Collaborative Research – BC5 laboratory studies of the optical properties and ice nuclei activity of carbonaceous particles as a function of mixing state and phase state

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Introduction and Methods

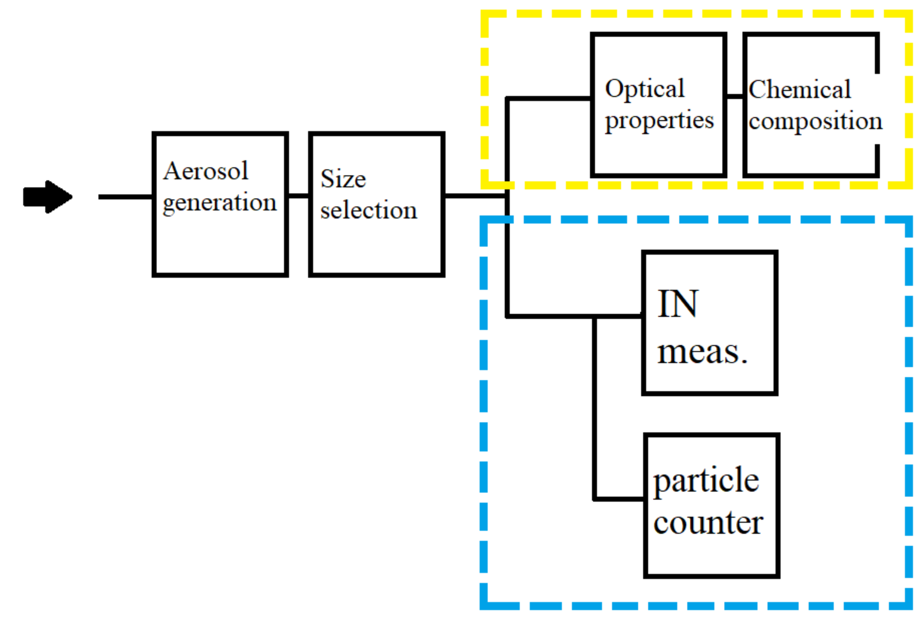
We are developing new techniques for studying the formation, chemical composition, phase state, optical properties and cloud activity, including the ice nuclei (IN),of atmospherically relevant particles.

(1) We conducted collaborative studies on black carbon containing particles optical properties and mixing states, resulting in manuscripts on modeling coagulation in a laboratory environment (with Prof. Reimer at UIUC) and the charring of absorbing aerosol in SP2 instruments (with Drs. Sedlacek and Lewis at BNL) (presented elsewhere).

(2) We use the broadband dielectric spectroscopy to study the effects of cooling rates on the glass transition of atmospheric relevant organic aerosols. Such study provides theoretical evidence for how the cooling rates and the phase state of the organic aerosols could potentially change their ice nucleation potential.

(3) We are combining our new method of measuring SOA glass transitions with IN activity to study the effects of organic particle phase states on IN activities. Recent work by our research group and others investigating ice nucleation of glassy organic aerosols suggest that the phase state of SOA particles from biogenic sources may influence ice (e.g., cirrus) and mixed phase cloud formation.

