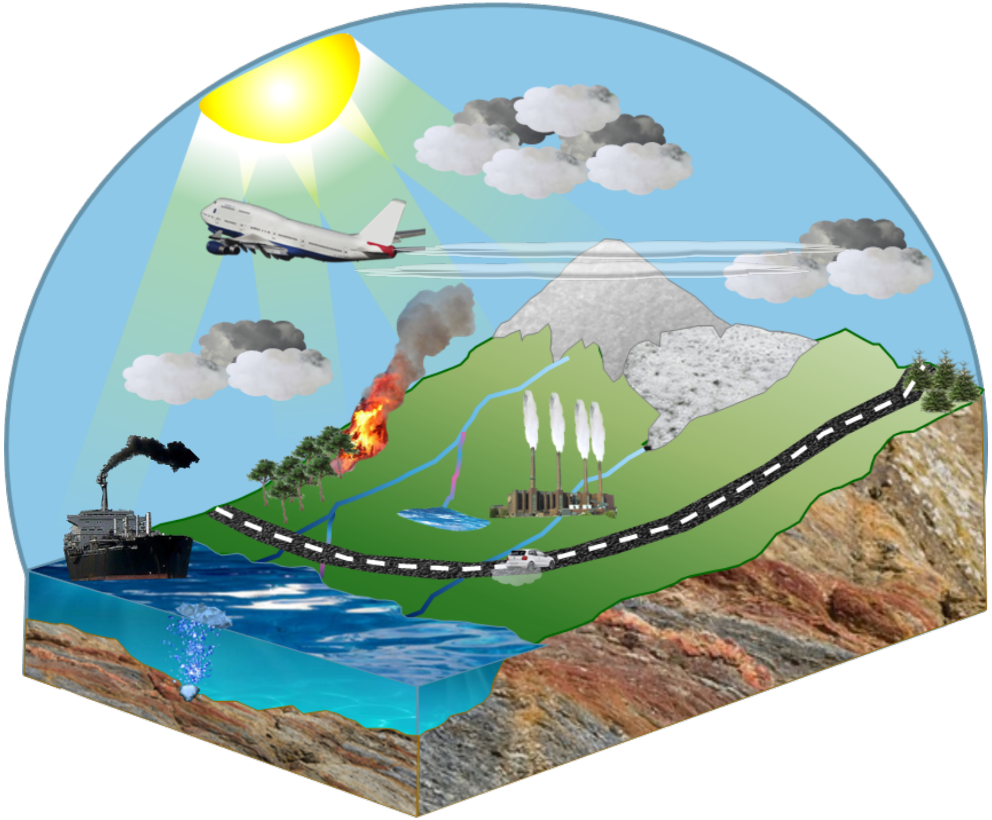
Ice nucleation abilities of soot particles and crystal habits



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PhLAM Physique des Lasers Atomes et Molécules
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MERMOSE Measurement and rEasearch on aircRaft engine eMissiOnS rEactivity
Labex CaPPA
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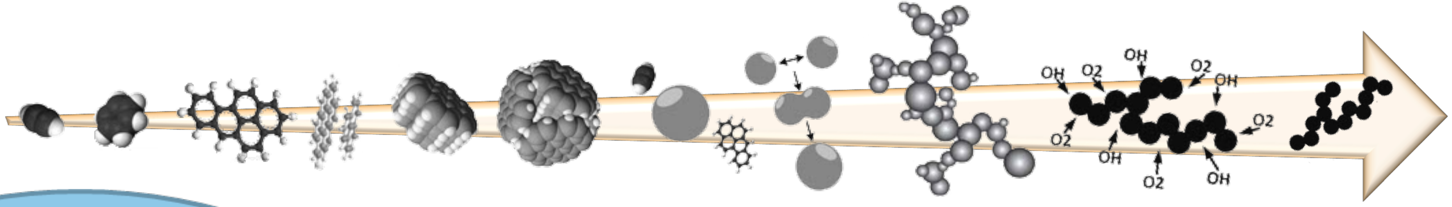
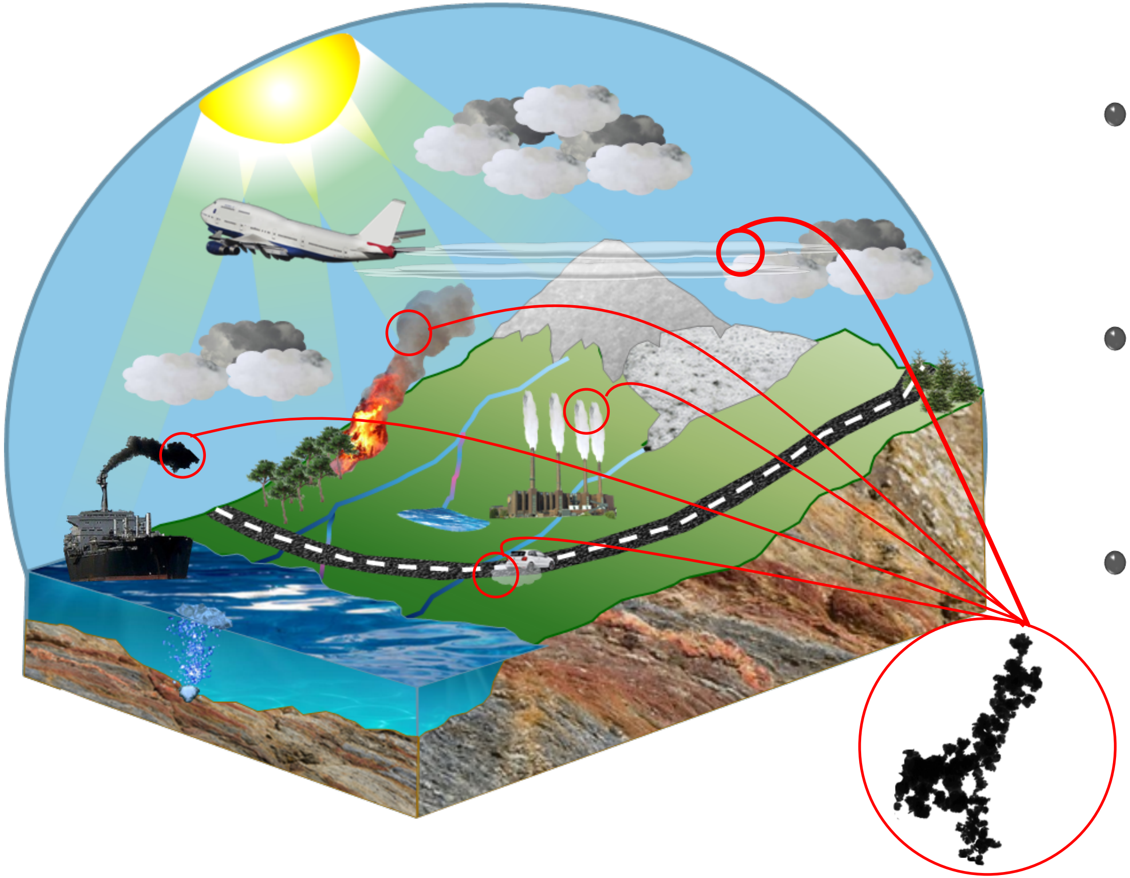
Context



