

**Response to 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**

Dear Editor,

Thank you for your time and understanding during the review process. The authors wish to reiterate that the paper as it stands presents the first quantitative demonstration that meteoric material is a sufficiently active heterogeneous nucleus to explain atmospherically observed PSC (which has been hypothesised in a large number of studies over the last 3 decades). In addition we have identified meteoric fragments, a class of aerosol previously unrecognised in the stratosphere, as an alternative to meteoric smoke in this heterogeneous nucleation. The findings, methodology and techniques presented in this study could pave the way for answering atmospherically relevant questions which have been outstanding for several decades.

Of the two reviewers, one was willing to see the paper published, with only minor reservations. The second reviewer was rather more critical. Some of the comments from this second reviewer will lead to clarification and overall improvement of the text, and we are happy to implement these. However, other suggestions are not practicable: we are not able to satisfy the reviewer's request for further experiments since they are either not relevant to our aims, not achievable within a reasonable timescale (the CODITA grant which funded this research ended in March 2017) and in some cases, not achievable by any experimental technique which we are aware of. Here we present a generalised response to many of the reviewer's comments, followed by specific responses to those which have been addressed in the revised manuscript.

- The reviewer repeatedly states that referring to the equilibrium phase diagram and the use of saturation ratios is inappropriate. We are disappointed to see such a fundamental criticism being brought up so late in the review process. In fact, vast quantities of data are available from multiple chemical fields which show that increasing saturation ratio increases the probability of nucleation events occurring. The formulation of classical nucleation theory is entirely based on this premise and we do not know of any published literature that disputes the idea that the probability of nucleation increases with increasing supersaturation, in any system. Saturation (the ratio of free energy of the metastable liquid phase to the solid phase, as commonly defined in immersion mode nucleation) is recognised throughout the heterogeneous nucleation community as the variable which controls the probability of nucleation [e.g. (Koop et al., 2000)]. Hence we consider the use of saturation, based on phase diagrams, to be a reasonable way to parameterise the nucleation process.
- On the identity of the initially nucleating phase: in the previous version we stated that it is "likely" that NAT is the primary nucleating phase. We then made the assumption that this is so in order to parameterise our data and compare to atmospheric observations. We have edited the text (see below), stating that a different nitric acid hydrate may form first and clarifying that formation of NAT is a necessary assumption to allow atmospheric implications of the study to be probed. However we are not aware of any technique which can experimentally identify the critical cluster, the solid phase at the point of nucleation, since this is both very small (nm radius) and very short lived. This is an issue well understood in a range of nucleation communities. As a measure of the sensitivity of the atmospheric

implications to this assumption we have added a statement that if NAD is assumed to nucleate first, we see several orders of magnitude more solid particles in our atmospheric prediction. To assume that a different phase formed first we would have to guess at the thermodynamic properties of that phase and program these into the e-AIM model, a very time consuming task with little scientific basis.

It also seems that the reviewer is conflating our discussion of the observed melting with our identification of the phase. The purpose of including that observation in the paper is the confidence which it gives in the temperature measurement and control. Since the two eutectic points occur within such a small range of temperature, this is not affected by the identity of the phases melting. We have added (see below) a statement explicitly stating that our tentative identification of the nucleating phase does not rely on the observed melting point.

- A number of comments suggest that the reviewer continues to misunderstand the aims of our study:

The reference to the “stabilization afforded by the presence of water ice” shows that the reviewer continues to misunderstand our clearly stated aim of studying clouds which form in the absence of water ice (at least 20% of denitrification [ref. Mann]). This also links to the question of performing experiments over a range of concentrations, where we already explicitly state that the choice of concentration is designed to facilitate identification of the phase which forms by excluding the possibility that water ice initially nucleates.

Regarding alteration of the surfaces of particles during grinding: our explicitly stated aim is to survey a range of materials to assess which may be active enough to cause nucleation in the atmosphere (which we have achieved). Examining the exact mode of action of those materials, toward which these studies would indeed be valuable, is explicitly stated as a subject of future study. We are also puzzled by the continued references to “rendering amorphous” materials which are already amorphous in the bulk. This is also evident in the statement that our experimental observations are “too pedestrian to deduce details of the mechanistic details on nucleation”. We might not choose this experiment to answer that question, but it is explicitly not the question we are trying to answer! It is worth noting that in the much more thoroughly studied system of water-ice nucleation such mechanistic details remain a very open question (Slater et al., 2016).

We now present responses (in blue font) to the majority of the reviewer’s comments (in black font) along with details of changes made to the paper. Comments which have been generally responded to above and did not result in changes to the text have been omitted.

## **Reviewer 1**

I acknowledge the effort of the authors to amend the manuscript in the sense suggested by both referees.

We are pleased that the reviewer appreciates the significant work which went into this review process.

We are dealing with a manuscript that examines ocular (by eye) freezing and melting observations of a single known HNO<sub>3</sub> 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.

