School of Chemistry
Faculty of Maths and Physical Sciences
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What controls nucleation of ice and nitric acid hydrates by meteoric material?

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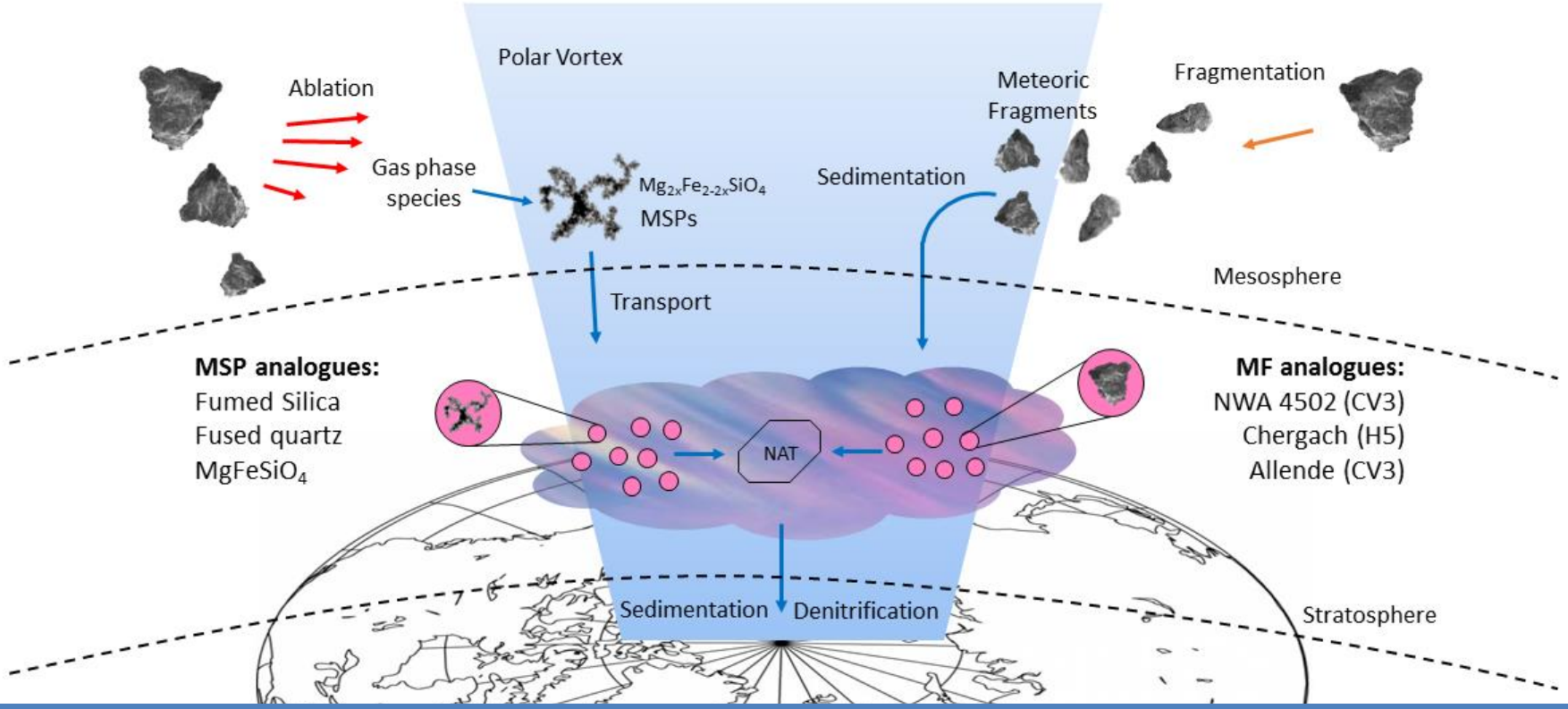
Graham W. Mann, John M. C. Plane, and Benjamin J. Murray



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Motivation

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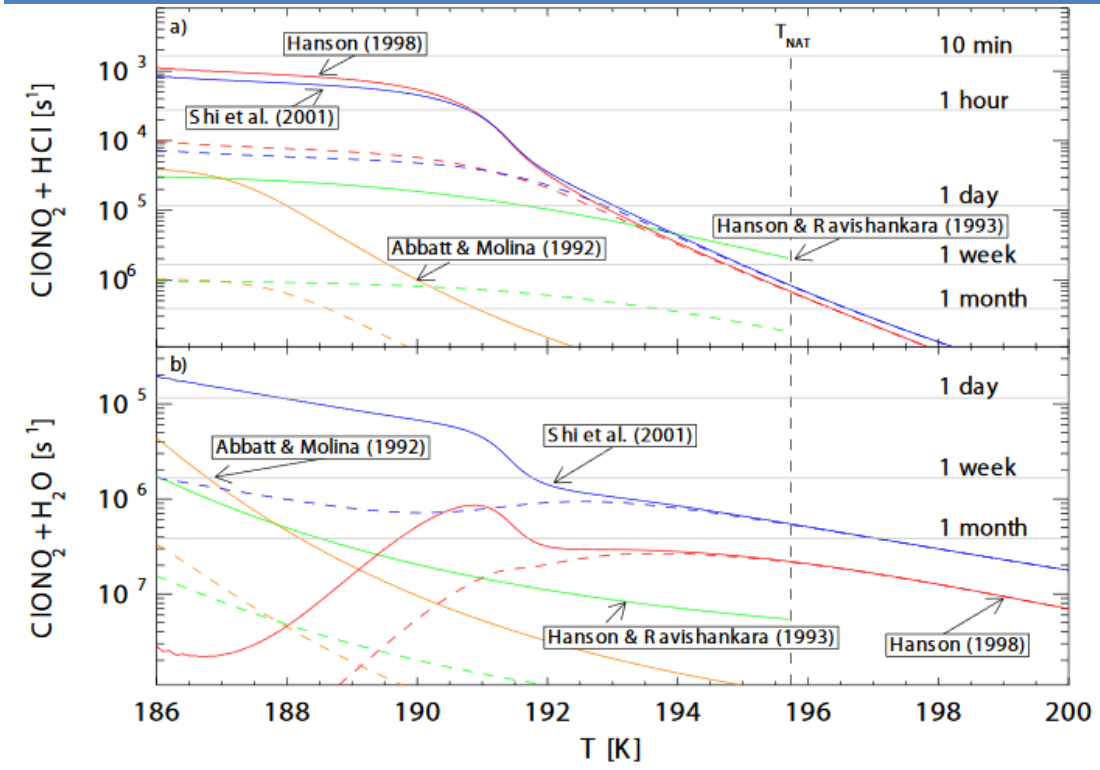
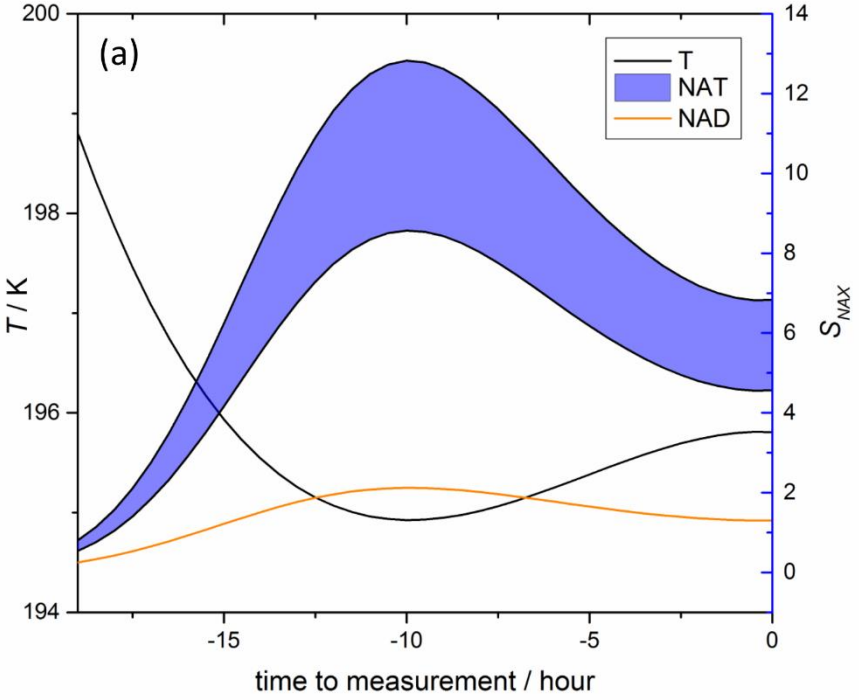
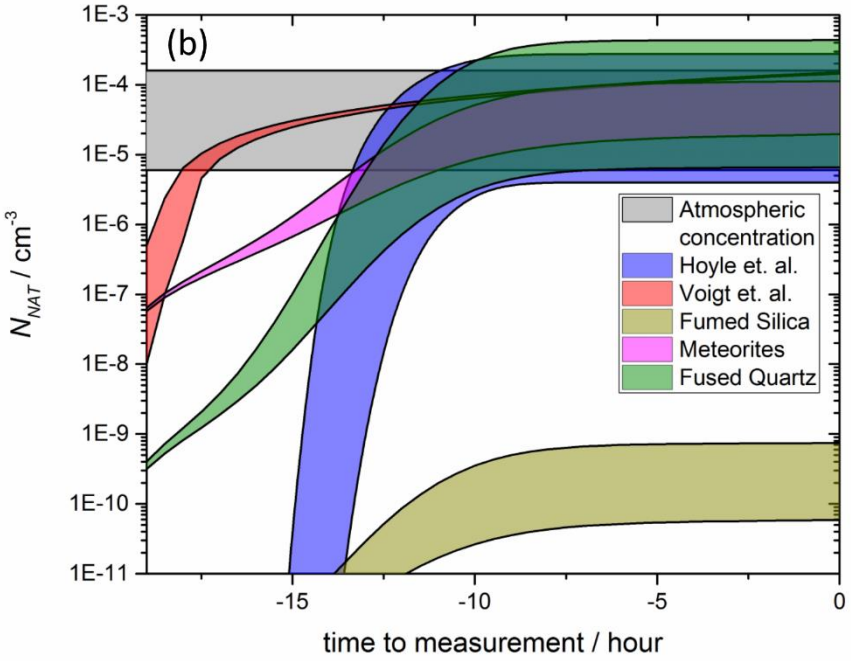