Soot formation process, adapted from Thomson Lab. U. Toronto

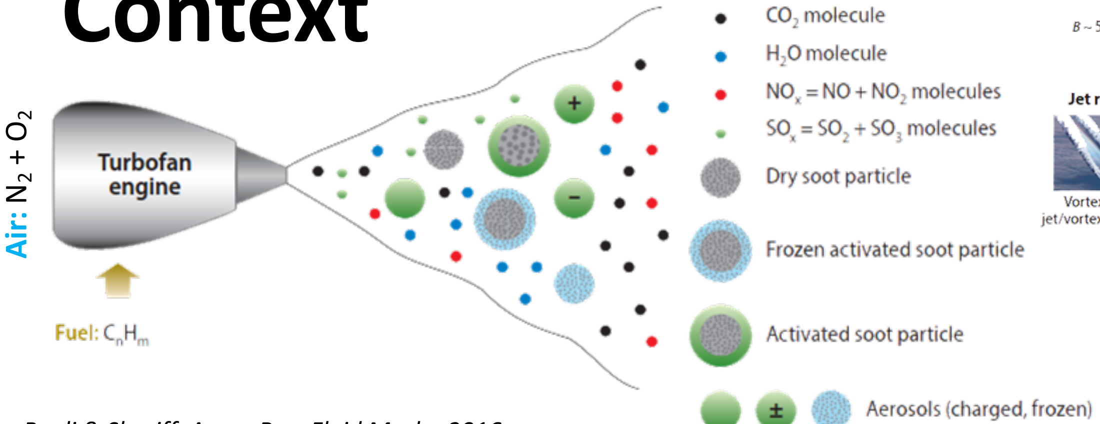


- **Soot particles:** carbonaceous particulate matter produced by incomplete combustion of hydrocarbons, often found covered in a surface layer of adsorbed molecules;

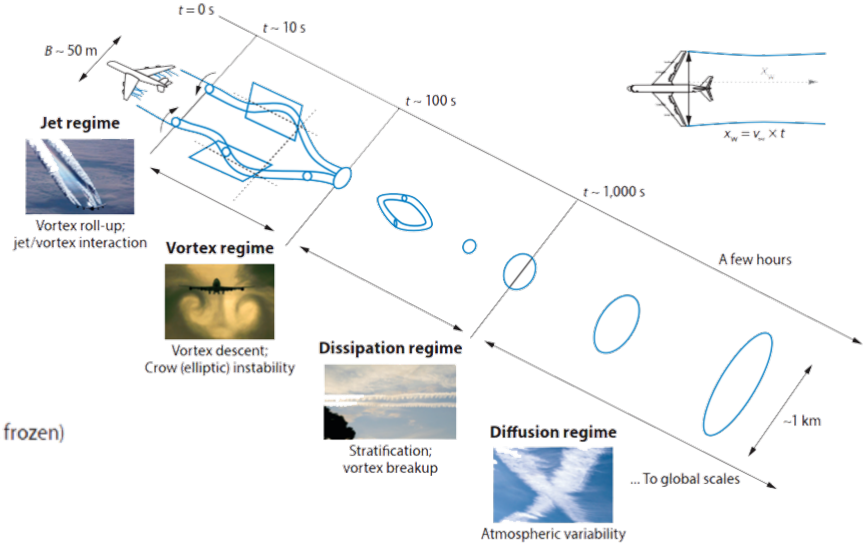
- **Natural and anthropogenic sources:** biomass burning , exhausts emissions from aircraft or automobile engines, ships, industrial combustion or domestic fires;

- **Environmental Impact:** particles are involved in many physical and chemical processes that can affect the atmospheric radiative forcing or the formation of clouds and their lifetime expectancy.

Context



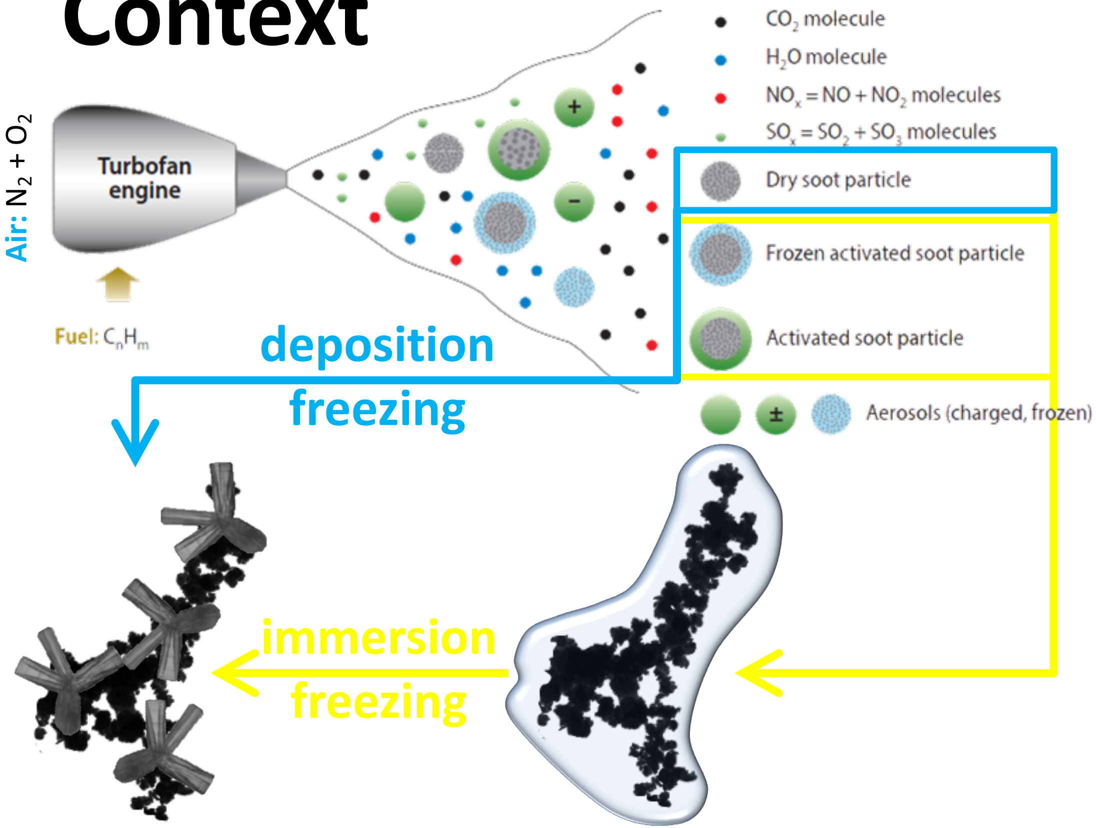
Paoli & Shariff, Annu. Rev. Fluid Mech., 2016

