little impact, and it is necessary for calculating statistical measures of the variability. This will be elaborated in the revised paper.

Page 4071, line 18: Yes, run-to-run changes were meant, and the qualifier omitted for brevity.

Figure 9: Sigmas were chosen for illustration, but it is a fair suggestion to use values that match the actual data.

Section 6: As detailed in my responses to Reviewer #1, only the shape of the derived nucleation rate curve contains useful information in this study.

Page 4082, lines 10-13; This is an important point, and goes to the heart of the issue addressed in the paper. Indeed, experiments with constant temperature or with steady cooling can yield rate information if (!) the stochastic model applies. The argument in the paper is stated for heterogeneous nucleation. To my knowledge, no material has been found so far for which the stochastic model is the correct one, but the possibility exists in principle.

Page 4082, lines 14-21: The important parallel between the Marcolli et al. results and those I present on this paper is the emphasis on the fact that nucleation sites, even on the same material, differ from one another, whether this difference is expressed in terms of a characteristic temperature or an assumed contact angle. The former is found by direct observation and is combined with a rate function derived from statistical analysis of the behavior of a population of similar sites. The latter approach uses an assumed frequency distribution of contact angles, and other parameters of CNT, to yield a rate function. Neither description is fully satisfactory, since the observed characteristic temperature is only a diagnostic that reveals no specific information about what factors control the activity of a specific site. In the same vein, I consider contact angle to be a surrogate for a compositional and structural definition of a site. Underlying the latter statement is the recognition that the spherical cap model used in CNT is only an idealized description of what an ice germ actually looks like.

Brief addition:

Data included in this paper were obtained with two slightly different soil suspensions and with a distilled water sample. Key results are consistent for all three samples, even though they contained materials of various chemical composition and physical state. This fact indicates that the concepts arrived at in the paper are likely to be applicable for materials of different composition. The purpose of this short note is to reinforce that expectation by extending the list of materials for which experiments have yielded similar results. The tests here included are less comprehensive than those in the manuscript, and only statistical data are available, not the individual drop histories.

Samples of silver iodide (AgI), P. syr. bacteria (strain T2304), and a cell-free bacterial preparation were used. The cell-free sample was produced as described in Phelps et al. (1986) and provided for these tests by Dr. Ray Fall. Essentially, this sample retained fragments containing the nucleating protein from the outer membrane of Ps. syr. bacteria but had most of the original cell material removed. The samples were suspended in distilled water at concentrations that yielded freezing temperatures in the range -4...-6°C. Between 30 and 80 drops were tested in 7 to 11 re-freezing cycles.

Results are expressed in terms of the standard deviation of the distribution of run-to-run changes of freezing temperatures, compared to the value of this parameter that would be expected if the sample drops froze in a random sequence while retaining the actual frequency distribution of the freezing temperatures. When the observed value is smaller than the one for random variations, that can be interpreted as an indication that the nuclei contained in the drops preserved, within some variation from run to run, their original freezing temperatures. Because of the stochastic element and the slow alterations (cf. Section 6.2 of the paper) are superimposed on the characteristic temperatures, a sample that has all the drops freezing within a temperature interval of only a few degrees can be expected to have a relatively small difference between the observed and randomly shuffled values. These samples all had such narrow ranges of freezing temperatures, while the samples analyzed in the paper had temperature spreads of 10°C or more.

For AgI, the observed standard deviation and the same for the randomly rearranged temperatures are (in °C): 0.39/0.99. For two samples of P. syr. the values are 0.36/0.68 and 0.85/1.48. For the cell-free sample the values are 0.83/1.20.

As these data indicate, all of the observed values are smaller than the those for random variations. Given the argument in the preceding paragraph about the impact of a narrow range of freezing temperatures, and with the caveat that these were a limited set of observations, it seems warranted to extend the conclusions of the paper to the samples here reported. The fact that these additional test included a simple inorganic (AgI) of well- known properties, a bacterial ice nucleant, and a cell-free derivative of that, support general validity of the singular character of heterogeneous freezing nucleation, while certainly do not exclude the possibility that with for some materials the definition of a characteristic temperature is less meaningful because of the labile nature of the nucleating sites on that substance. Clearly, this is a subject for further exploration.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 4059, 2008.

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