School of Earth and Environment
INSTITUTE FOR CLIMATE & ATMOSPHERIC SCIENCE
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Microfluidics for ice nucleation

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Properties of water

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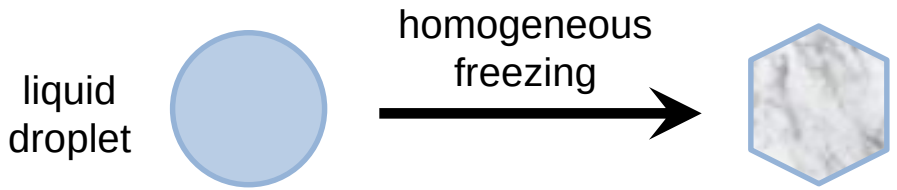
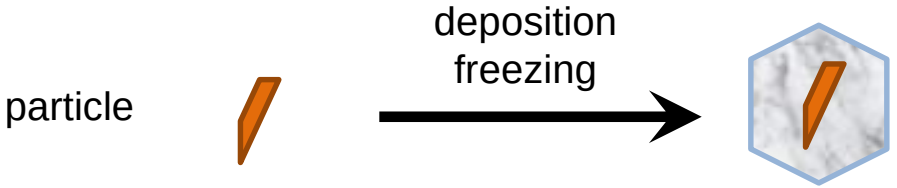
❄ In the absence of nucleation sites, water can **supercool** to temperatures well **below 0 °C**

❄ ***Homogeneous*** freezing of water occurs below about −35 °C



❄ **Ice-nucleating particles (INPs)** cause ***heterogeneous*** freezing at higher temperatures



Ice nucleation in mixed-phase clouds

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http://earthsky.org/earth/andrew-heymsfield-on-hole-punch-clouds-made-by-jets

Sources of INPs

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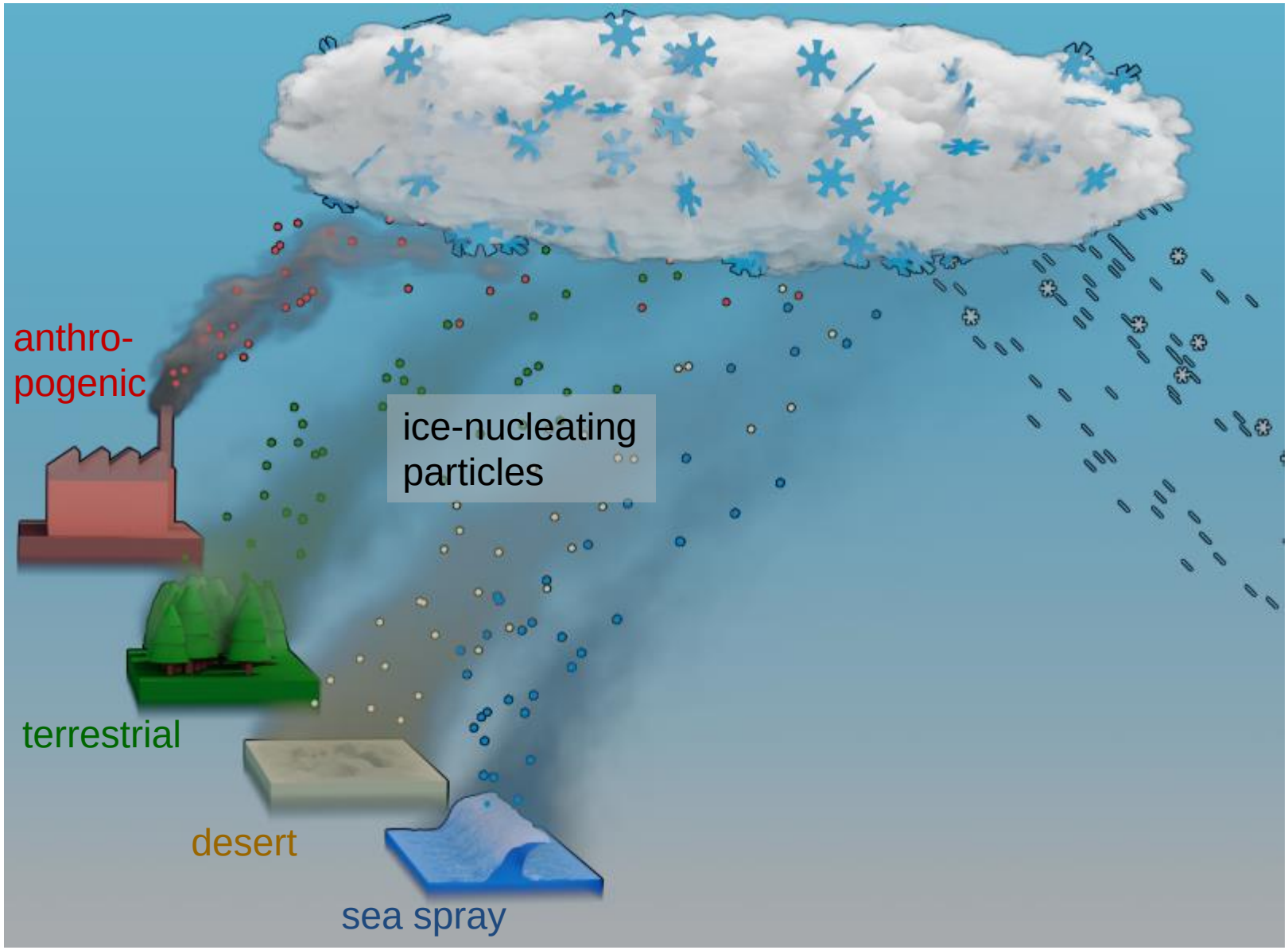

Figure by Jamie Ridley (2018)

Sampling of INPs

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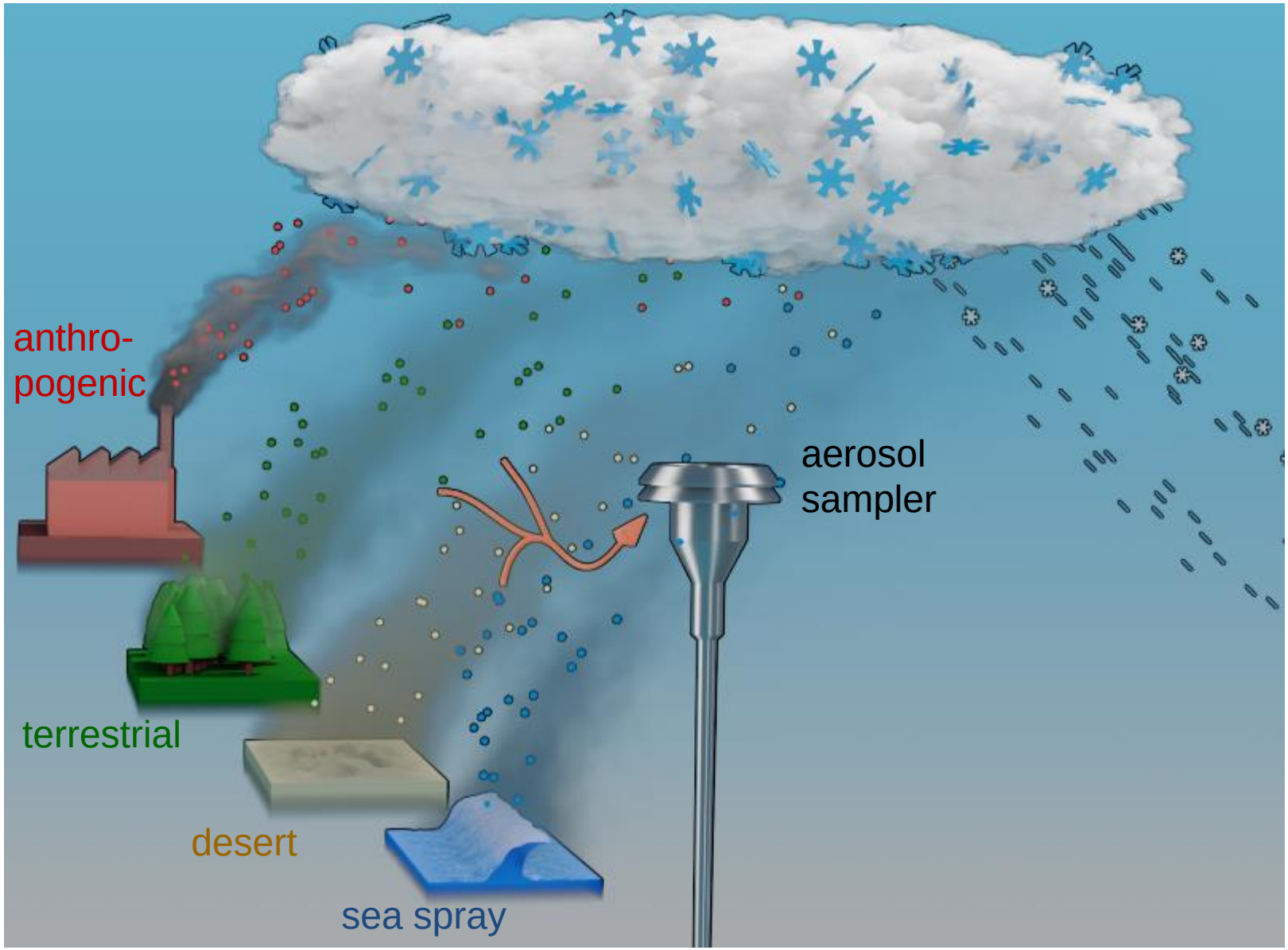

Figure by Jamie Ridley (2018)

Analysis of INPs

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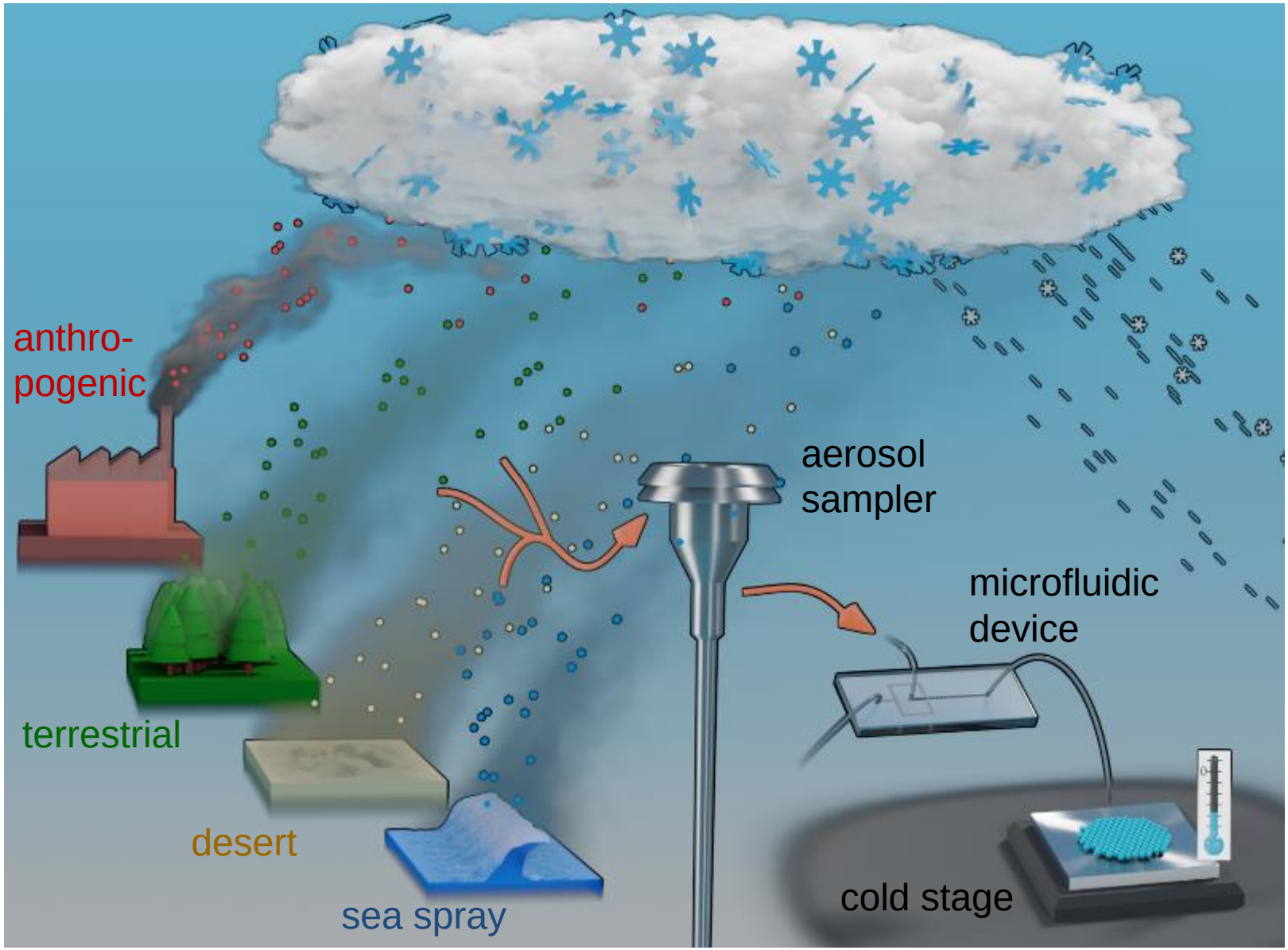

Figure by Jamie Ridley (2018)

Measurement of INPs in droplets

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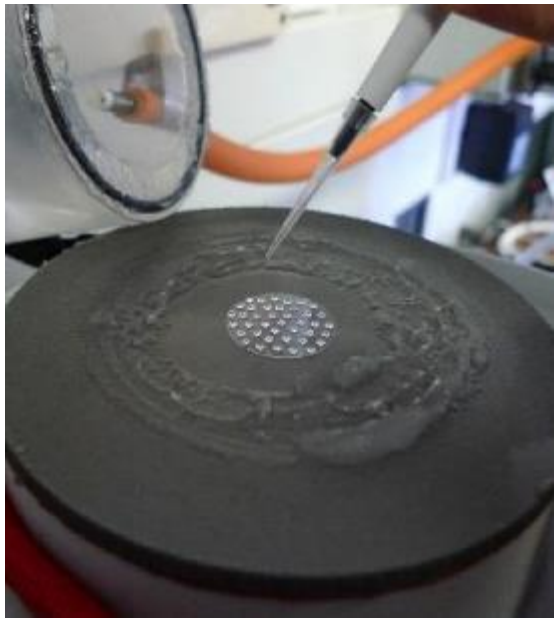
Microlitre Nucleation by Immersed Particle Instrument (μL-NIPI)

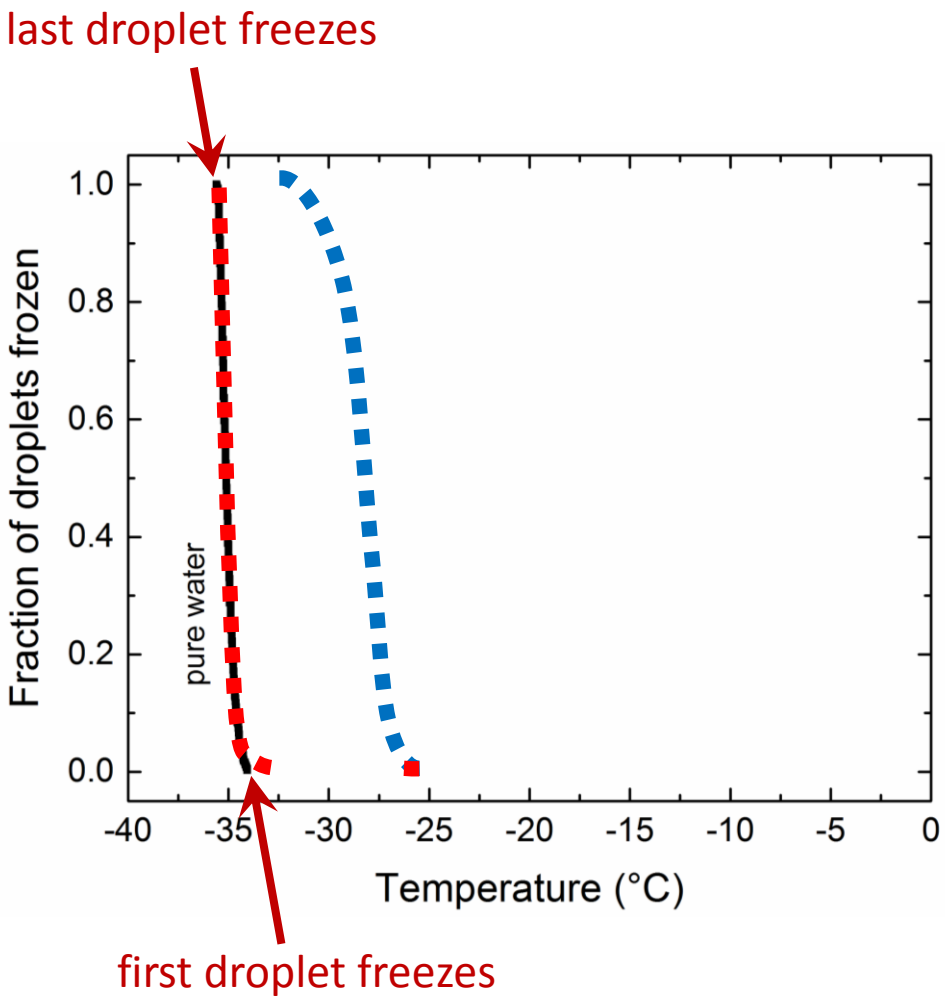
Wilson et al., *Nature*, 2015, **525**, 234-238

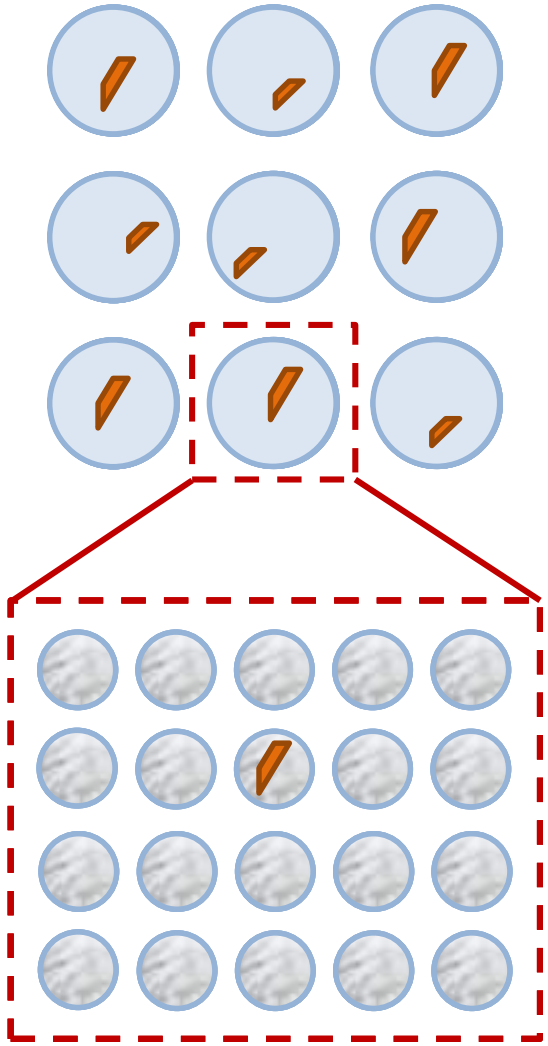


reduce temperature

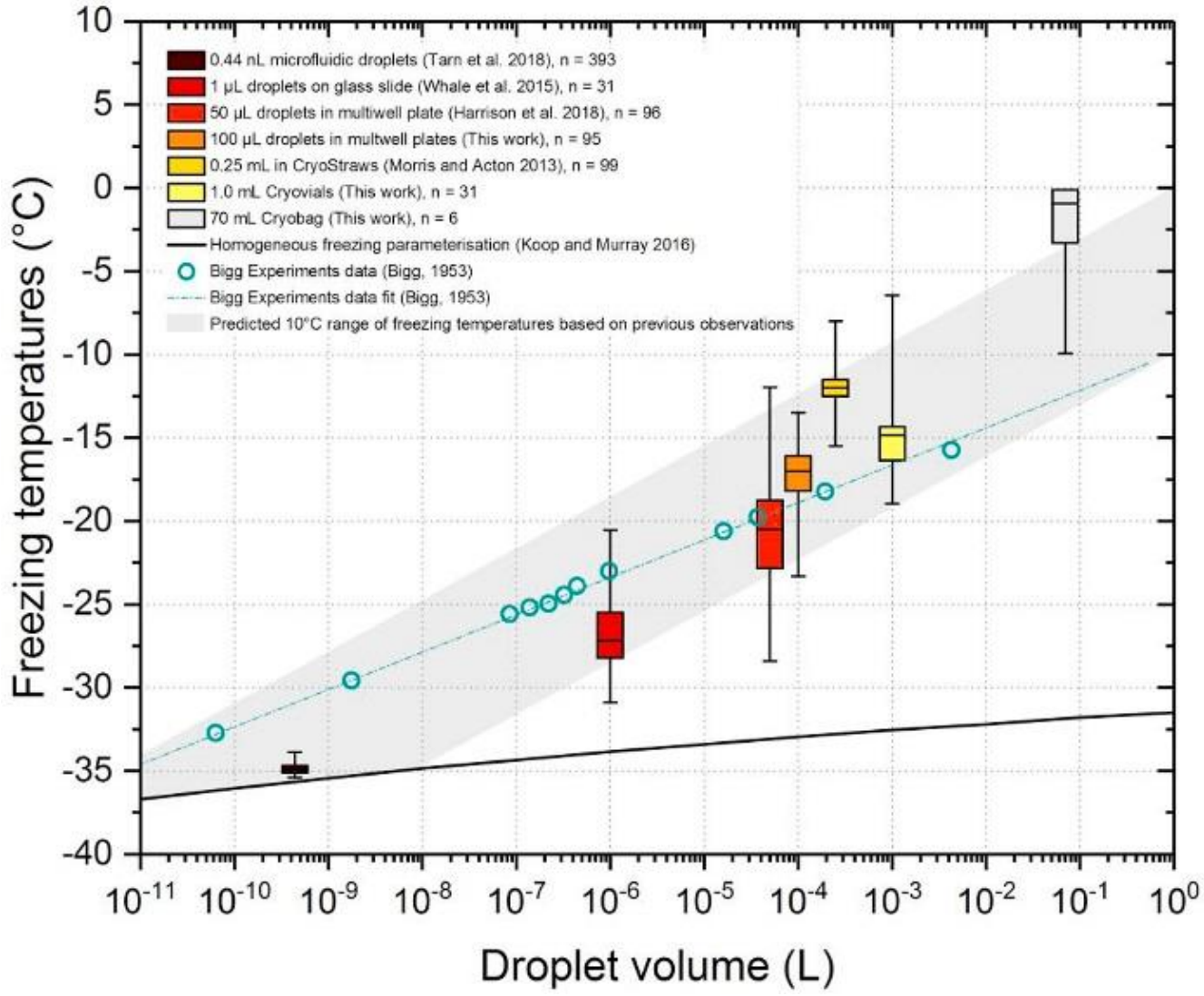
- ❄ μL droplet volumes
- ❄ Simple method
- ❄ **Limited number of droplets**
- ❄ **Poor background signal due to contaminants**

Background signal of pure water





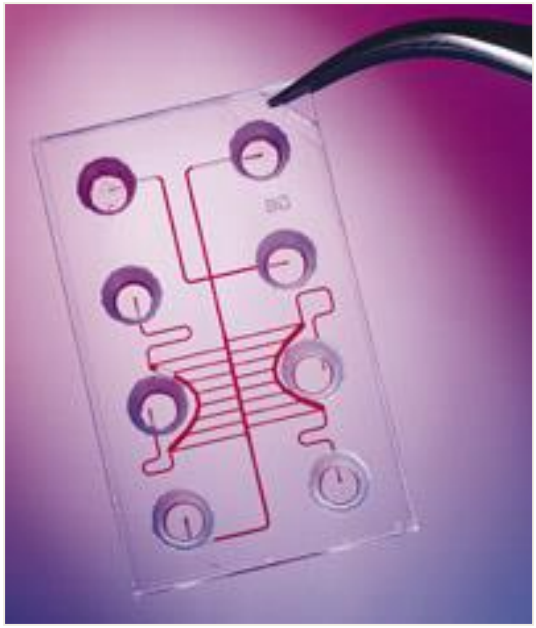
Droplet volume vs. freezing temperature



Daily et al., *Cryobiology*, 2020, **93**, 62

❄ See "Barry et al., *Atmos. Res.*, 2021, **250**, 105419"