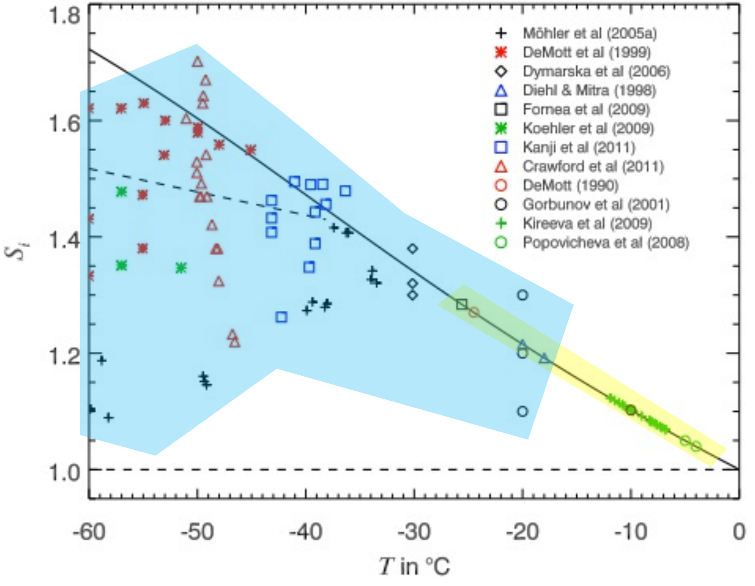


- Soot emissions from aircraft engines enhance background concentration of carbonaceous particles in the troposphere *(Hendricks et al., ACP, 2004)*
- Projected values for aircraft soot particles emissions ≈ 8.3-29 $Gg.yr^{-1}$ by 2050 (Brasseur et al., BAMS, 2016)
- Contrails may develop into contrail cirrus clouds with similar properties than those of native cirrus clouds provided sufficient ambient humidity *(Schumann, Contrail cirrus. Cirrus, 2002)*

→ **Studies that address the role of soot in cirrus formation are important to assess Aircraft-induced perturbations**

Context





Hoose & Möhler, ACP 2012

→ No clear consensus as to whether soot particles promote ice nucleation at low sursaturation ratios with respect to ice (S_i) in **deposition mode**

≠ **origins for soot particles** (chemical composition + morphology because ≠ combustion processes)
≠ **instruments used to probe nucleation events** (diffusion chambers, cold stages, wind tunnel, …)
≠ **parameters used to characterize soot activity** (nucleation onset, activated fractions : 1%, 10%)

Objective & Methodology

Step 1 - Build a versatile experimental setup suited to test ice nucleation activities

Step 2 - Analyze soot particles before being processed in the nucleation chamber using complementary techniques (Raman, FTIR, Two-Step Lasers Mass Spectrometry [L2MS], Secondary Ion Mass Spectrometry [SIMS])

Step 3 - Choose laboratory soot surrogates representative of soot particles emitted by aircraft engines based on their **surface chemical composition** and/or **structure**

Step 4 - Simulate temperature (**T°C**), humidity ratios (**RH**) and pressure (**P**) found in the upper troposphere to **test** soot particles' **ice nucleation activity** in the lab.

Are soot samples ice active in deposition mode?

Which parameter(s) predominantly drive(s) nucleation events?

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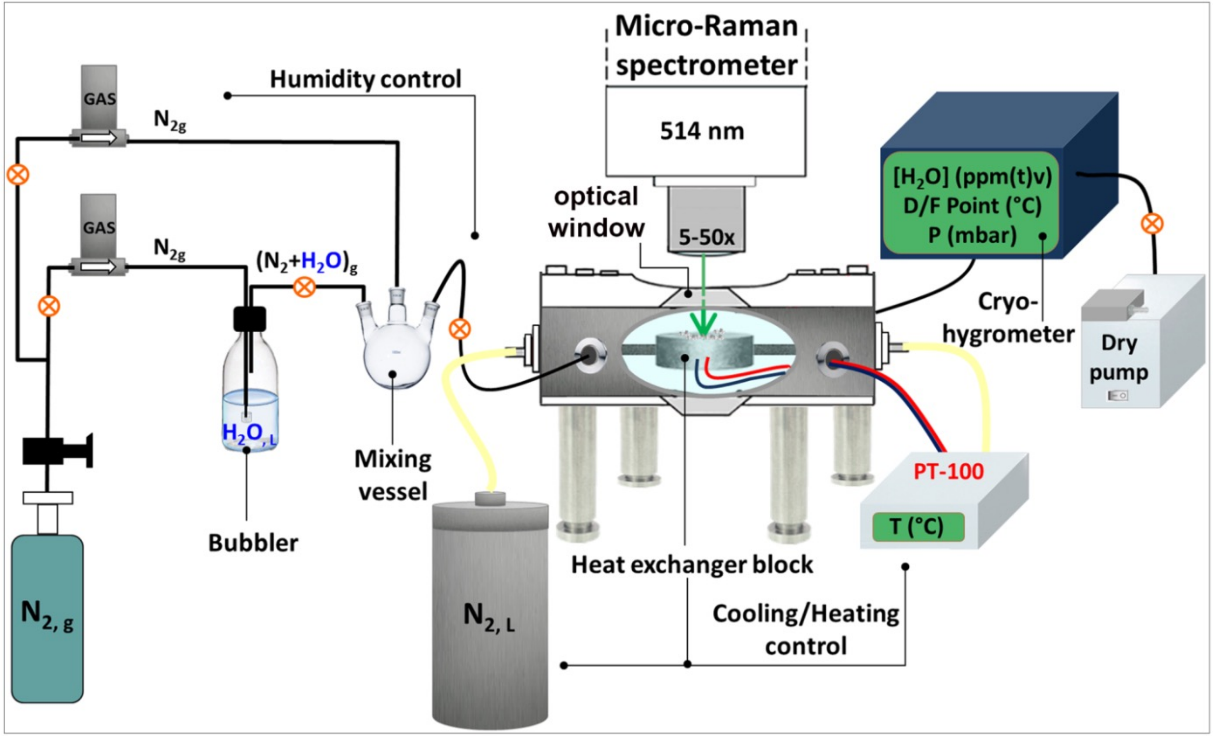
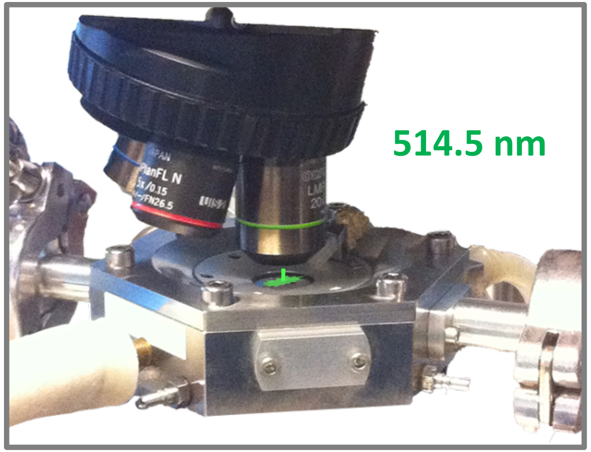
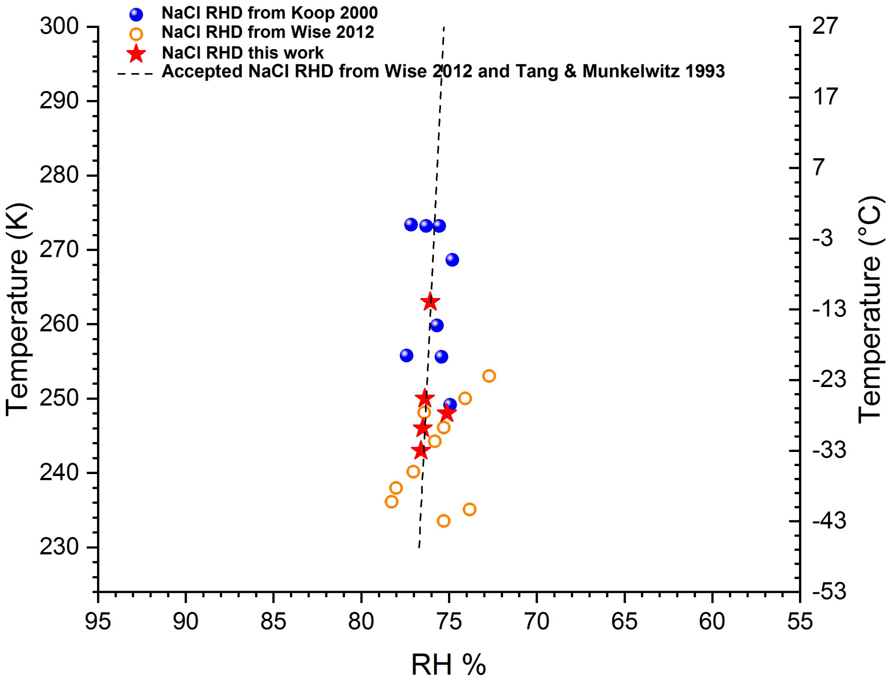
Step 1: IDroNES (Ice and Droplet Nucleation Experimental Setup)

