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The sensitivity of ice-nucleating minerals to heat and implications for the detection of biogenic ice-nucleating particles

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Ice nucleating minerals' response to heat – why?

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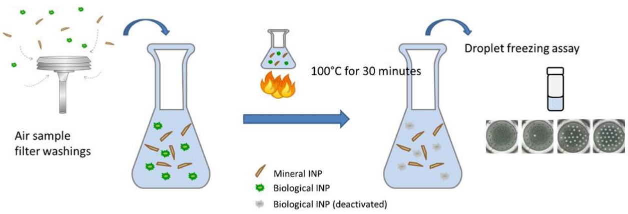
- We want to know what type of particles contribute to ice nucleating activity when sampled in the environment - mineral or biological?
- These have different sources so this would enable us to refine our understanding of global atmospheric INP sources and abundance
- A widely used method for this is to treat sample with heat as a 'stress' test – Deactivation interpreted as presence of 'biological' INP

Aerosol sampler



Assumptions of INP heat test:

Mineral INP → Unaffected by heating

Biological INP → Deactivated by heating

What are the important INP types in the atmosphere?

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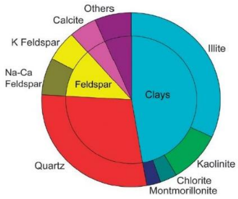
- Mineral dust (high volume, low ice nucleating efficacy)

Desert dust plume

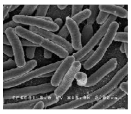
Murray *et al.*, 2012

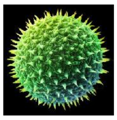


Global average mineralogical composition of mineral dust

Ice nucleating efficacy of mineral components: Feldspar > Quartz > Clays

- Biogenic (low volume, high ice nucleating efficacy)
  - Include proteinaceous (bacteria, fungal spores, lichen, viruses) or non proteinaceous (pollen, cellulose)
  - Exist as intact primary biological aerosol particles, fragments and ice nucleating macromolecules
  - Bacteria, such as *Psuedomonas syringae,* are amongst the most efficient INP known – nucleate as warm as -2 °C



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Recent examples of bioaerosol INP 'detected' by using heat

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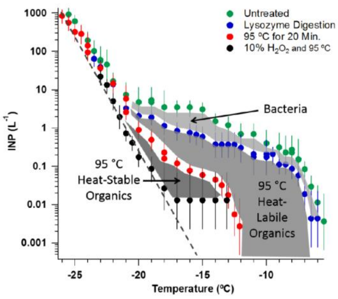
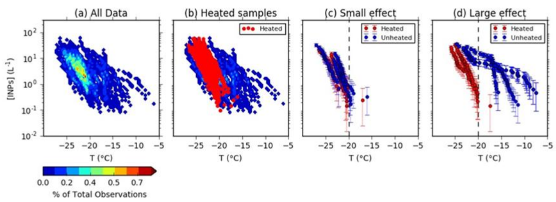


Ice nucleating activity of aerosol collected at a farm in the USA during harvest before and after heat treatments (Suski et. al. (ACP) 2018)



Ice nucleating activity of aerosol collected at a farm in the UK during harvest before and after heat treatments (O'Sullivan et. al. (Nat. Sci. Reps) 2018)

- Bioaerosol acting as INP at high temperatures very likely to be present
- As well as identify their presence some workers quantified bio INP L^{-1} air using magnitude of heat deactivations[1,2]
- However often more 'heat labile' INPs are detected than can be explained by bioaerosol content[3,4,5,6]

1 Christner et. al. (2008) Geographic, seasonal, and precipitation chemistry influence on the abundance and activity of biological ice nucleators in rain and snow. Proc Natl Acad Sci U S A 105 (2008) 18854-9.
2 Du et. al. (2017) Evidence for a missing source of efficient ice nuclei. Sci Rep 7 (2017) 39673.
3 Garcia et al. (2012) Biogenic ice nuclei in boundary layer air over two U.S. High Plains agricultural regions. Journal of Geophysical Research: Atmospheres 117 (2012)
4 Joly et. al. (2014) Quantification of ice nuclei active at near 0 °C temperatures in low-altitude clouds at the Puy de Dôme atmospheric station. Atmos. Chem. Phys. 14 (2014) 8185-8195.
5 Lu et. al. (2016) The Diversity and Role of Bacterial Ice Nuclei in Rainwater from Mountain Sites in China. Aerosol and Air Quality Research 16 (2016) 640-652.
6 Šantl-Temkiv et al. (2015) Characterization of airborne ice-nucleation-active bacteria and bacterial fragments. Atmospheric Environment 109 (2015) 105-117.