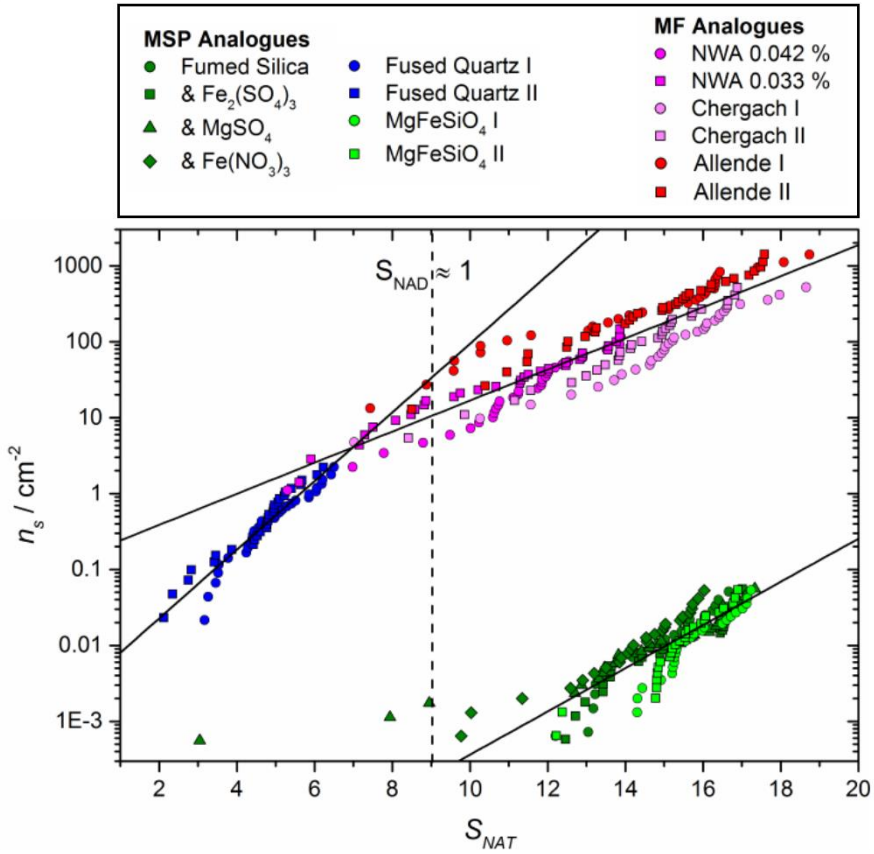
Fig. 1. First order loss rates for $ClONO_2$+HCl **(a)** and $ClONO_2$+H_2O **(b)** for different parameterizations and aerosol types for typical stratospheric conditions (50 hPa, 5 ppmv H_2O, 1 ppbv HCl, 0.5 ppbv $ClONO_2$, 10 ppbv HNO_3, 0.15 ppbv H_2SO_4 and 10 background aerosol particles cm^{-3}). Solid red and blue lines depict ternary aerosol, dashed lines binary aerosol. Solid green and orange lines represent NAT particles with density 10^{-1} cm^{-3}, dashed lines 10^{-4} cm^{-3}. Adapted from Dameris et al. (2007).

Chlorine activation depends strongly on the type and number density (surface area) of Polar Stratospheric Cloud (PSC) particles present. This means that aerosol microphysics and nucleation in particular are key uncertainties in predicting ozone recovery.

Wegner, T., Grooß, J.-U., von Hobe, M., Stroh, F., Sumińska-Ebersoldt, O., Volk, C. M., Hösen, E., Mitev, V., Shur, G., and Müller, R.: Heterogeneous chlorine activation on stratospheric aerosols and clouds in the Arctic polar vortex, Atmos. Chem. Phys., 12, 11095–11106, https://doi.org/10.5194/acp-12-11095-2012, 2012.







We previously showed that meteoric fragments have sufficient activity to explain observed crystal number concentrations.

James, A. D., Brooke, J. S. A., Mangan, T. P., Whale, T. F., Plane, J. M. C., and Murray, B. J.: Nucleation of nitric acid hydrates in polar stratospheric clouds by meteoric material, Atmos. Chem. Phys., 18, 4519–4531, https://doi.org/10.5194/acp-18-4519-2018, 2018.

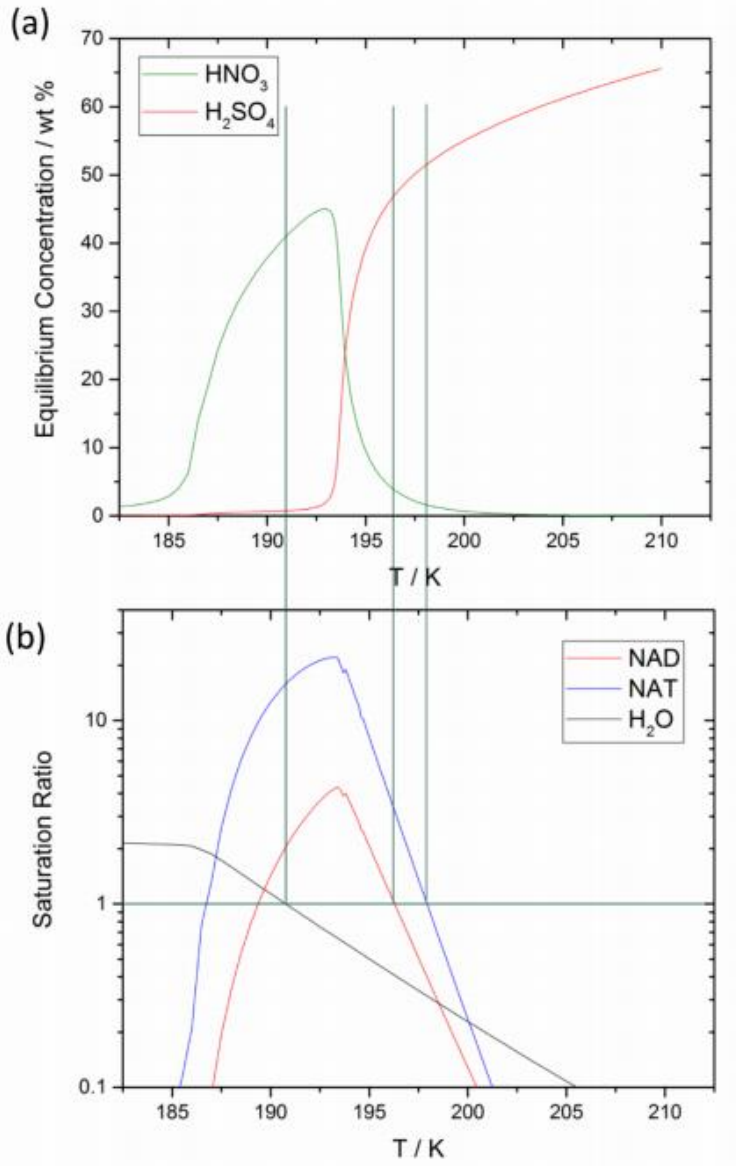


Figure 1.10: Concentration (a) and associated saturation ratio (b) of droplets in equilibrium with a gas phase containing 0.4 ppb HNO_3, 0.1 ppb H_2SO_4 and 4 ppm H_2O as a function of temperature. Horizontal and vertical green lines demonstrate the temperature and concentration at which the solution is saturated with respect to Nitric Acid Trihydrate (NAT), Nitric Acid Dihydrate (NAD) and H_2O ice. After *Carslaw et al.* [1997].

- Our study made three key assumptions which must be tested before we can produce a rigorous treatment of nucleation to test in global modelling.
- Firstly, we used binary HNO_3/H_2O solutions to approximate liquid PSC, which actually contain significant H_2SO_4 at the temperatures where crystals form.
- Secondly, the n_s parameterisation used assumes that the nucleation process is stochastic, with the thermodynamic saturation of the solution with respect to the crystalline phase, S_x, as the only determinant of nucleation, and time dependence relatively unimportant.
- Thirdly, to assess the atmospheric implication of the observed nucleation, we had to assume the phase which forms first, and chose Nitric Acid Trihydrate (NAT).

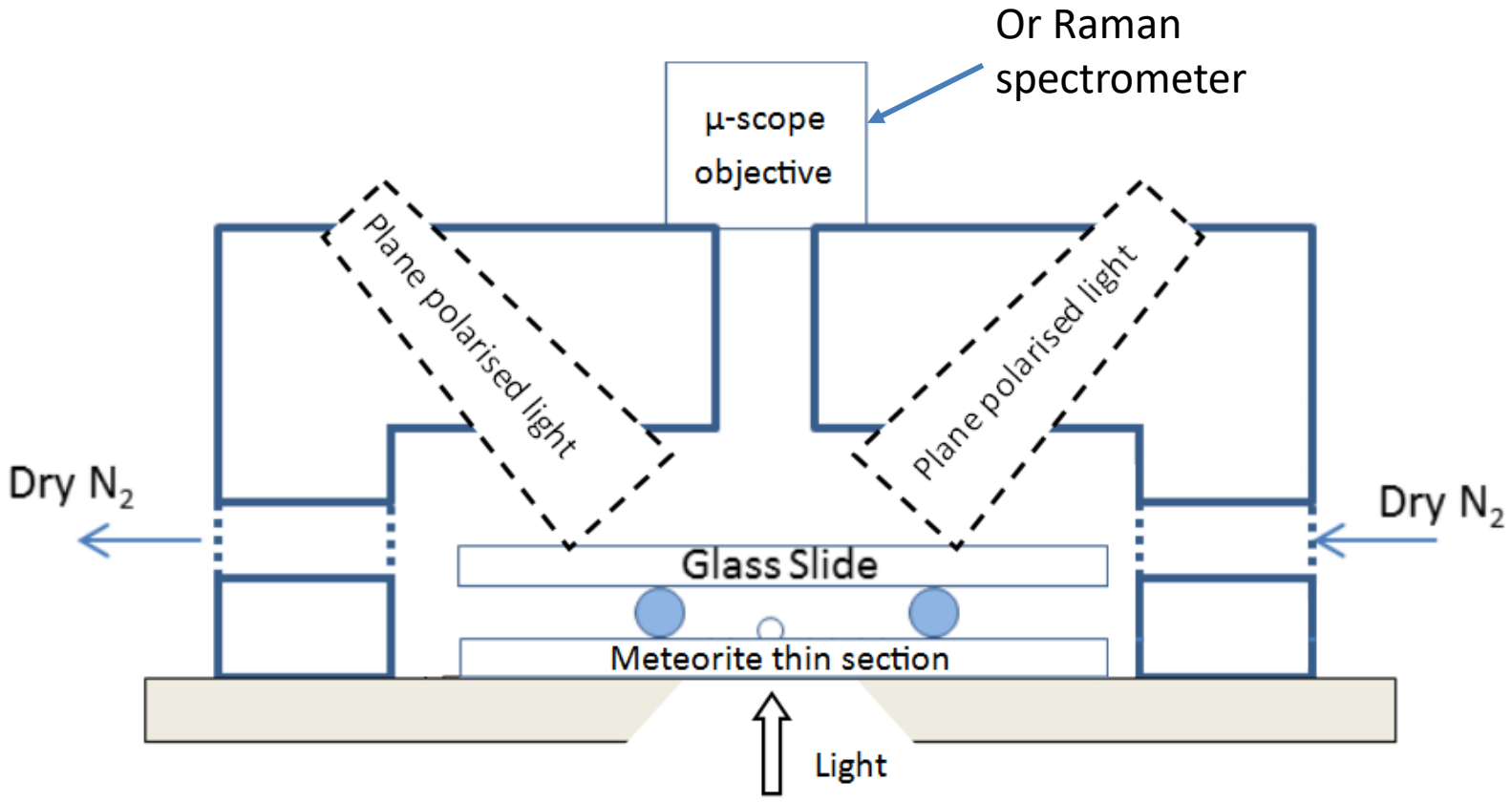
Aims

- Investigate impact of H_2SO_4 content.
- Investigate which phase forms first.
- Investigate time dependence, i.e. CNT vs. n_s parameterisations.

