The Ice Nucleation Pathway of Different Amorphous Secondary Organic Aerosol
The Role of Oxidation Level and Sulfate Content

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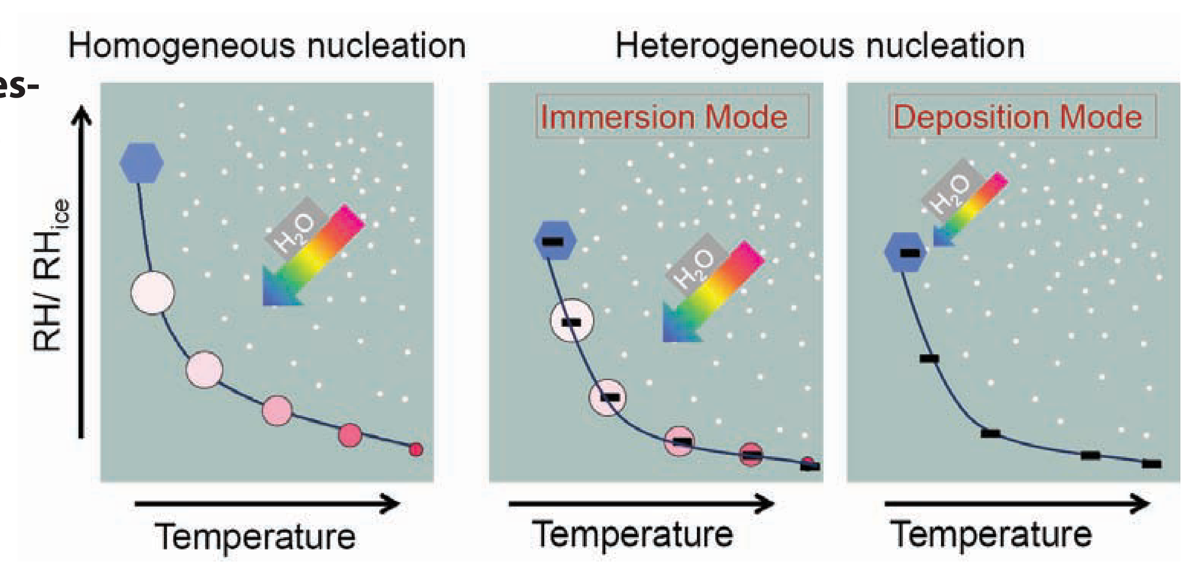
Motivation

Secondary organic aerosol (SOA) is ubiquitous in the atmosphere
Anthropogenic derived SOA can contribute to cold cloud formation and nucleate ice (Knopf et al., GRL, 2010; Wang et al., JGR, 2012)
Anthropogenic and biogenic SOA can exhibit various amorphous phase states ranging from liquid to solid (Virtanen et al., Nature, 2010, Saukko et al., ACP, 2012, Wang et al., JGR, 2012)

We investigate the potential of laboratory generated SOA from biogenic presursor gases **isoprene**, **α-pinene**, and **longifolene** reacted with **OH** with and without SO_2 present to take up water and nucleate ice for tropospherically relevant conditions. These data are set in context with estimated glass transition points.

Ice nucleation pathways investigated in this study.