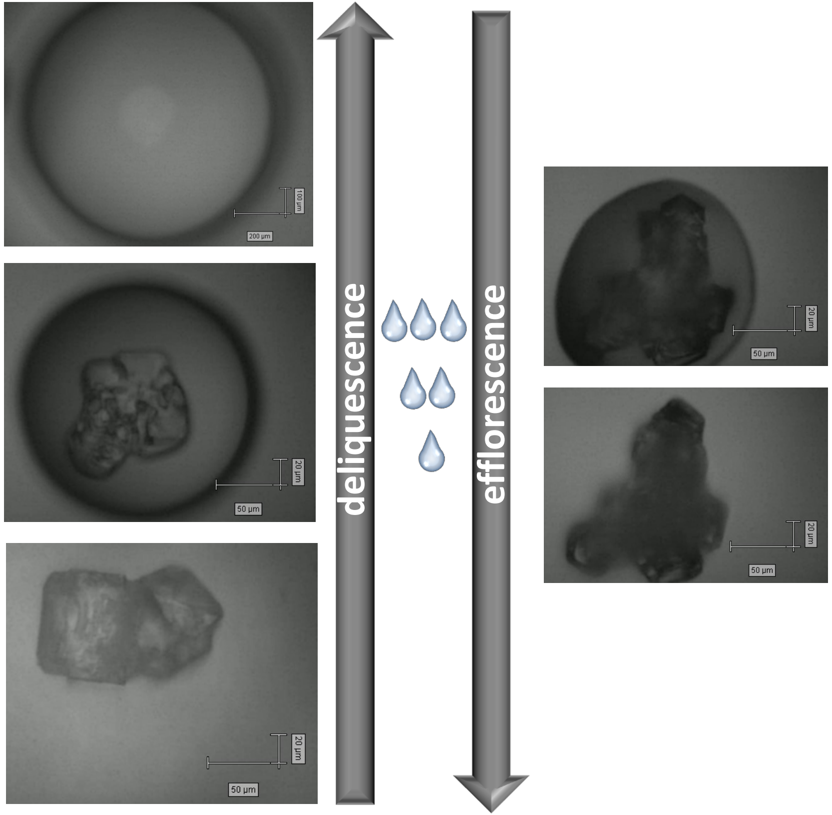




Step 1: IDroNES (Ice and Droplet Nucleation Experimental Setup)

Test 1 → relative humidity (RH) needed to observe deliquescence and efflorescence phenomena from NaCl crystals at a given temperature





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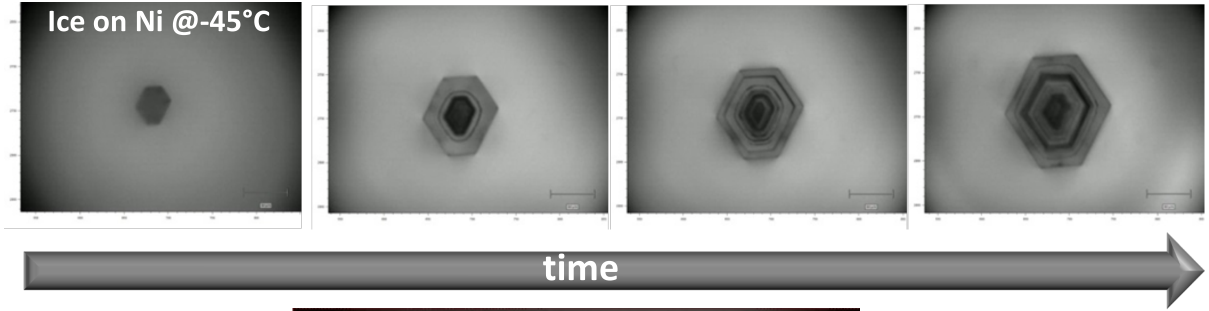
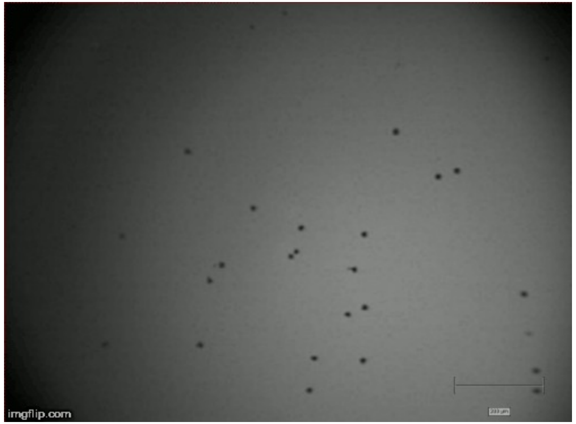
Step 1: IDroNES (Ice and Droplet Nucleation Experimental Setup)