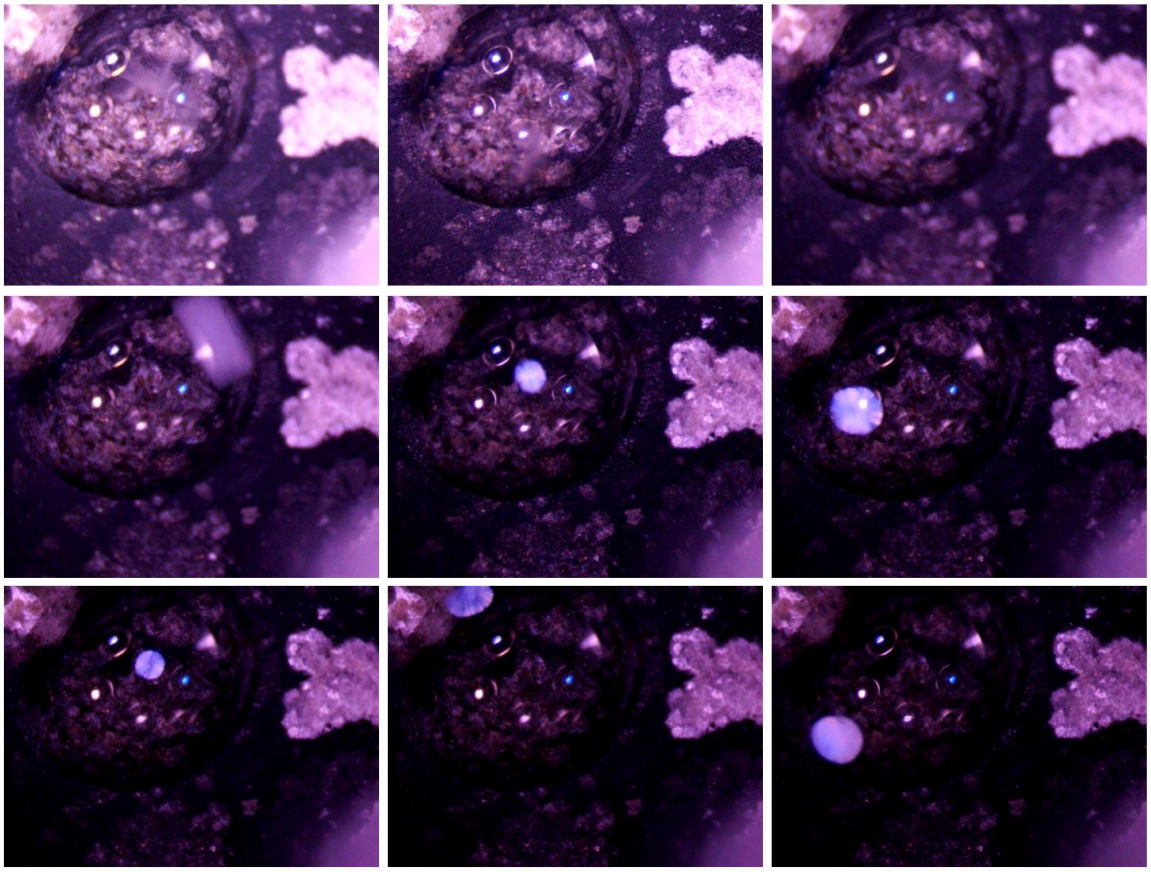
This is a significant body of work to carry out with complex, heterogeneous materials like meteorite samples, so:

- Investigate preferential nucleation of individual phases on individual mineral content of meteoric fragments.

Experimental method – nucleation by components of fragments?



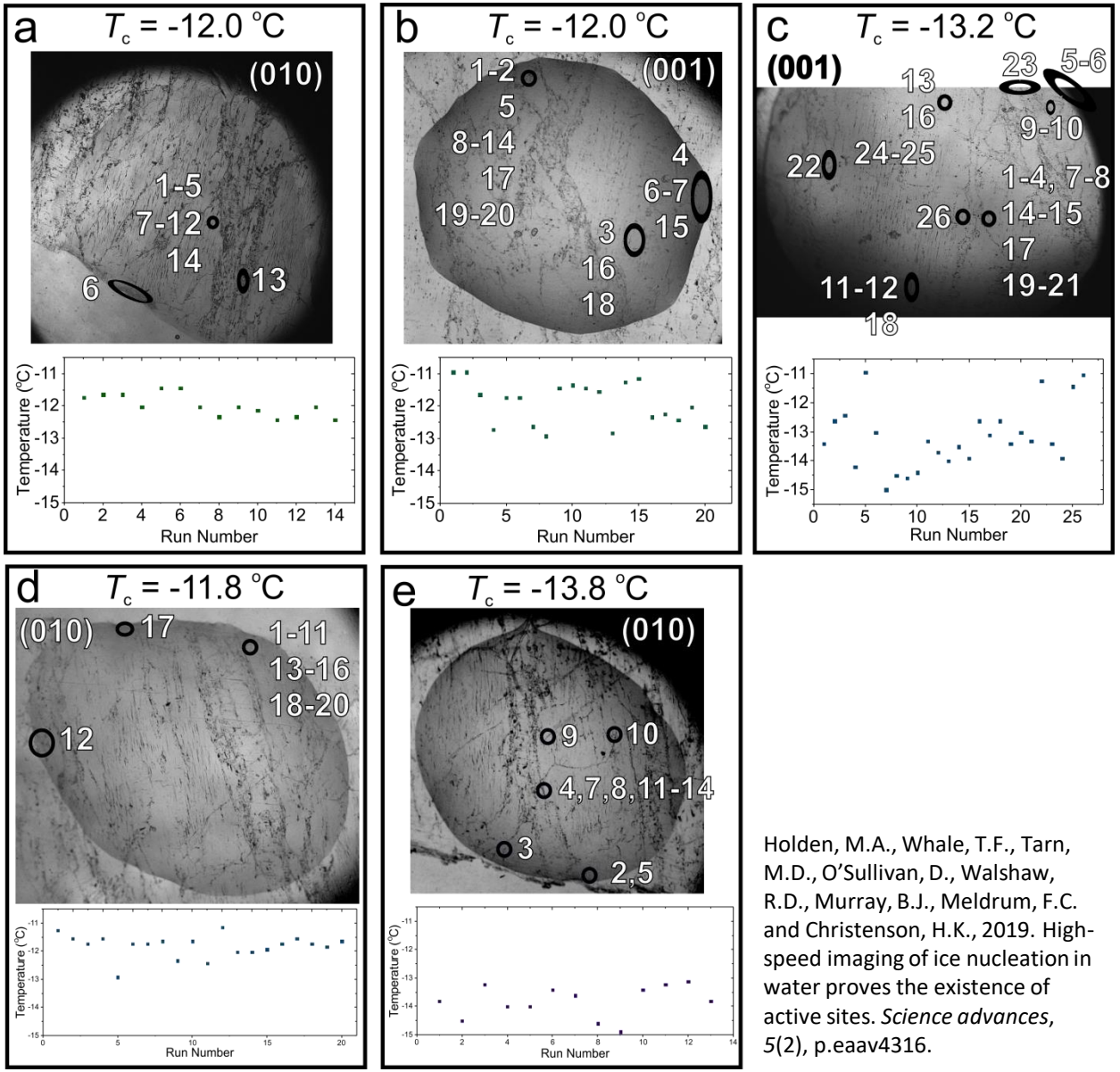
- Plane polarised reflected light microscope
- Liquid droplets on meteorite thin section



- We observed repeated nucleation and melting in droplets of binary HNO_3 / H_2O on thin section of the Allende meteorite.
- A total of 37 nucleation events have been observed so far, with up to 9 repeats on individual droplets.

- Nucleation did not show preference for particular sites on the surface, suggesting that either a distribution of similarly active sites exists, or that the sites are destroyed by the acid solution or the nucleation process.
- In addition the crystals which form have some distinct visual differences.

Comparing to other recent work

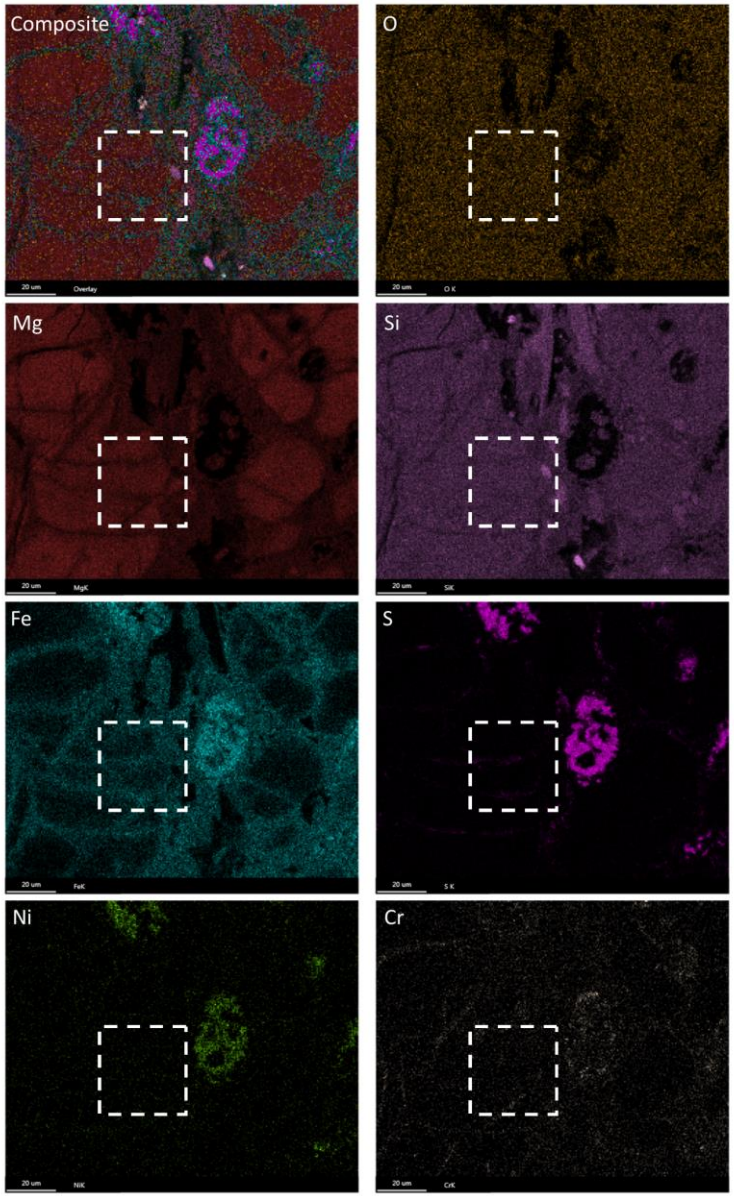


In contrast, Holden et al. tended to see nucleation on preferred sites for H_2O ice on K-feldspar (occasionally moves but often returns).

This suggests that nucleation in different systems can proceed by rather different mechanisms.