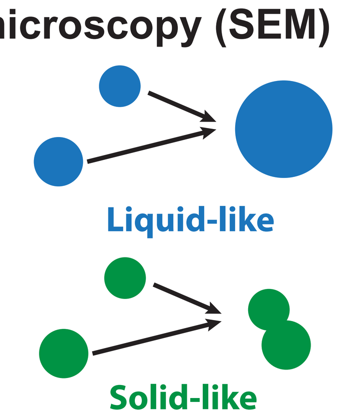


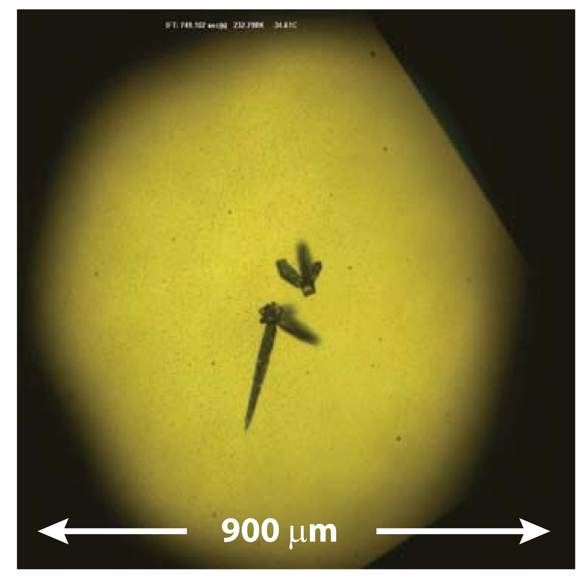
Physical-Chemical Characterization of SOA Particles with STXM/NEXAFS and SEM

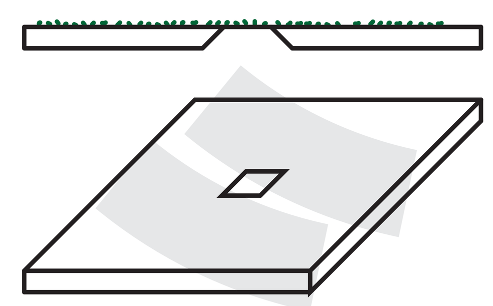
Scanning transmission X-ray microscopy coupled with near edge absorption fine structure spectroscopy (STXM/NEXAFS) and scanning electron microscopy (SEM) was used to characterize SOA particles at Lawrence Berkeley National Laboratory.

STXM/NEXAFS allows:
i) discrimination of the inorganic and organic phase
ii) particle mixing state
iii) organic carbon speciation

Scanning electron microscopy (SEM)
Rounded morphology or coallesced particles indicate a liquid like phase. While coagulated particles may be highly viscous or glassy.