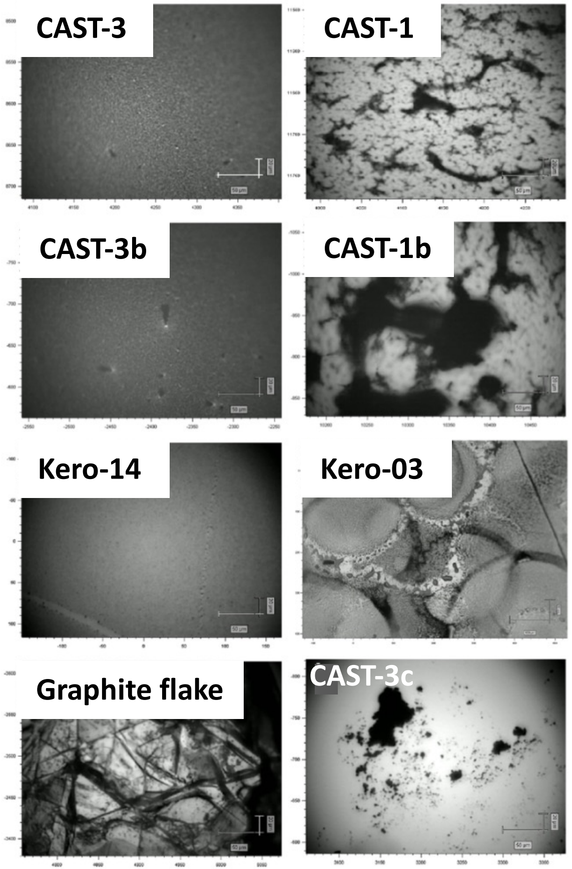
Test 2 → Nucleation on sample stage (nickel) at T= -45°C (228 K)

Growth rate along 1 dimension : 0.12 µm /s (7,2 µm/min), S_i =1.25 @-45°C

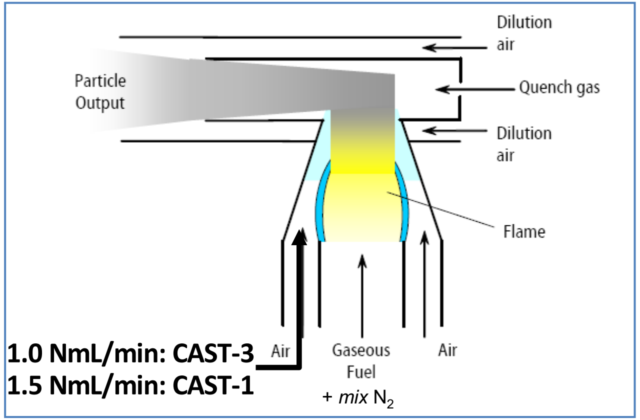




Step 2: Soot particles collection …



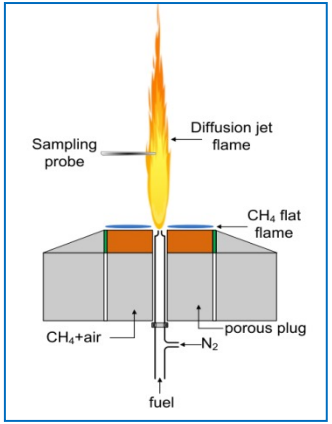
miniCAST generator



Fuel: propane gas (C_3H_8)