The language in the text (final paragraph of Section 3) has been altered to clarify that the assumption of NAT as the primary phase which nucleates is made in order to allow investigation of atmospheric implications. We have also expanded the discussion (same paragraph) on how reasonable this assumption is. A statement has also been added (penultimate paragraph of Section 4.2) describing the effect of assuming that NAD nucleates first. The unchanged conclusions of the study suggest that the model is reasonably insensitive to the assumption of primary nucleating phase, which increases confidence that our conclusions are robust. We have adjusted the conclusions section to make it clear that we ‘suggest’ that NAT nucleates.

The altered paragraphs read as follows:

#### Section 3:

“In order to assess the atmospheric implications of these observations, the assumption has been made that the nucleation events observed in this study were direct nucleation of NAT. While observations indicate that NAT is the phase which exists in PSC (Höpfner et al., 2006), it is possible that other metastable nitric acid hydrate phases (Nitric Acid Dihydrate,  $\alpha$ - or  $\beta$ -NAD) may form initially, then transform to the stable NAT phase (Grothe et al., 2008; Weiss et al., 2016). We note that the  $820\text{ cm}^{-1}$  feature used by Höpfner et al. (2006) to identify atmospheric NAT is present for both the  $\alpha$ - and  $\beta$ - polymorphs (Iannarelli and Rossi, 2015). Since the equivalent  $816\text{ cm}^{-1}$  feature for  $\beta$ -NAD has not to our knowledge been compared to the atmospheric spectra there is still uncertainty regarding the relevant atmospheric phases. In fact, NAD nucleation has been observed under atmospheric conditions for homogeneous nucleation (Stetzer et al., 2006). However, in our experiments some nucleation events were observed under conditions where NAD is not thermodynamically stable ( $S_{\text{NAD}} < 1$ ), and since there is no significant discontinuity in the trend in  $n_s$  at  $S_{\text{NAD}} = 1$ , the assumption of direct nucleation of NAT seems reasonable. Since it is possible that a different nitric acid hydrate phase formed in these experiments we have examined the sensitivity of our atmospheric conclusions to the assumption of NAT as the primary nucleating phase. Some metastable NAD may form when  $S_{\text{NAD}} > 1$  (or some other metastable nitric acid phase may form); however, the consistent melting onset of droplets in agreement with the NAT / ice or NAT / NAM eutectic suggests that if any NAD did form it converted to NAT (note that the melting point is not taken to be supporting evidence of which phase nucleated initially). We did not attempt to identify directly the phase of the acid hydrate in the frozen droplets, since the polymorph resulting from crystallisation may not be the same phase which initially nucleated. In fact, if a metastable phase nucleates, it often converts to a more stable phase during the crystallisation process (Murray and Bertram, 2008). The parameterisations of  $n_s$  as a function of  $S_{\text{NAT}}$  shown in Figure 4 were therefore used to investigate the activity of meteoric material in heterogeneously nucleating PSC formation in the atmosphere.”

#### Section 4.2:

“To test the sensitivity of the system to the assumption that NAT was the primary nucleating phase, parameterisations of  $n_s$  as a function of  $S_{\text{NAD}}$  were produced for the meteorite samples and the fumed silica. Note that a parameterisation was not produced for the fused quartz since with this material heterogeneous nucleation was always observed under conditions too warm (by up to 10 K) for NAD to be thermodynamically stable. These parameterisations were then implemented in the same atmospheric scenarios (temperatures and concentrations). The result was that the onset of nucleation was predicted 1.2-1.7 K colder, but that by the point of measurement around 250 times higher  $N_{\text{NAX}}$  was predicted (data not shown). This means that the conclusions remain the same for both the meteorites (which are sufficiently active to explain observed cloud) and fumed silica (which is not), suggesting that the atmospheric conclusions of this study are reasonably insensitive to the choice of primary nucleating phase.”

Conclusions:

“Heterogeneous nucleation by analogues for Meteoric Smoke Particles (MSPs) and Meteoric Fragments (MFs) in binary  $\text{HNO}_3$  /  $\text{H}_2\text{O}$  solutions has been measured in the laboratory. Both MSPs and MFs immersed in nitric acid solution droplets were found to nucleate crystalline nitric acid hydrates. Given nucleation occurred under conditions where the metastable nitric acid dihydrate (NAD) is unstable, we suggest that the nitric acid trihydrate (NAT) initially nucleated, although we cannot rule out the nucleation of other metastable phases. Parameterisations of the resulting activity were used to show that heterogeneous nucleation on meteoric material is a potential pathway to forming observed number densities of NAT crystals in Polar Stratospheric Clouds (PSCs) in the absence of water ice.”

In a stricter sense the chosen title is misleading because nucleation is never investigated.

It is true that we do not directly observe nucleation, we observe the result of nucleation – i.e. crystallisation. It is a very common approach to take the crystallisation of a droplet as evidence of nucleation since crystallisation could not occur without nucleation. Hence, we intend to keep the title unchanged.

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

Regarding the use of a single  $\text{HNO}_3$  solution I point out that known equilibrium phase diagrams are NOT a good guide to interpret observations on nucleation which is a kinetic process.

We discuss this point in the first of this response. We think that the changes mentioned above clarify these issues.

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.