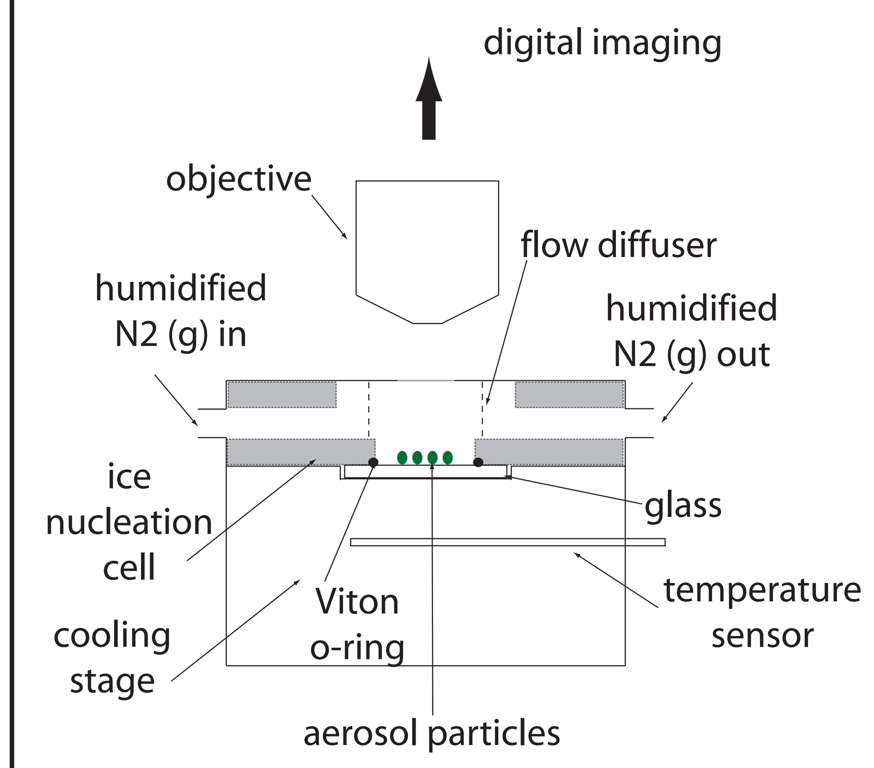




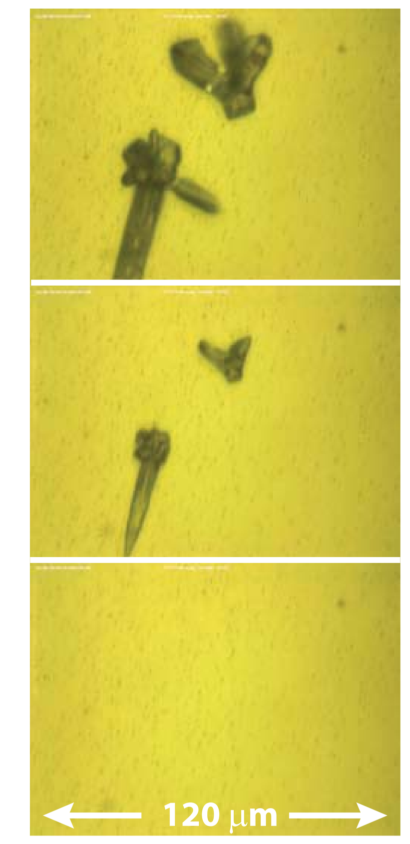
Impacted particles on silicon nitride windows can be mounted in the ice nucleation cell. The same sample can then be used for STXM/NEXAFS analysis.

Ice Nucleation on α-Pinene and Longifolene SOA Particles

Particles on various substrates, e.g. silicon wafers, hydrophobically coated glass slides, and 100 nm thick silicon nitride window membranes, were used in ice nucleation experiments.



Scematic of the ice nucleation cell. Particles are exposed to a constant water vapor partial pressure and cooled resulting in increasing RH_{ice}.