Microfluidics



- fluid-carrying channels
- width and depth
  = 10s-100s μm
- pL to nL ranges

Motivation

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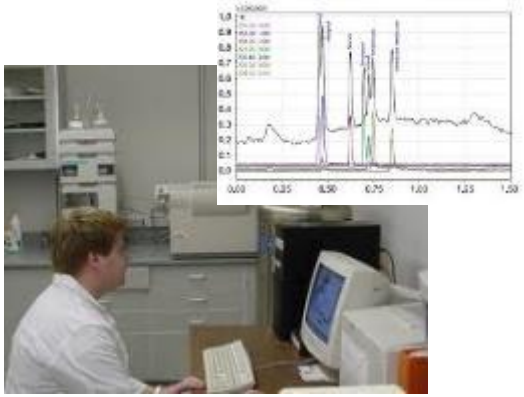
sampling

transport

sample pretreatment

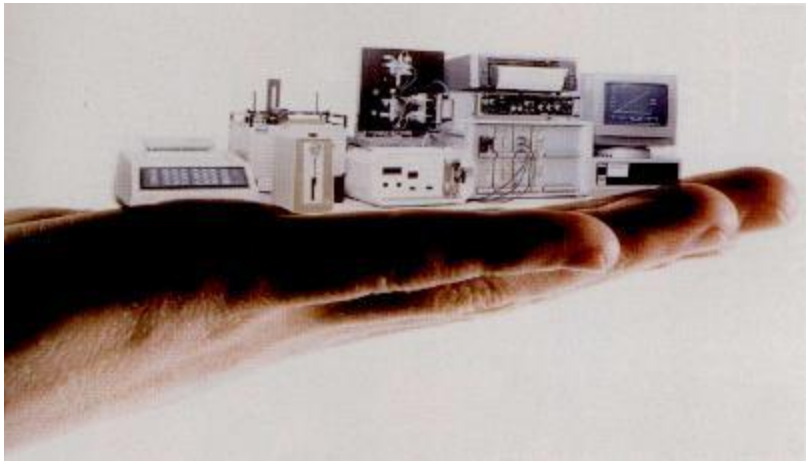
chemical reactions

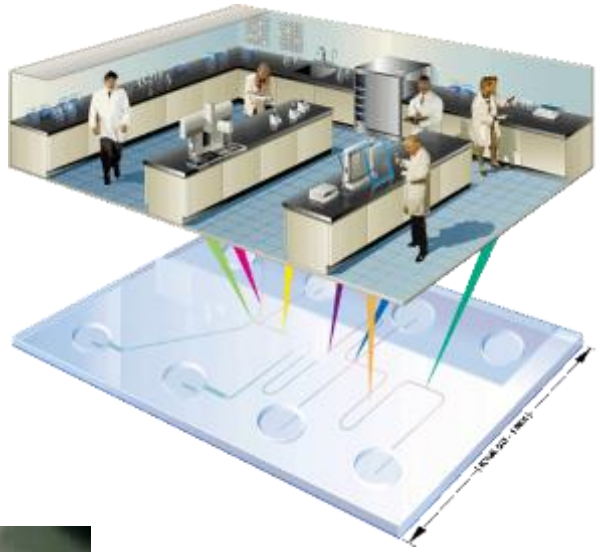
separation and detection



data analysis and output

Miniaturisation





Integrate all analytical steps into a miniaturised device

- microfluidics
- lab-on-a-chip
- micro Total Analysis Systems (μTAS)

The early days…

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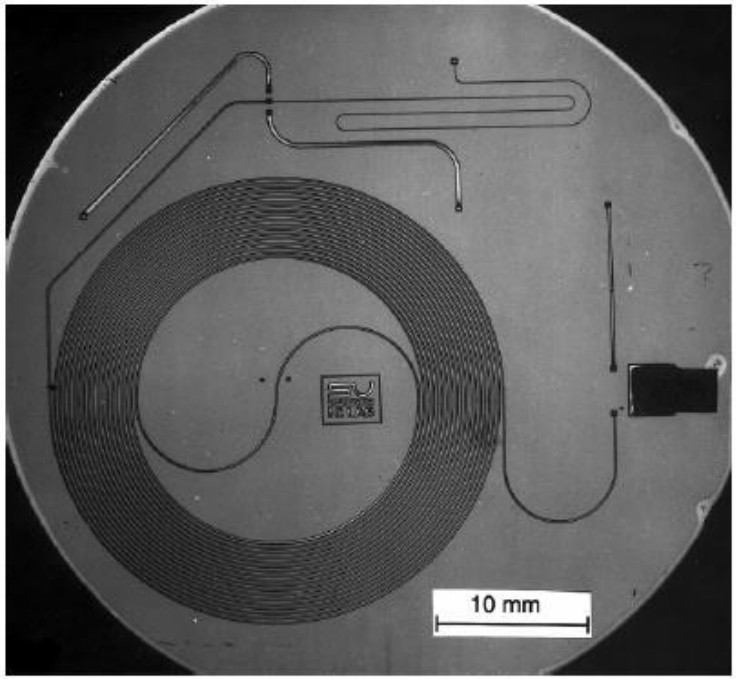
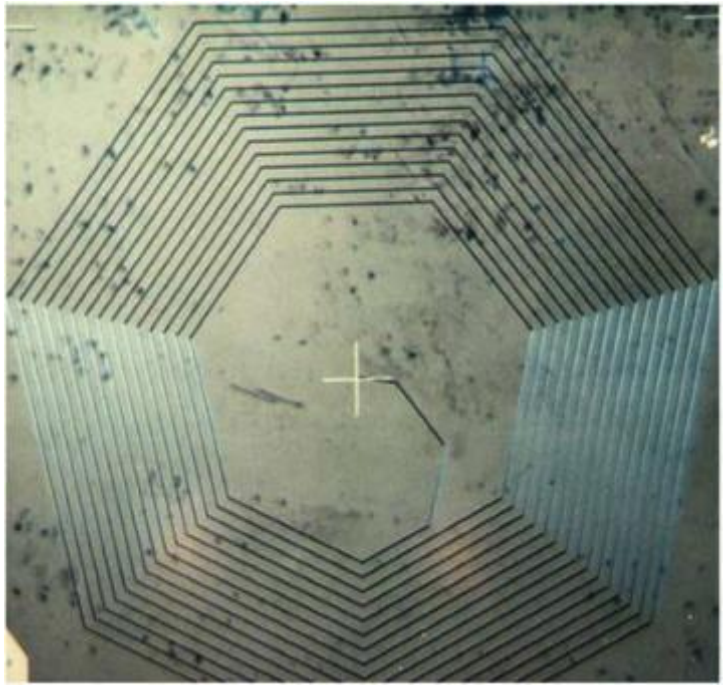
Gas chromatography



S.C. Terry et al., *IEEE Trans. Electron Devices*, 1979, **26**, 1880

Liquid chromatography



A. Manz et al., *Sens. Actuators A*, 1990, **80**, 84

Microfluidics

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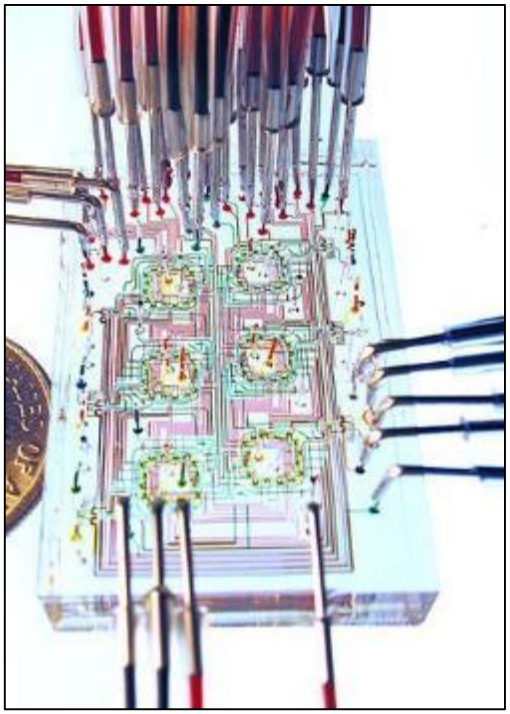
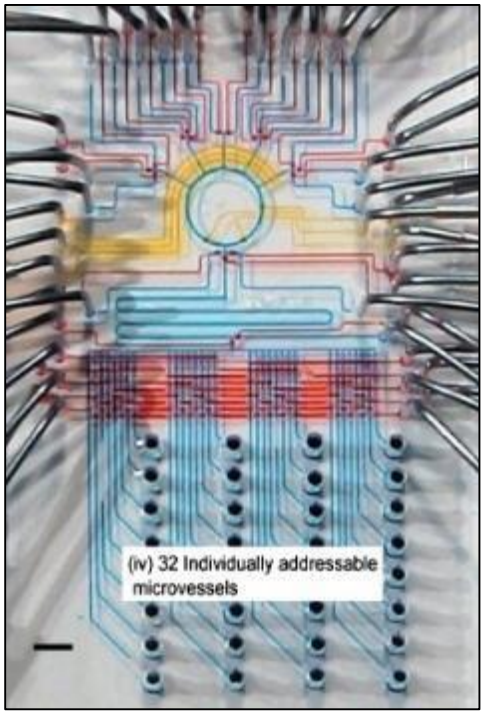
❄ Enable complex procedures on-chip



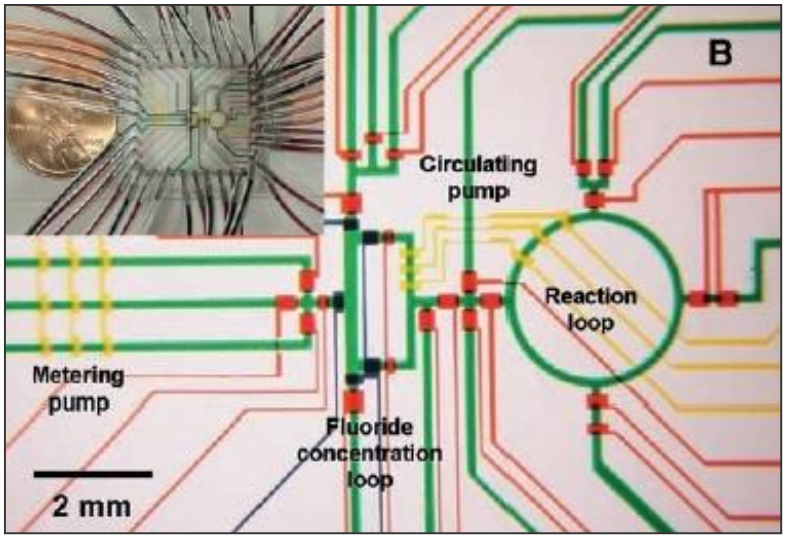
Science, 2005, **309**, 137

monitoring bacteria undergoing population control



Angew. Chem., 2006, **45**, 5276

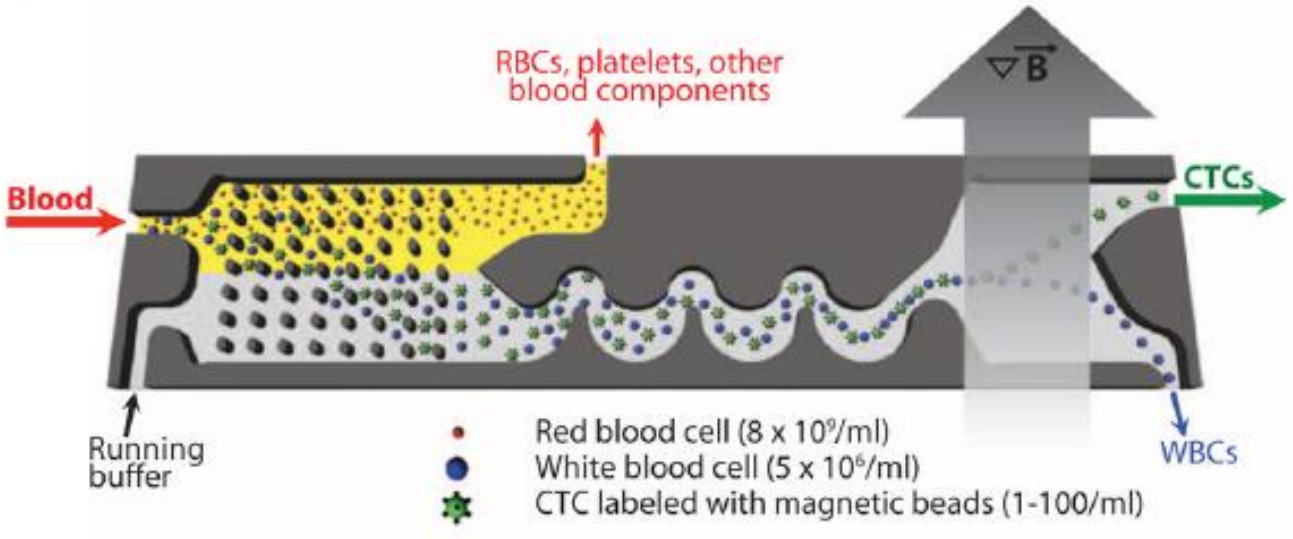
parallel screening of 32 click chemistry reactions



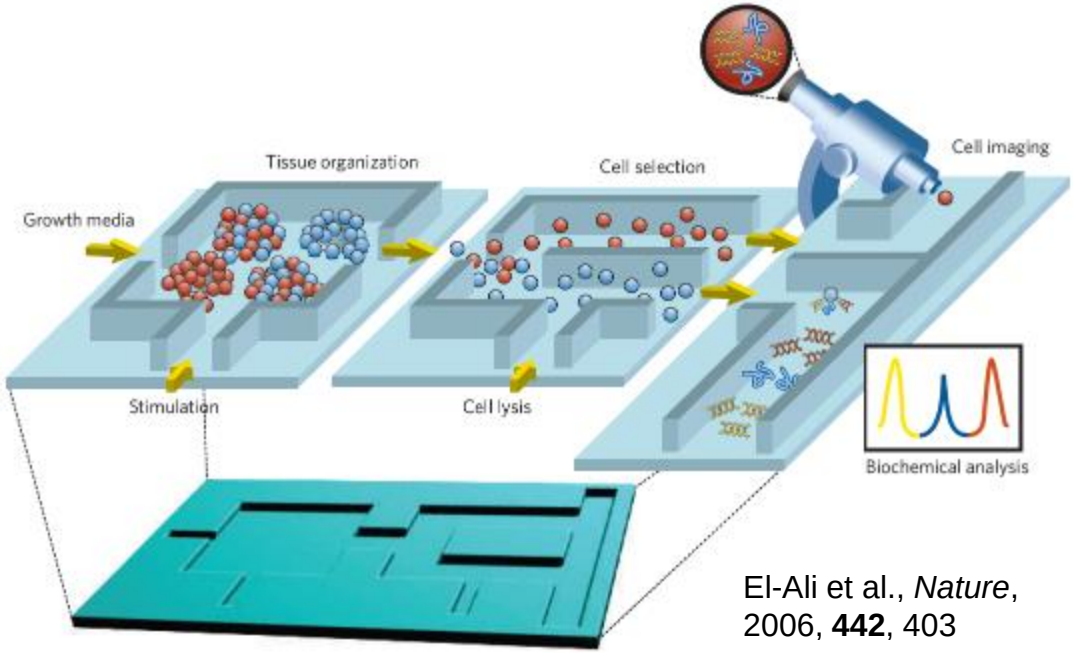
Science, 2005, **310**, 1793

synthesis of radioactive tracers for positron emission tomography (PET)

Droplet/particle/cell sorting

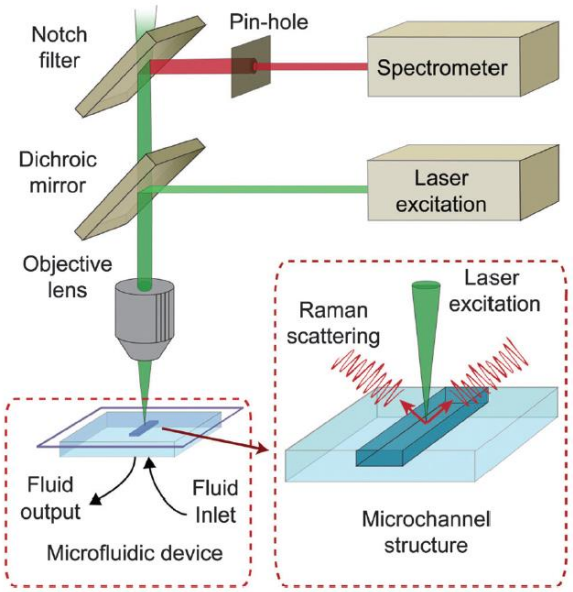


Ozkumur et al., *Sci. Transl. Med.*, 2013, **5**, 179ra7



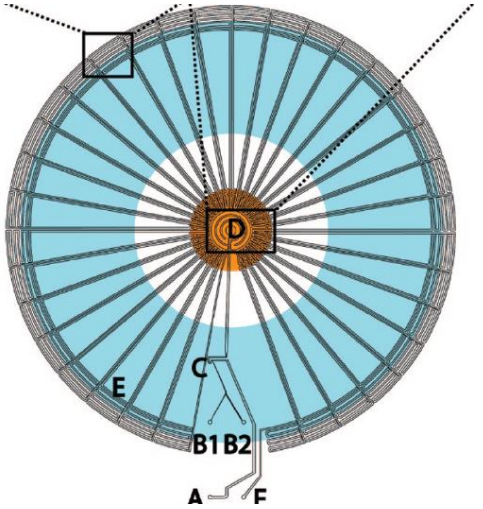
El-Ali et al., *Nature*, 2006, **442**, 403

Microfluidic analysis

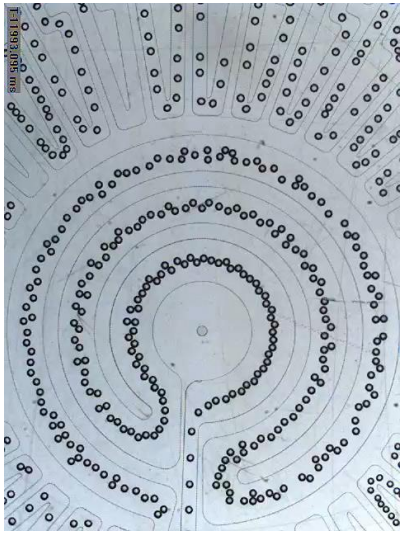


Chrimes et al., *Chem. Soc. Rev.*, 2013, **42**, 5880

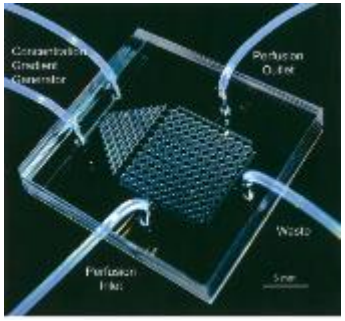
Spectroscopy

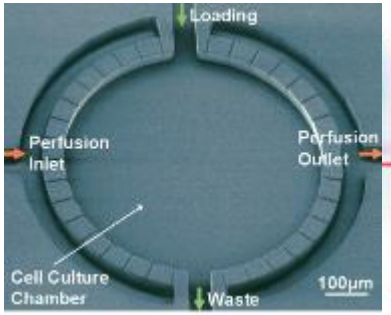


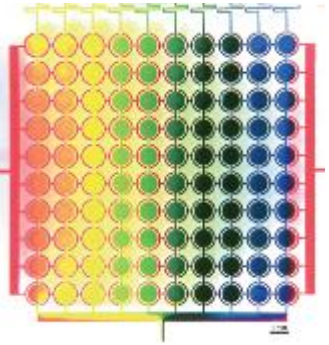
Continuous flow droplet PCR



Schaerli et al., *Anal. Chem.*, 2009, **81**, 302

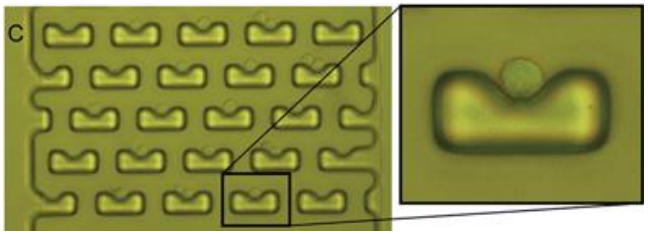






Hung et al., *Biotechnol. Bioeng.*, 2005, **89**, 1

Cell culture



Single cell analysis

D. di Carlo et al., *Lab Chip*, 2006, **6**, 1445

Microfluidics in the real world

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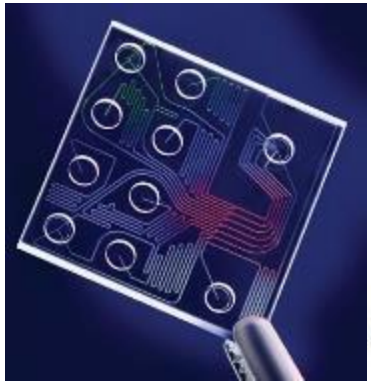

Agilent
(DNA, RNA, protein analysis; HPLC)

Covid-19 vaccine production

Fluidigm
(single cell analysis

Bio-Rad
(droplet-based PCR)

Abbott i-STAT
(point-of-care blood analysis)

My background

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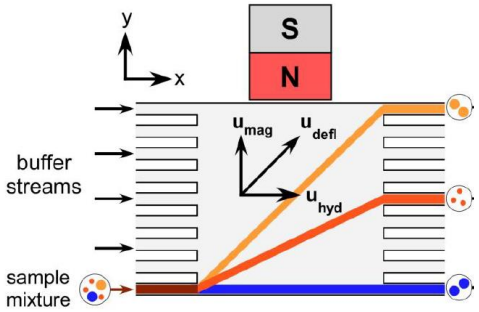
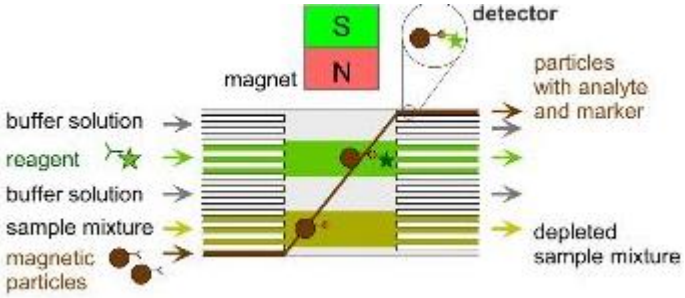
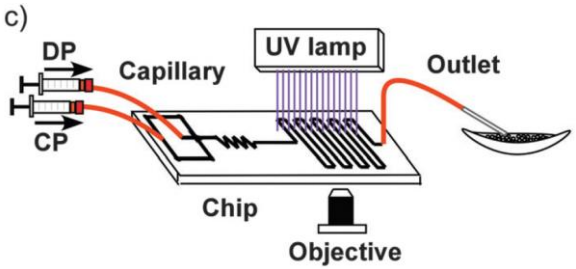
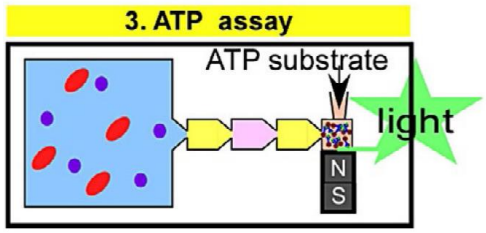




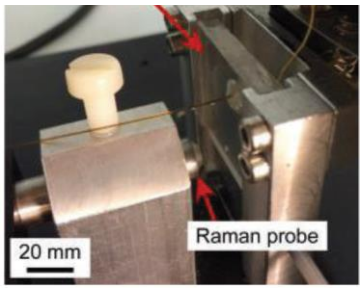
Magnetic particle/droplet separations and assays



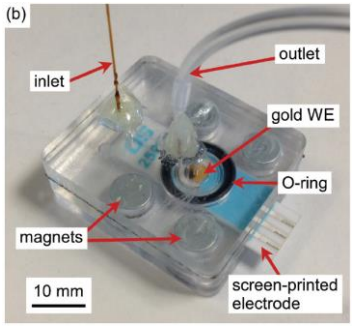
Microgel production



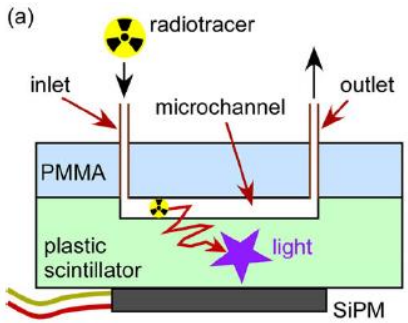
Bacterial detection



Absorption & Raman spectroscopy



Electrochemical detection



Radiopharmaceutical analysis

What is old is new again

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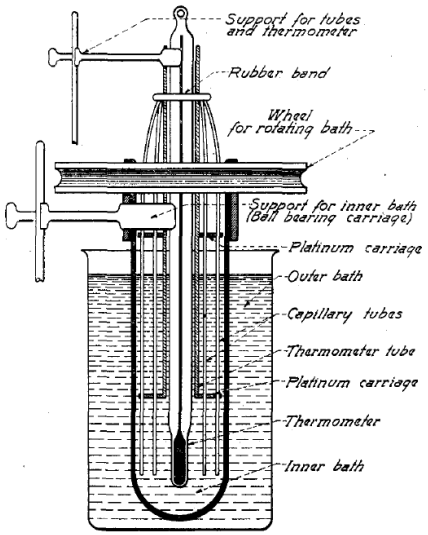
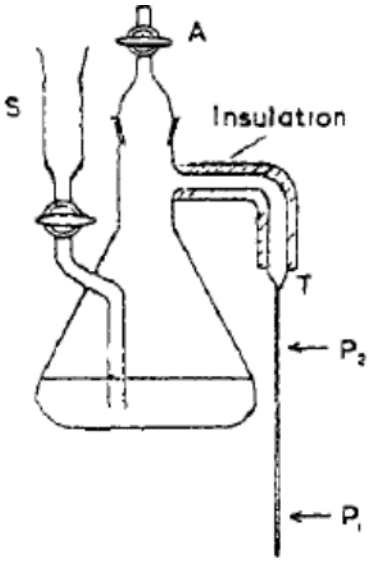
- **Fahrenheit (1721):** Observed supercooling of rainwater in a sealed vial
- **Mousson (1858):** Supercooled <500 μm droplets on hydrophobic surface
- **Sorby (1859):** Observed supercooling in capillaries
- **Dufour (1861):** Supercooled droplets in emulsions