Ice Nucleation of Soot

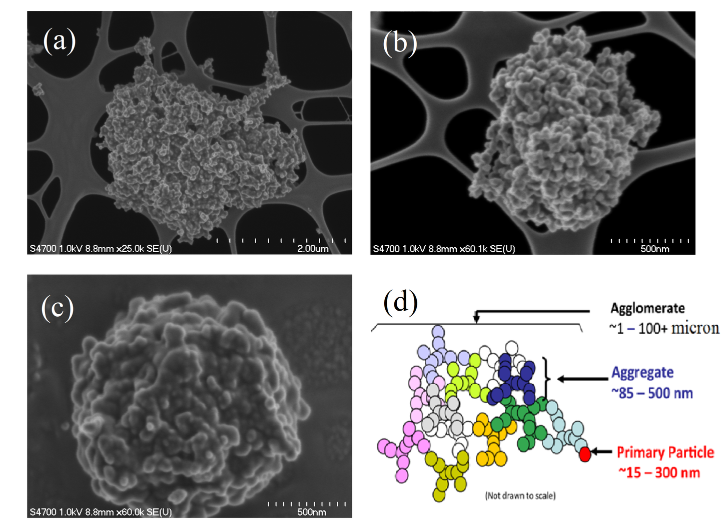


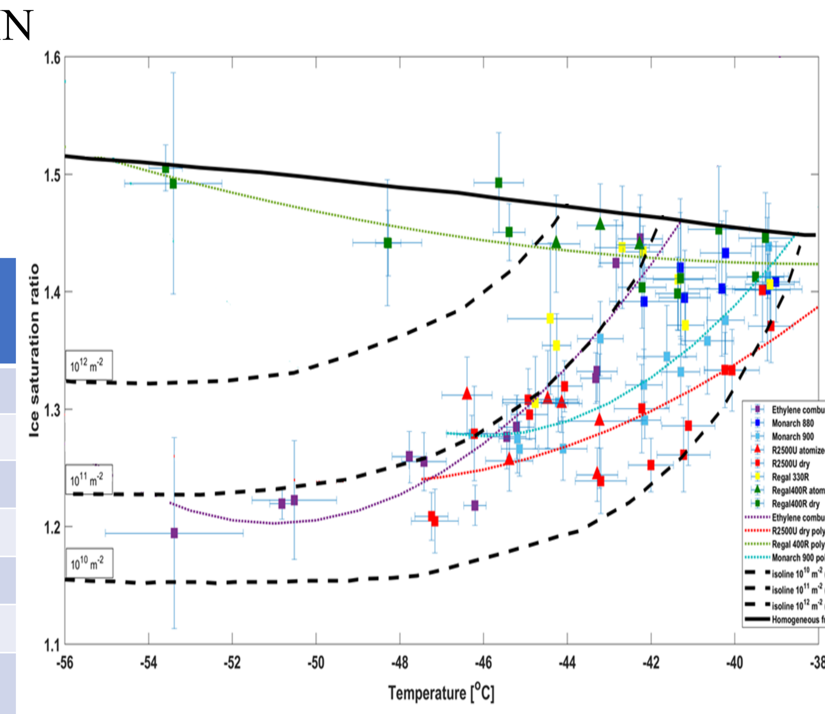
A systematic study of ice nucleation by BC particles. Particle characterization (yellow) was followed by IN measurements (blue).

Black carbon samples used in this study and their properties are listed in the table below

Sample	SSA [m²/g]	OAN [ml/100 g]	Surface type
Regal 250R	60	45	Non-oxidized
Regal 330R	90	65	Non-oxidized
Regal 400R	90	70	**Oxidized**
Monarch 880	240	110	Non-oxidized
Monarch 900	240	70	Non-oxidized
Raven 2500 Ultra	270	67	---------
Ethylene combustion	---------	-----------	---------

SEM images of (a)soot (b)Regal 400 (c) R2500U (d) agglomerate, aggregate, and spherule illustration reproduced from Long et al., 2017.

