Referee Report on manuscript no. acp-2017-816 « Nucleation of nitric acid hydrates in Polar Stratospheric Clouds by meteoric material » by A.D. James, J.S.A. Brooke, T.P. Mangan, T.F. Whale, J.M.C. Plane and B.J. Murray submitted to Atmospheric Chemistry and Physics

I acknowledge the effort of the authors to amend the manuscript in the sense suggested by both referees. However, I think that the problems lie at a deeper level where cosmetic changes to the text just won't do. We are dealing with a manuscript that examines ocular (by eye) freezing and melting observations of a single known HNO_3 concentration (40%wt) as a function of temperature in the presence of processed meteoric material and some of its analogues. The identity of the nucleating phase remains unexamined, and conjectures on the presence of the stable phase are made after thermodynamic relaxation according to published phase diagrams. In a stricter sense the chosen title is misleading because nucleation is never investigated.

In the following I would like to raise a few significant points:

Regarding the use of a single HNO_3 solution I point out that known equilibrium phase diagrams are NOT a good guide to interpret observations on nucleation which is a kinetic process. Rather, a cascade from one or more metastable states towards a final thermodynamically stable state is observed according to Ostwald's rule. The formation of NAD (α and β-modification) via homogeneous nucleation of a stoichiometric gas mixture (HNO_3:H_2O =1:3) in the AIDA chamber (Stetzer 2006) and metastable α-NAT via heterogeneous immersion and deposition freezing (Grothe 2008, Weiss 2016) are examples. Given the fact that the authors intend to examine the nucleation, a kinetic process, I think that a concentration range from 33 to 45%wt would be more appropriate in order to free themselves from the narrow range given by equilibrium considerations that certainly kick in later in the process upon thermodynamic relaxation. The authors report the onset (eutectic) melting at 231.2 K, however, the phase diagram (Beyer, 2002) reveals an eutectic tie line at the same temperature in the range 0 to 78%wt spanning the range all the way from ice, NAT, NAD and NAM. This makes the observation of the onset of melting ambiguous in nature.

In addition, at 40%wt of HNO_3 these workers spot an unknown hydrate having a peritectic point (incongruent melting) that they claim is unimportant at equilibrium, but which cannot be ruled out as a nucleation phase. Soleley based on that fact it is absolutely unjustified to conclude that NAT is nucleated "directly" without the implication of metastable phases that have been found in both homogeneous and heterogeneous nucleation experiments. The present underdiagnosed laboratory observations do not provide a basis for the statement of spontaneous nucleation of NAT (see pg. 8, line 2: pg. 10, line 25), all the more so that there are numerous potential metastable states whose eutectic melting starts at 231 K (Beyer 2002). The chosen laboratory methods in this work are just too crude in order to sort out what is going on upon nucleation of an aqueous HNO_3 solution.

Regarding the abscissa of Figure 4 I do not understand the insistence of the authors to codify the temperature in terms of saturation ratios of NAT or NAD. The temperature is the independent variable in this case and should be used in Figure 4. The equilibrium phase diagram is irrelevant here and is grossly misleading the reader by suggesting that nucleation is an equilibrium phenomenon. Saturation of a NAT or NAD phase has nothing to do with the process at hand which will depend on the adsorption of HNO_3 and H_2O vapor to the interface of meteoric materials and their analogues (proxies). Hoyle (2013) has used the "theory of active sites" successfully which is nothing else than a simple Langmuir-Hinshelwood model that has to be extended to allow for multilayer adsorption!

The authors are dismissing a bit too rapidly my original observation that the interface of the refractory samples may have been modified (rendered amorphous) in the course of the grinding process. In a stricter sense all the examined meteoric materials as well as the "analogues" are atmospherically irrelevant because they may have undergone changes in the grinding process. Sometimes this manifests itself in surface-sensitive diffraction processes where one observes line-broadening (for instance in small particles or powders offering large surface-to-bulk ratios). I must admit that the analogue $MgFeSiO_4$ does not fit that scheme as it still is fairly inactive! It is possible that the argument is more complicated and that grinding is perhaps not the only salient parameter! However, to take the single example of the above olivine material as a reason to dismiss the argument seems superficial and not justified. The one and only material that is not processed in fumed silica and its doped congeners (displayed in the first column on top of Figure 4).

In the end I would like to emphasize a point made by Grothe (2008) and reiterated by Weiss (2016) that the reason for the transient stability (metastability) of NAD or α-NAT is the stabilization afforded by the presence of water ice. DFT calculations in Weiss (2016) have quantified the interaction of α-NAT with water ice and have found it to be larger than for β-NAT which itself is more stable than α-NAT. There is a delicate balance of energetic terms on the way of a metastable phase to its relaxed (stable) final phase in view of the fact that the implied energy differences are small, albeit significant at the low temperatures of interest. Along these lines Iannarelli (2016) have examined the spontaneous formation of NAT and NAD on thin water ice films and have found consistently that α-NAT is always formed before phase transition to the stable final phase that starts in the range 190 to 195 K. A few degrees may make a large difference in the kinetic stability of a metastable phase.

Regarding the introduction I would like to emphasize that both Grothe (2008) and Weiss (2016) dealt with heterogeneous nucleation of HNO_3-hydrates, reportedly in the immersion or contact freezing mode (liquid N_2) as well as in deposition freezing (cold metal support). The authors make it sound as if homogeneous nucleation was involved (pg. 2, line 2). I will not dwell on this "classical" characterization (Pruppacher) as these terms are devoid of any meaning in a mechanistic sense.

References are missing: Peter and Gross (2012); Lambert et al. (2016).

In conclusion, my problem with the present work is that the claims are not supported by established facts as well as experimental observations by the authors that are too "pedestrian" to deduce mechanistic details on nucleation of HNO_3 hydrates on meteoric materials and their analogues. The experimental material at hand is interesting though, but does not make a "story" at this stage owing to its fragmentary nature. The modeling part is OK if it were not "punished" by the rash experimental conclusions. The absent proof for the existence of an (expected) effect cannot be construed as an argument in favor of its contrary! Science is deductive by nature and cannot accept negative differential diagnostics ("This must be the reason by exclusion because I cannot think of a positive fact supporting my hypothesis"). There is too much speculation owing to the absence of experimental evidence!