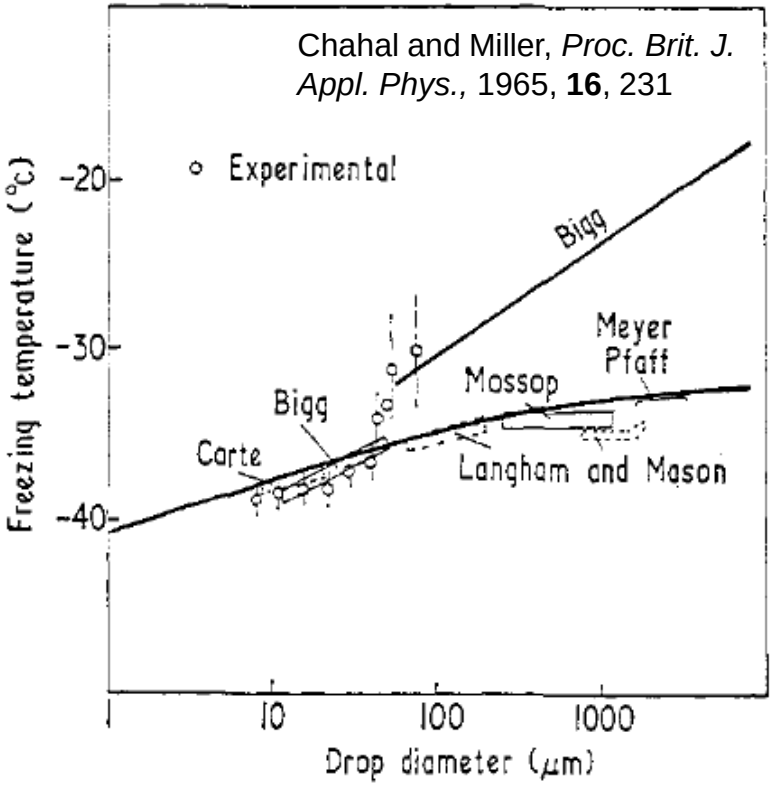


Bigelow and Lawrence, *J. Phys. Chem.*, 1917, **21**, 474

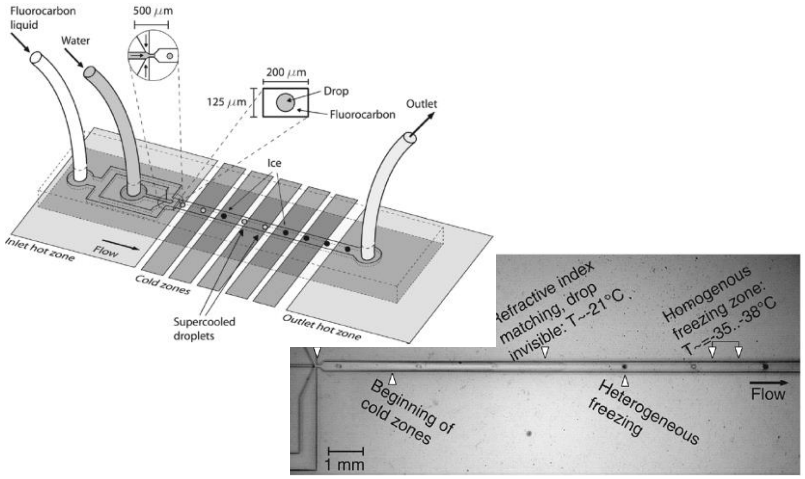


Mossop, *Proc. Phys. Soc. B*, 1955, **68**, 193

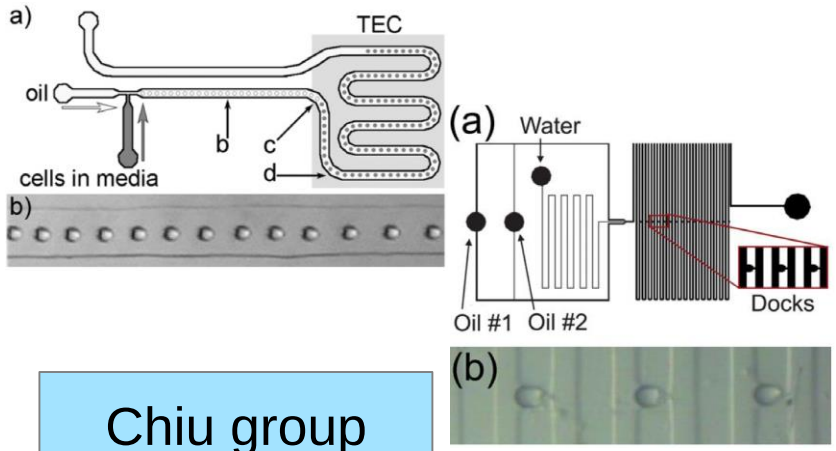
Chahal and Miller, *Proc. Brit. J. Appl. Phys.*, 1965, **16**, 231



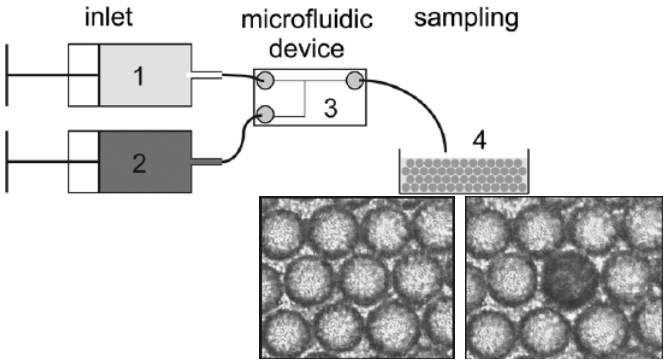
Early microfluidics for ice nucleation (2007-2013)



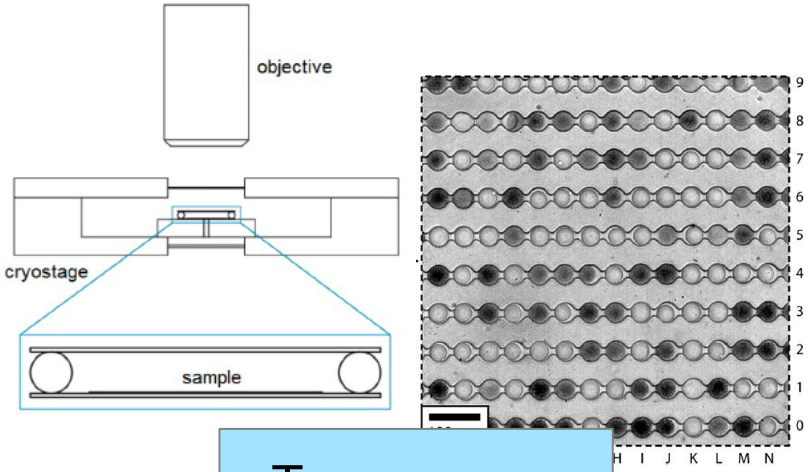
Whitesides group



Chiu group



Koop team



Toner group

Microfluidics for INP analysis (2016-)

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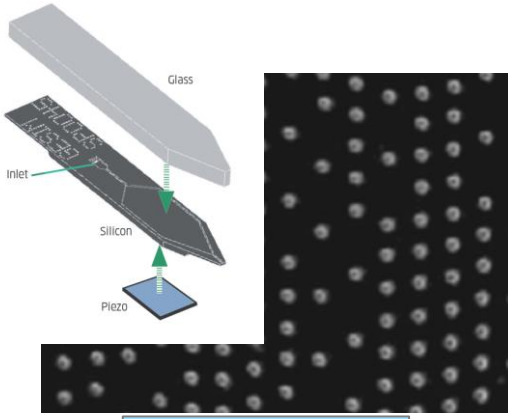
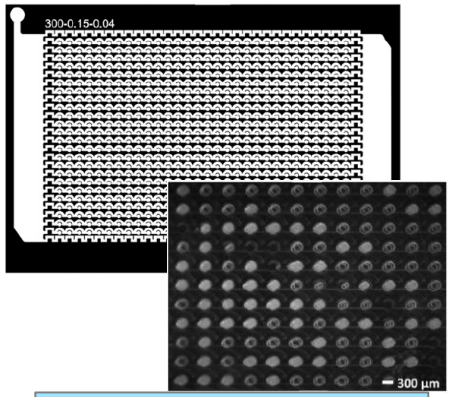
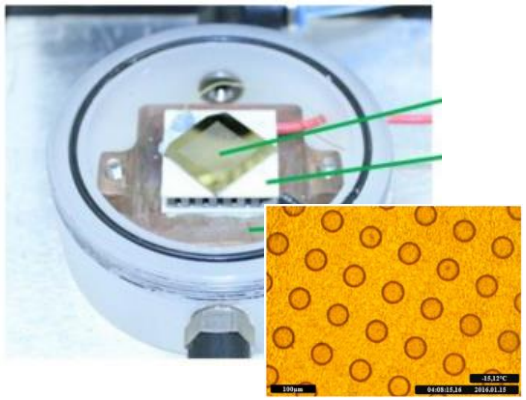


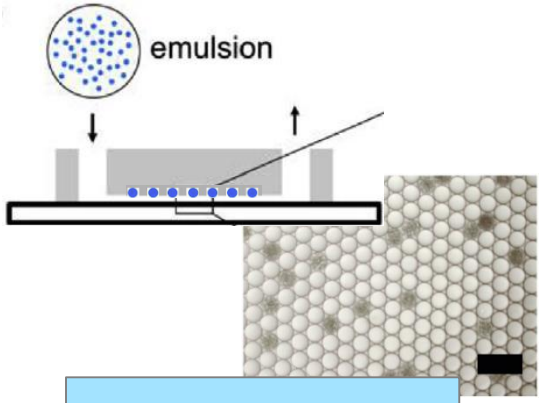
KIT



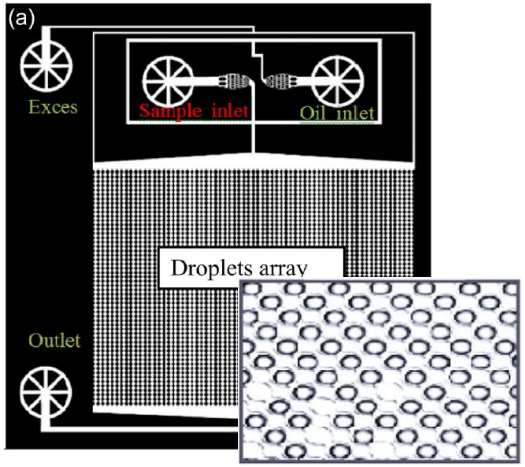
Sullivan group



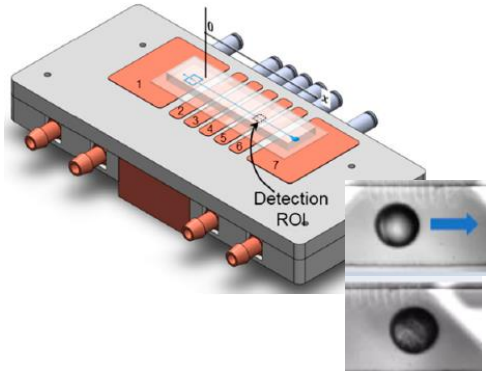
Grothe group



Toner group



Rudich group



Dutcher group

INP analysis in Leeds: pL-NIPI

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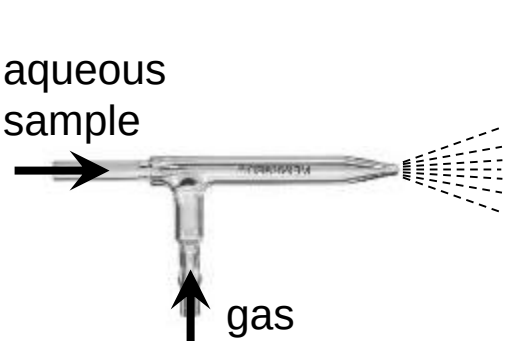
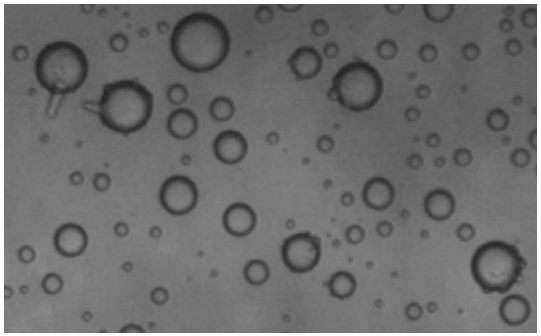
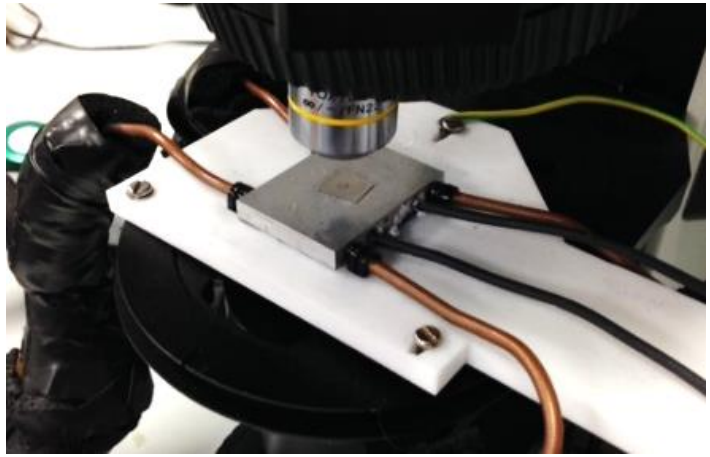
Nebulisation

Atkinson et al., *J. Phys. Chem. A*, 2016, **120**, 6513



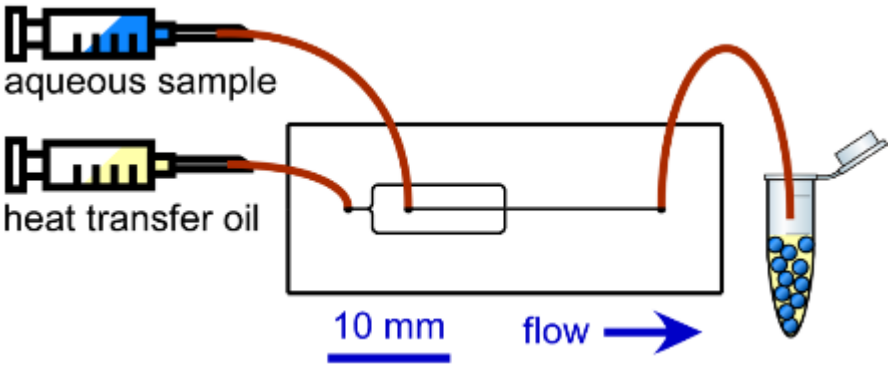


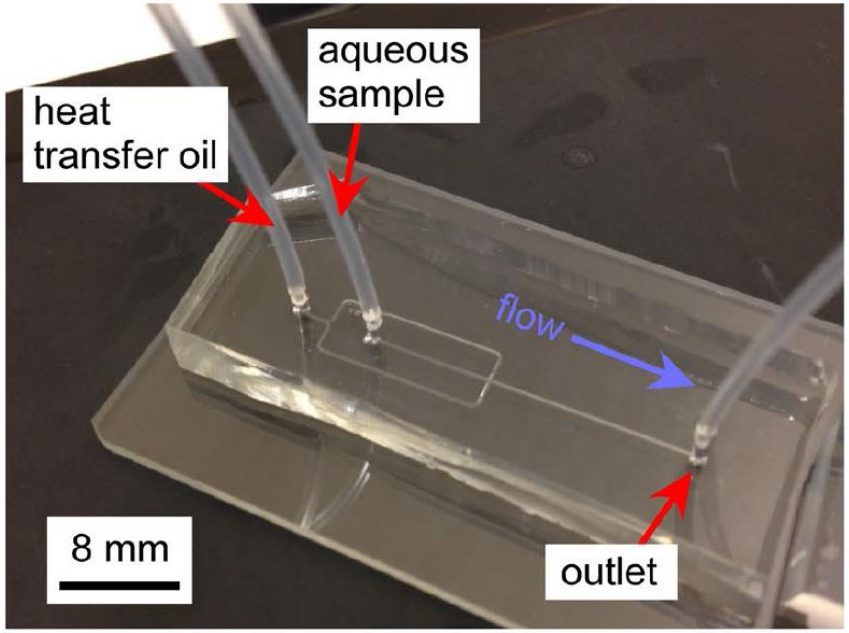


- pL droplet volumes
- **Non-trivial method**
- **Polydisperse droplets**

LN_2 cryomicroscope stage

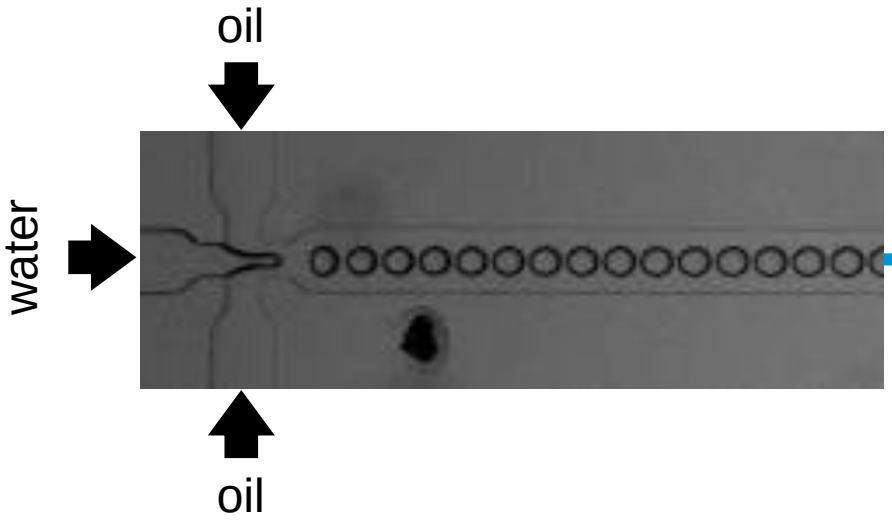
Microfluidic pL-NIPI



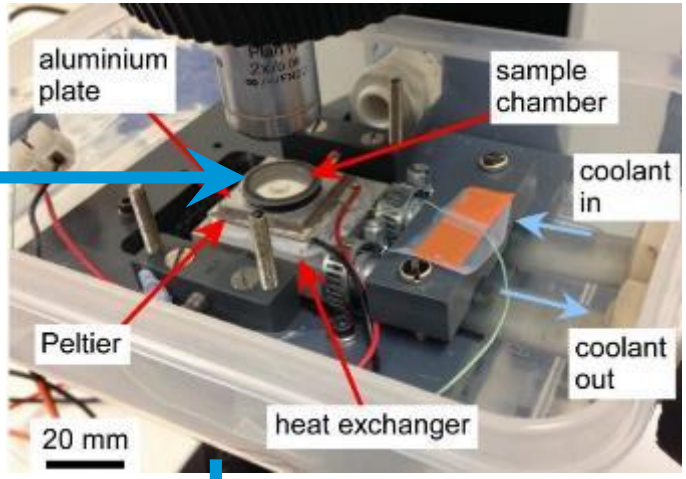


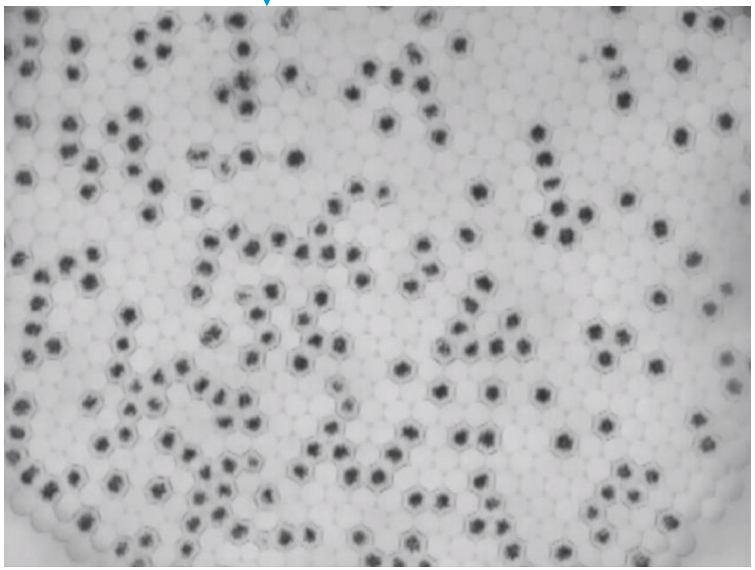
Tarn et al., *Microfluid. Nanofluid.*, 2018, **22**, 52

Microfluidic pL-NIPI



Peltier cryomicroscope stage





- Straightforward method
- Analyse hundreds of pL volume droplets
- Monodisperse population

Tarn et al., *Microfluid. Nanofluid.*, 2018, **22**, 52

Measurements of various INPs

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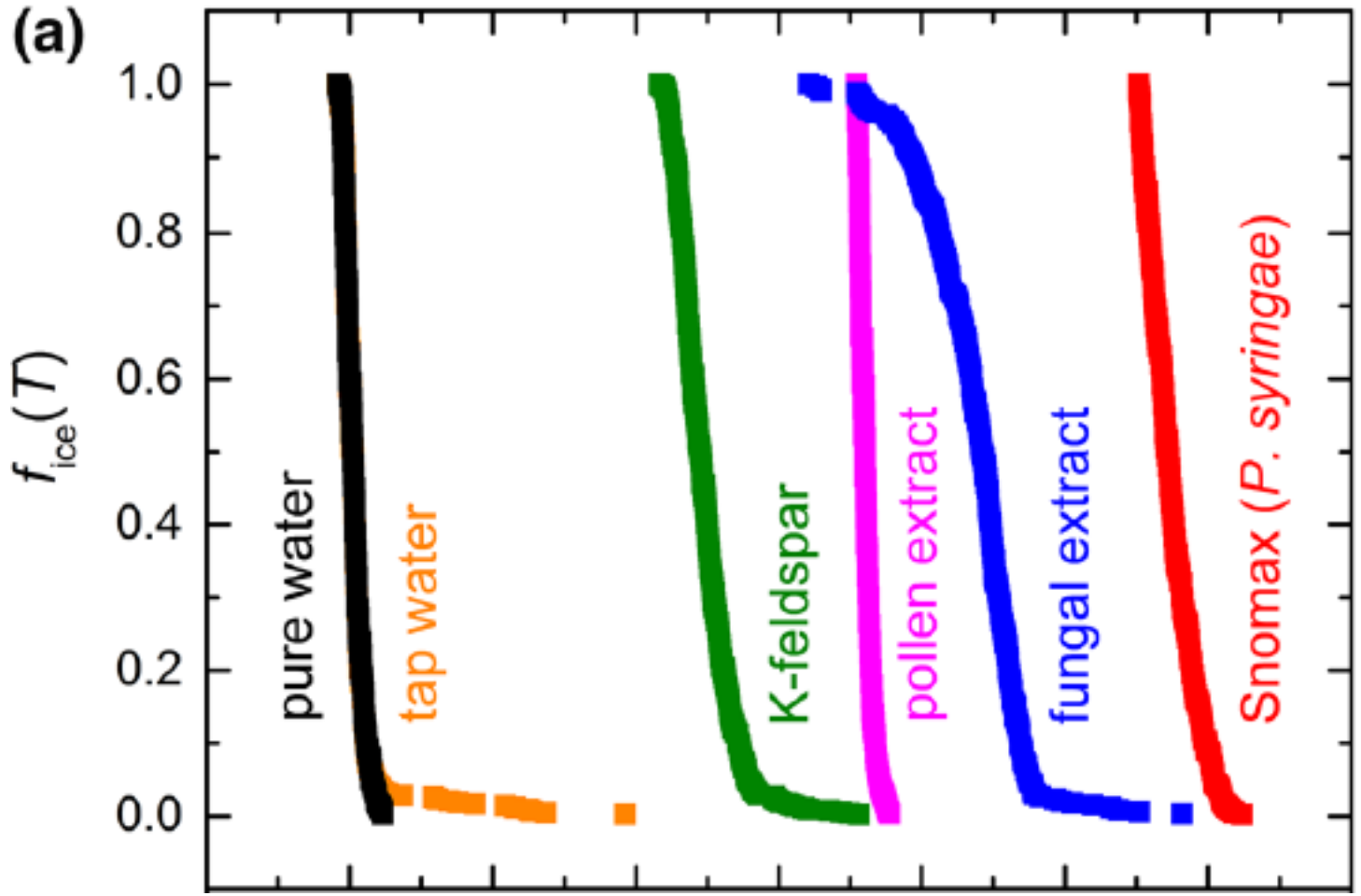
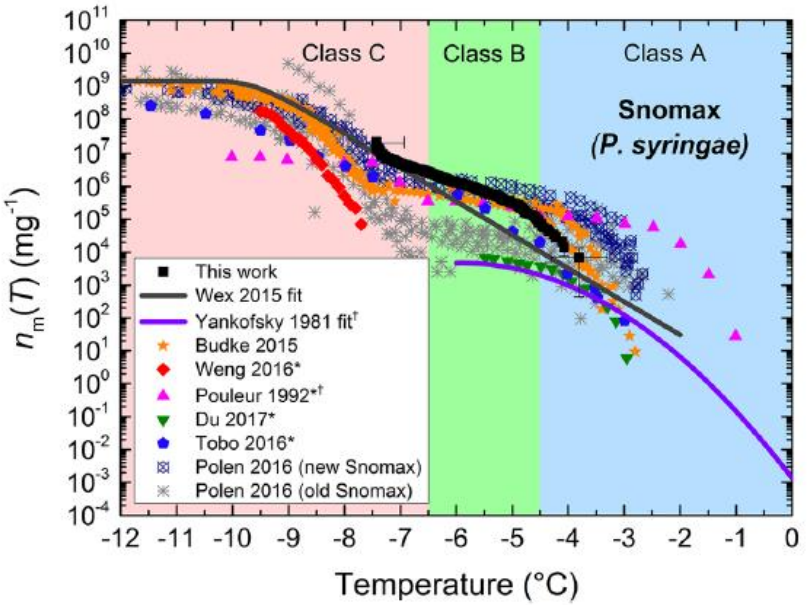
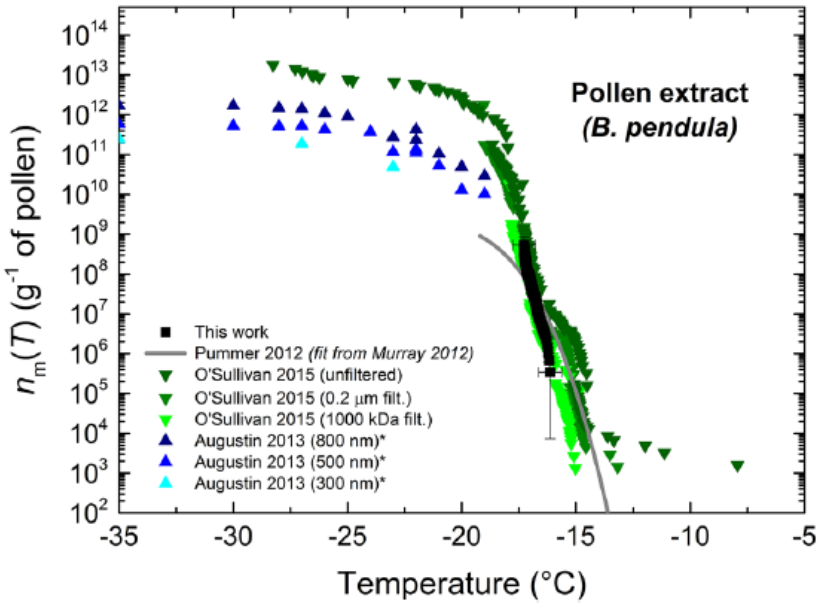
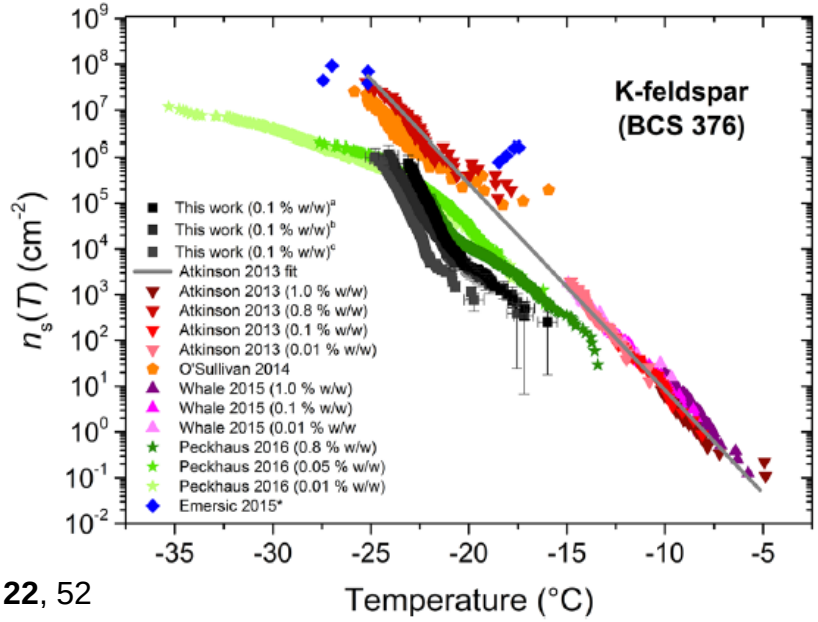