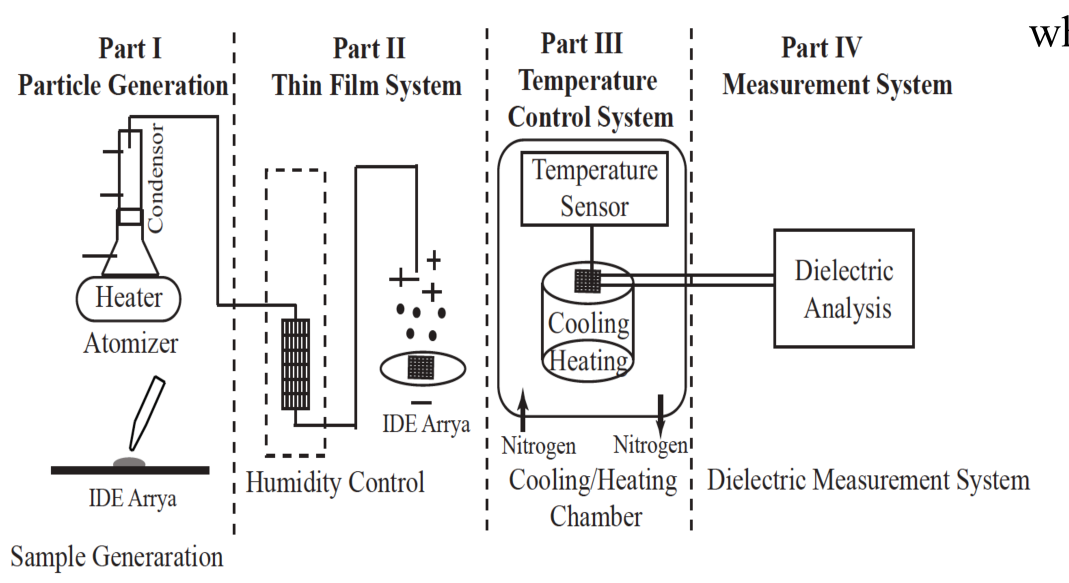




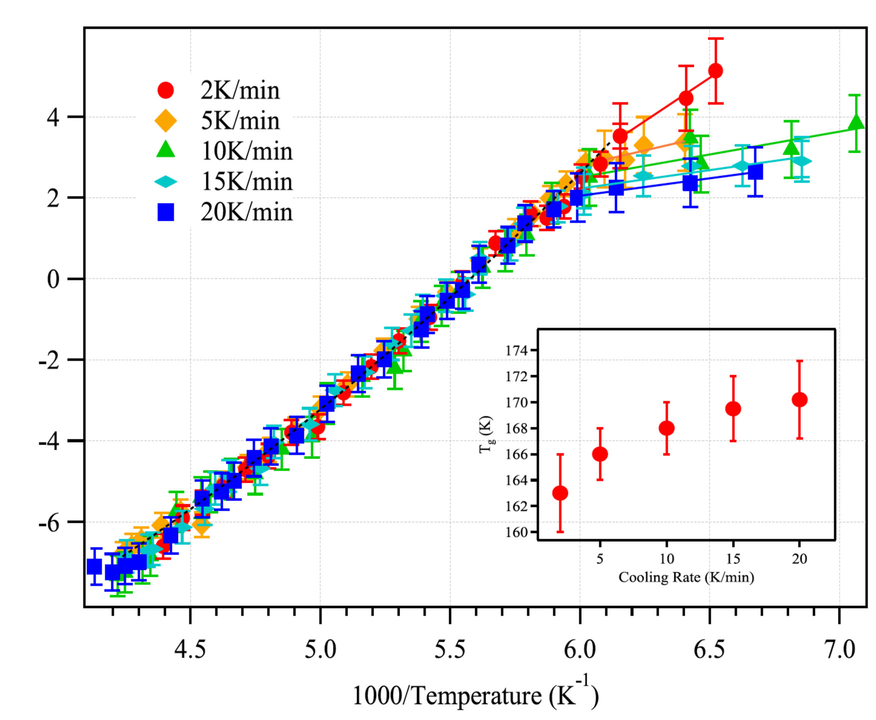
The plot below shows ice nucleation data collected in the deposition mode, at water sub-saturated conditions, relevant to cirrus cloud regime. Clear temperature dependence hints on a pore condensation and freezing (PCF) mechanism in most BC particles tested. The oxidized sample froze homogeneously in all scenarios while a non-oxidized sample with the same morphology showed heterogeneous behavior. The morphological properties affect the dimensions of water confinement in cavities and therefore the onset of ice nucleation. Organic coatings enabled inhibition or enhancement of IN activity.

