

## ***Interactive comment on “Nucleation of nitric acid hydrates in Polar Stratospheric Clouds by meteoric material” by Alexander D. James et al.***

### **Anonymous Referee #1**

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This short paper deals with a subject of current interest and reads well in its present concise version. It will in all likelihood find an interested community within the circle of readers of acp as the authors propose a novel and potentially important class of ice nucleation materials of extraterrestrial origin. However, the report gives a highly fragmentary view of the posed problem, whether or not meteoric material and its likely surrogates may make a significant contribution to NAT nucleation under suitable UT/LS conditions. The authors use a very limited data set (a single aqueous HNO<sub>3</sub> concentration, no check for possible dependence of results w/r to cooling rate) associated with visual observation of the phase transition (liquid to solid and vice versa) leading to an unexplained result as far as fused quartz and fumed silica particles are concerned. The authors do not seem to attach great importance to the physical-chemical proper-

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ties of the interface of the ice nucleating particles, instead they bring bulk properties into play (X-Ray diffraction and EDX) that are not informative or relevant in the present context. The reader is left with a snapshot of potentially interesting results without confidence that the authors are not prone to or victim of artefacts in the wake of the processing/handling of all tested materials except fumed silica, the only material used as is (I am assuming that the supplier of the quartz powder has ground the macroscopic sample using a ball mill as well!). In fact, according to Figure 4 all materials that have been ground to some extent except the “used as is” fumed silica samples (including “doped” ones) show a much larger nucleation activity than the latter at constant S(NAT). The authors should at least touch upon this fact in the discussion portion of the manuscript and include possible explanations. Please see below how one could at least in the case of fused silica particles make sure how to remove a potentially contaminated and/or amorphous interface by etching away a few molecular monolayers. I believe that the authors should include a more profound discussion as the present version is short on details and comes across as “superficial” (no pun intended!). Papers reporting limited aspects of nucleation like the present work abound throughout the literature, and the take-home lesson for the reader remains uncertain and unclear, if not confusing. The modeling part is informative but critically hinges upon the accuracy and veracity of the experimental results. It underlines the impact of the experimental results, if confirmed.

The following points/questions listed below need particular attention on the part of the authors. In my opinion it is necessary to include answers or explanations to every single point raised in the following in the revised version:

- A single aqueous 40%(wt) HNO<sub>3</sub> concentration (corresponding to H<sub>2</sub>O-rich NAT) has been used, presumably to correspond to typical concentration/temperature conditions of HNO<sub>3</sub> in the UT/LS of between 10 to 15 ppb (v/v). A burning question might be whether or not there is a HNO<sub>3</sub> concentration range that could lead to NAT nucleation as well according to the Liquidus curve for NAT spanning roughly the HNO<sub>3</sub>

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concentration range of 33 to 72%(wt) with the stoichiometric solution of 53.85%(wt) lying in-between (see for example Beyer and Hansen, J. Phys. Chem. A 2002, 106, 10275). There are measurements to the effect that strata of different atmospheric trace gas concentrations do exist in the UT/LS, among them for HNO<sub>3</sub>.

- Regarding the detection of the phase transition as well as the identification of the molecular composition of the binary mixture NAT/ice the manuscript leaves wanting. Considering first the identification of the condensate, the H<sub>2</sub>O-rich NAT binary mixture has an eutectic melting point of roughly 231 K and a final melting temperature of approximately 245 K (where the NAT surrounded in pure H<sub>2</sub>O is melting). As a complication, there is another eutectic melting point at 72% HNO<sub>3</sub> between the Liquidus curves of NAT and NAM. It is not clear to this reviewer how the observation of melting by eye can distinguish between these two alternate nitric acid hydrates as the observation of the “melting” temperature is ambiguous in regards to identification of the molecular composition of the condensate. Which “melting” temperature was observed: eutectic or final? How was the new apparatus validated anyway (which nucleation system. Please disclose)? How did the authors, in the absence of any spectroscopic evidence, determine the HNO<sub>3</sub>/H<sub>2</sub>O condensate as NAT? It seems crucial to spend some time and effort at positively identifying the molecular composition of the condensate going beyond merely visual observation. An FTIR microscope might help in this regard, all the more so as absolute cross sections for alpha- and beta-NAT have been measured (Iannarelli and Rossi, JGR, 2016). (My guess is that beta-NAT is the relevant NAT modification in this work considering the temperature). On pg. 6 and 9 (third paragraph) the authors invoke their belief of “direct formation of NAT”, that is shunting the formation of intermediate NAD: based on which observations?

- Regarding the freezing process the authors took a specific experimental protocol without spanning a range of time scales for the freezing process (First paragraph on pg. 4). In order to make a point I will briefly exaggerate: If there a single site leading to NAT nucleation on the meteoric material or its surrogate a single collision of HNO<sub>3</sub>

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with this special site will lead to the construction of the NAT lattice if it “sticks” and does not desorb. However, this event may require a long time for it to happen, hence the importance of probing several (especially slow) temperature ramps. I could not find a single experimental run dedicated to this question. It is true that atmospheric time scales may never be duplicated in the laboratory, but I would like to see an effort in this direction!

- According to Figures 3 and 4 fumed silica offers ns values roughly four orders of magnitude lower than all other examined materials at  $S(\text{NAT}) = 10$ . As alluded to above this may occur because all high-nucleation rate materials have been mechanically ground, either by hand (pestle and mortar) or in a ball mill. Pure fused silica offers the unique advantage to wet-etch the possibly amorphous interface layer of ground fused silica using aqueous (concentrated) HF with our w/o H<sub>2</sub>O<sub>2</sub> (so-called Piranha solution used routinely in the microelectronics industry to clean Si-wafers). In this way (after several washing cycles with ultraclean H<sub>2</sub>O) one may restore the “native” or natural fused silica interface. The challenge remains to explain the significant difference in the number of ns sites between fused and fumed silica despite the “normalization” to unit surface area using  $f(T) = 1 - \exp(-n(s) s)$ . A serious method of interface characterization before performing nucleation experiments would seem in order, at least for meteoric surrogate material. “The apparent agreement between the active MSP analogue fused quartz and the meteoric samples is likely coincidental” (see pg. 6, second paragraph): Is it?

- I am unable to follow the author’s explanations regarding the “morphology” as well as their differences on pg. 6, second paragraph. Please try again!

- The authors use “saturation” a lot. Please always indicate WHAT is saturated? Is saturation w/r to condensation of a vapour onto its own condensed phase (e.g.  $S(\text{NAT})$ ), or w/r to the site occupancy of ns (pg. 5, line 30)?

- Pg. 6, line 17: It is a binary system, therefore always NAT/ice at the used HNO<sub>3</sub> concentration!!

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- Pg. 8, line 27: Parametrization of what? Using which variables? Too vague!

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