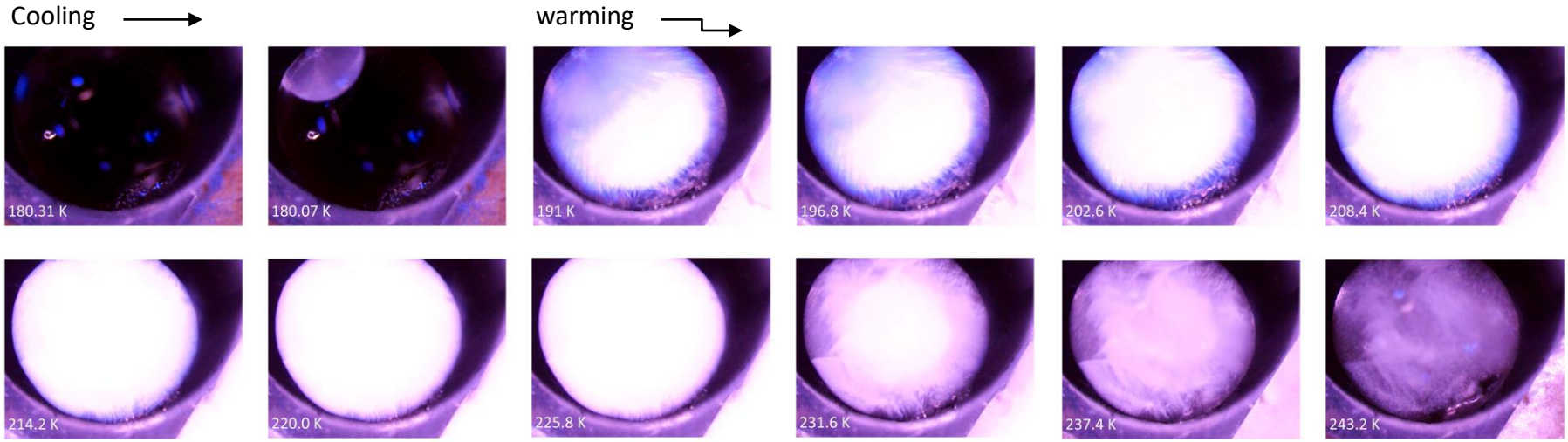
Holden, M.A., Whale, T.F., Tarn, M.D., O'Sullivan, D., Walshaw, R.D., Murray, B.J., Meldrum, F.C. and Christenson, H.K., 2019. High-speed imaging of ice nucleation in water proves the existence of active sites. *Science advances*, *5*(2), p.eaav4316.

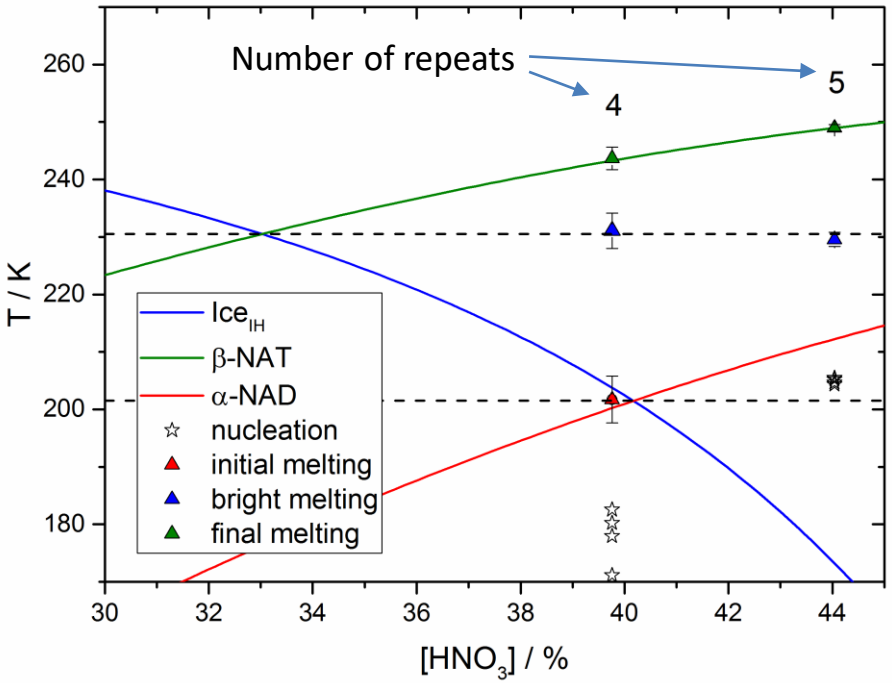
Nucleating regions are heterogeneous



- Narrowing down to active regions by examining electron microscopy of thin sections used for 9 events, we find three kinds of region:
- The highly processed edge of chondrules.
- Olivine / pyroxene boundaries within chondrules.
- The edge of metal sulfide inclusions in chondrules. (e.g. left figure, white box shows region where crystal formed)
- Since these features are unique to meteorites, it is not possible to substitute more easily obtainable proxies for meteoric fragments.

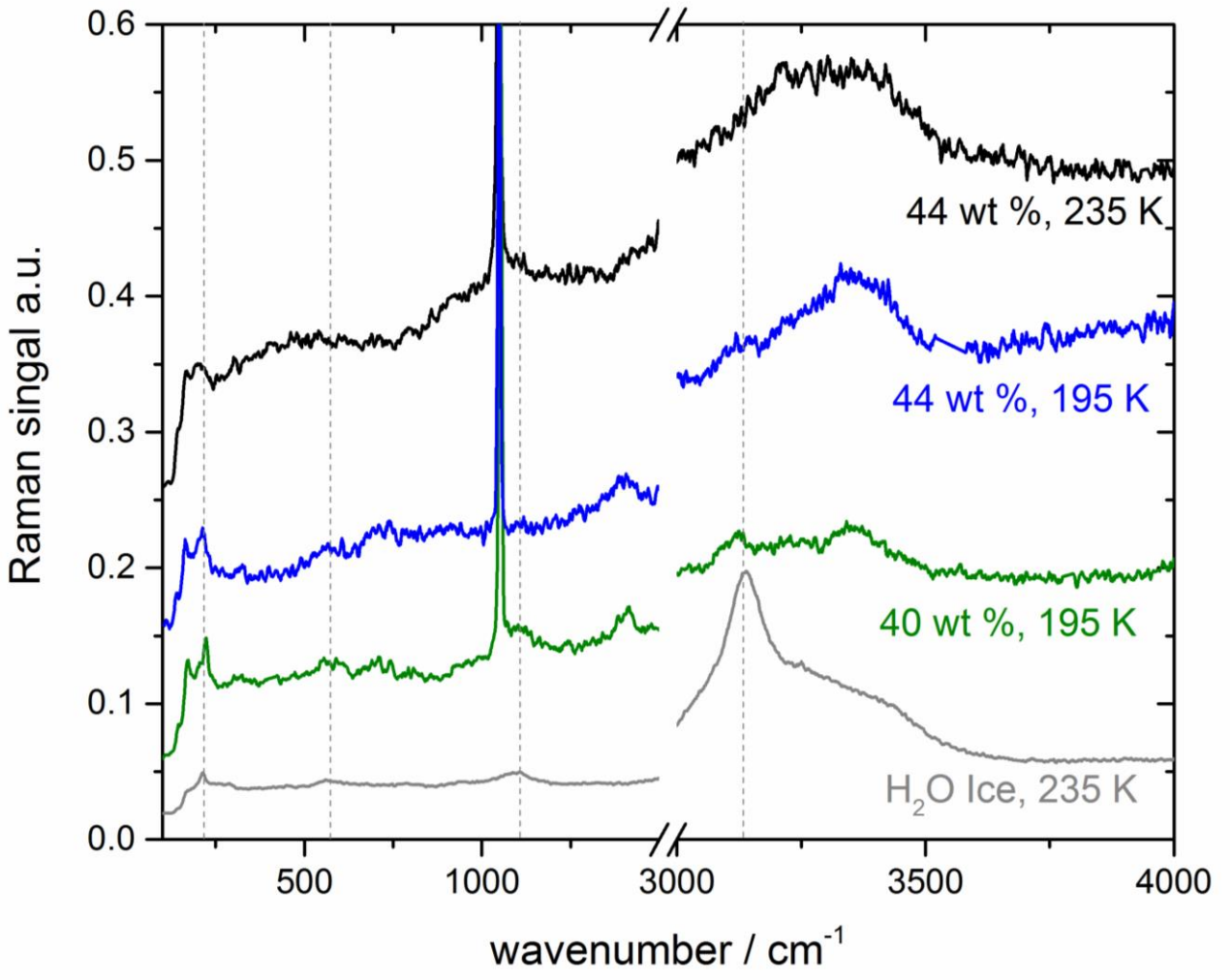
“blank” results – no thin section





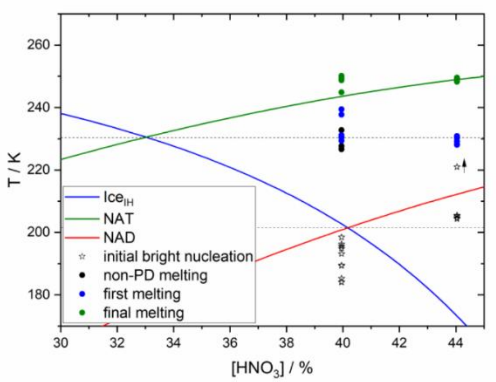
- Microscope observations of nucleation events may also give some information about the phase which nucleates.
- Sometimes see a “bright” phase form initially on nucleation. Melting behaviour suggests this is H_2O ice. Often also observe this phase as a secondary nucleation of further cooling.

Raman spectra of phases



Confirms that phase melting at eutectic temperature is H_2O ice, we were not able to observe good enough signal to noise to identify nitric acid hydrates.

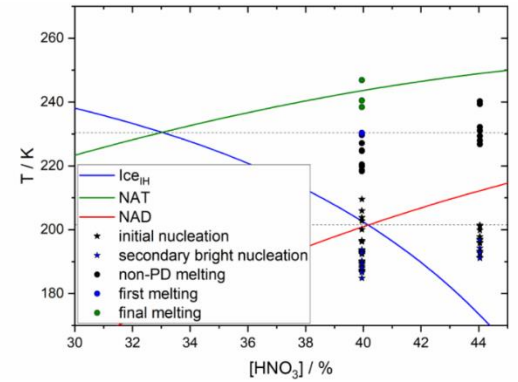
Probability tree



Yes: 16, 46 %

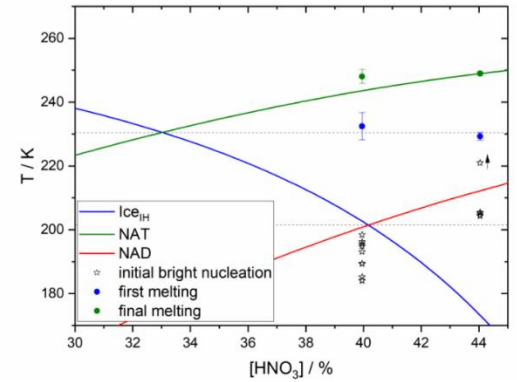
Does a "bright" phase form initially?

No: 21, 54 %



Are there two distinct melting events?