Tarn et al., *Microfluid. Nanofluid.*, 2018, **22**, 52

Measurements of various INPs







Tarn et al., *Microfluid. Nanofluid.*, 2018, **22**, 52

INPs in sampled aerosol

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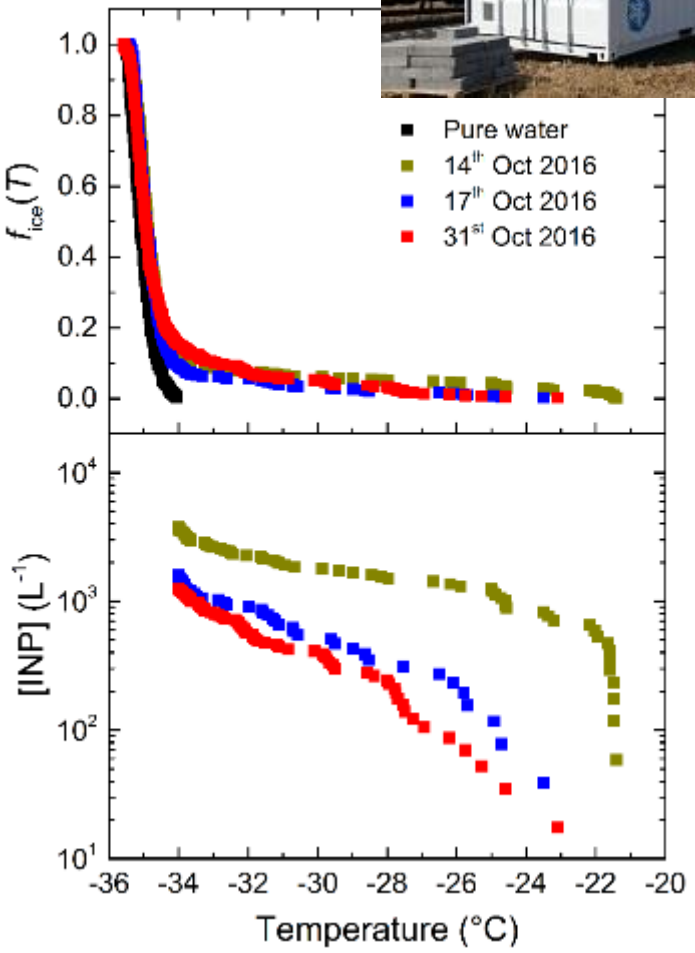
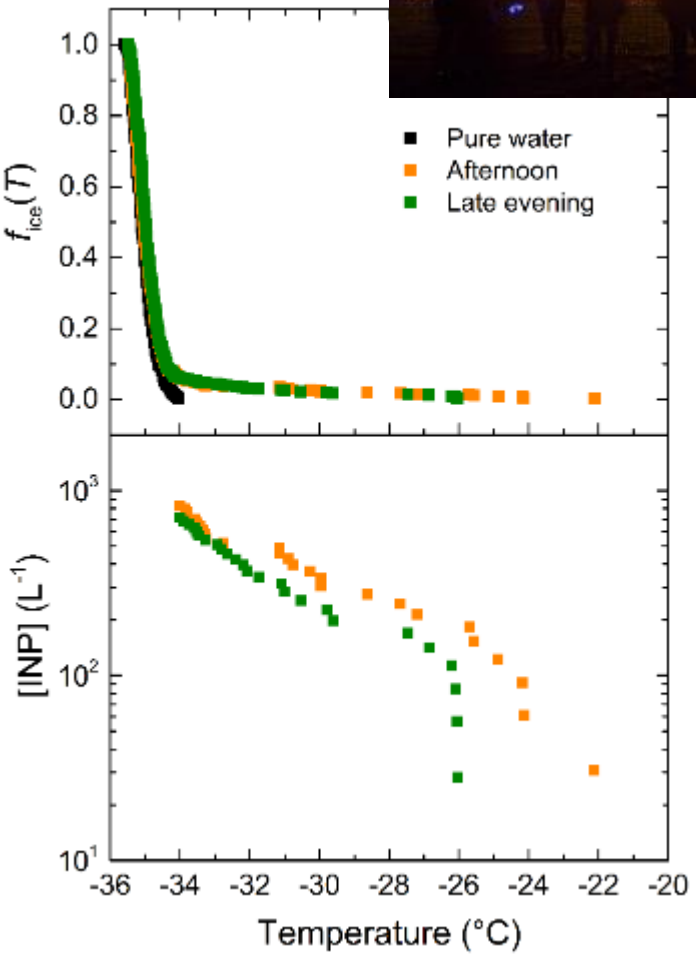
Leeds University Research Farm



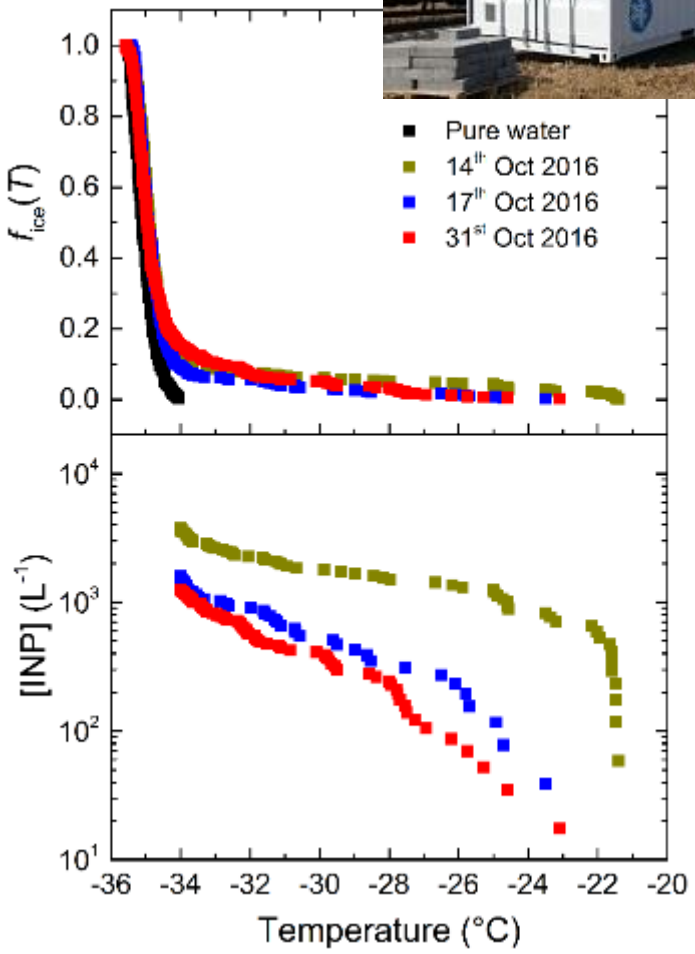
Bonfire Night 2016 (Leeds)



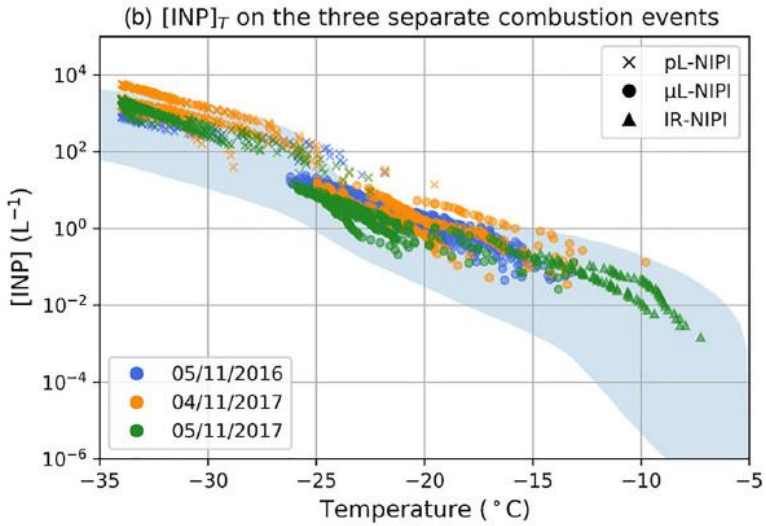
INPs in sampled aerosol

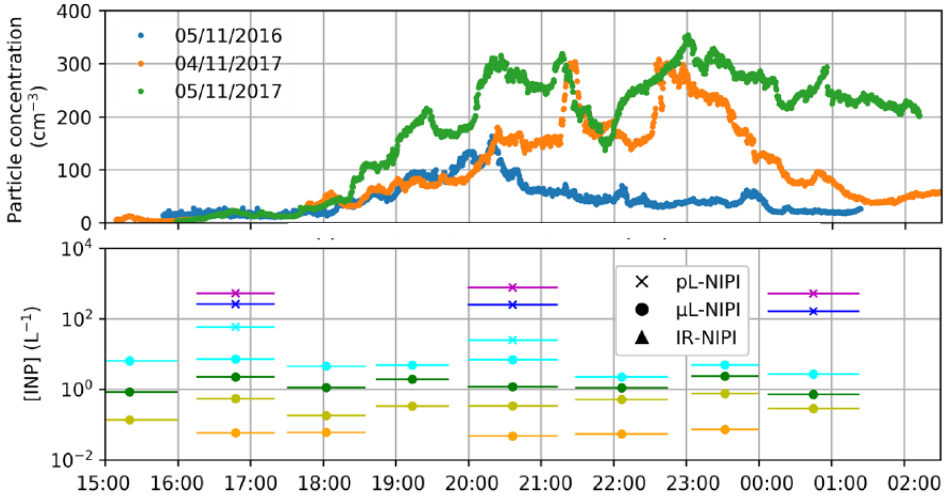
UNIVERSITY OF LEEDS

Leeds University Research Farm



Bonfire Night 2016-2017





Adams et al., *J. Geophys. Res. Atmos.*, 2020, **125**, e2020JD032938

Continuous flow analysis platform

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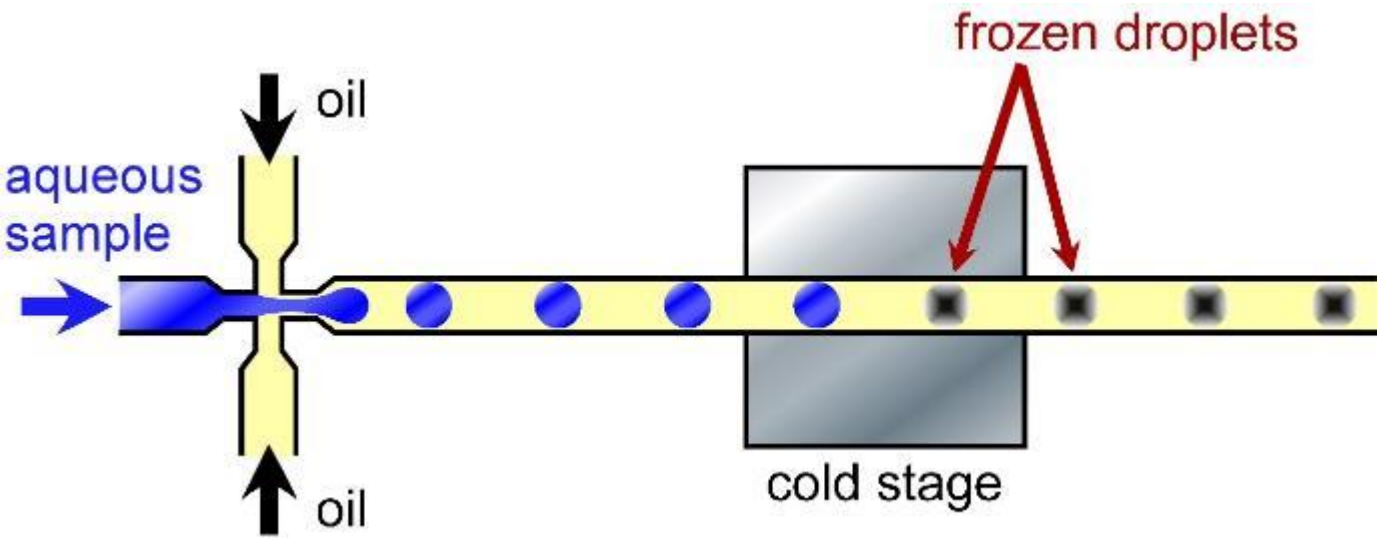
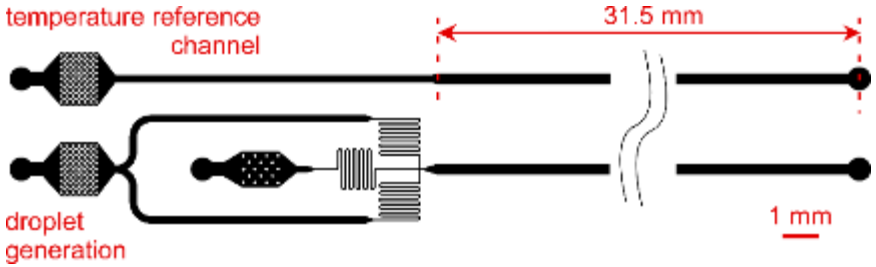
Lab on a Chip Nucleation by Immersed Particle Instrument (LOC-NIPI)

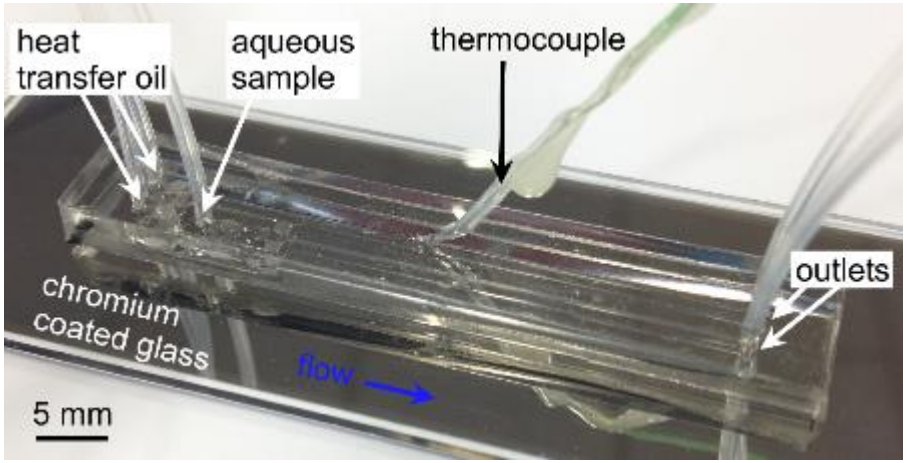


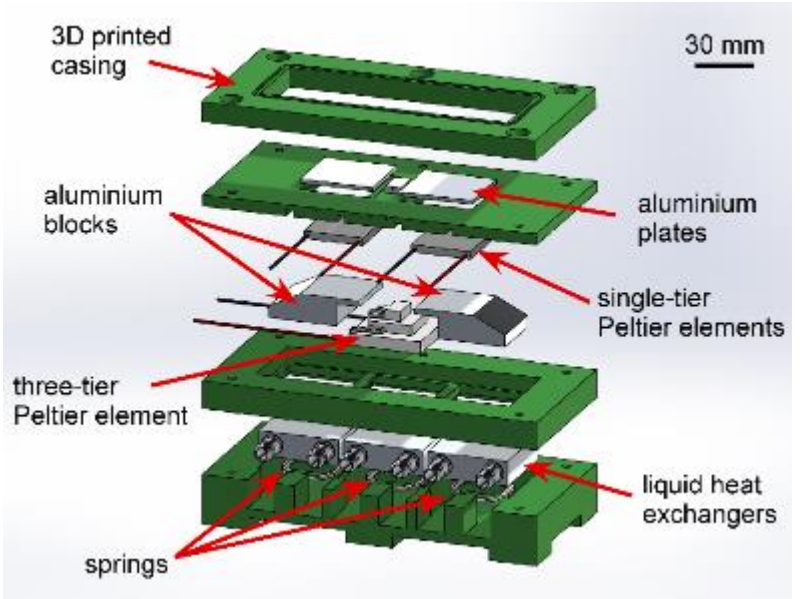
- Droplets continuously generated and frozen at a set temperature
- Ratio of *frozen vs. unfrozen* droplets counted to give fraction frozen

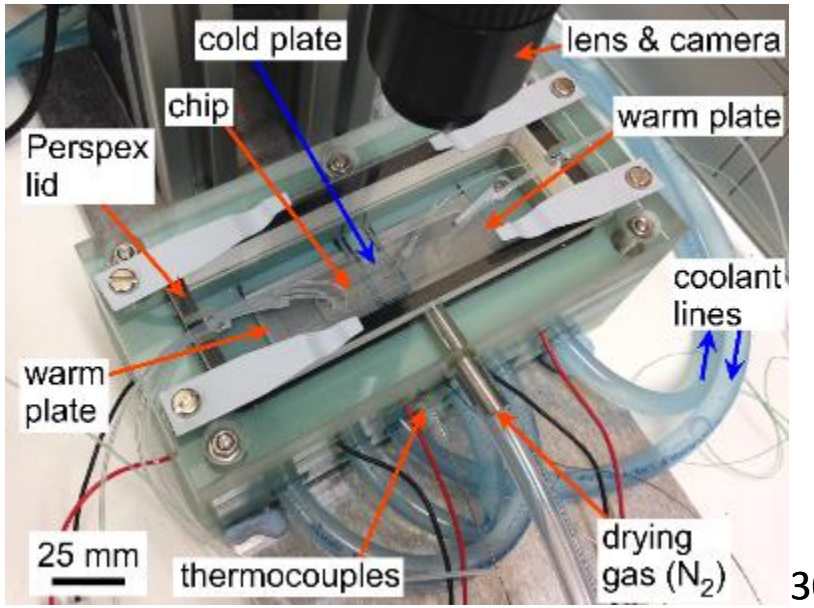
- High throughput
- User-defined number of droplets to be analysed
- Amenable to automation and continuous monitoring

Chip design and setup









Tarn et al., *Lab Chip*, 2020, **20**, 2889

Design and setup

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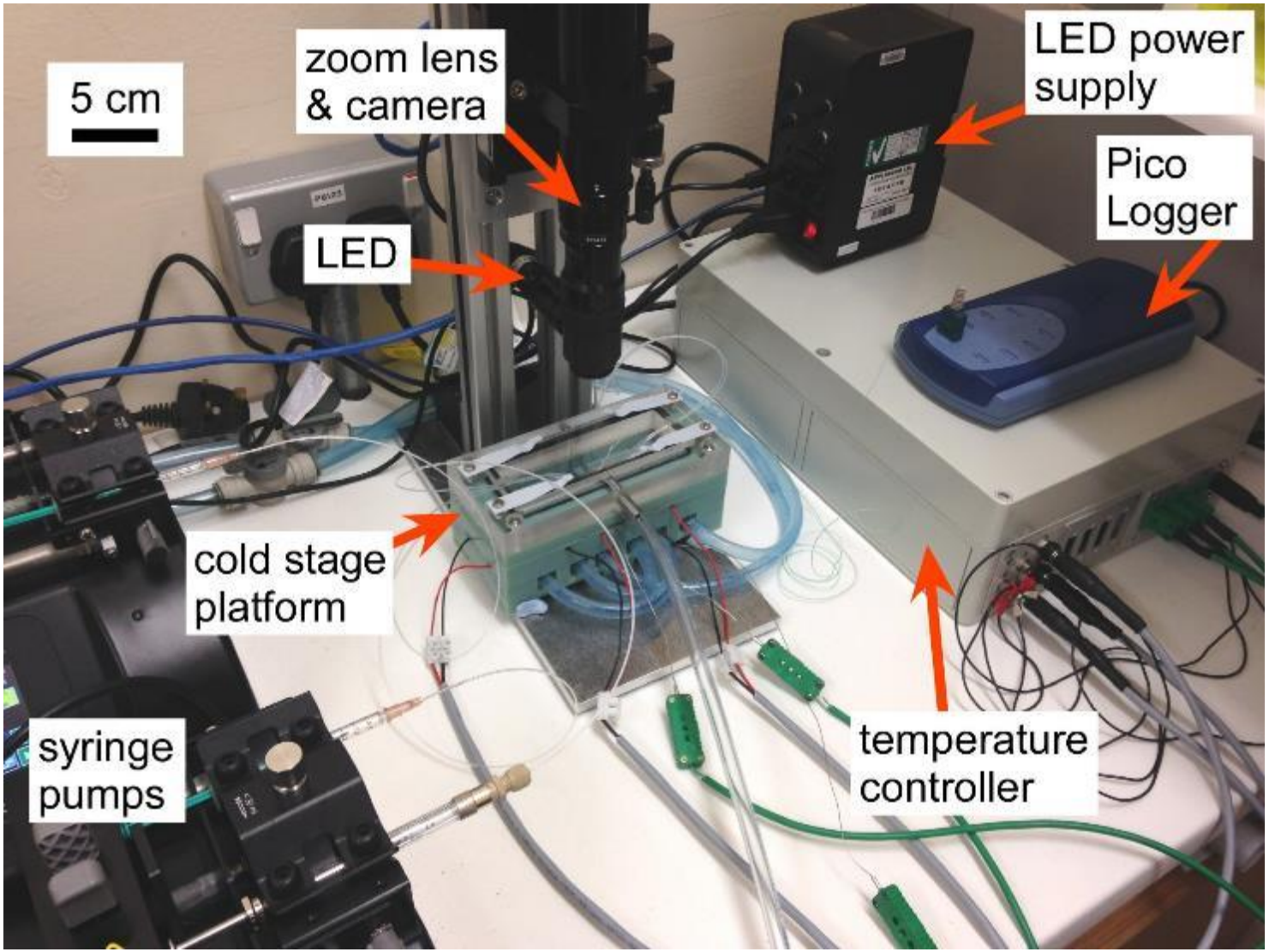

Tarn et al., *Lab Chip*, 2020, **20**, 2889

Droplet freezing in flow

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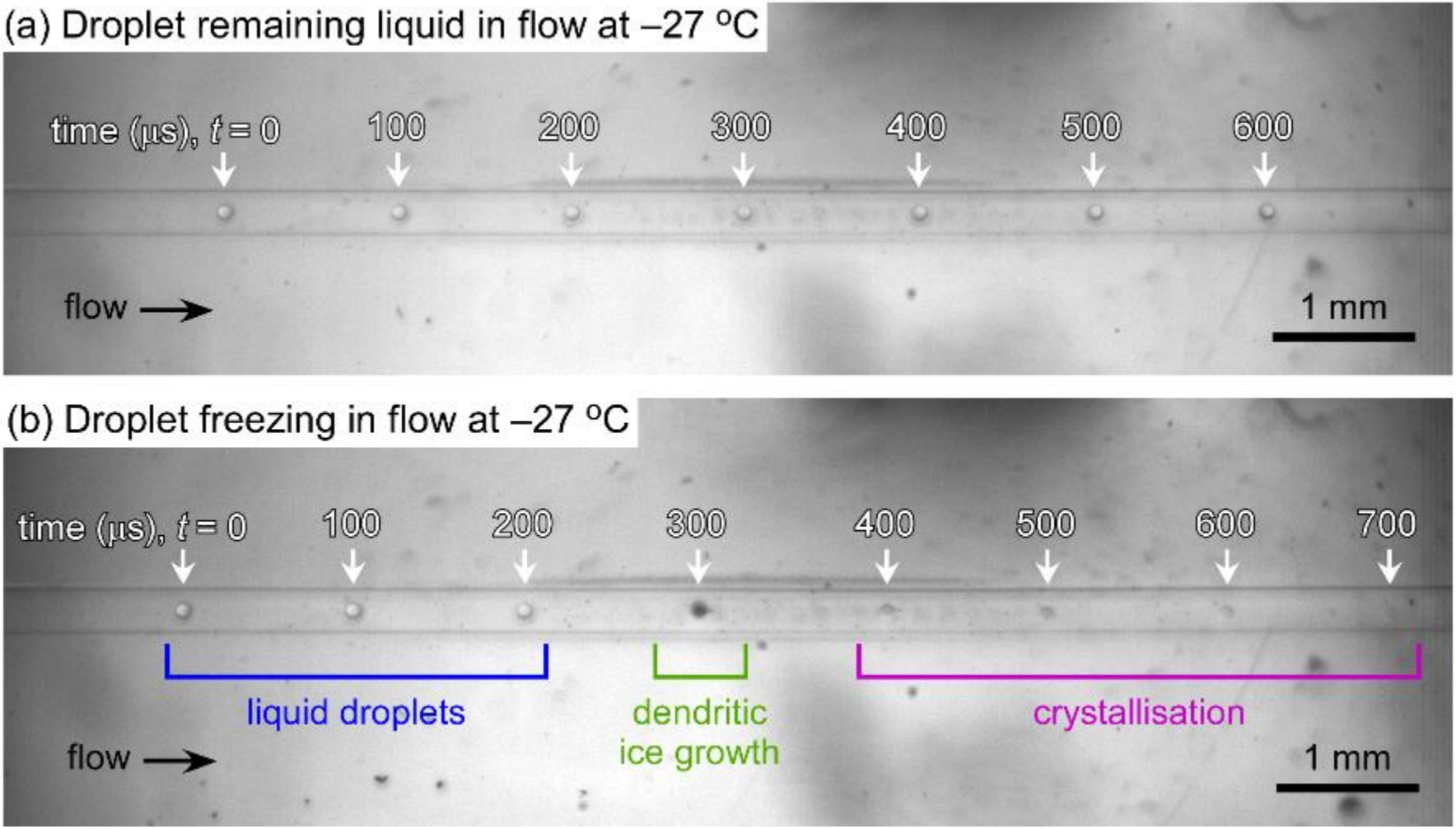

