

Referee Report on manuscript acp-2022-598 “The importance of acid processed meteoric smoke relative to meteoric fragments for crystal nucleation in polar stratospheric clouds” by A.D. James, F. Pace, S.N.F. Sikora, G.W. Mann, J.M.C. Plane and B.J. Murray submitted to Atmospheric Chemistry and Physics Discussions

The present work deals on the one hand with the old, but as yet unanswered question about the nucleation rate of PSC I (NAT) clouds that are necessary, together with ice particles (PSC II) and other H₂SO₄-containing aerosols (frozen ternary solutions or glasses), to explain the rapid and recurrent seasonal stratospheric ozone loss, both in the Antarctic and, to a lesser extent, also in the Arctic. In this paper nucleation rates are measured in deposited microdroplet plate experiments under satisfactory temperature control using visual observation on the fraction of frozen droplets as a function of temperature. On the other hand, the paper deals with the application of Classical Nucleation Theory (CNT) to literature data (James, 2018) and to results obtained in this study starting with section 4 of the present paper. CNT is a formally thermodynamic network cast into a kinetic theory (akin to transition state theory) that uses scarce, scattered and inconsistent macroscopic data such as contact angles and surface energies that do not constrain anything, but leaves the bewildered reader on a heap of unexplained and less than intuitive physical pictures. Even though I concur with most if not all of the conclusions of the authors that are deemed to be plausible there seems to be a disconnect between the two parts which seems to be a sign of incomplete “integration” of the two halves of this publication. The paper is well written, but sometimes needs additional explanations in order for the reader to grasp the experimental development and evaluation of the data (see below). I believe that the paper, if reworked and partially reformulated, would be of significant interest to the community of atmospheric chemists and numerical modelers trying to understand the physical-chemical basis and circumstances such as the locus of nucleation of PSC I clouds because several interesting facts about nucleation are presented, both in the first experimental and further in the second theoretical (CNT) section. The second modeling part needs to be streamlined, but at the same time has to be linked to intuitive and plausible concepts (see below). I am willing to support the publication of this two-pronged paper once the authors have had a chance to address my several questions and suggestions in a revised manuscript. However, I request to inspect the improvements and alterations before this publication is given the green light to proceed.

Here are my main points I would like to raise in the order of the presentation of the text:

- Addressing the first part of the manuscript a discussion of experimental uncertainties is nowhere to be found throughout the manuscript. Every scientific quantification needs one in view of the many parameters that control the measured nucleation rate. From Figure 2 it is apparent that per run 40 droplets in total are considered leading to a minimum of the random error of observation at the 50% point of fraction frozen. The experimental error at the fringes of the measurement domain become larger, and it behooves the authors to label a random error to selected data points such as displayed in Figure 3.
- Regarding the method I wonder about the gas-tightness of the cover plate swept with dry nitrogen gas during measurements. Have the authors performed tests in this regard? If gas-tightness would be only partial it may be conceivable that the HNO₃ and/or HNO₃/H₂SO₄ concentration would increase over time because the partial pressure of H₂O is much larger than that of HNO₃, and even more so for H₂SO₄ according to the pertinent phase diagram. Have any attempts at measuring the pH value before and at the end of each experimental run been undertaken? Or before and after adding the meteoric fragments (line 148)! Owing to the high acidities the authors probably would have to work with Hammett acidity functions (possibly negative pH values).

- The symbols, especially referring to the control runs in Figure 3, are too faint and all characters are too small (adjust font size) to read-off the given chart. Please anticipate the drawing in print! Line 182 mentions a factor of ten in nucleation temperature when adding H₂SO₄. I for one am able to “find” at most a factor of five difference, so I request that the authors specify which points they are comparing in Figure 3. Regarding Figure 3 I observe a certain irreversible change in nucleation behavior in consecutive runs. The authors never venture out into a possible reason for this behavior when going from run 1 to 2 to 3.
- On line 137 the authors mention an average of 18 μm (microns) dimension of the added meteoric material. Do they have any idea about size dispersion and shapes from imaging of meteoric material? Any BET measurement for total external and internal surface of the used material? How do the authors proceed to evaluate n_s, the number of active sites per unit surface area of solid inclusion? This screams for an explanation and in my view is a show-stopper when presenting Figure 4. What is the definition of n_s used, and what is it based on?
- One of the most interesting aspects of this work is the conversion of the relative results presented in Figure 3 to absolute values in Figure 4. The authors have to stepwise explain how they arrive at the surface area of 0.2 μm² cm⁻³ as a minimum surface area from their data in relation to the observed crystal concentration of 6 · 10⁻⁶ cm⁻³. The authors do not explain where these numbers emerge from. Please oblige as the connection to absolute numbers is an important aspect of the results as the primary observable (fraction frozen) is a relative finding.
- A semantic point: Lines 288 and 293 mention “meteoroids”? What is the definition compared to meteoric materials? Why do you need to use an additional terminology here?

Regarding Section 4 onwards I have only two questions:

- The authors repeatedly write about size-dependent effects on parameters feeding into macroscopic CNT such as σ_{NAT} , θ , r_{NP} . As far as I see it the only size-dependent parameter is σ_{NAT} from which all size-dependence follows according to equations (1) to (4) in the Introduction. Is this equivalent to the effect of curvature of ever smaller particles that becomes dominant for sizes below 20 nm or so when evaluating the surface energy σ_{NAT} ? From what the authors tell me I am not sure about it as they never attribute the size-dependence to any physical or geometrical parameter. If this is the case the next step would be to point out the conundrum of CNT for small (curved) particles as the classical picture of a smooth envelope fails owing to the molecular view of a surface with its molecular asperities. In any case, Table 2 yields instructive examples which the authors should comment on in depth in order to enhance understanding of the CNT results. Their treatment reminds me of Fletcher theory of touching spheres of ice in order to describe capillarity effects and condensation phenomena.
- One of the main conclusions of this work is that quartz particles of several hundred nm’s and possibly silicates do not lend themselves as nucleating substances for PSC I formation over the poles owing to insufficient numbers whereas much smaller and more numerous MSP particles would be the favored nucleating substrate. In view of the fact that by far the most abundant atmospheric dust source is from terrestrial crustal material whipped up by winds could it be that the fine fraction of this atmospheric dust could possibly be responsible for PSC I nucleation in the stratosphere after some strat-trop exchange? In contrast the Meteoric Input Function (MIF) is highly uncertain as the authors convincingly point out. A statement by the authors admitting or refuting this terrestrial source as well as the reasons for it would be helpful to clarify the situation.
- The Herbert et al., 2015 reference is missing. The last reference Wood, S.E. is incomplete.