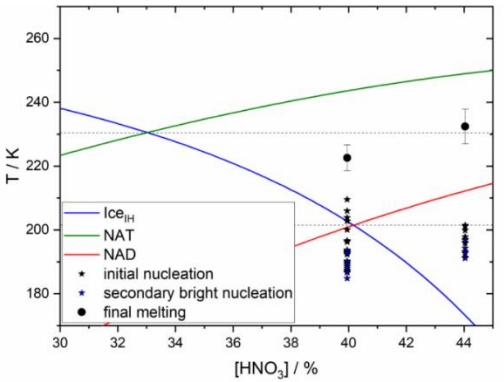
Yes: 7, 32 %



No: 3, 14 %

Also see melting behaviour which does not agree with phase diagram, implying metastable phase formation

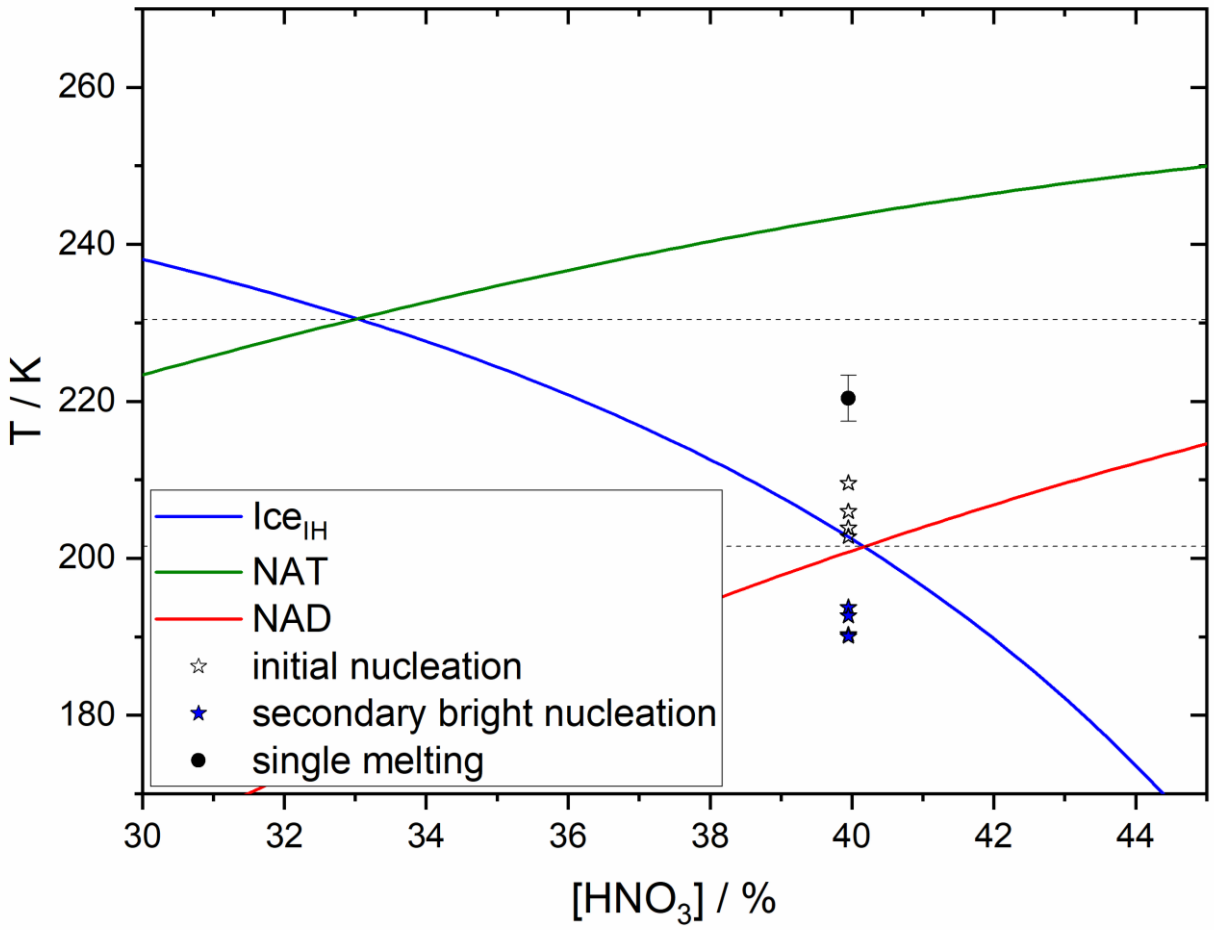
Yes: 3, 14 %



No: 9, 41 %

Complex, poorly reproducible behaviour makes gathering statistically useful data on the phase which forms extremely difficult

A new metastable phase?

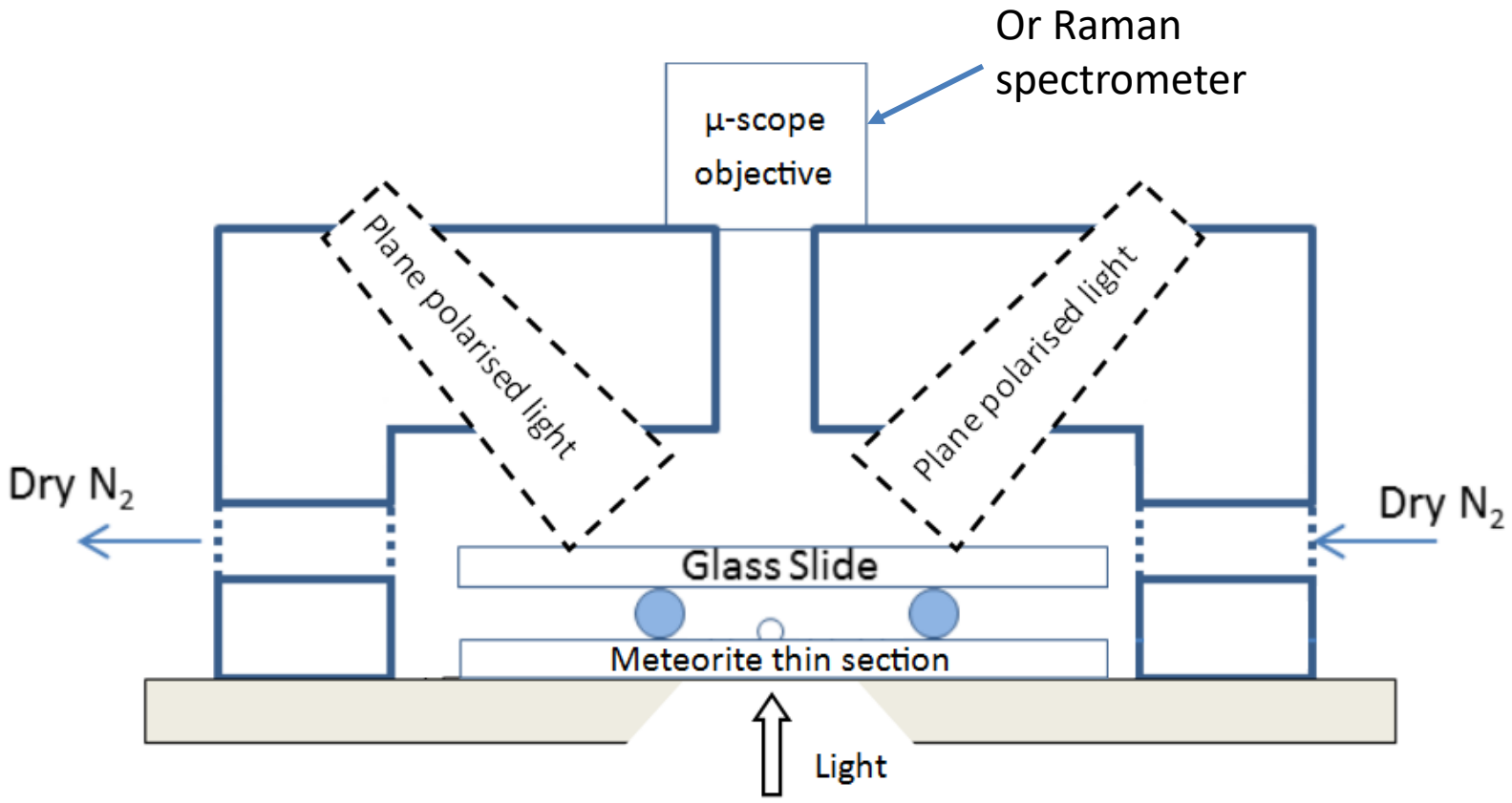


- Three runs from different droplets on different thin section samples nucleated at H_2O ice and NAD sub-saturated conditions, and did not melt as any known phase.
- This could indicate the presence of a previously unknown phase, or that thermodynamics of α-NAT or β-NAD are not well represented by the equilibrium phase diagram.

Conclusions – thin section work

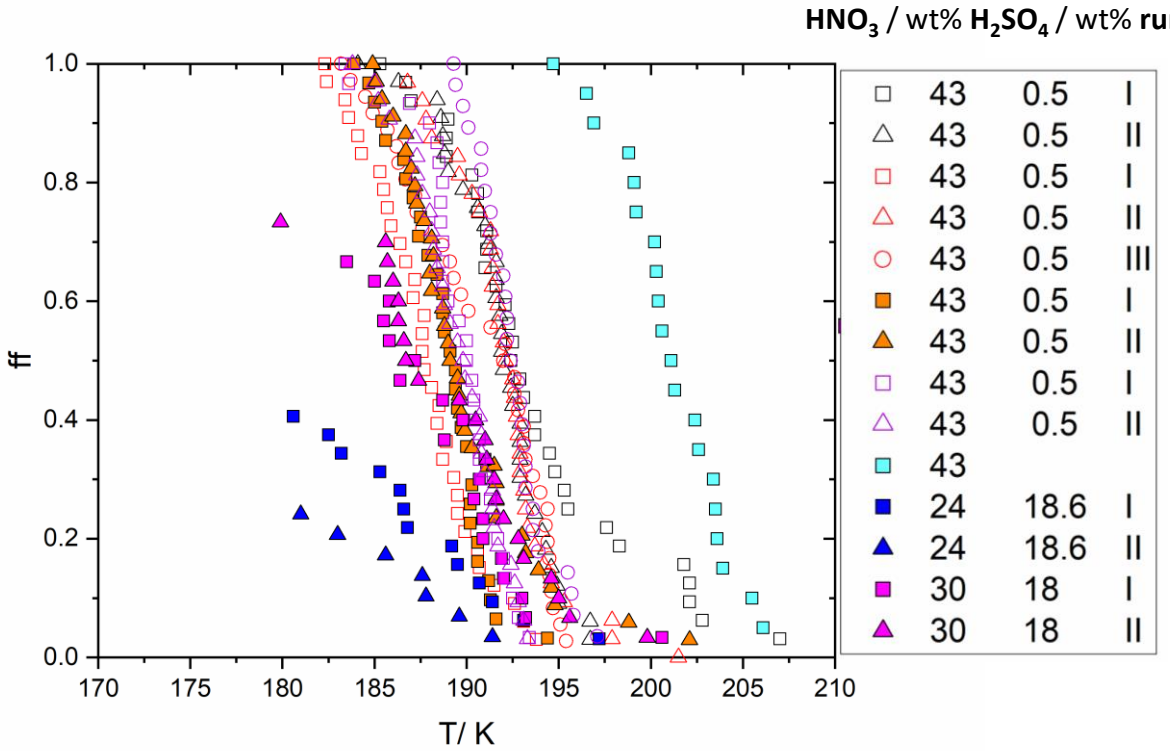
- Competitive nucleation of different phases by meteoric fragments makes for a very complex system.
- Nucleation does not appear to occur preferentially on one type of region e.g. one mineral.
- Nucleation observed in James, ACP (2018) was likely a variety of phases, so parameterising as NAT is a simplification… still the best we can do.