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Questions to validate the 'heat test'

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- **Q1. Does heat always deactivate biogenic INP?**

Answer from literature: ✓ / ?

- Proteinaceous INP deactivate when heated above 70 °C
- Polysaccharide INP such as pollen may require 200°C + to deactivate
- No data for cellulose

- **Q2. Does heat never deactivate mineral INP?**

Answer from literature: ?

If mineral INP, particular K-feldspars, deactivate upon heating this could *potentially* lead to false positive detection of biological INP

- No systematic study yet done
- Not considered that minerals can physically and chemically change with heat
- Dry and aqueous/wet heating considered equivalent treatments
- Already evidence that quartz and feldspar can 'weather' and lose ice nucleating efficacy over time in water[1,2,3,]

1 Harrison et al. (2016) Not all feldspars are equal: a survey of ice nucleating properties across the feldspar group of minerals. Atmospheric Chemistry and Physics 16 (2016) 10927-10940
2 Harrison et.al. (2019) The ice-nucleating ability of quartz immersed in water and its atmospheric importance compared to K-feldspar. Atmospheric Chemistry and Physics Discussions (2019) 1-23.
3 Perkins et al. (2020) The Labile Nature of Ice Nucleation by Arizona Test Dust. ACS Earth and Space Chemistry 4 (2020) 133-141.

Methodology – Sample selection and heat treatments

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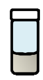
Aim:
Test ice nucleation efficacy of range of atmospherically relevant minerals and biogenic INP proxies after parallel dry and aqueous (wet) heating treatments

Ground mineral samples are 1 wt% dry powder suspended in ultrapure water

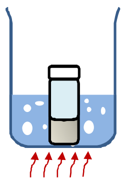


Sample Class	INP sample tested
Feldspar	K-feldspar (x5), Na/Ca feldspar
Silica	Quartz (x3), Chalcedony
Clays	Kaolinite (x2), Montmorillonite (x2), Chlorite
Other	Calcite, Volcanic Ash (x2)
Dust analogues	NX Illite, Arizona Test Dust
Biogenic (proteinaceous)	Snomax* , Lichen
Biogenic (non-proteinaceous)	Microcrystalline cellulose (MCC), Birch pollen washing water (BPWW)

*Non viable *Pseudomonas syringae* extract

INP sample heating treatments:

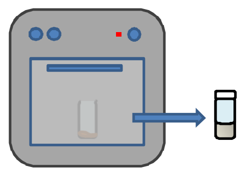
'Wet' heat treatment



Suspension made then heated at 100°C for 30 minutes

Vs.

'Dry' heat treatment



Heated as dry powder at 250°C for 4 hours then suspended in water

Methodology – Drop Freezing Assays

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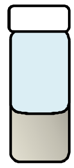
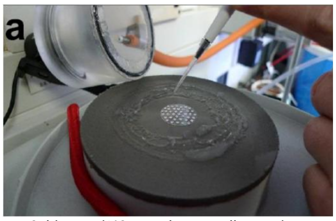
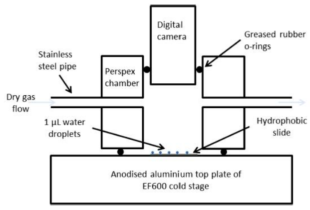
Nucleation by Immersed Particle Instrument – microlitre droplets (µL-NIPI) (Whale et.al, AMT 2015)

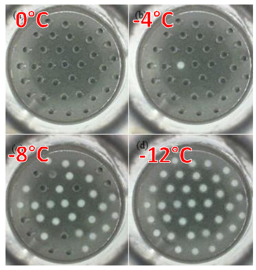


INP suspension



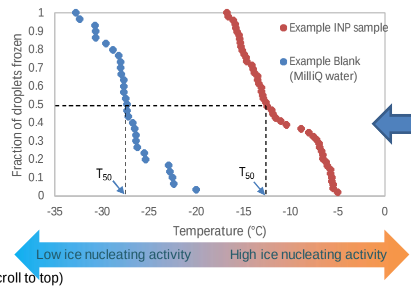
Cold stage (1°C per minute cooling rate)