Tarn et al., *Lab Chip*, 2020, **20**, 2889

Validation tests

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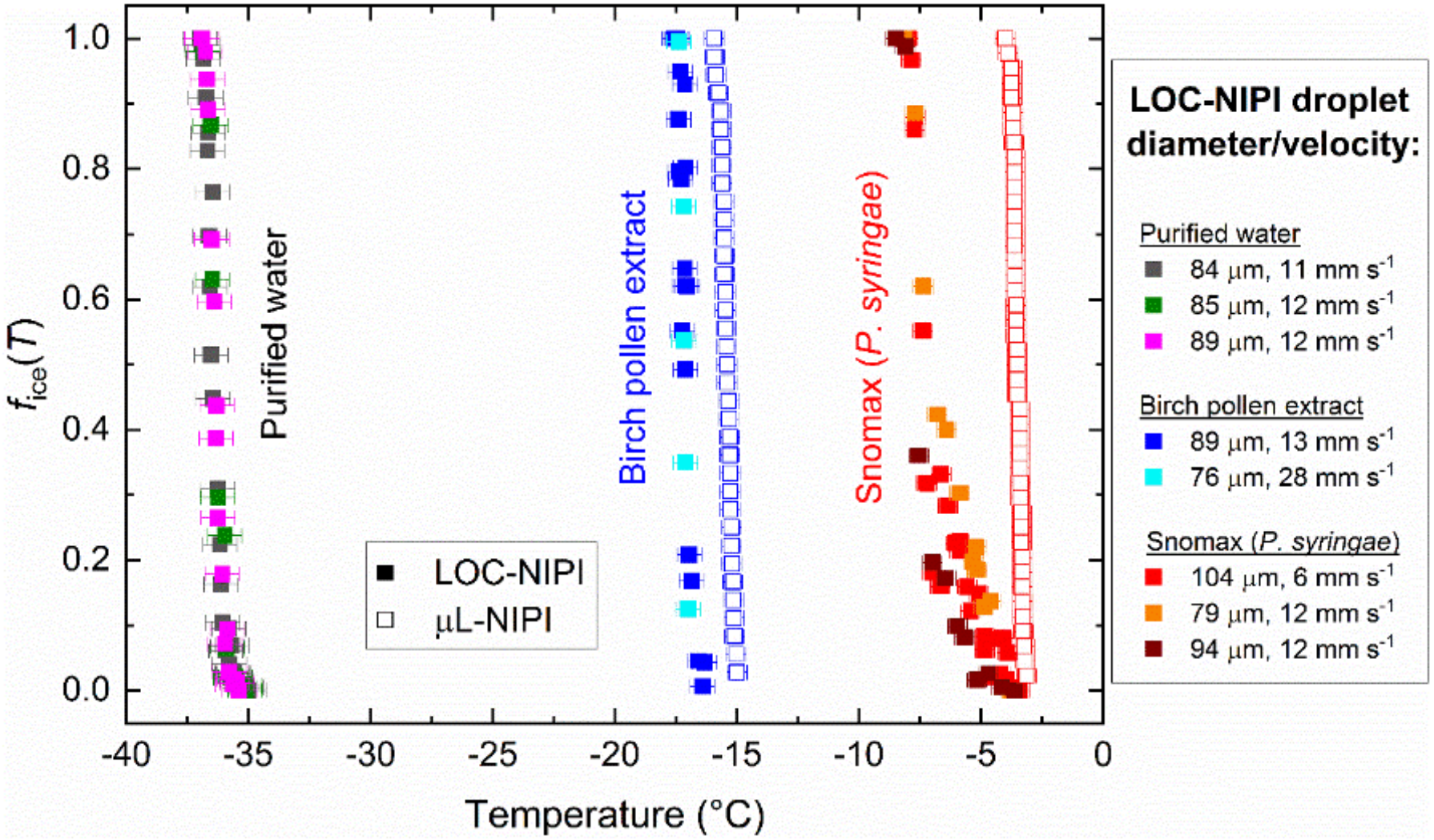
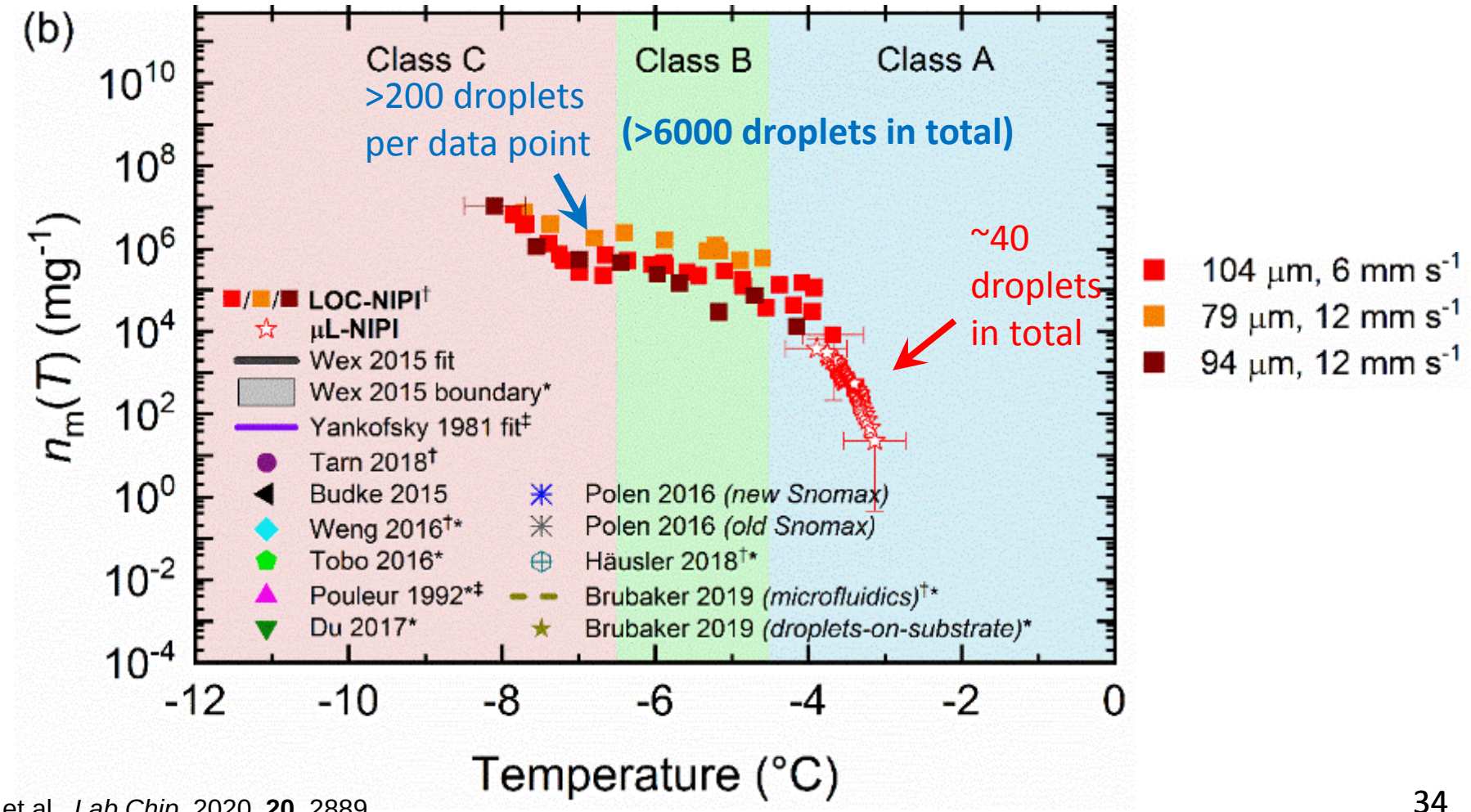


Tarn et al., *Lab Chip*, 2020, **20**, 2889

Snomax results

UNIVERSITY OF LEEDS

❄ Non-viable form of *Pseudomonas syringae* bacteria

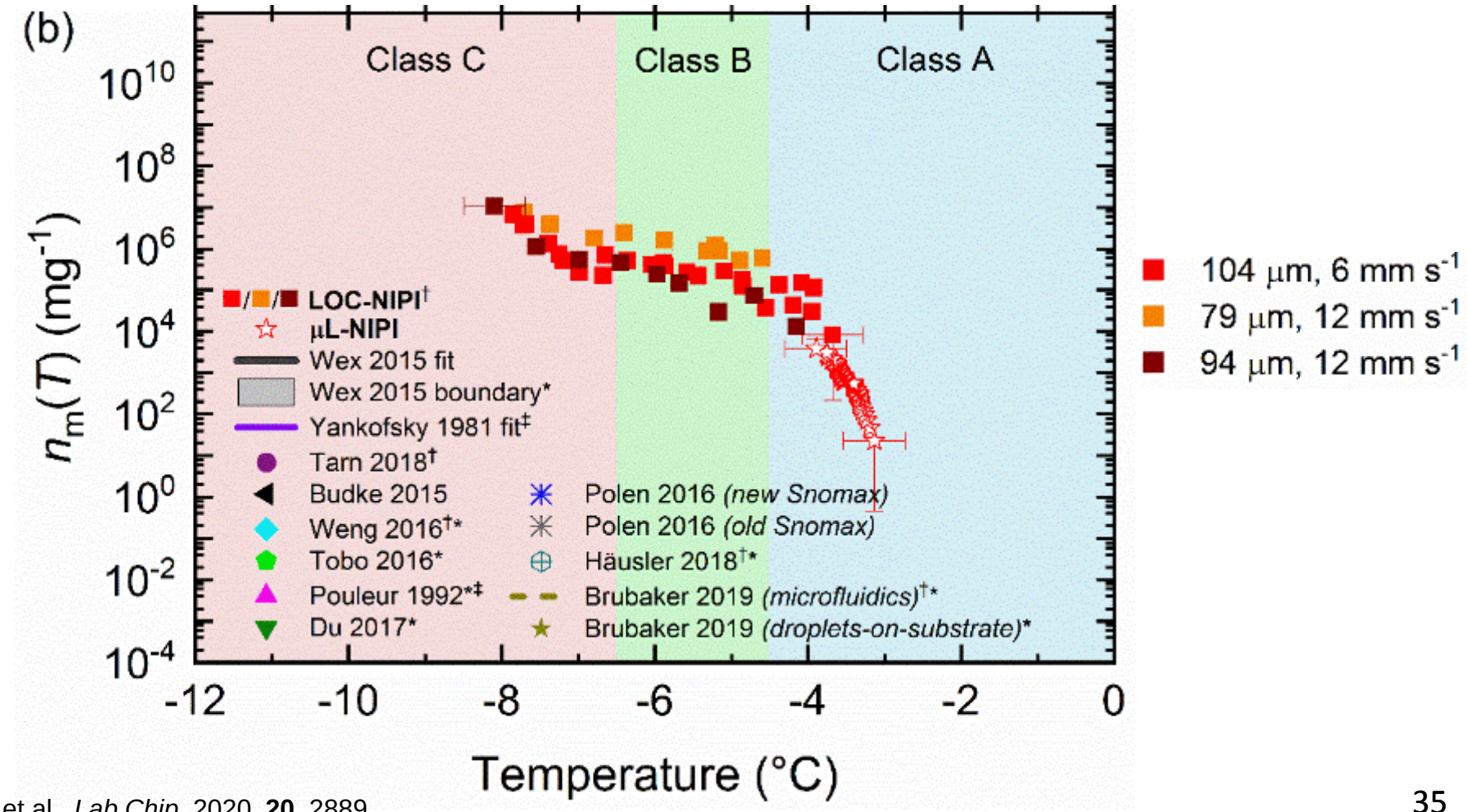


Tarn et al., *Lab Chip*, 2020, **20**, 2889

Snomax results

UNIVERSITY OF LEEDS

❄ Non-viable form of *Pseudomonas syringae* bacteria

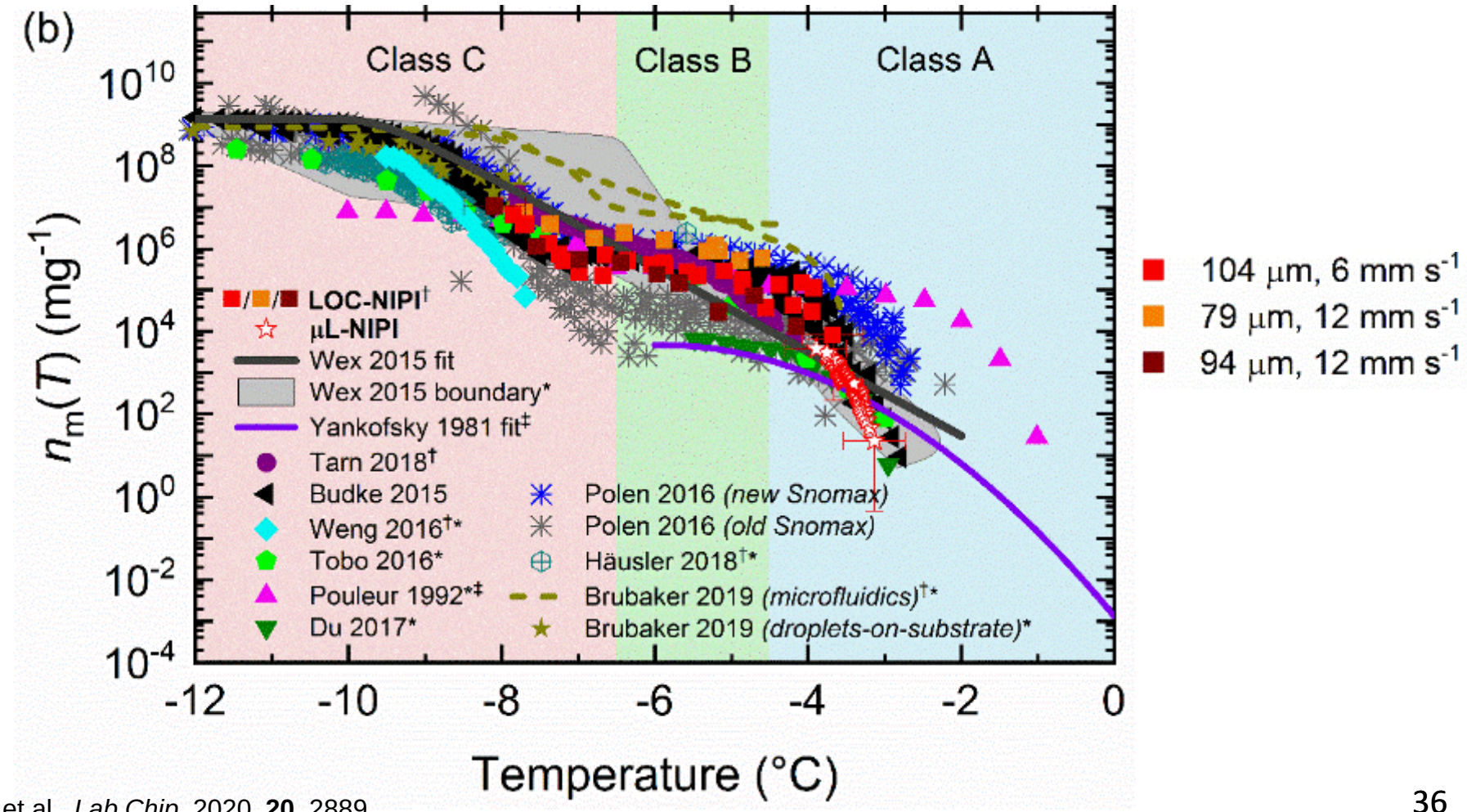


Tarn et al., *Lab Chip*, 2020, **20**, 2889

Snomax results

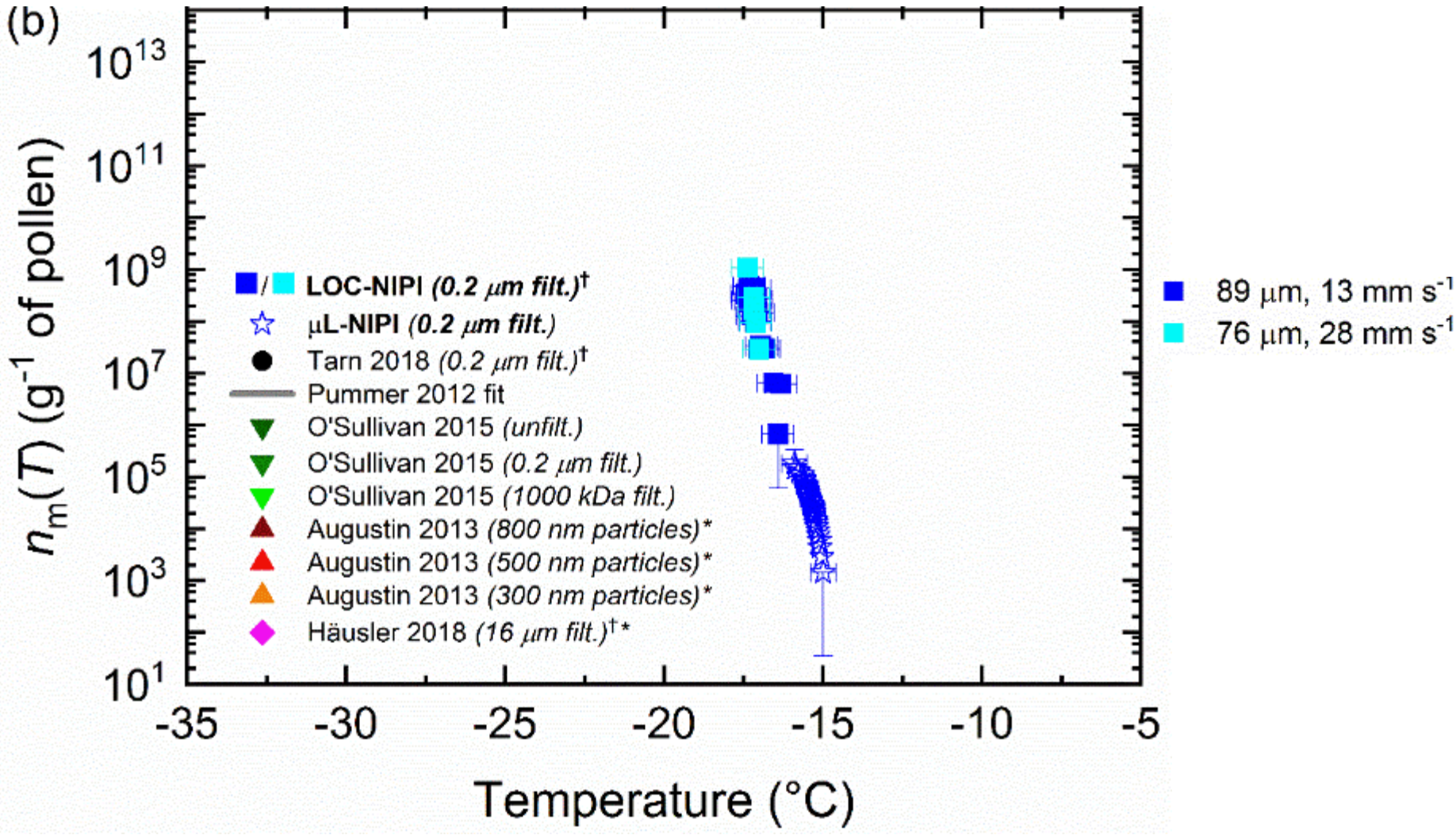
UNIVERSITY OF LEEDS

❄ Non-viable form of *Pseudomonas syringae* bacteria



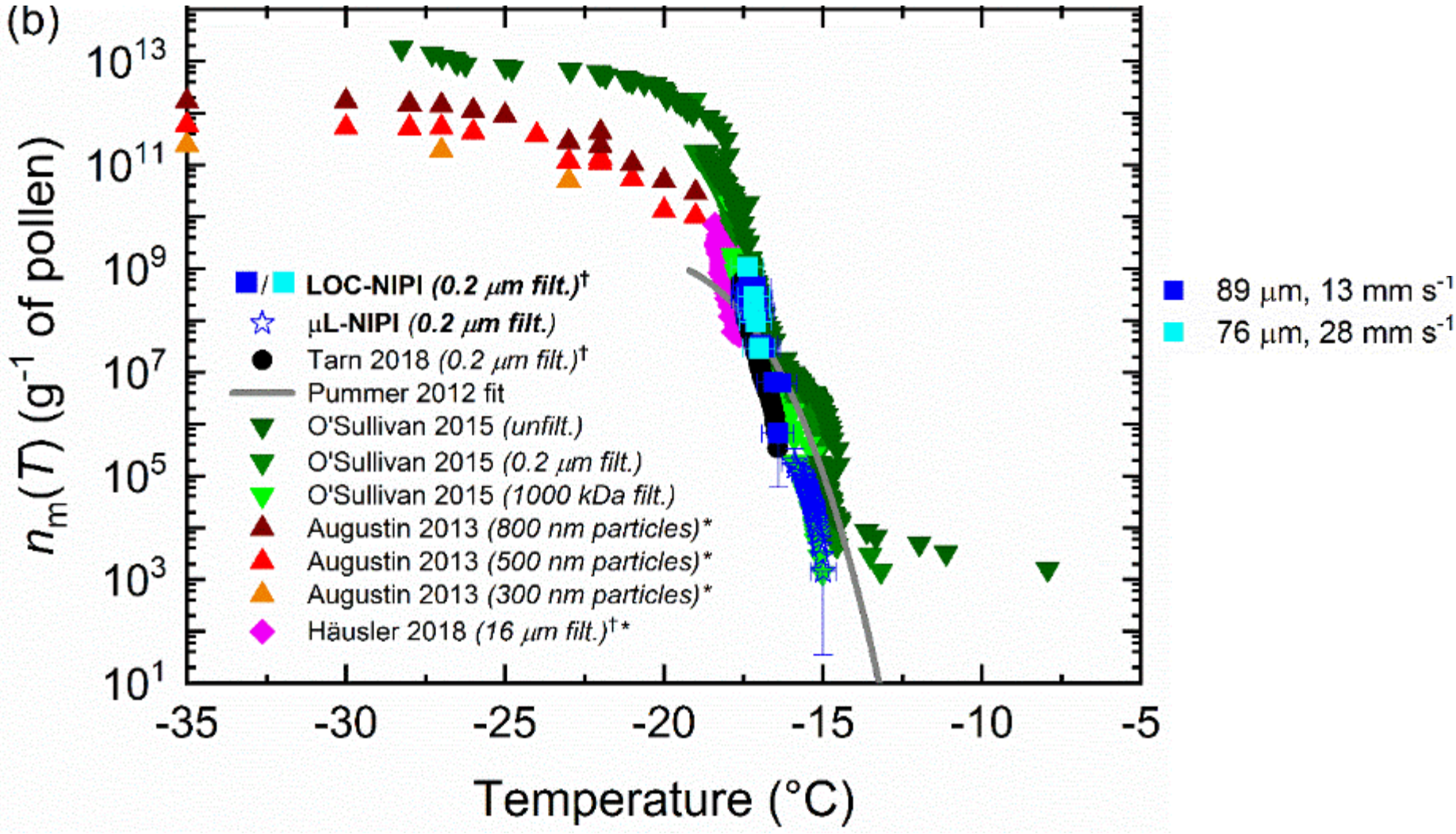
Tarn et al., *Lab Chip*, 2020, **20**, 2889

Birch pollen results



Tarn et al., *Lab Chip*, 2020, **20**, 2889

Birch pollen results



Tarn et al., *Lab Chip*, 2020, **20**, 2889

Preliminary field campaign tests

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❄ Israel, Oct-Nov 2018

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WEIZMANN INSTITUTE OF SCIENCE