Experimental method – effect of H_2SO_4?



- Plane polarised reflected light microscope
- Array of droplets on glass slide

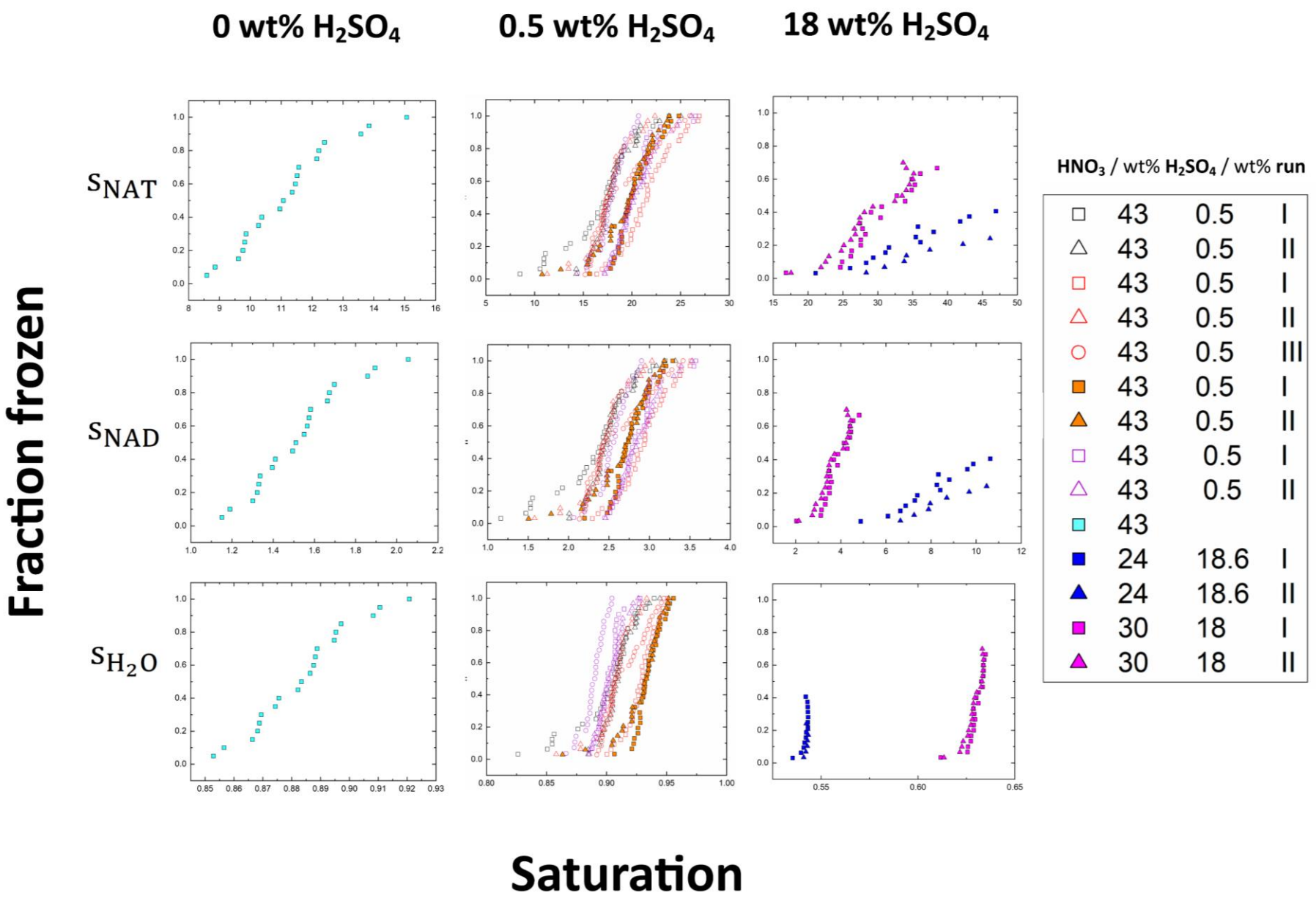
H_2SO_4 deactivates meteoric fragments



- Open symbols = controls
- Filled shapes contain 1 wt% NWA 2502 meteorite
- Symbol shape indicates repeats (same solution after several hours at variable cold bath temperature)

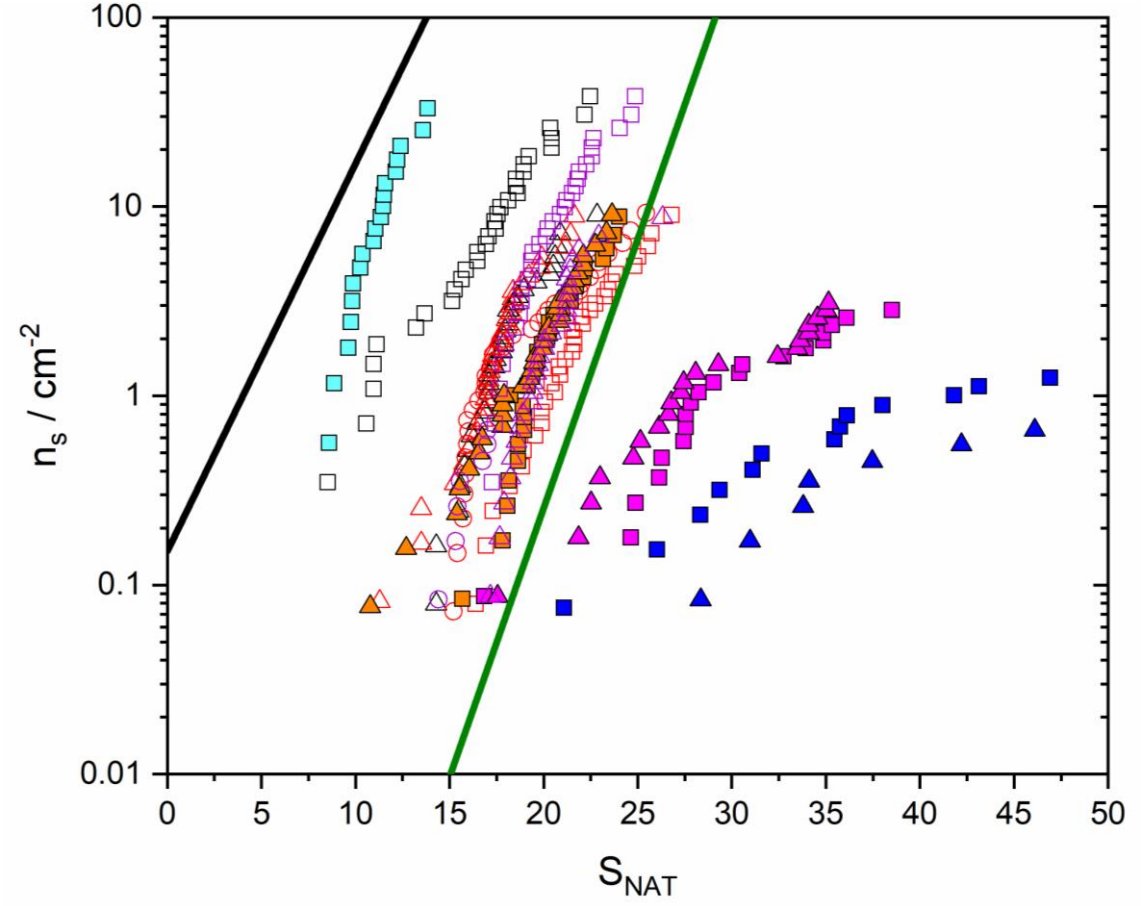
- 43 wt% HNO_3 used to suppress H_2O ice formation.
- Adding 0.5 wt% H_2SO_4 deactivates the heterogeneous nucleating ability of H_2SO_4.
- Initially samples were made up at room temperature. To investigate the temperature sensitivity of this deactivation, solutions were made up in a cold bath.
- For cold bath T below 0 °C, meteorite was added to 60 wt% H_2SO_4, then mixed with HNO_3 and H_2O, such that crystalline phases were never thermodynamically stable in bulk samples.
- Cold bath T of 253 K did not restore heterogeneous activity.

H_2SO_4 deactivates meteoric fragments



H_2O was never stable & NAD was always stable for the observed nucleation events

H_2SO_4 deactivates meteoric fragments

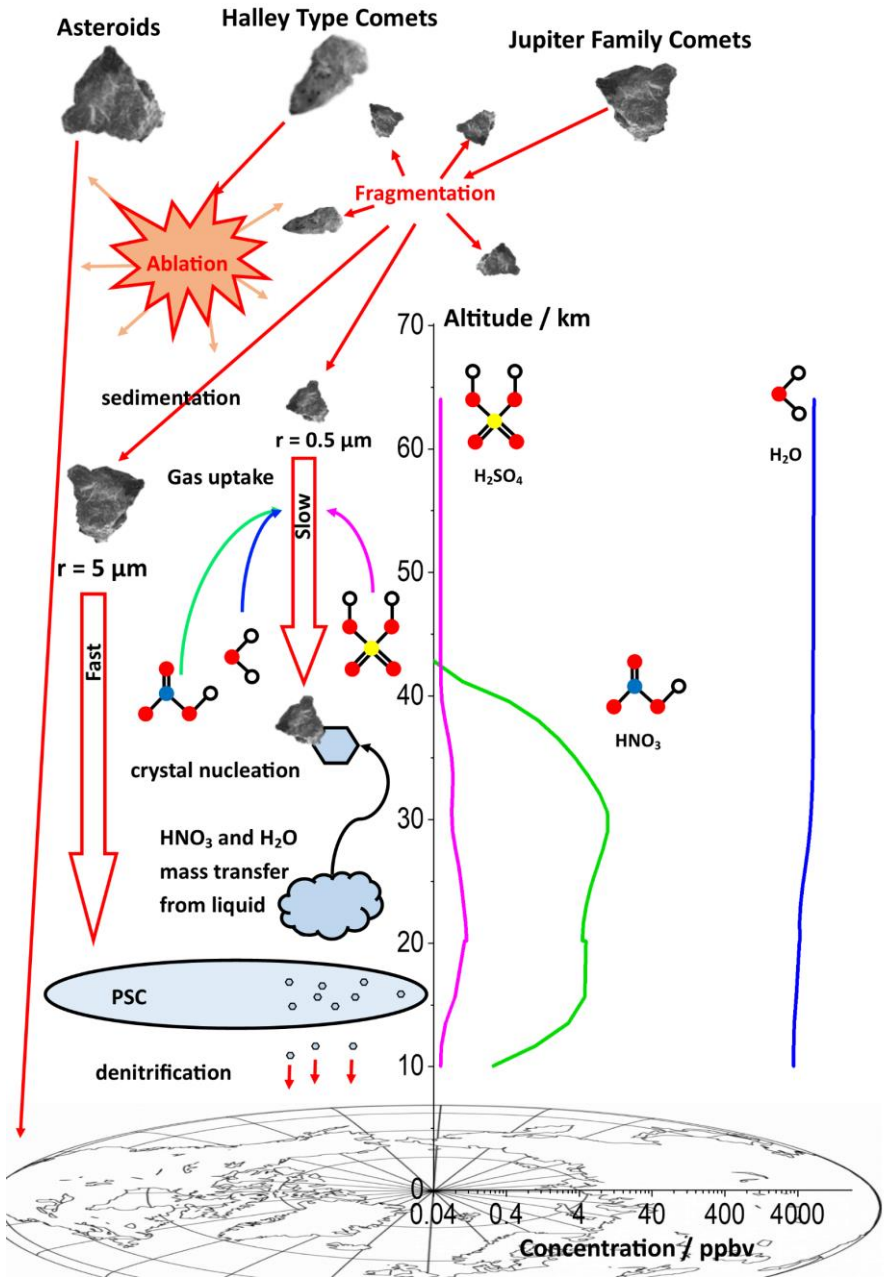


HNO_3 / wt%	H_2SO_4 / wt%	run
43	0.5	I
43	0.5	II
43	0.5	I
43	0.5	II
43	0.5	III
43	0.5	I
43	0.5	II
43	0.5	I
43	0.5	II
43		
24	18.6	I
24	18.6	II
30	18	I
30	18	II

- Straight lines are parameterisations of meteorite fragments (MFs, black) and meteor smoke particles (MSPs, green) from previous work. An upper limit based on the background here would not give sufficient number concentration in the atmosphere.
- H_2SO_4 deactivates heterogeneous nucleation activity of meteoric fragments.