Droplets containing INP cooled at 1°C / min

Fraction of droplets frozen as function of T



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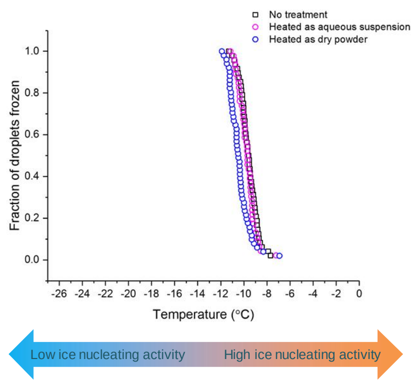
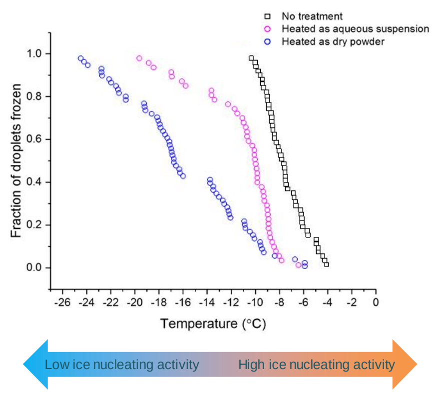
If an INP sample was insensitive to heat treatment…

The result would look like this



If an INP sample was deactivated by heat treatment…

The result would (for example) look like this



Summary of results - Mineral INP are not universally heat resistant!

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Mineral INP

Sample	Class	ΔT_{50} Wet heat	ΔT_{50} Dry heat
Microcline (Amazonite)	K-feldspar	-1.5	-5.6
Microcline (BCS-376)	K-feldspar	+0.2	+0.2
Microcline (TUD#1)	K-feldspar	-1	-1.2
Microcline (TUD#3)	K-feldspar	-0.1	-1.9
Sanidine	K-feldspar	+0.8	-0.4
Plagioclase (BCS-375)	Na/Ca Feldspar	-1.2	-0.6
a-Quartz	Silica	-7.3	+0.1
Fluka quartz	Silica	-4.1	+1.3
Fused quartz	Silica	-4.4	-1.1
Bombay chalcedony	Silica	+0.1	-0.9
Montmorillonite (CMS)	Clay	-2.3	-0.3
Kaolinite (kga-1b)	Clay	+0.5	+1.8
Calcite	Other	-1.9	+0.2
Volcanic ash	Other	-6.2	+0.9
ATD	Dust analogue	-4.5	-1.4
NX illite	Dust analogue	0.0	-0.8

Biogenic INP

Sample	Class	ΔT_{50} Wet heat	ΔT_{50} Dry
Snomax	Biogenic (proteinaceous)	-4.6	-20.3
Lichen	Biogenic (proteinaceous)	-3.9	-6.8
Microcrystalline cellulose (MCC)	Biogenic (non-proteinaceous)	0.0	-1.4
Birch pollen washing water (BPWW)	Biogenic (non-proteinaceous)	-1.3	-2.8

Minor deactivation (> 1.2 °C)

Large deactivation (> 2.0 °C)

Instrumental error ±0.4 °C

- Some mineral INP are significantly deactivated by wet heat treatment but are in general less sensitive to dry heat treatment
- Only consistent trend is seen in silica samples (quartz)
- Biogenic INP react as expected to same heat treatments

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Results – Biogenic INP Samples react as expected – mostly!

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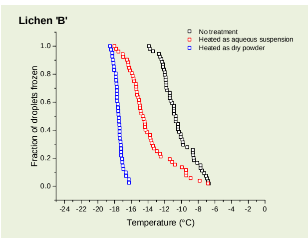
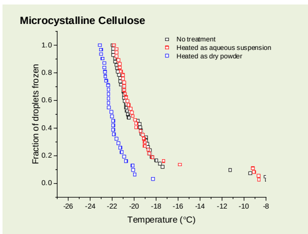
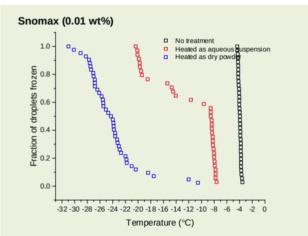


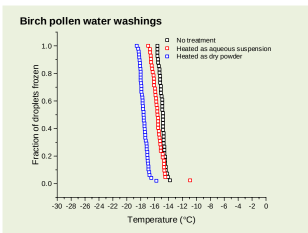
ΔT_{50} Wet = -3.9 °C
ΔT_{50} Dry = -6.8 °C