Samples: CAST-1 & CAST-3

McKenna burner

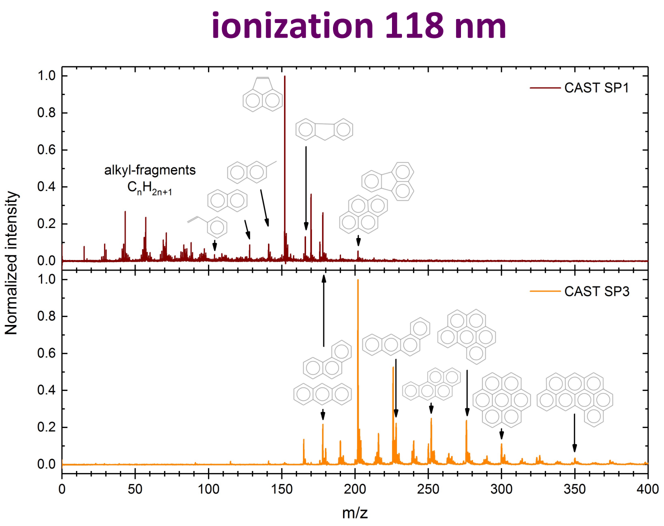


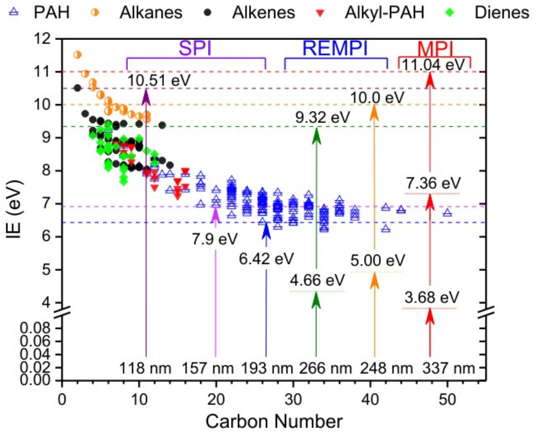
Fuel: Jet A-1 Kerosene

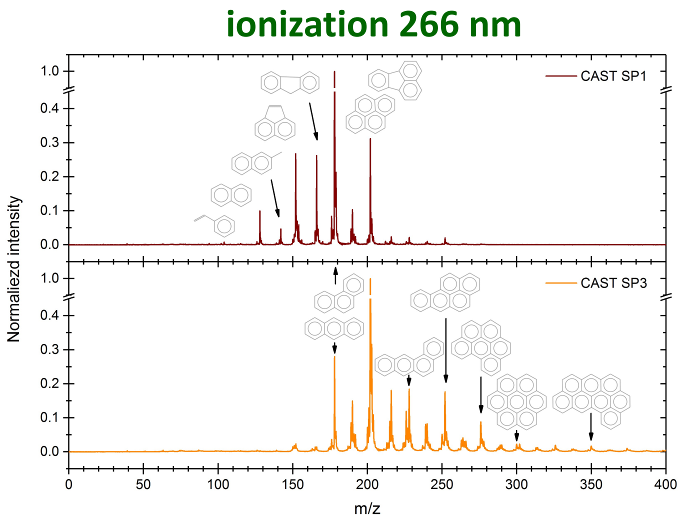
Samples: Kero-03 & Kero-14

All samples collected onto 185 µm-thick silicon wafers

Step 2: … and analyses: surface composition





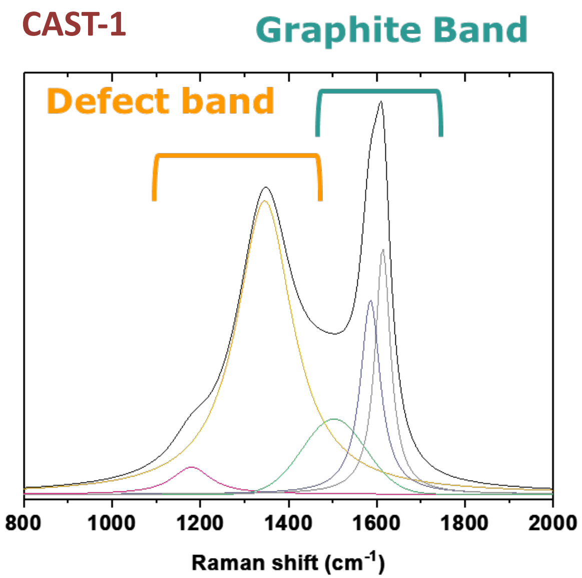


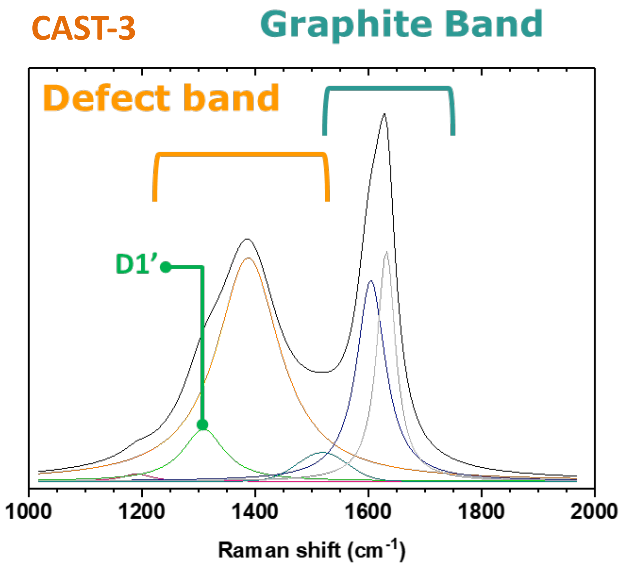
L2MS + SIMS + NEXAFS + Raman + FTIR:

- **PAH content**: CAST-3 >> CAST-1; Kero-14 >> Kero-03
- **PAH distribution**: CAST-3 (heavy), CAST-1 (light), Kero-14 (light), Kero-03 (heavy)
- Presence of **alkanes + alkyl-PAH**: CAST-1
- **Oxygen content**: CAST-3 (10 at%), CAST-1 (4 at%), observed in Kero samples
- Correlation between mass spec PAH content+distribution and Raman spectra

Ikhenazene et al. *JPhysChemC* 2020
Marhaba *et al.* Combust.Flame 2019
Parent *et al*. Carbon 2016
Ouf *et al.* Sci Rep. 2016
Ess et al. Carbon 2016
Desgroux *et al.* PCI 2013

Step 2: … and analyses: structure





→ G Band (ideal graphite - L)

→ D1 Band (edges defects - L)

→ D2 Band (surface defects - L)

→ D3 Band (fraction of small graphitic domains / interstitial defects - G)

→ D4 Band (chemical defects - L)

→ D1' Band (aromatic units weakly bound to the surface - L) ≈ 1280 cm^{-1}

Raman + TEM + Surface reconstruction

- **Crystallite order**: CAST-3 (poor), CAST-1 (turbostratic), presence of defects observed in graphite flakes
- **Porosity**: about the same for CAST-3 and CAST-1
- **Mean pore size** (hydraulic diameter) estimate: 0.66 µm (CAST-3), 2 µm (CAST-1)
- **Surface available for nucleation**: about the same for CAST-3 and CAST-1

Chazallon *et al.* in prep
Ikhenazene et al. *JPhysChemC* 2020
Marhaba *et al.* Combust.Flame 2019
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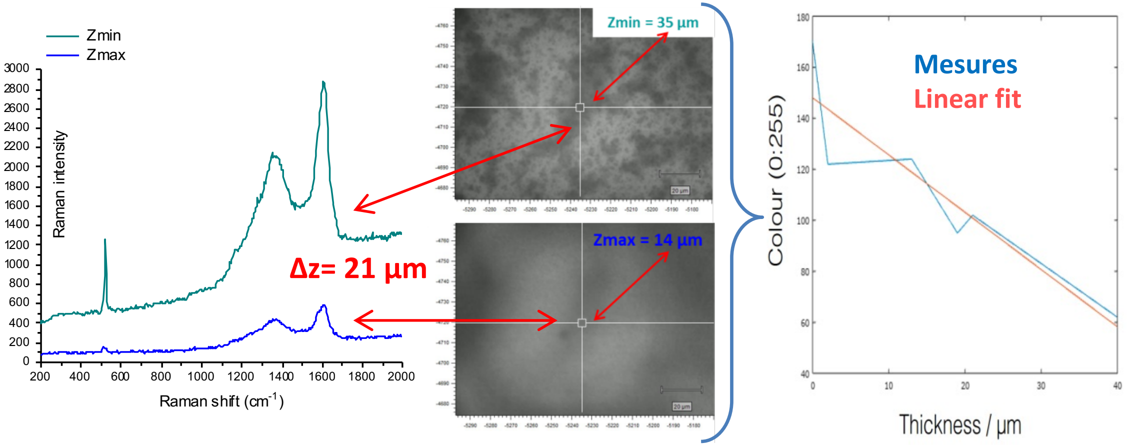
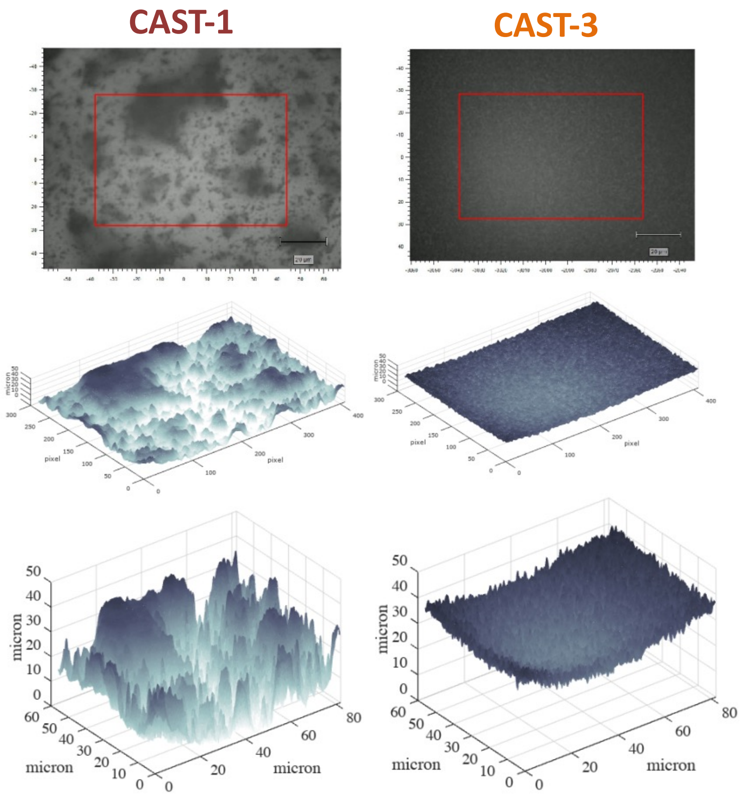
Step 2: … and analyses: structure