James, A. D., Brooke, J. S. A., Mangan, T. P., Whale, T. F., Plane, J. M. C., and Murray, B. J.: Nucleation of nitric acid hydrates in polar stratospheric clouds by meteoric material, Atmos. Chem. Phys., 18, 4519–4531, https://doi.org/10.5194/acp-18-4519-2018, 2018.

Pathway to nucleation



- Proposed mechanism for heterogeneous nucleation in PSC:
- Meteoric fragments sediment rapidly through the mesosphere and upper stratosphere, but slow at PSC altitude.
- Fragments then take up HNO_3 and H_2O from the gas phase, whilst H_2SO_4 remains in liquid droplets.
- Highly dependent on the size (sedimentation velocity) of meteoric fragments. If too big, stratospheric lifetime will be too short, if too small, will take up H_2SO_4 and be deactivated.

Smallest fragments

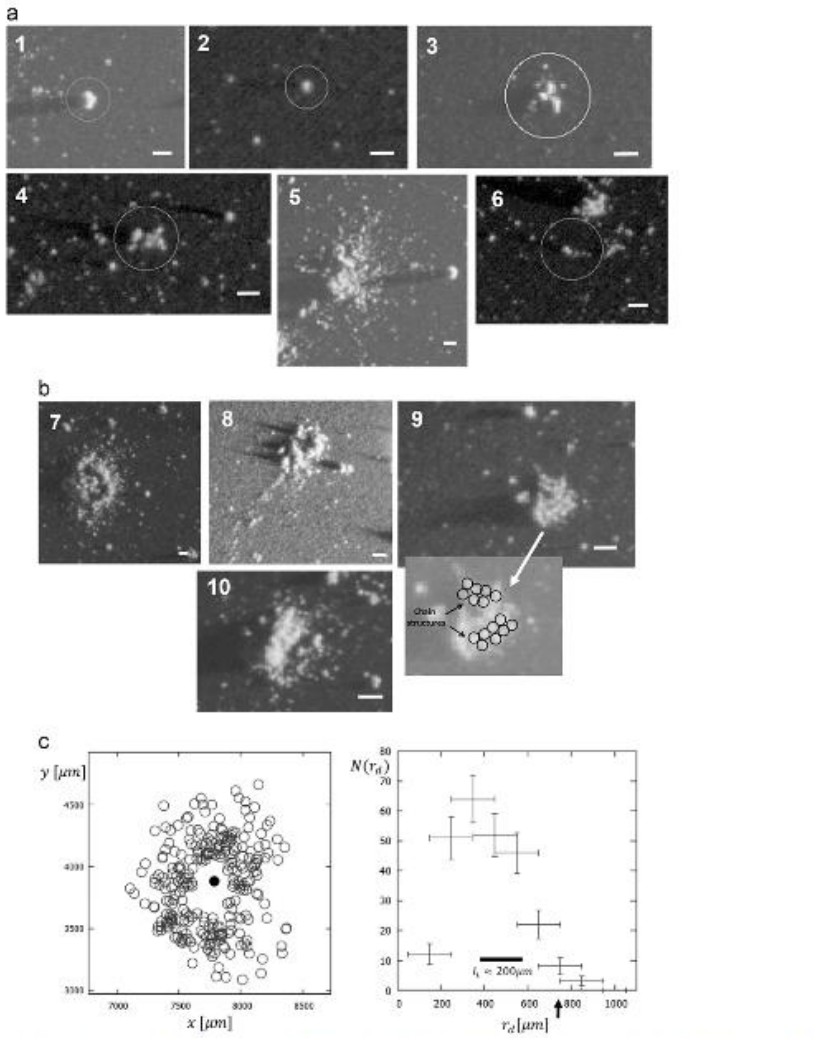


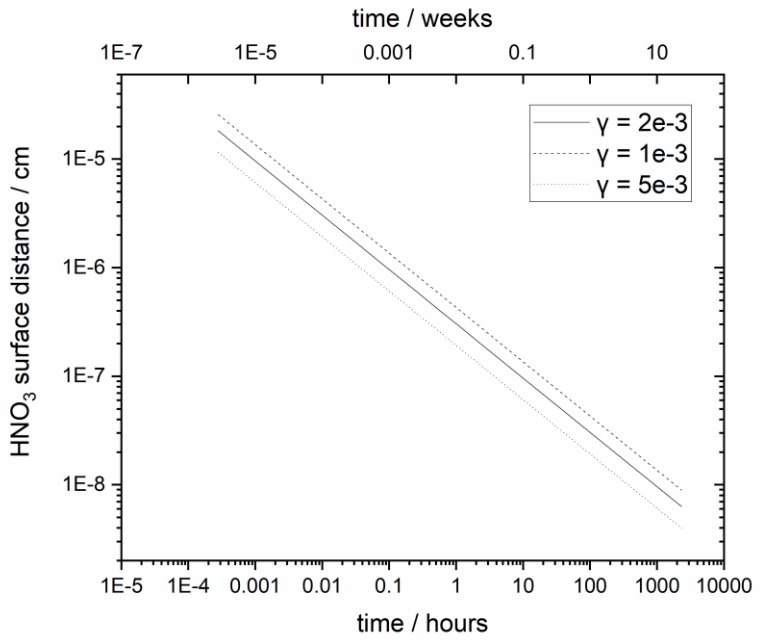
Fig. 2. **(a) 1:** no breakup: 2CF Lambert Kolima.3, $d\approx108$ µm, $h\approx115$ µm. **2:** no breakup: 1CF Pecine Ala Kitka, $d\approx41$ µm, $h\approx45$ µm. **3:** simple breakup: 2D0 Stefanie Saimaa, $d\approx87$ µm, $h\approx45$ µm, fragment sizes 15–40 µm (diameter). **4:** simple breakup: 2CF Pertti Kolima.3, $d\approx89$ µm, $h\approx40$ µm, fragment sizes 20–35 µm. **5:** catastrophic breakup: 2CF Nilda Kolima.3, $d\approx309$ µm, $h\approx140$ µm, fragment sizes 10–35 µm (the compact spherical particle to the right is Lambert, see panel 1 and is not part of Nilda). **6:** shedding upon rolling: 2CF Clarence Kolima.3, $d\approx63$ µm, $h\approx68$ µm, fragment sizes 15–20 µm. $d=\left(\frac{a}{\pi}\cdot a\cdot b\cdot e^{2}\right)^{1/3}$, a = area in image plane, h = height as derived from shadow, e = geometry factor ($\varepsilon\approx0.5$ assumed, see text). All scale bars 100 µm. Collection periods of examples shown: (date of begin + days of exposure): Kolima.3 (24 Jan 2015 + 1.0); Ala Kitka (16 Dec 2014 + 3.7); Saimaa (29 Oct 2014 + 4.7); Lummene.2 (26 Jan 2015 + 1.0); Ukonvesi (10 Nov 2014 + 4.0).
(b): 7: depression at center: 2CF Jessica Lummene.2, $d\approx207$ µm, $h\approx40$ µm, element sizes 15–40 µm. **8:** depression at center: 3D0 Kamil Ukonvesi, $d\approx179$ µm, $h\approx50$ µm, element sizes 15–30 µm. **9:** linear chains of elements: 2CF Adeline Kolima.3, $d\approx120$ µm, $h\approx50$ µm, element sizes ≈20 µm. **10:** shedding from a stronger core: 2CF Jean-Baptiste Kolima.3, $d\approx214$ µm, $h\approx100$ µm, element sizes ≈15–40 µm. All scale bars 100 µm
(c): Fragment spatial distribution around 2CF Nilda Kolima.3 (see Fig. 2a-5). Left: Positions of fragments on target 2CF. Zero point of coordinate system is the lower left corner of the 1×1 cm² target plate (see Langevin et al., 2016). The full central circle marks the fragment's "source center" from which the sum of distances to all fragments is a minimum. Right: Number of fragments within a ring of 100 µm width as a function of radial distance from the source center (horizontal error bars are +100 µm; vertical error bars: $\pm\sqrt{N}$). l_f: characteristic travel length of the fragments, defined by N dropping to half of its maximum value. The arrow indicates where the mean ambient particle area number density of about 20/mm² is reached.

- COSIMA (aboard ROSETTA) has shown that smaller interplanetary dust is likely stronger, made up of units 0.5 µm or larger, so this can be taken as the lower limit of meteoric fragment size.

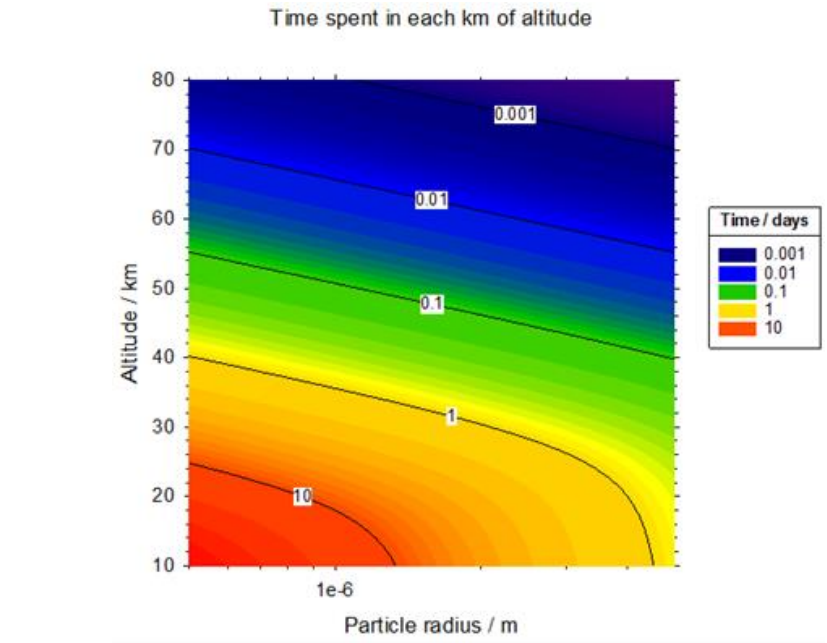
- The larger limit to fragment size is poorly constrained. see presentation by David Bones on Wednesday afternoon https://meetingorganizer.copernicus.org/EGU2020/displays/36521

Hornung, K., Merouane, S., Hilchenbach, M., Langevin, Y., Mellado, E. M., Della Corte, V., ... & Silen, J. (2016). A first assessment of the strength of cometary particles collected in-situ by the COSIMA instrument onboard ROSETTA. *Planetary and Space Science*, *133*, 63-75.