ΔT_{50} Wet = 0.0 °C
ΔT_{50} Dry = -1.4 °C



ΔT_{50} Wet = -4.6 °C
ΔT_{50} Dry = -20.3 °C



ΔT_{50} Wet = -1.3 °C
ΔT_{50} Dry = -2.8 °C

- Proteinaceous INP samples deactivated by both wet and dry heat – much more by dry heat.
- Non-proteinaceous INP samples resistant to wet heat, more resistant to dry heat than expected

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Results – Feldspars are (largely) heat resistant

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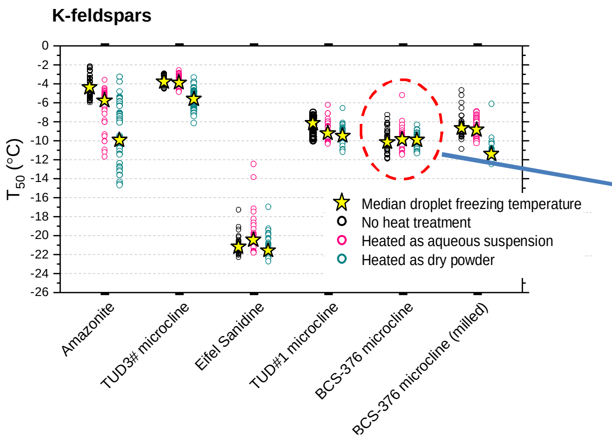
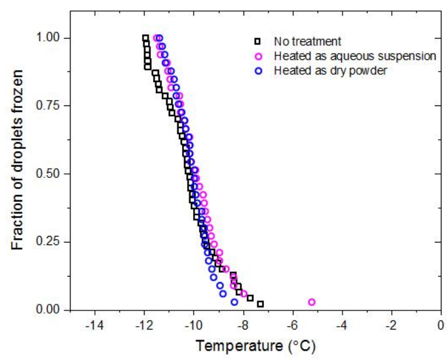
ΔT_{50} Wet = +0.2 °C
ΔT_{50} Dry = +0.2 °C





- 'Representative' samples of K-feldspar show no deactivation upon both wet and dry heating
- Minor deactivations of other samples by dry heating
- 'Hyperactive' varieties show some sensitivity, especially to dry heating

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Results – Quartz is deactivated by heating in water

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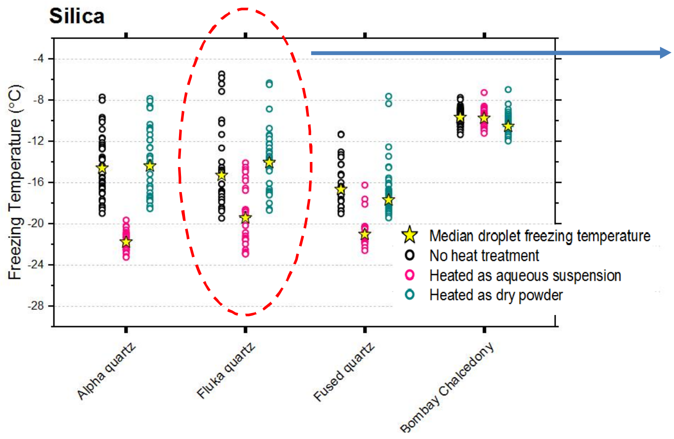

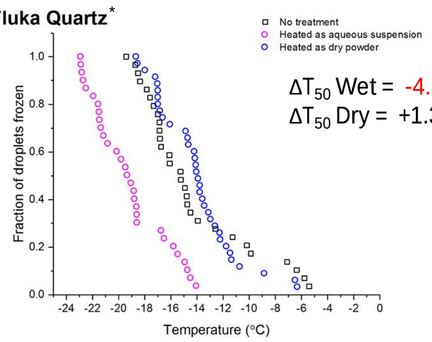

ΔT_{50} Wet = -4.3°C
ΔT_{50} Dry = +1.3 °C

* *Reagent grade quartz powder (Honeywell Fluka Cat. 83340)*

- Quartz samples are sensitive to wet heat but NOT to dry heat
- Dry heat resistance suggests organic/biological contamination unlikely

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Results – If Quartz INP loses activity in water it is accelerated by heating