Sample surface reconstruction





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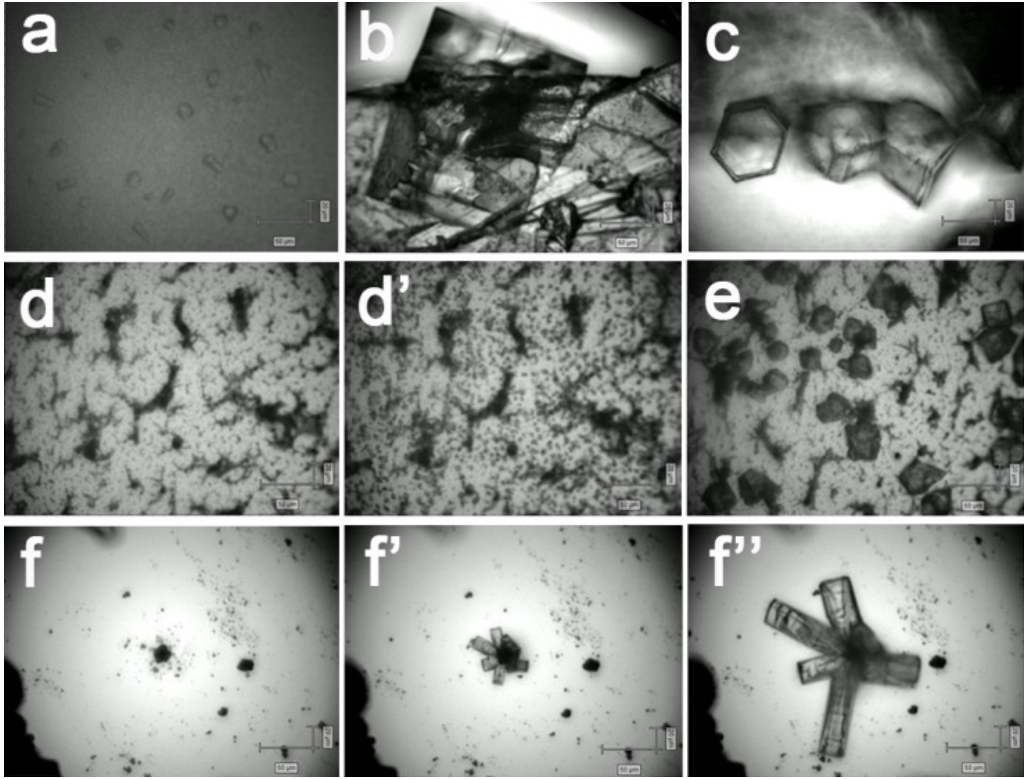
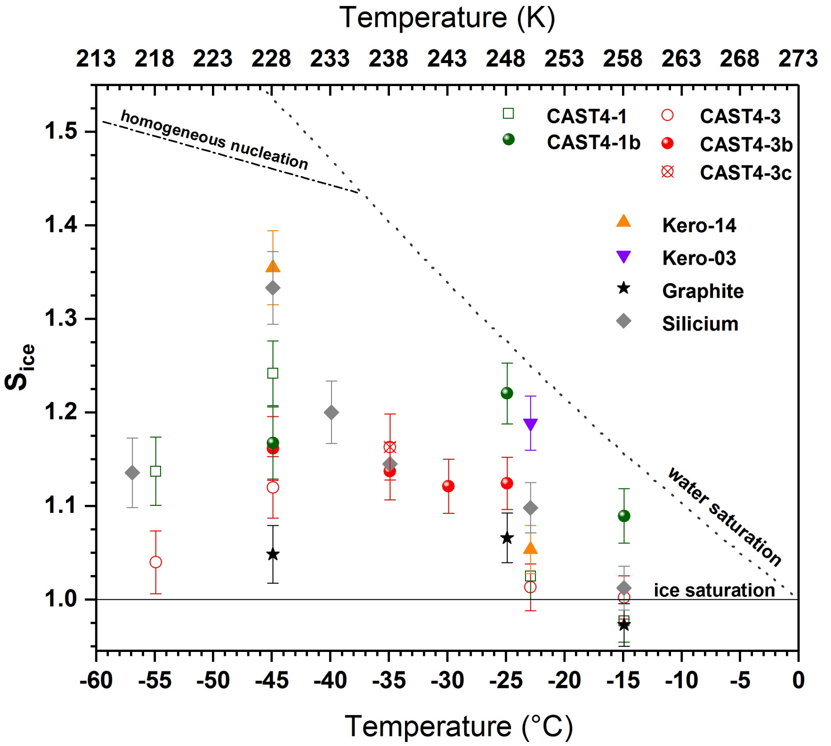
Step 3-4: Nucleation activity of aircraft soot surrogates





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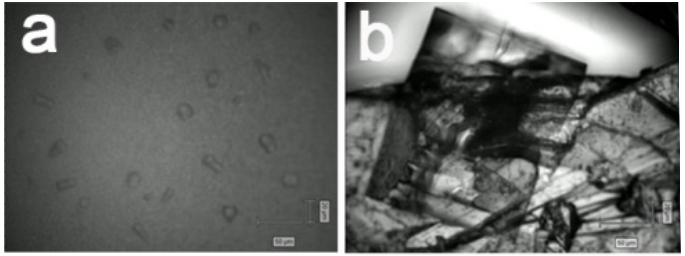
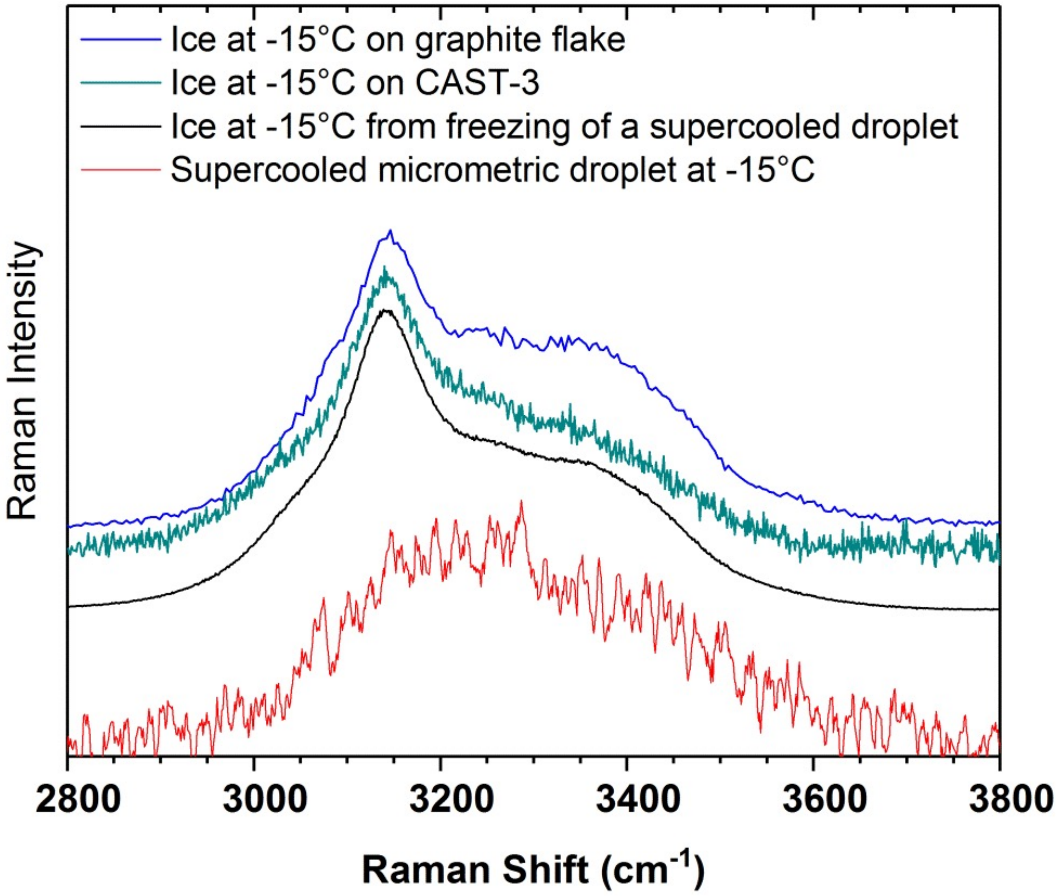
a) CAST-3 at -45°C, b) graphite flake at –35°C and c) at –45°C. d) + e) CAST-1, preferential crystal growth on soot islands at -55 and -45°C, respectively, f) CAST-3c at -45°C. prime and double prime symbols = time lapse pictures of the same areas