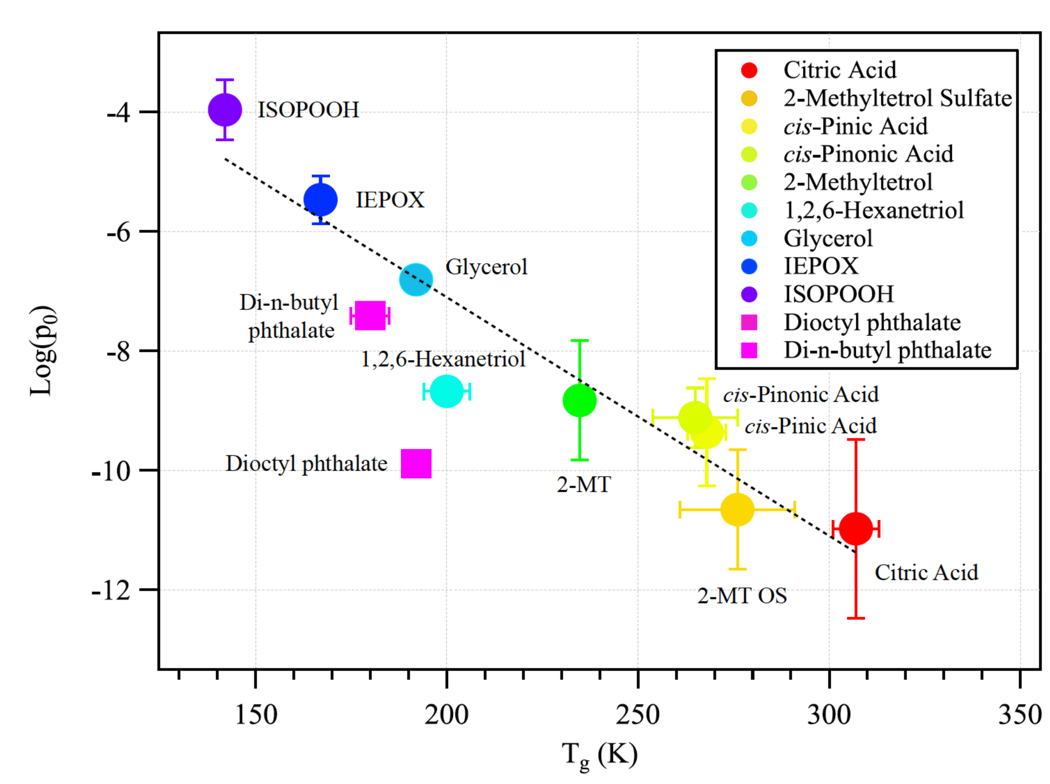
The Effects of Cooling Rates on Glass Transition of Organic Aerosols

Schematic of the Experimental Setup



Effects of cooling rates on the glass transition temperatures of isoprene-derived epoxide (IEPOX), which shows cooling rate could change T_g by 5-6 K.





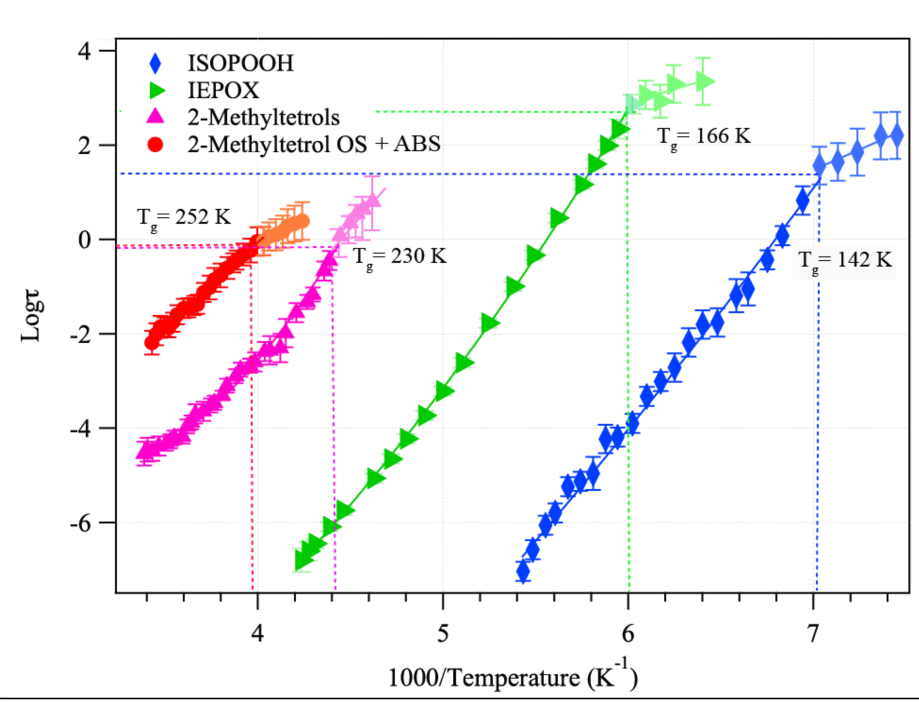
The plot to the left shows the relationship between the saturation vapor pressure and the glass transition of the organic compounds determined from this study and literature, with R^2=0.9