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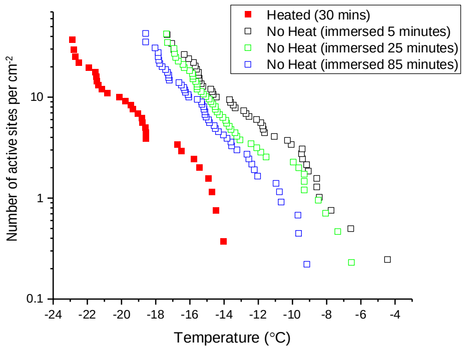
Fluka Quartz – room temperature water 'ageing' vs heating



- Quartz may slowly lose its ice nucleating efficacy anyway when immersed in room temperature water[1]
- Heating appears to accelerate this process

1 Harrison et al. (2019) The ice-nucleating ability of quartz immersed in water and its atmospheric importance compared to K-feldspar. Atmospheric Chemistry and Physics Discussions (2019) 1-23.

Results – Are heat sensitive Mineral INP responses consistent over a range of suspension concentrations?

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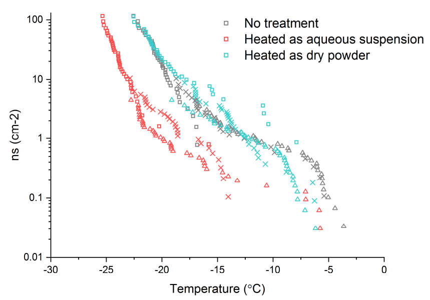
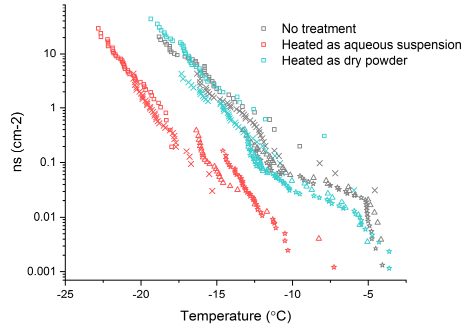
Fluka Quartz: 0.1% to 2.5% w/w suspensions



Arizona Test Dust (ATD): 0.01 to 1 % w/w suspensions



- For quartz and ATD wet heat deactivations were consistent over 3+ orders of magnitude of $n_s(T)$
- Suggests heat deactivations are not a result of aggregation effects or solute release which would scale with concentration

Discussion

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- What's going on?
  - Only able to speculate on mechanisms of INP deactivation without further physical/chemcal analysis
  - Quartz – combination of dissolution and grain morphology? Release of silicic acid?
- What does this mean for using heat for field detection of biogenic INP?
  - The *good news* is that **K-feldspar (the most active type of mineral INP) is not affected by the heating method commonly used.**
  - However **some minerals acting as INP are 'heat labile' and some biogenic INP are heat resistant**
  - INP active > -10°C are likely to be proteinaceous anyway, but **if INP active < -15°C deactivate after wet heat test, interpret with caution.**
  - **Could dry heating samples on filters be a more selective method** for distinguishing between mineral and biogenic INP?

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Conclusions

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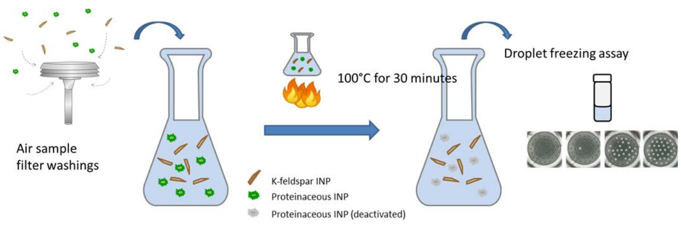
- Using aqueous heat to detect the presence of **proteinaceous** ice nucleating bioaerosol **is a valid methodology** because the activity of the most active mineral component (K-feldspar) is preserved
- BUT wet heating may not be able to distinguish between mineral INP and non-proteinaceous ice biogenic INP

Refined assumption for heat test:

Mineral INP → K-feldspar unaffected by heating

Biological INP → Proteinaceous INP deactivated by heating



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Summary

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- **Cloud reflectivity and precipitation can be affected by presence of INP of inorganic and biological origin** which are not yet fully understood
- **A heating test is a valid and practical tool for detecting presence of biogenic INP** if processing large volume of samples, for example, on a field campaign
- The heat test could **be adapted to utilise dry heat instead of wet heat** as a more selective way to distinguish INP types