Aerosol sampling and analysis

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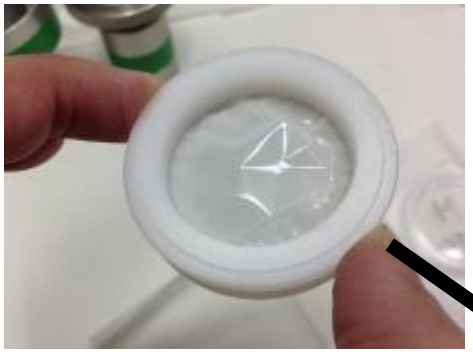
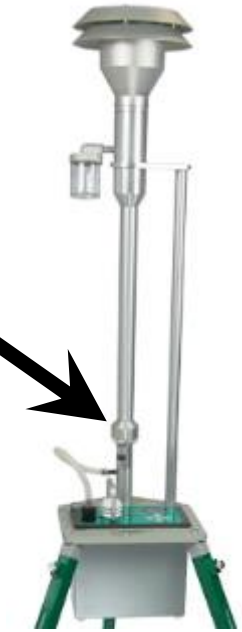
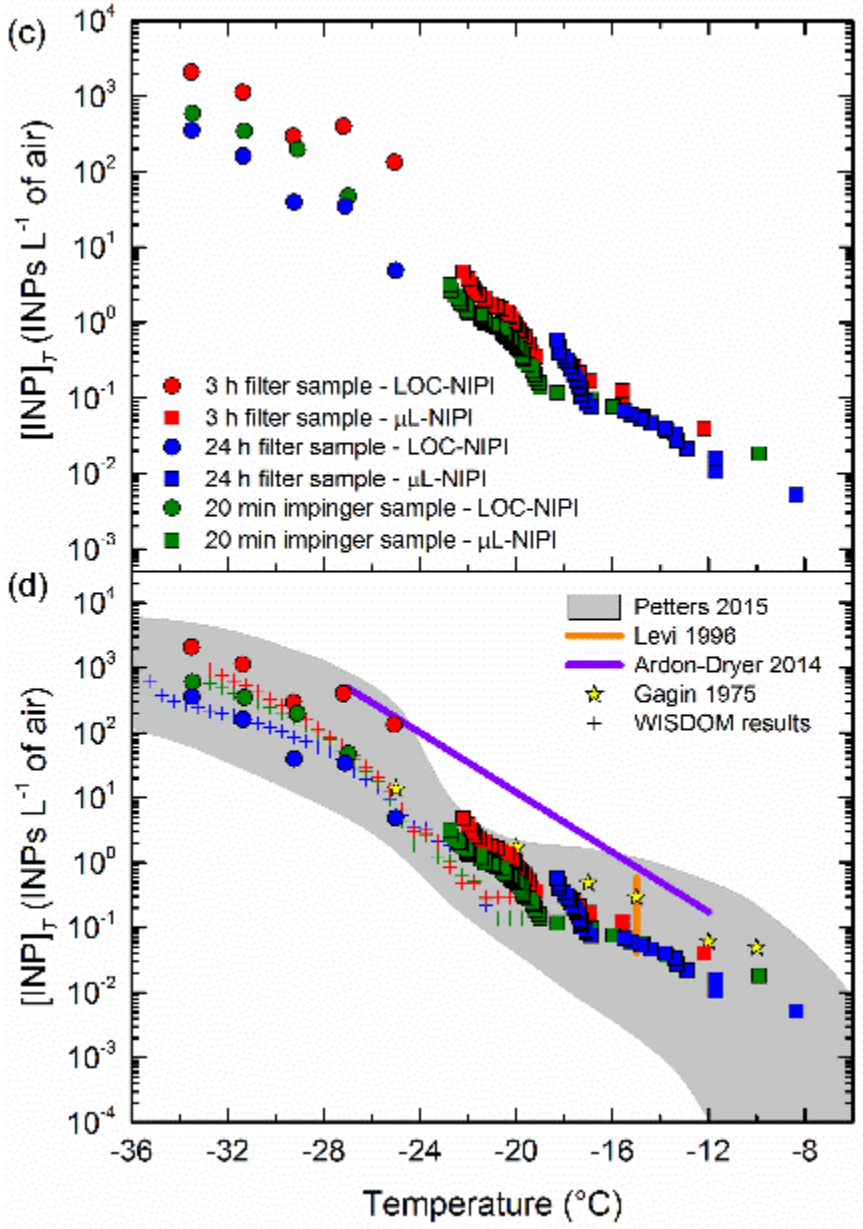


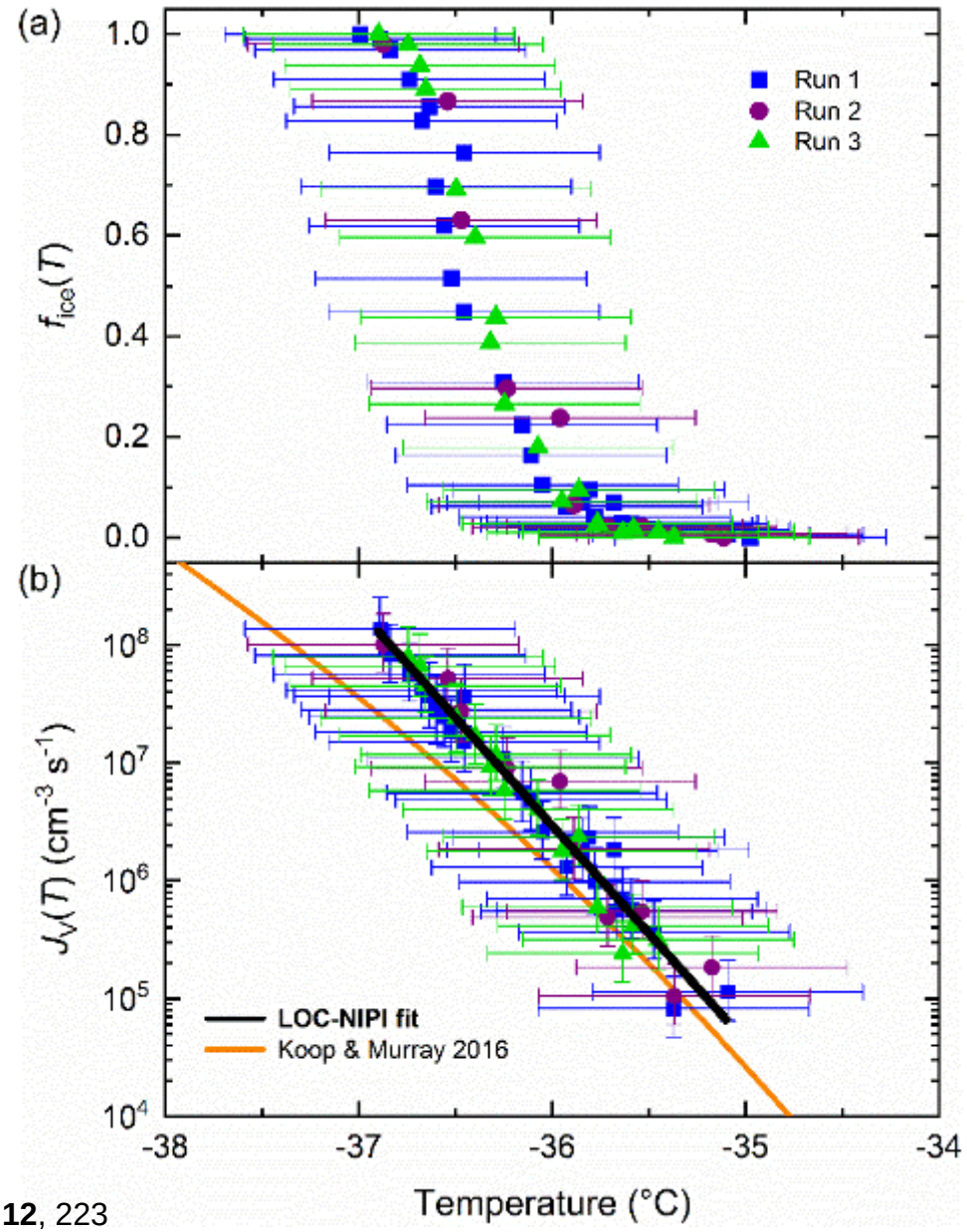


Filter-based sampling

Impinger-based sampling



Homogeneous ice nucleation

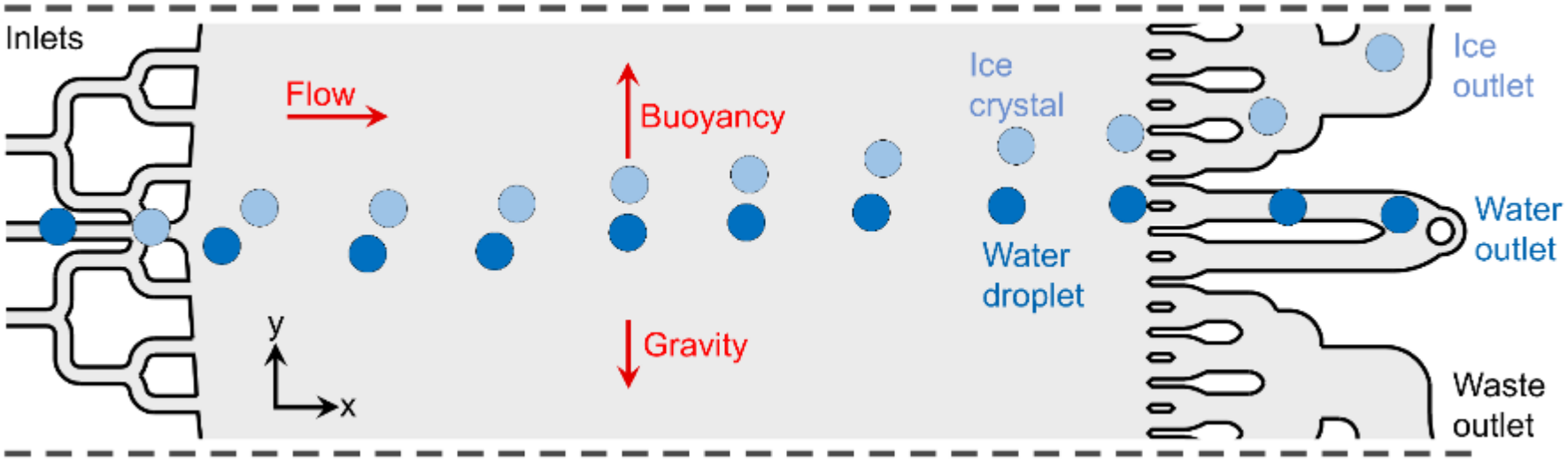


Tarn et al., *Micromachines*, 2021, **12**, 223

Sorting droplets and ice crystals

Grace Porter

- **Aerosol sampling:** INP concentrations can be calculated, but it is difficult to determine what the active INP is, *e.g. dust, bacteria….*
- Sorting frozen from unfrozen droplets could allow characterisation of the components that caused freezing in the former but not the latter



Porter et al., *Lab Chip*, 2020, **20**, 3876

Buoyancy force (F_{buoy})

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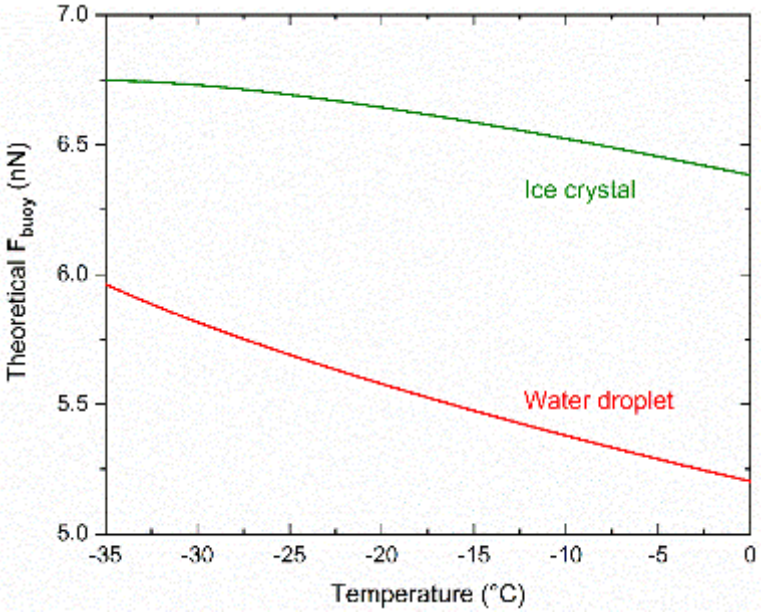
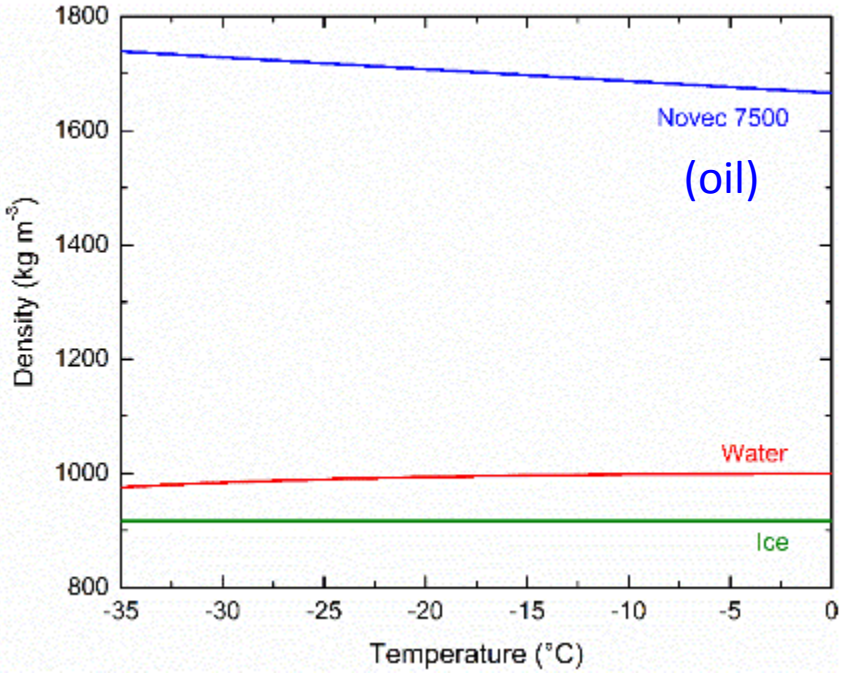
density of droplet

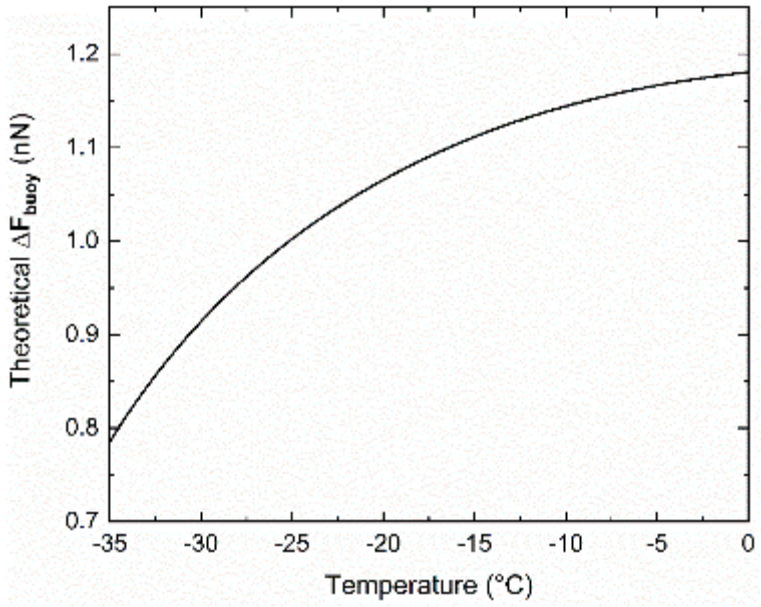
volume of droplet

$$\mathbf{F_{buoy}} = (\rho_p - \rho_m)\, V_p\, g$$

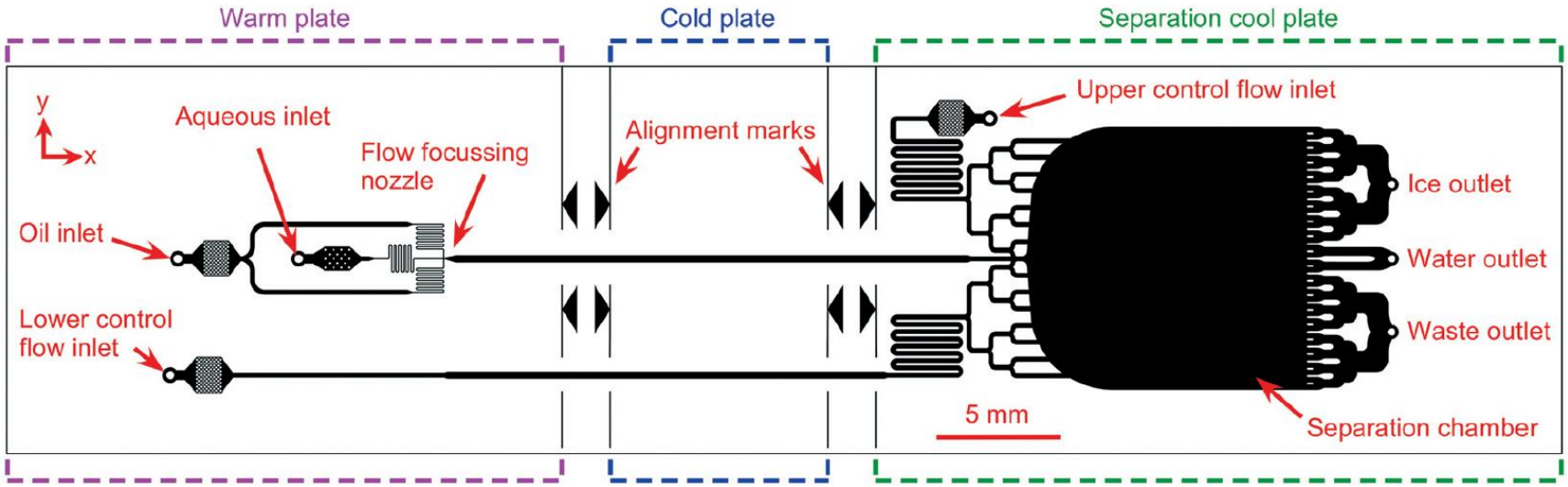
density of oil

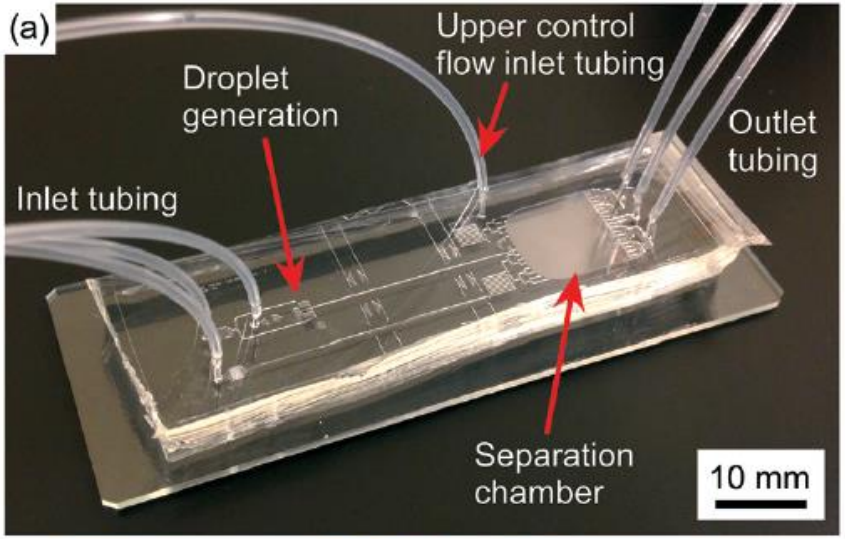


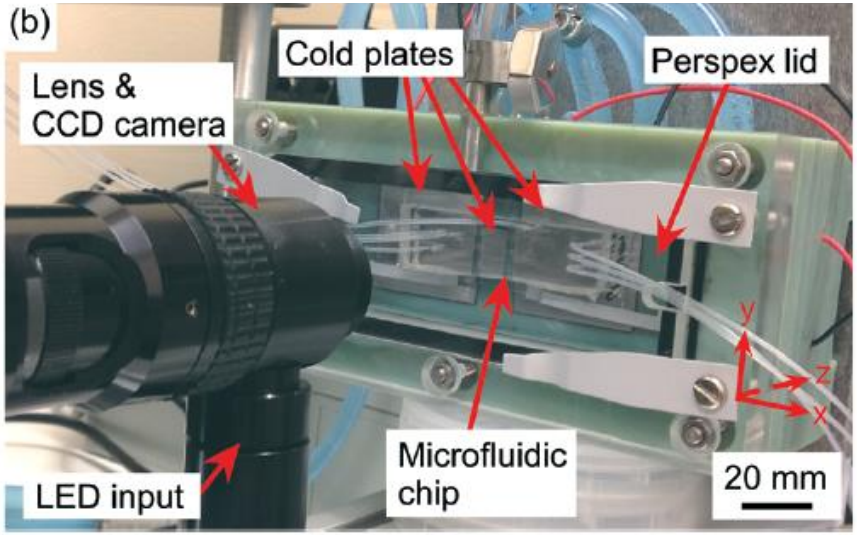




Sorting droplets and ice crystals







Porter et al., *Lab Chip*, 2020, **20**, 3876

Sorting droplets and ice crystals

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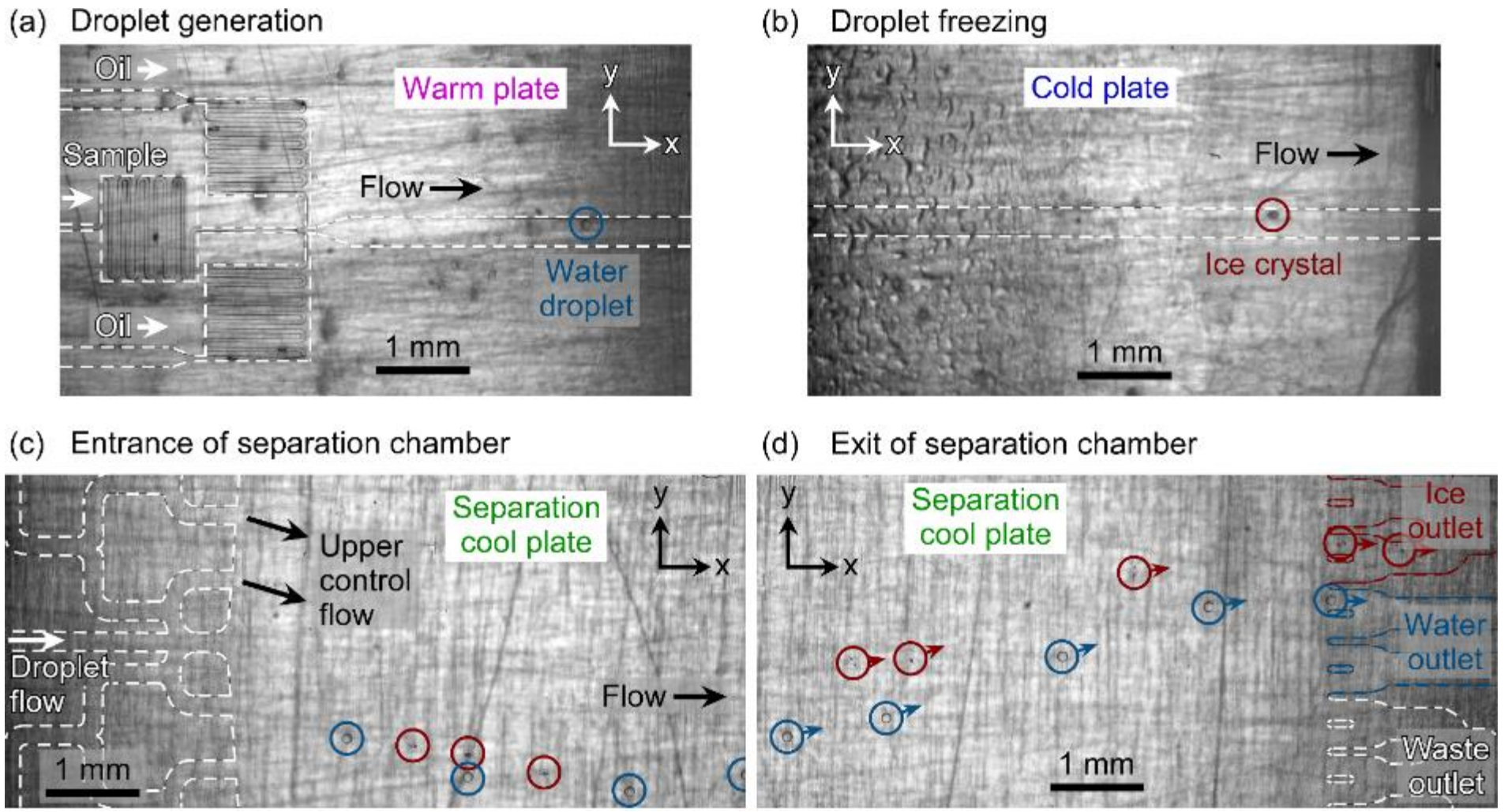

Porter et al., *Lab Chip*, 2020, **20**, 3876

Sorting droplets and ice crystals

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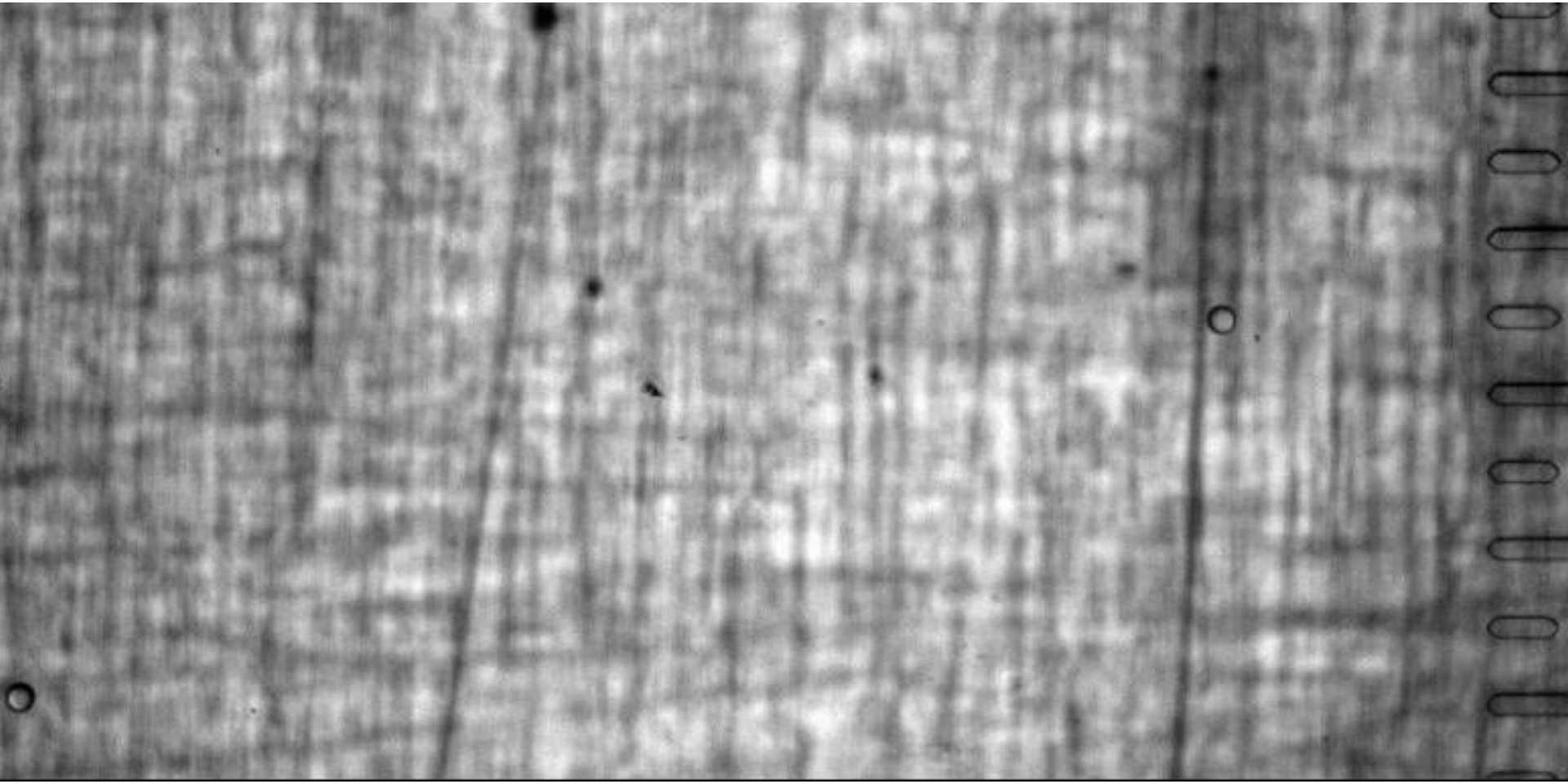

gravity

Porter et al., *Lab Chip*, 2020, **20**, 3876

Sorting droplets and ice crystals

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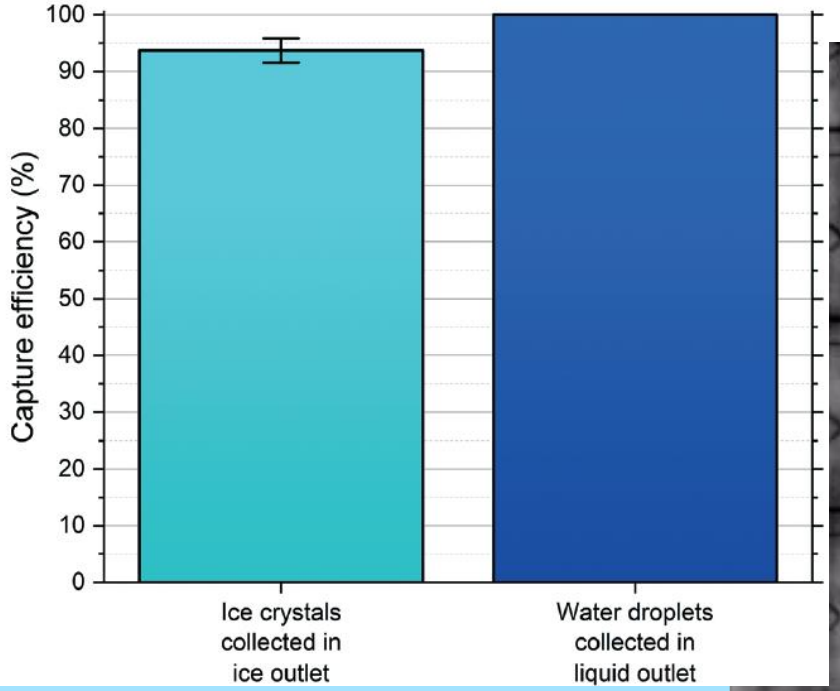

- **Separation efficiency of 92 %**
- ***Next steps:***
  - → Analyse and characterise collected droplet populations
  - → Improve separation efficiency

gravity

Porter et al., *Lab Chip*, 2020, **20**, 3876

Possibilities….