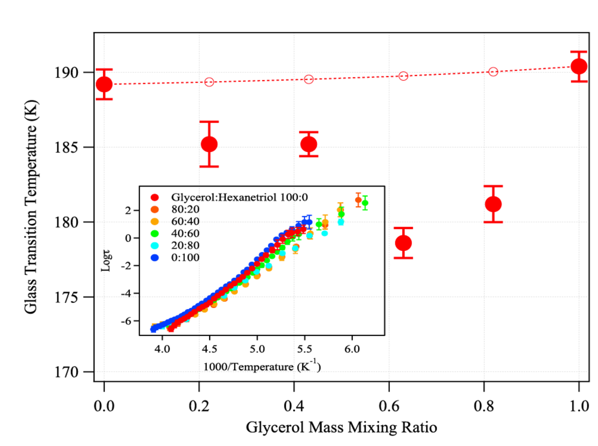
$$\text{Log}(p_0/\text{atm}) = 0.910 - 0.0400 \times (T_g/\text{K})$$

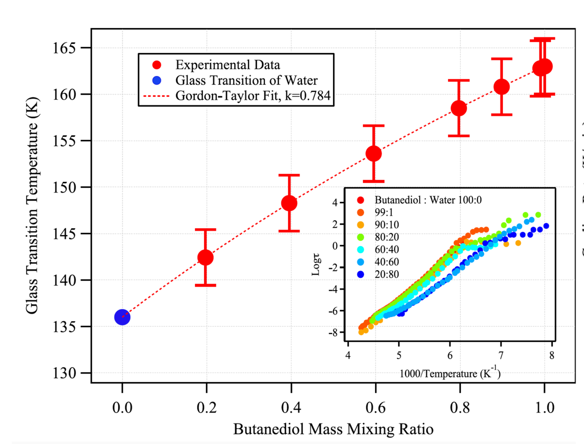
The equation can also be related to the effective saturation vapor pressure and T_g

$$T_g = 25 \times log_{10}\left(\frac{M}{RTC^*}\right) + 172.75 \text{ (K)}$$

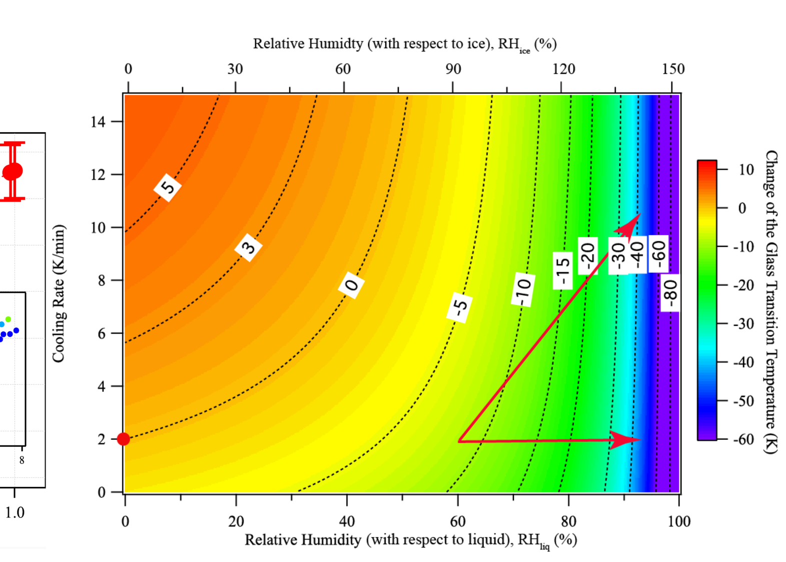
The glass transition temperature of ambient relevant organic aerosols, shown below. 2-Methyltetrol organosulfates (2-MT-OS) have the highest T_g