Preliminary study of ice habits and metastable water





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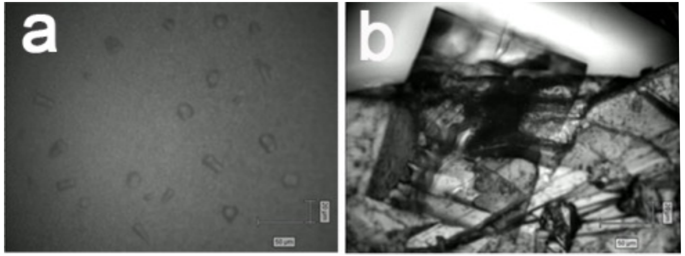

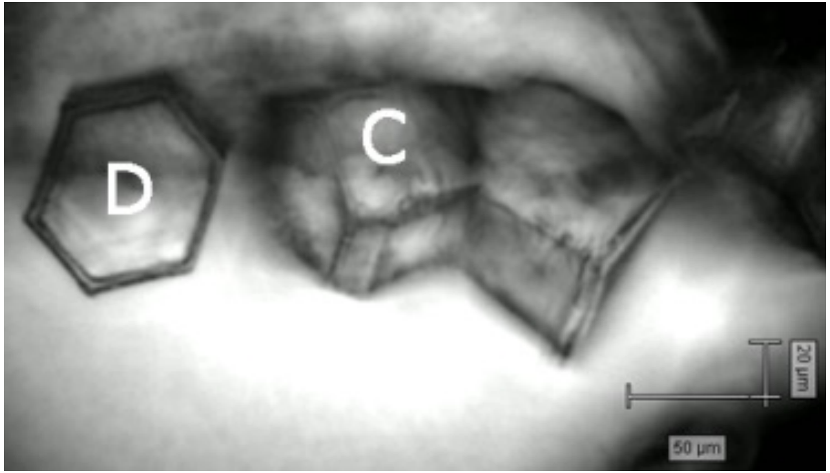

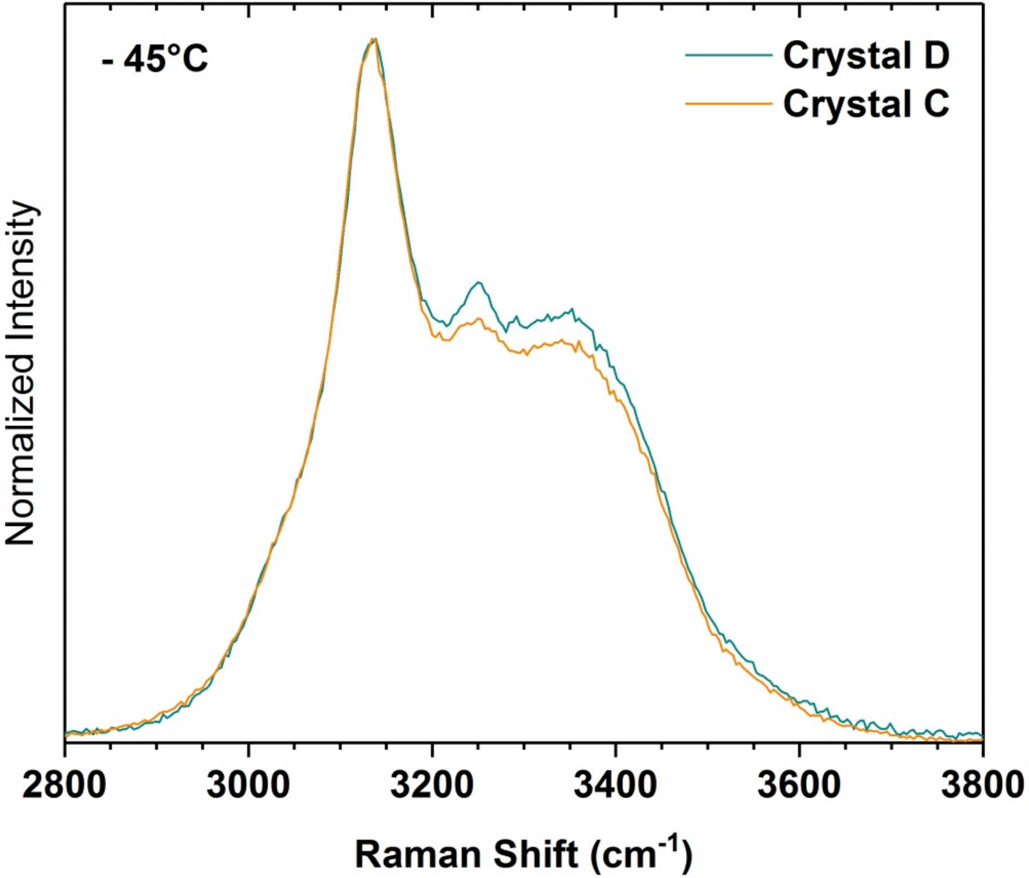

Are soot samples tested here ice active in deposition mode?

→ Yes, here soot particles do not need high partial water pressure to trigger ice crystal growth at their surface

→ Slight differences in activity between different types of soot are observed at moderate temperatures (warmer than -38°C)

→ hydrophobic substrate in immersion mode does not necessarily imply icephobic substrate in deposition mode (Ramachandran et al. 2016, Nosonovski et al. 2012, Farhadi et al. 2011)

Which parameter predominantly drives nucleation events?

→ Unclear from these experiments since soot samples differ in both their chemical composition and their structure:

Surface chemical composition

→ influences water affinity (alkanes, branched PAH vs PAH)

→ provides potentially optimized surface bonding (chemical templates) for stable ice structures to grow

→ offers active sites (heteroatoms) to which water molecules may preferentially attach

Structure

→ provides active sites (defects) with various defect densities

→ surface roughness and pores in which the pore condensation freezing mechanism (PCF) might take place

→ Need for systematic studies limiting the number of parameters changing between ≠ soot samples ←

Acknowledgements

Climibio

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MERMOSE Measurement and rEasearch on aircRaft engine eMissiOnS rEactivity

CORAC Aéronautique Environnement Recherche

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SAFRAN Snecma

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CINaM

F.-X. Ouf, E. Therssen, N. Nuns

Thanks for your attention!

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