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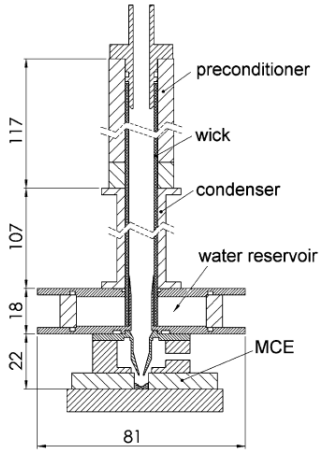
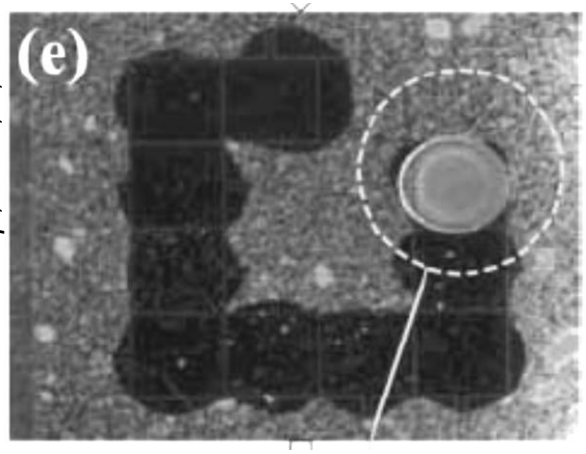
Interfacing aerosol collection to microfluidics

Noblitt et al., *Anal. Chem.*, 2009, **81**, 10029

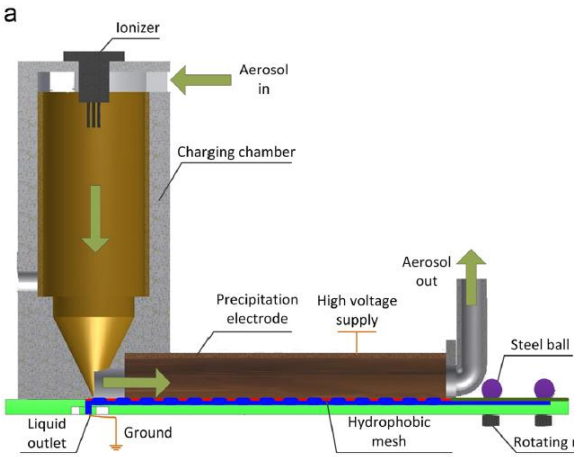


Growth tube collector

Zhao and Cho, *Lab Chip*, 2006, **6**, 137



Electrowetting-on-dielectric (EWOD)

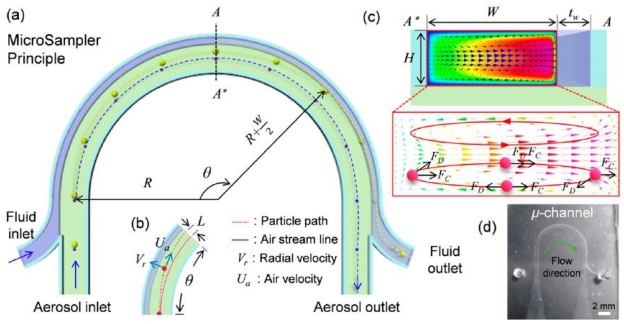


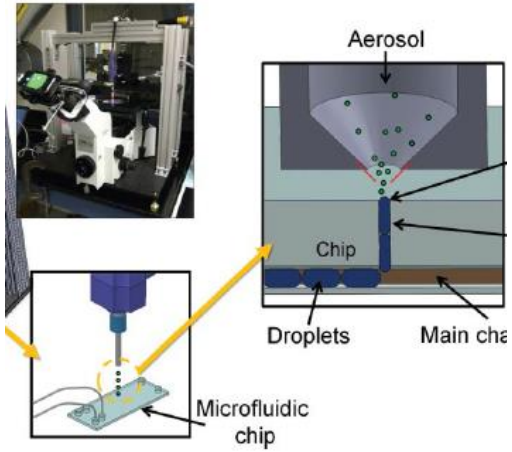
Choi et al., *J. Aerosol Sci.*, 2016, **95**, 84

Electrostatic sampler

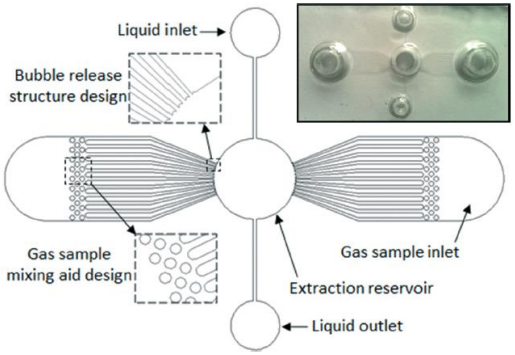
Microfluidic impingers

Choi et al., *ACS Sens.*, 2017, **2**, 513



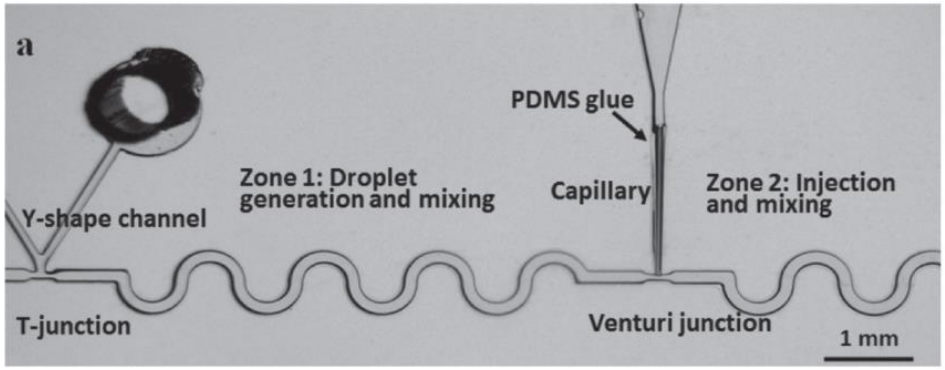


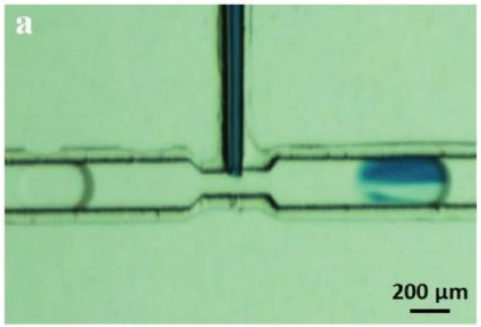
Damit, *Aerosol Sci. Technol.*, 2017, **51**, 488

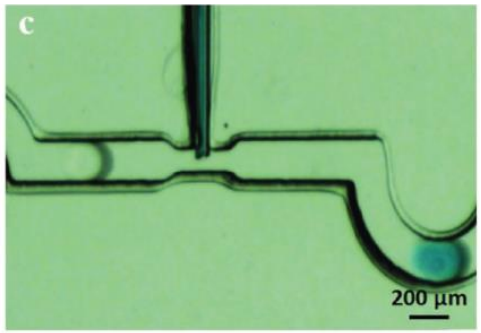


Mirzaee et al., *Lab Chip*, 2016, **16**, 2254

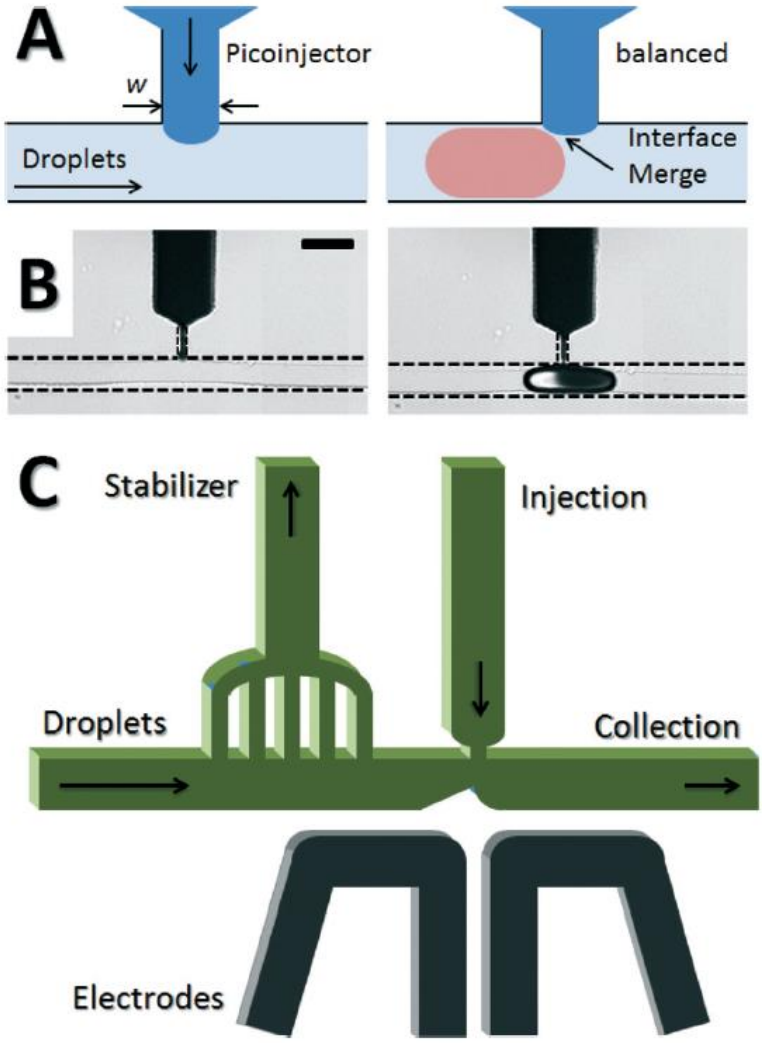
Picoinjectors







Li et al., *Lab Chip*, 2017, **14**, 4533



Rhee et al., *Lab Chip*, 2014, **14**, 4533

Droplet / cell / particle analysis

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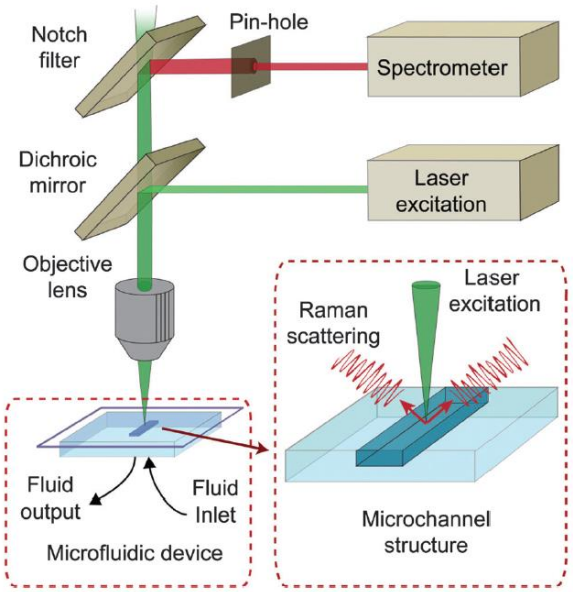
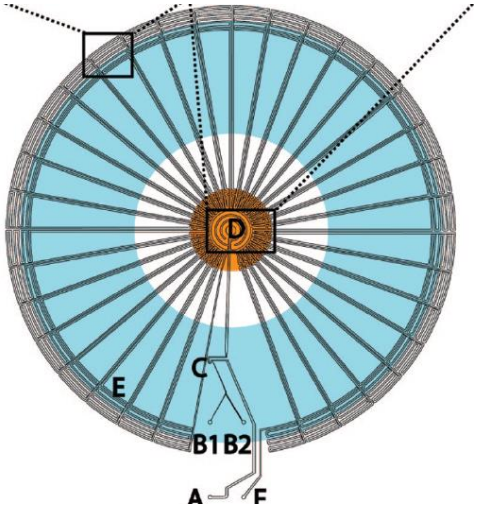
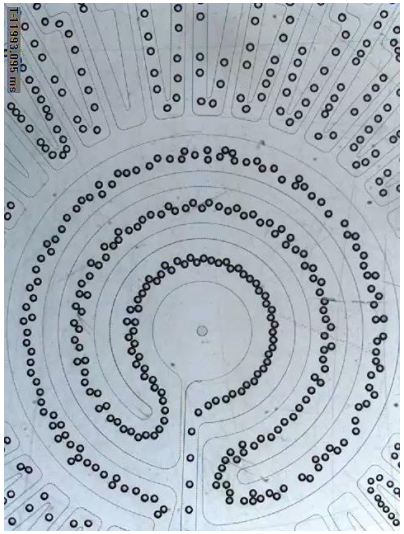


Chrimes et al., *Chem. Soc. Rev.*, 2013, **42**, 5880

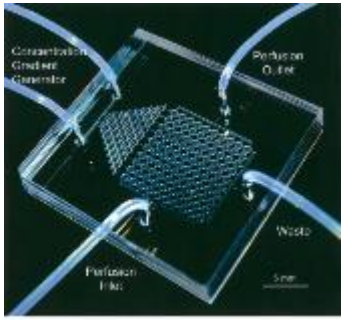
Spectroscopy

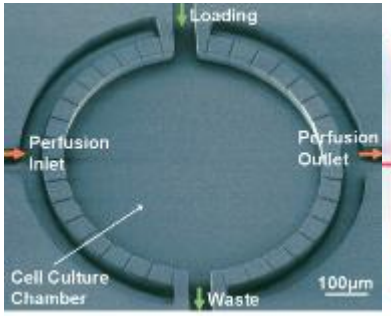


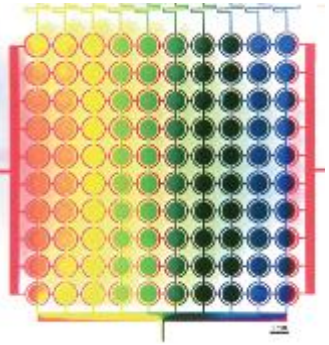
Continuous flow droplet PCR



Schaerli et al., *Anal. Chem.*, 2009, **81**, 302

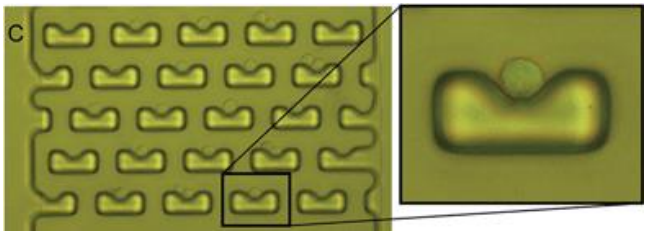






Hung et al., *Biotechnol. Bioeng.*, 2005, **89**, 1

Cell culture



Single cell analysis

D. di Carlo et al., *Lab Chip*, 2006, **6**, 1445

The vision….

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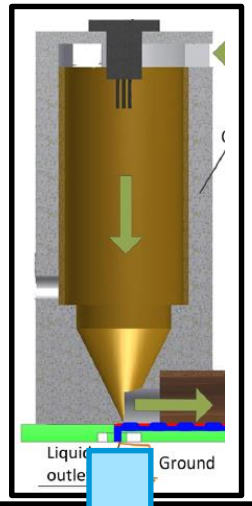
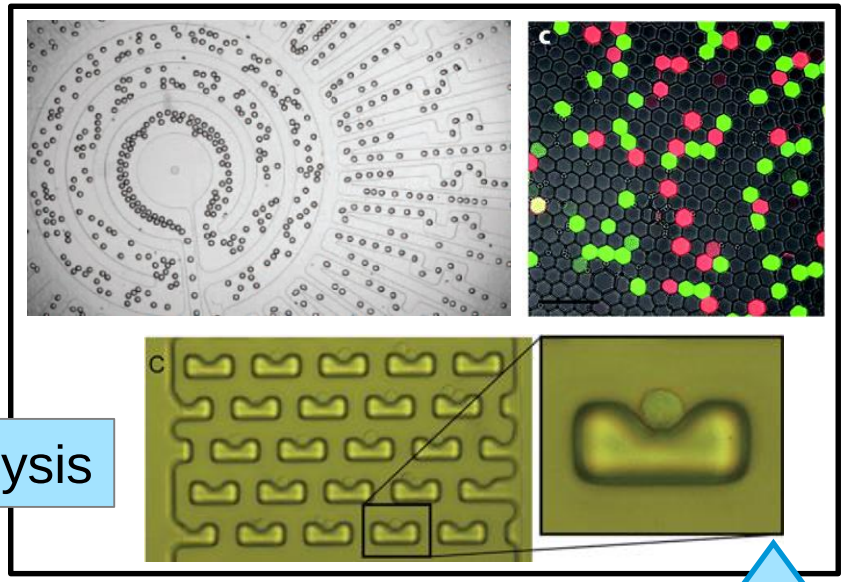
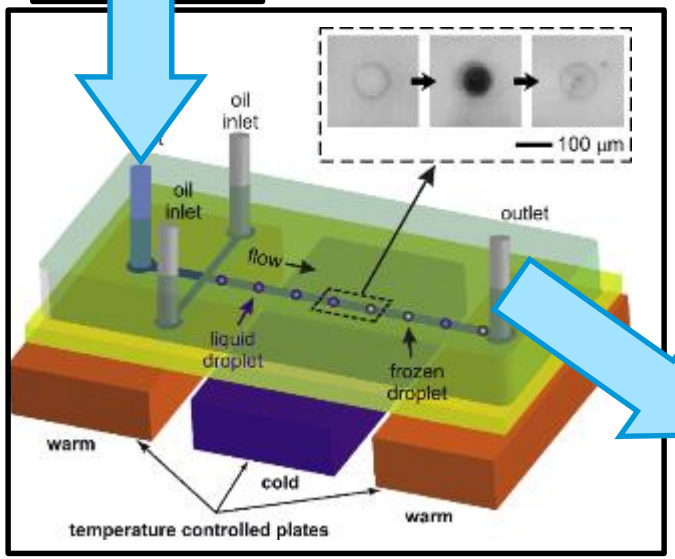


On-chip sampling

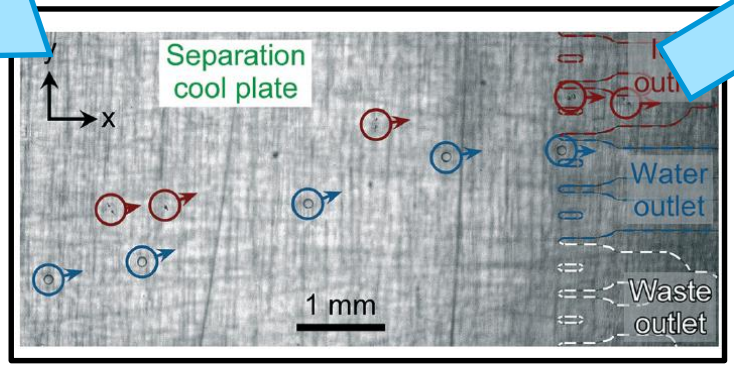


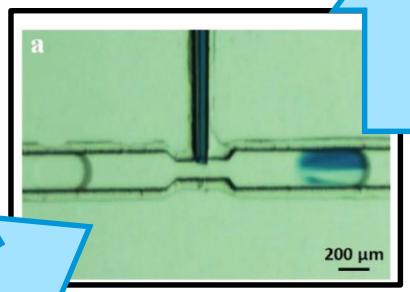
Analysis



INP counting

Sorting





Pico-injection

Characterisation of ice active sites

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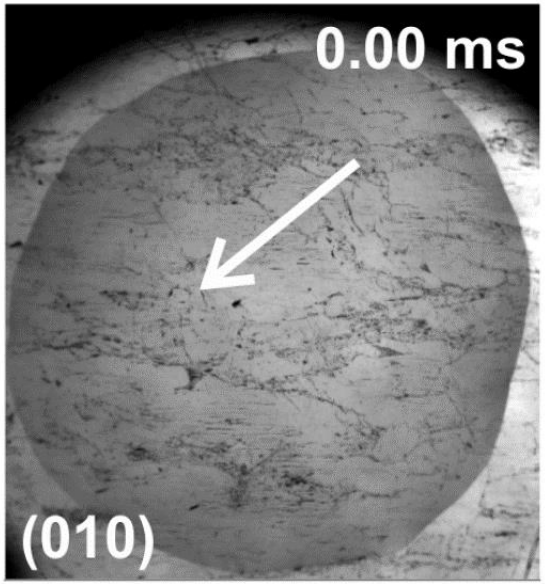

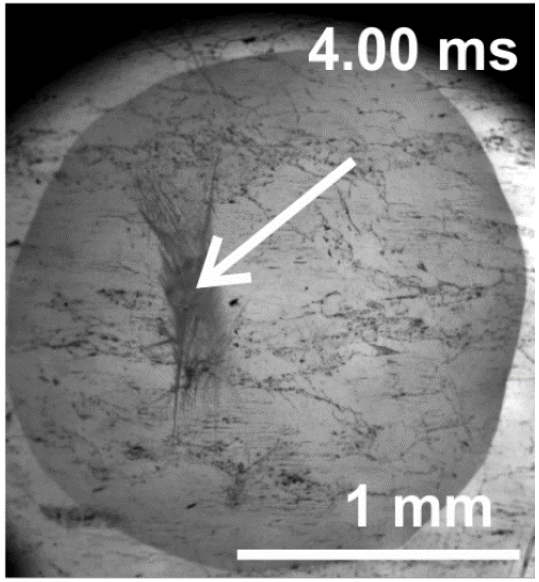

uclan

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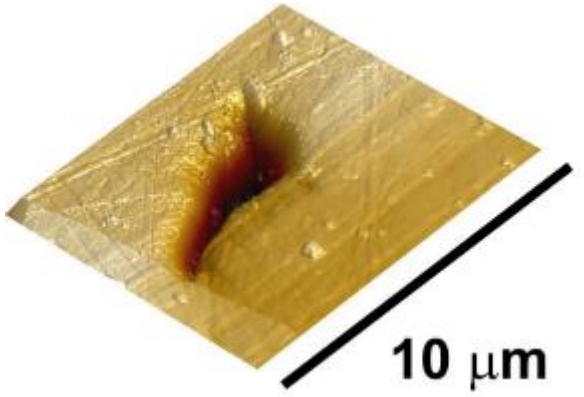
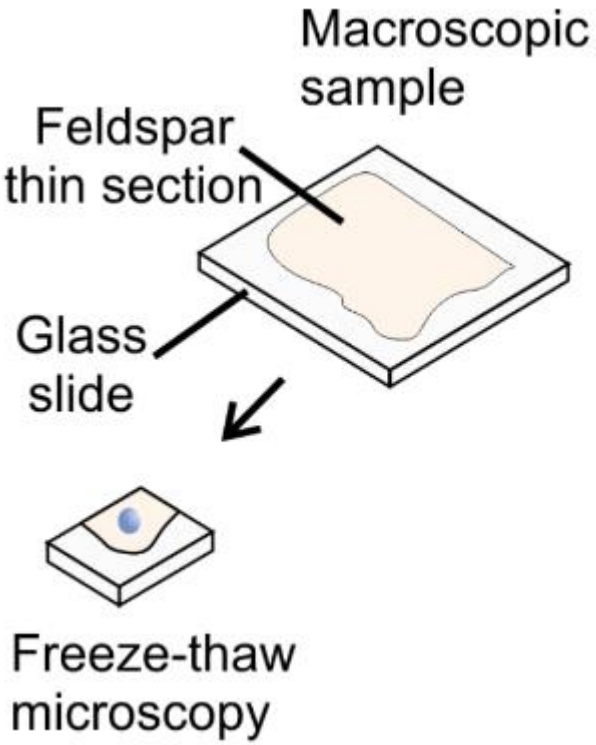
- Observed nucleation events/locations on a “thin section” of mineral using a 1 μL droplet