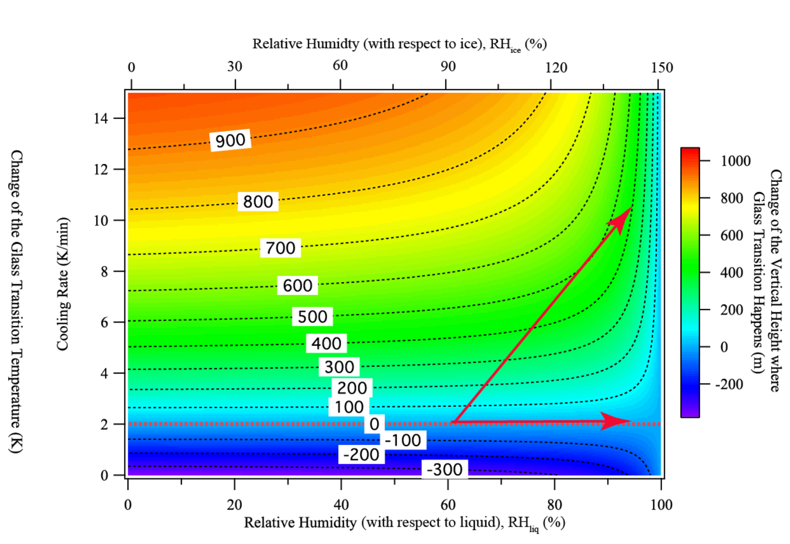






Compounds with similar T_g may not necessarily follow the Gordon-Taylor equation. Compounds with drastic different T_g (>10-20 K) follows better with the Gordon Taylor equation.

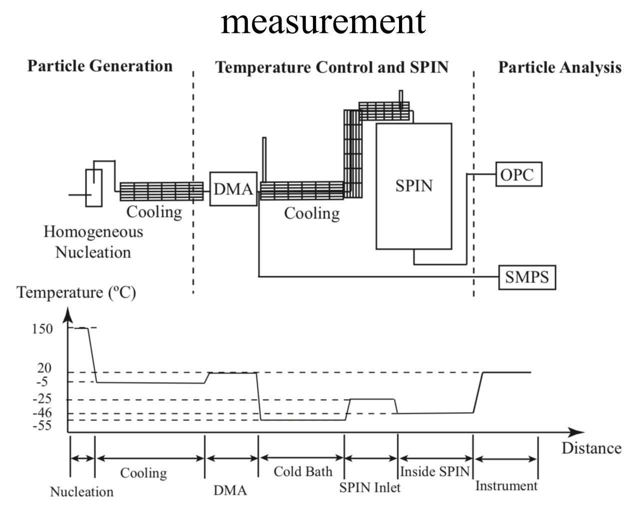




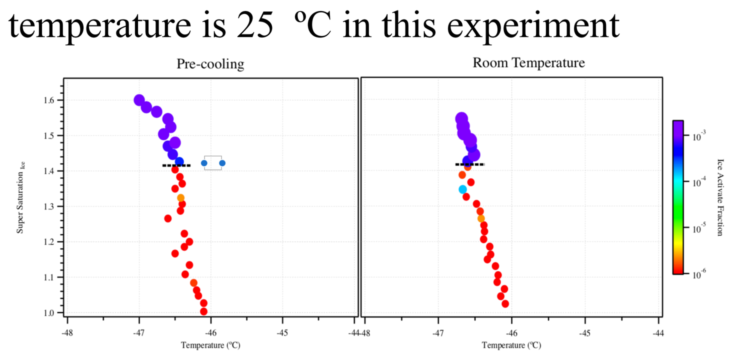
The plots above shows the possible effects of water content and cooling rates on the glass transition of organic aerosols, following the potential relative humidity trajectories. They show that cooling rate could change the glass transition by 400-800 meters.

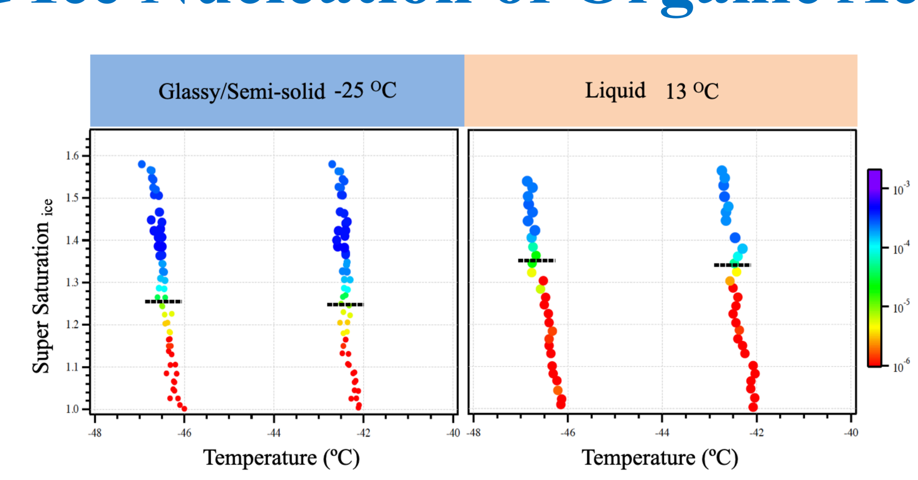
Glass Formation and Ice Nucleation of Organic Aerosols