The observation of the melting point is included in the text primarily to give confidence in the temperature measurement and control of the apparatus, which would still be relevant in the case of either eutectic point. The text in Section 2 has been revised to state that “The temperature at which changes start in the droplet is consistent with either the ice  $I_h$  / NAT or NAT / NAM eutectic”. See also changes above regarding changes to the final paragraph of Section 3.

Saturation of a NAT or NAD phase has nothing to do with the process at hand which will depend on the adsorption of  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  vapor to the interface of meteoric materials and their analogues (proxies).

Saturation ratios are entirely appropriate here and are not limited to defining gas phase adsorption. We stress that we are dealing with nucleation from a supersaturated solution, this is very clear in the manuscript.

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!

And

I will not dwell on this “classical” characterization (Pruppacher) as these terms are devoid of any meaning in a mechanistic sense.

These comment seems to be levelled more broadly at the extensive community that use these concepts. This paper is not the right place to open up this discussion. We have not made any changes in light of these comments.

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  $\beta$ -NAT is the stabilization afforded by the presence of water ice. DFT calculations in Weiss (2016) have quantified the interaction of  $\beta$ -NAT with water ice and have found it to be larger than for  $\alpha$ -NAT which itself is more stable than  $\beta$ -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.

The aims of the present study are to investigate formation of synoptic PSC in the absence of water ice: the final paragraph of Section 1 has been revised to “Here we investigate whether MSPs and / or MFs could provide a heterogeneous nucleation pathway to NAT in synoptic PSCs where water ice is not present” in order to clarify this.

Regarding the introduction I would like to emphasize that both Grothe (2008) and Weiss (2016) dealt with heterogeneous nucleation of  $\text{HNO}_3$ -hydrates, reportedly in the immersion or contact freezing mode (liquid  $\text{N}_2$ ) as well as in deposition freezing (cold metal support). The authors make it sound as if homogeneous nucleation was involved (pg. 2, line 2).

This has been corrected in the text and this section rewritten to make it clearer.

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!

We have provided the first experimental evidence that meteoric materials, both smoke and fragments, have the potential to trigger nucleation of crystalline nitric acid hydrate particles in the polar stratosphere. We think this is an important conclusion and will motivate future research to generate a more quantitative and fundamentally rigorous understanding of this process in the future. The work is not speculative, since we provide clear evidence of nucleation (we observe crystallisation, which must follow on from nucleation) and justify the assumptions made when exploring the atmospheric implications of this work.

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

This has been corrected.

## References

- Grothe, H., Tizek, H., and Ortega, I. K.: Metastable nitric acid hydrates-possible constituents of polar stratospheric clouds?, *Faraday Disc.*, 137, 223-234, 2008.
- Höpfner, M., Luo, B. P., Massoli, P., Cairo, F., Spang, R., Snels, M., Di Donfrancesco, G., Stiller, G., von Clarmann, T., Fischer, H., and Biermann, U.: Spectroscopic evidence for NAT, STS, and ice in MIPAS

infrared limb emission measurements of polar stratospheric clouds, *Atmos. Chem. Phys.*, 6, 1201-1219, 10.5194/acp-6-1201-2006, 2006.

Iannarelli, R., and Rossi, M. J.: The mid-IR absorption cross sections of  $\alpha$ - and  $\beta$ -NAT ( $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ ) in the range 170 to 185 K and of metastable NAD ( $\text{HNO}_3 \cdot 2\text{H}_2\text{O}$ ) in the range 172 to 182 K, *J. Geophys. Res.: Atmos.*, 120, 11,707-711,727, 10.1002/2015JD023903, 2015.

Koop, T., Luo, B. P., Tsias, A., and Peter, T.: Water activity as the determinant for homogeneous ice nucleation in aqueous solutions, *Nature*, 406, 611, 10.1038/35020537, 2000.

Murray, B. J., and Bertram, A. K.: Inhibition of solute crystallisation in aqueous  $\text{H}^+\text{-NH}_4^+\text{-SO}_4^{2-}\text{-H}_2\text{O}$  droplets, *Phys. Chem. Chem. Phys.*, 10, 3287-3301, 10.1039/B802216J, 2008.

Slater, B., Michaelides, A., Salzmänn, C. G., and Lohmann, U.: A blue-sky approach to understanding cloud formation, *Bull. Amer. Met. Soc.*, 97, 1797-1802, 10.1175/bams-d-15-00131.1, 2016.

Stetzer, O., Möhler, O., Wagner, R., Benz, S., Saathoff, H., Bunz, H., and Indris, O.: Homogeneous nucleation rates of nitric acid dihydrate (NAD) at simulated stratospheric conditions; Part I: Experimental results, *Atmos. Chem. Phys.*, 6, 3023-3033, 10.5194/acp-6-3023-2006, 2006.

Weiss, F., Kubel, F., Gálvez, Ó., Hoelzel, M., Parker, S. F., Baloh, P., Iannarelli, R., Rossi, M. J., and Grothe, H.: Metastable nitric acid trihydrate in ice clouds, *Angew. Chem. Int. Ed.*, 55, 3276-3280, 10.1002/anie.201510841, 2016.