- Characterise the nucleation site →



Holden et al., *Sci. Adv.*, 2019, **5**, eaav4316

Perform experiments on smaller scale

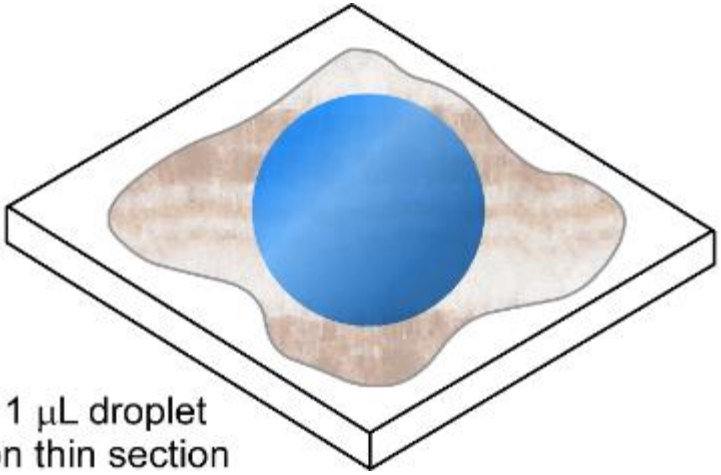


Dr Mark Holden

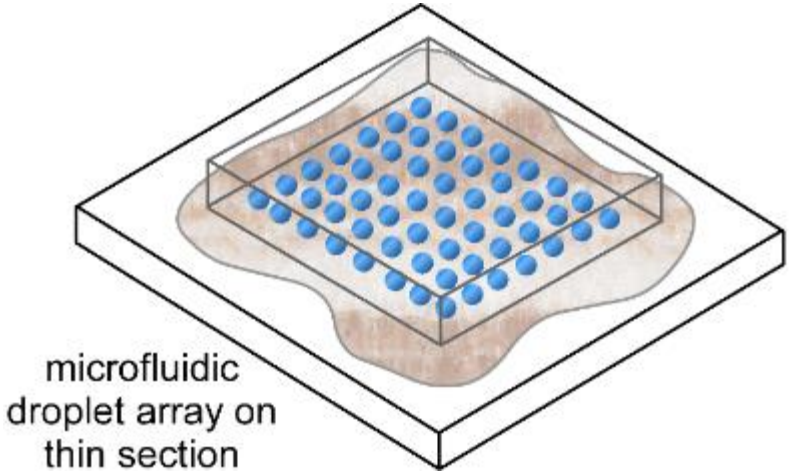
Holden et al., *Sci. Adv.*, 2019, **5**, eaav4316

Perform experiments on smaller scale

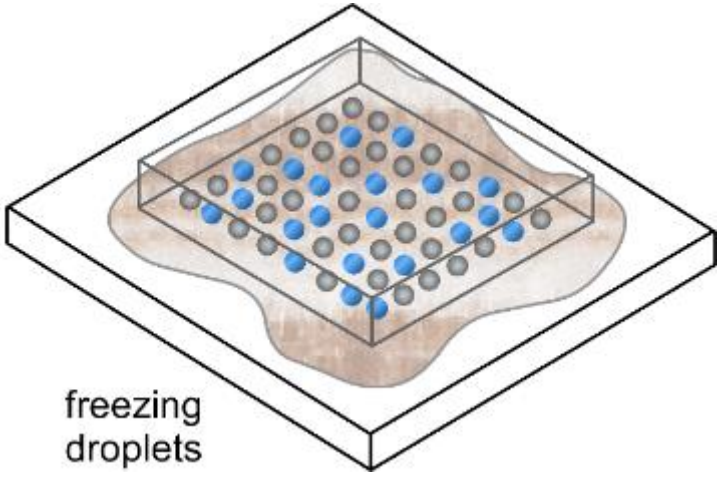
1 µL droplet



0.5 nL droplets

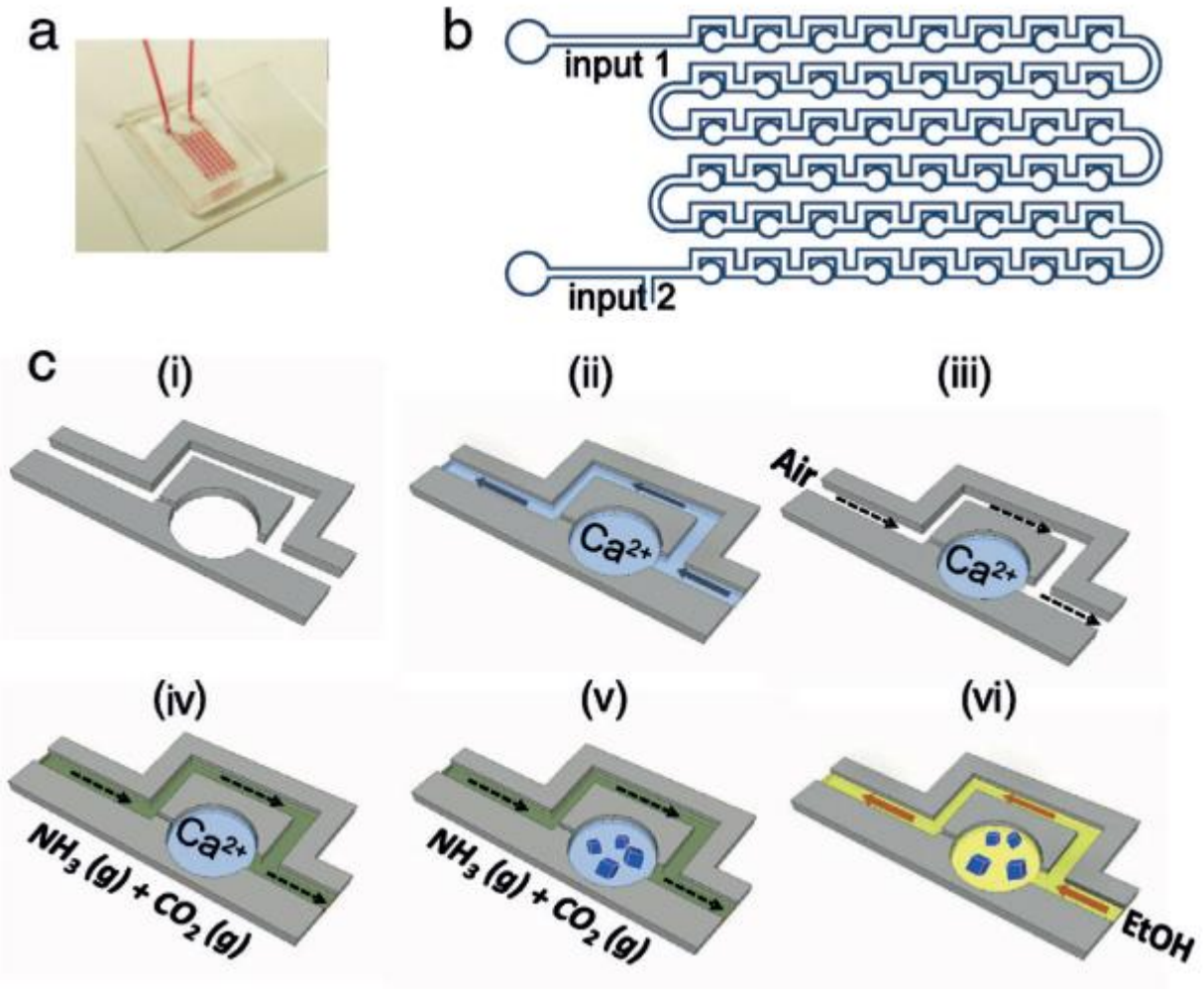


cool



- ❄ Reduce droplet volume to get higher spatial resolution
- ❄ Map the thin section surface in terms of ice-nucleating ability

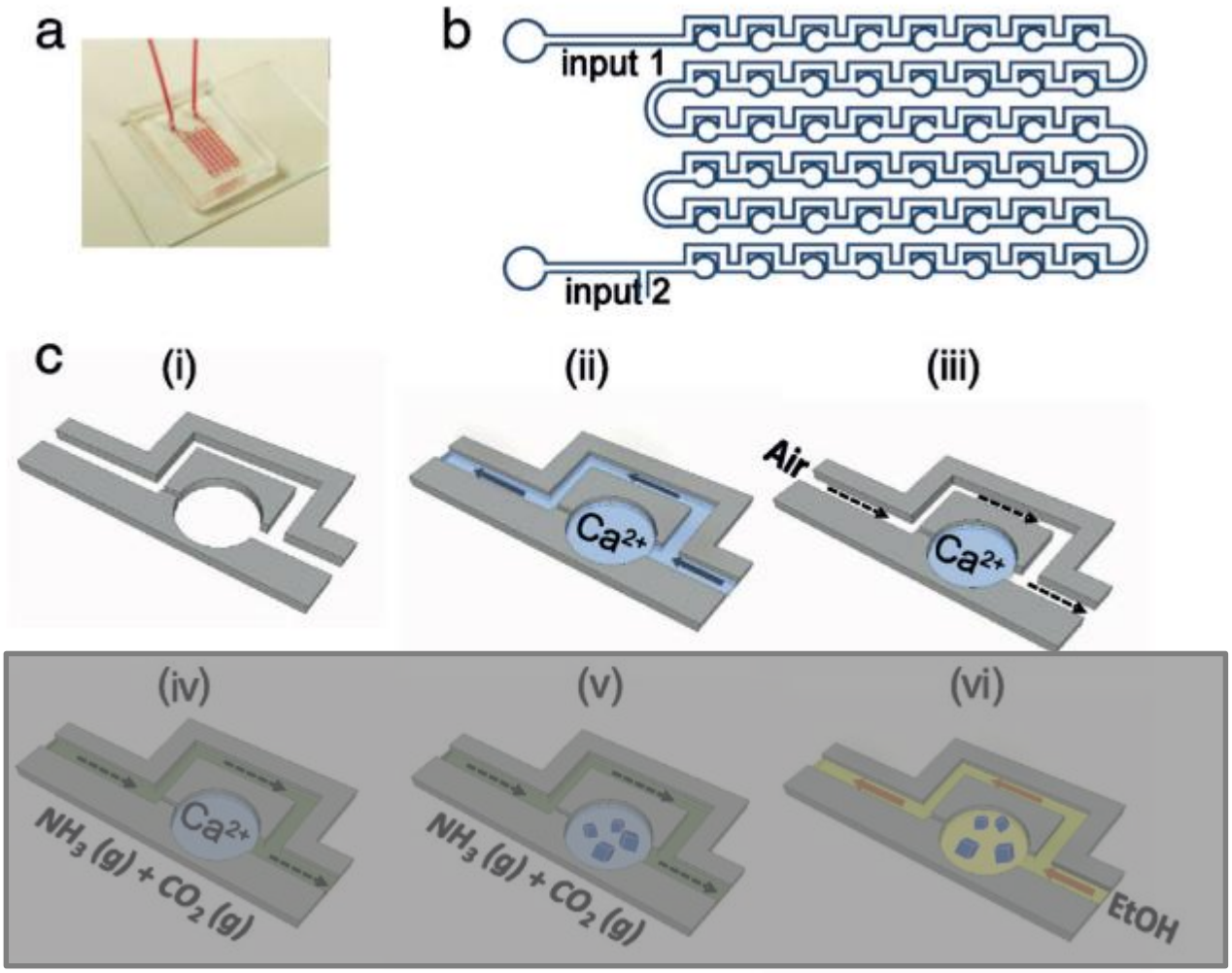
Crystal hotel



❄ Used to perform crystallisation studies in an array of droplets

Kim et al., *Angew. Chem.*, 2017, **56**, 11885

Crystal hotel



❄ Used to perform crystallisation studies in an array of droplets

Kim et al., *Angew. Chem.*, 2017, **56**, 11885

Polymer chip on thin section

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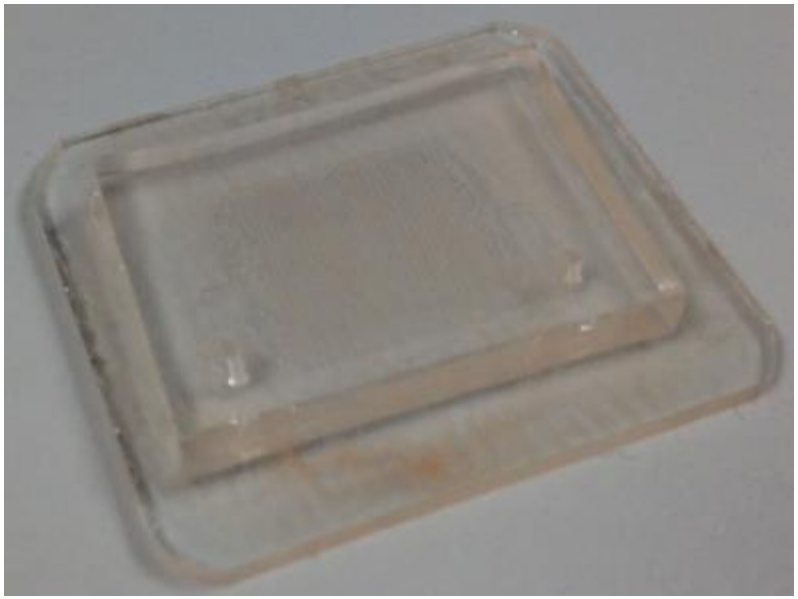
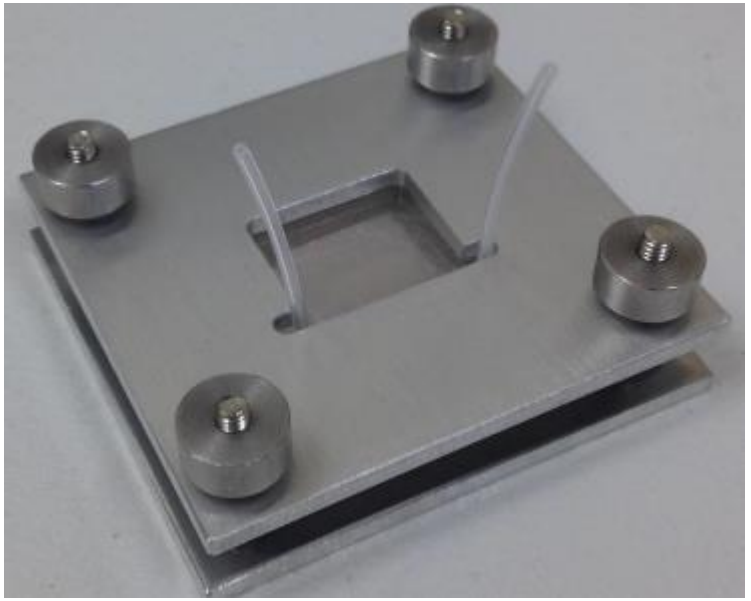
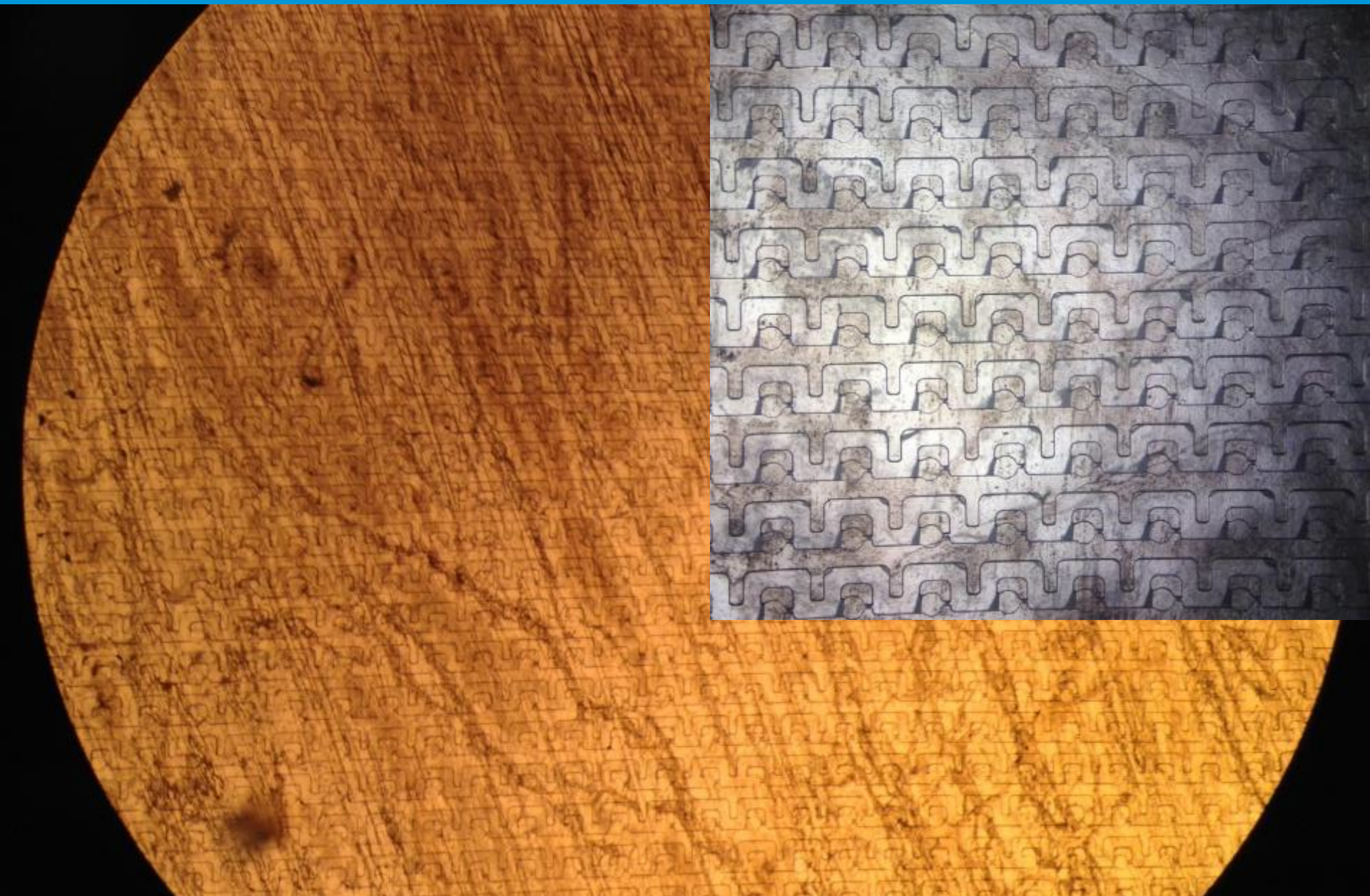




- Microfluidic chip on a K-feldspar thin section
- Placed in a clamp to seal the device
- Cooled on a Peltier-based cold stage

Water droplets on a mineral thin section



Freezing droplets

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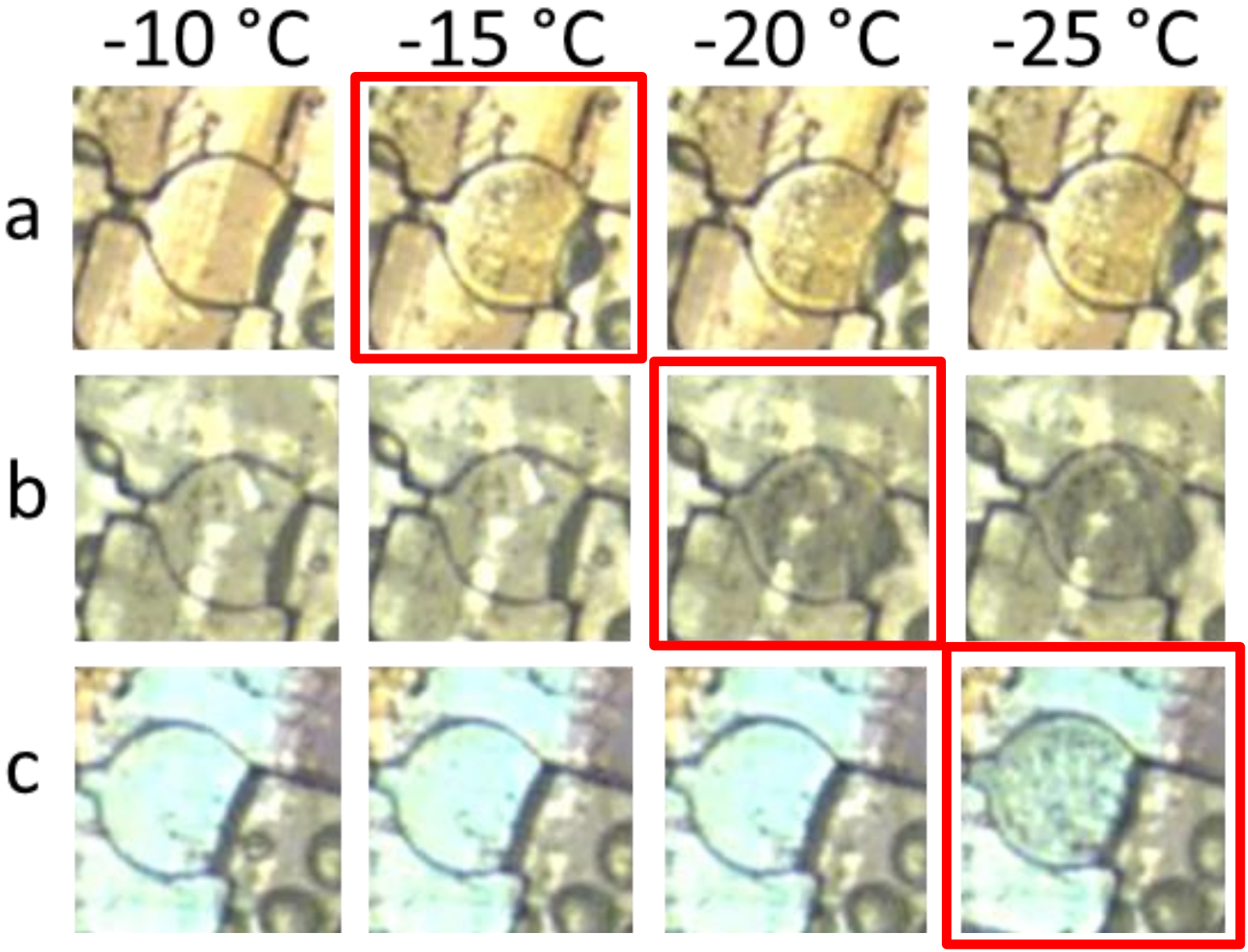

Summary

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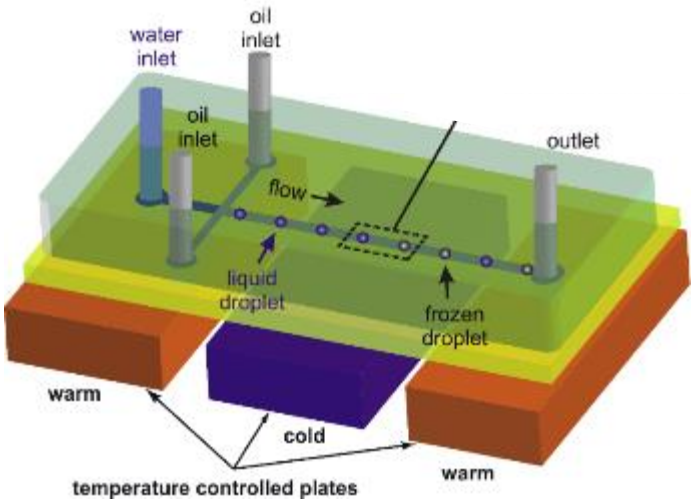
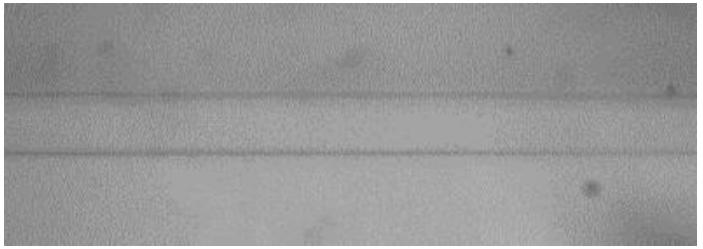
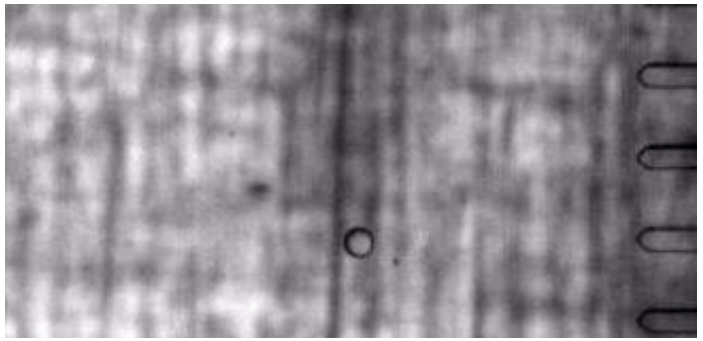
- Developed a new continuous flow INP analysis instrument: the LOC-NIPI
  - → low backgrounds
  - → high throughput
  - → user-defined droplet numbers
- Validated using INP standards and applied to preliminary field measurements
- Sorting of ice crystals from droplets







Future work:

- Optimisation and integration of processes
- Downstream analysis of separated ice/water populations for INP classification
- Automation of the LOC-NIPI for continuous INP monitoring in the field

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