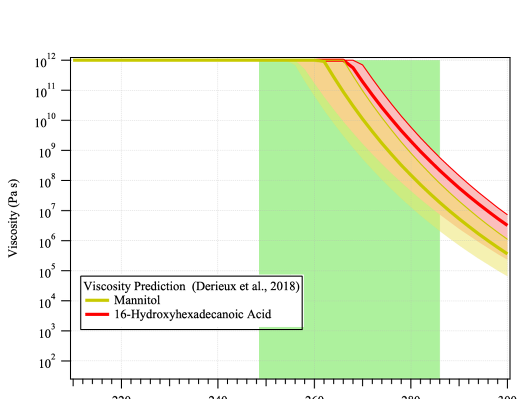
Experimental setup of the ice nucleation measurement



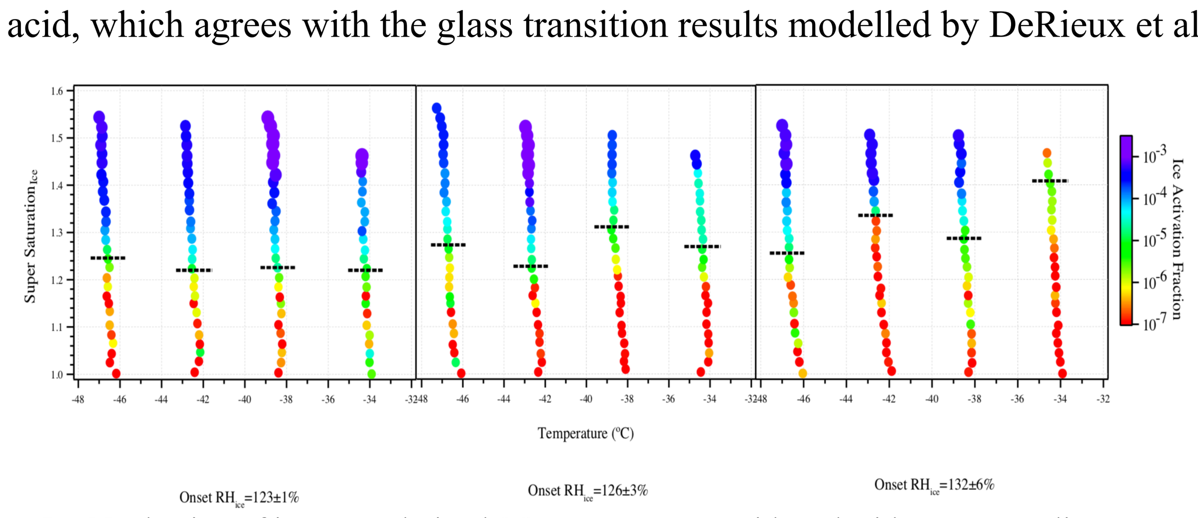
Sucrose is known to stay in liquid at -25 ºC (Pre-cooling temperature). Room temperature is 25 ºC in this experiment







An enhancement of the ice nucleation activity is observed for mannitol and 16-hydroxyhexadcanic acid, which agrees with the glass transition results modelled by DeRieux et al. (2018).



Ice Nucleation of isoprene-derived SOA components with and without pre-cooling

The results show that ice nucleation of 2-methyltetrol, a predominant isoprene-SOA component, is enhanced when the phase state changes.

Conclusions and Acknowledgement

•The systematic study of ice nucleation of black carbon particle types indicates that surface chemistry and microstructures of the soot play a role in ice nucleation properties.

•The glass transition temperatures of the organic aerosols can be influenced by cooling rate and relative humidity. Experimental study combined with modeling shows that an increasing cooling rate from 2 K/min to 10 K/min can reduce the glass transition by 4-6 K, equivalent to 400-800 meters of height in the troposphere.

•Controlling the temperature history of secondary organic aerosol particles, such that they can form glasses, increases their ice nucleation activity.

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