Largest particle – sedimentation lifetime

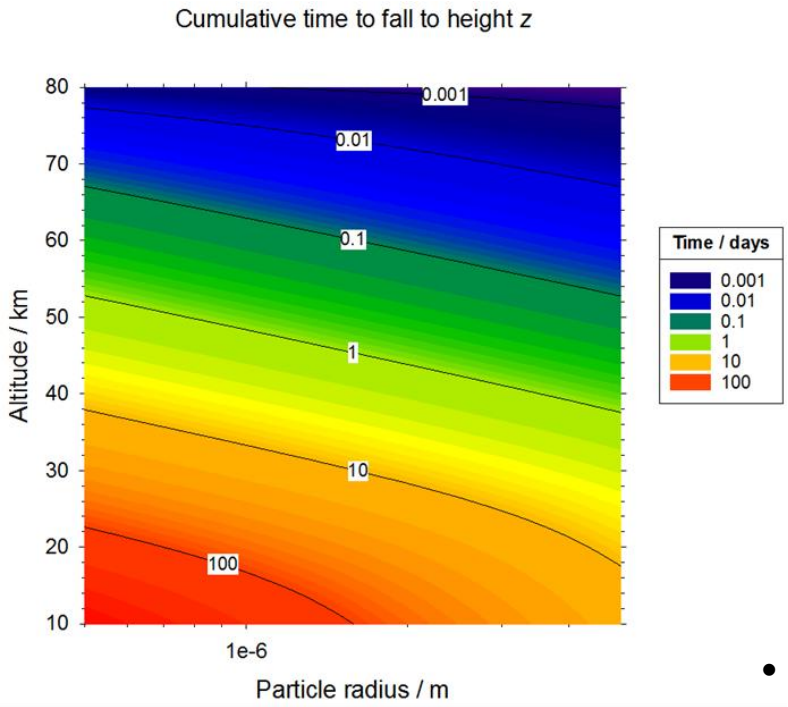


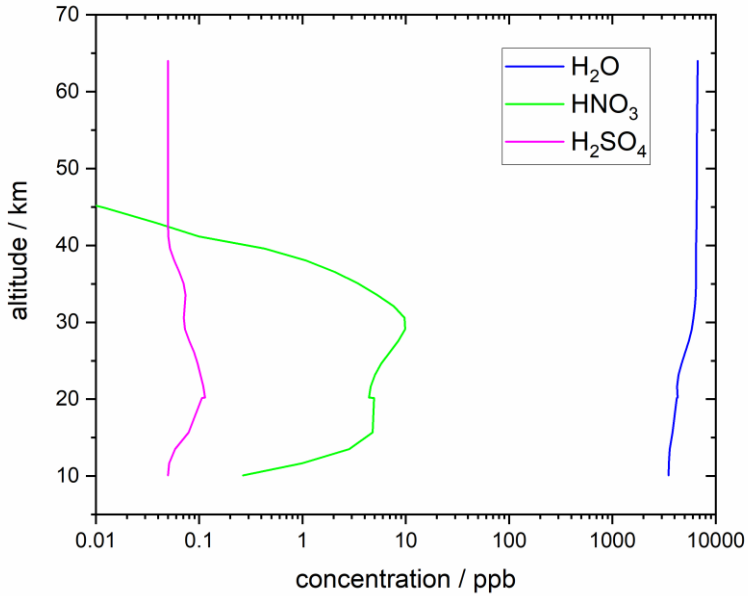
For a crystal to nucleate, HNO_3 must be on the order of <nm apart on the surface. This means that the largest particle capable of heterogeneous nucleation must have a sedimentation lifetime in the PSC altitude of hours to days. Uptake coefficients, γ from Frankland, V. L., James, A. D., Feng, W., & Plane, J. M. (2015). The uptake of HNO3 on meteoric smoke analogues. *Journal of Atmospheric and Solar-Terrestrial Physics*, *127*, 150-160.

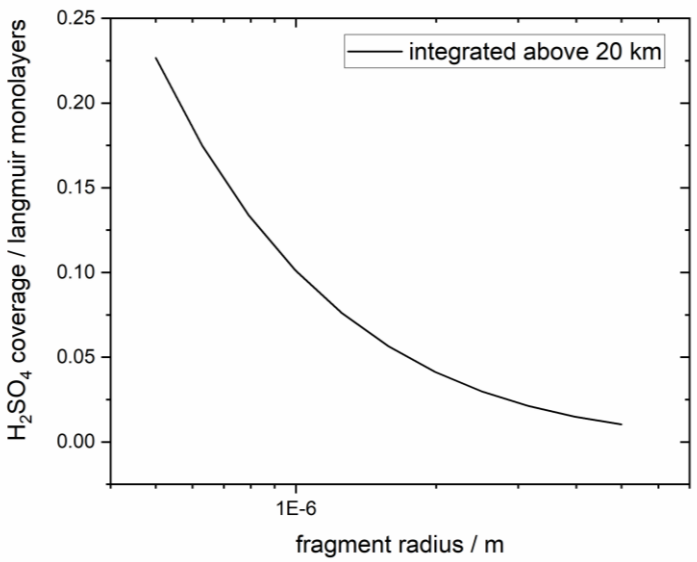


For a particle of the mass density of a meteoric fragment, we calculate sedimentation lifetime of one day at 20 km is possible for particles up to 5 μm radius.

Smallest particle – H_2SO_4 coverage

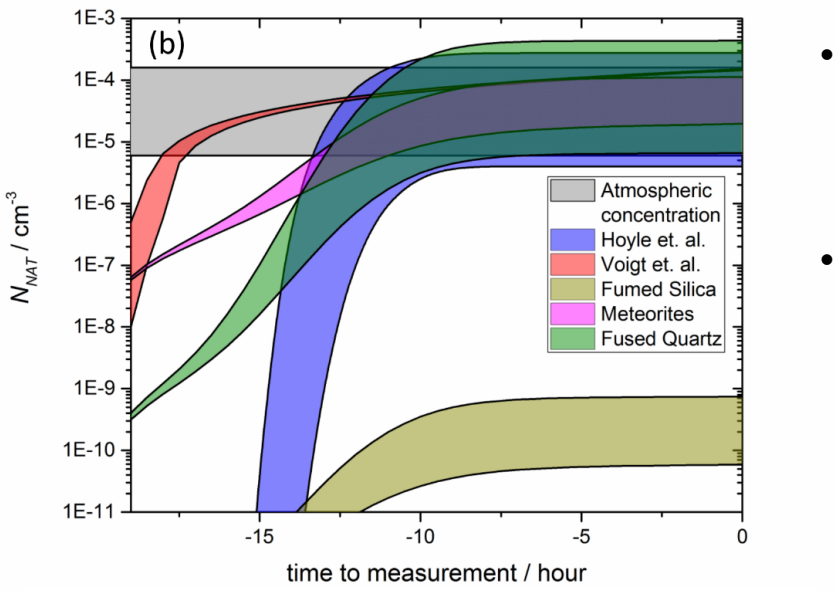


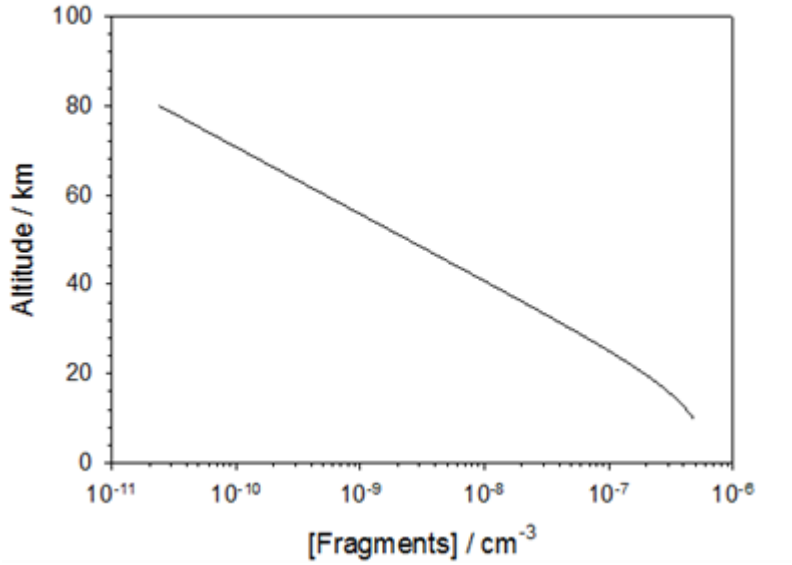




- Using the altitude dependent fall speed, $[H_2SO_4]$ and γ_{H2SO4} = 0.001 we calculate surface coverage and integrate as the particle falls to PSC altitude. This gives an upper limit since HNO_3 and H_2O uptake will compete for available surface area as the particle sediments.
- The smallest particles (0.5 µm) will not be significantly coated by H_2SO_4, so are available for heterogeneous nucleation.

Fragment number concentrations





- Atmospheric observations of the PSCs which have not reached H_2O saturation have found crystal number densities on the order of 1 x 10^{-4} cm^{-3}.
- The fragment flux and sedimentation speed can be combined to obtain a steady state concentration at each altitude. Using the established flux of Halley type comet particles (HTCs) and assuming that they fragment to a power law distribution with the largest particle 1/10th the parent mass gives the number concentration plotted. In addition HTCs produce the majority of ablated metals in the mesosphere, so significant fragmentation would require a significantly increased total flux.
- Jupiter family comet (JFC) input is, however, relatively poorly constrained, and may produce the number of fragments required to match observed cloud. This could mean that PSC can be used to constrain the JFC flux to the Earth.

Conclusions:

- Multiple phases nucleate competitively on different mineral components in meteoric fragments.
- H_2SO_4 deactivates heterogeneous nucleation by meteoric fragments under Polar Stratospheric Cloud conditions
- Fragments of Jupiter Family Comets may be in the correct size range to sediment rapidly to the stratosphere and cause nucleation without interacting with liquid H_2SO_4.

Thanks:

Murray and Plane groups & meteorstrat project

Lab experiments:

Tom Whale, Mark Holden, Sebastien Sikora, Mark Tarn

Mchem student Finn Pace

Measurements of PSC number concentration

CALIOP – satellite LIDAR data modelled with N_{NAT} >1 x 10^{-4} cm^{-3}

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