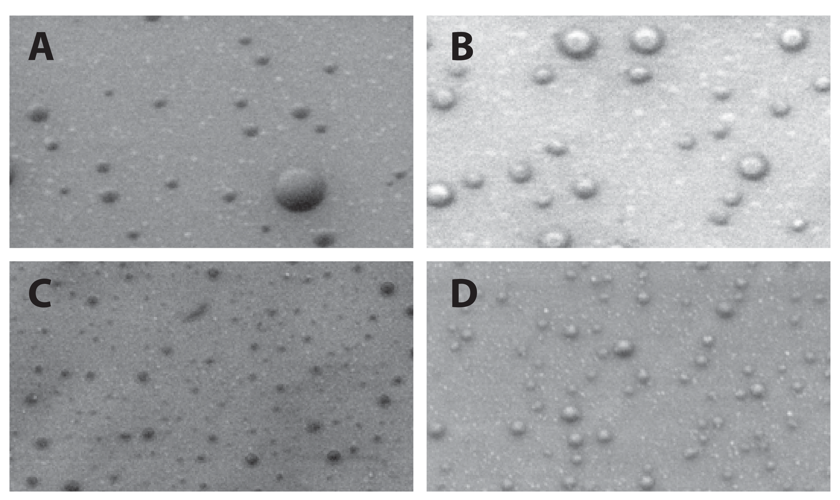


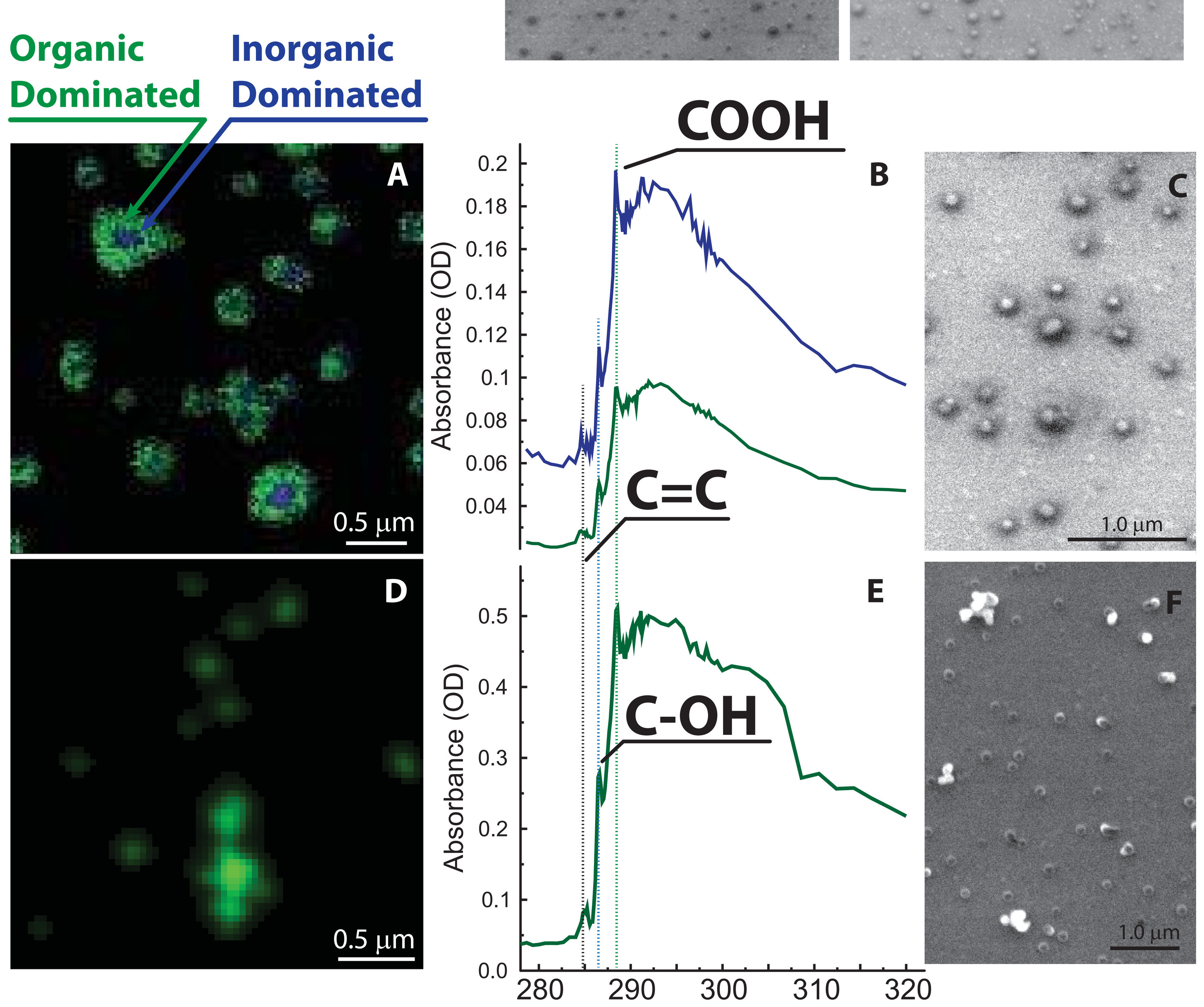
Sublimating crystals reveal the exact particles that nucleated ice.

Single Particle Image Analysis with SEM and STXM/NEXAFS

We used SEM and STXM/NEXAFS to observe single particle morpholgy, chemical composition, and internal microstructure. Isoprene and α-pinene SOA has rounded morphology and particle coallesced on substrates implying they were liquid-like. Longifolene SOA remained in a glassy phase as individual particles stuck together. STXM analysis reveals that longifolene SOA are purely organic. In the presence sulfates, longifolene SOA condensed around the seed particle forming an inorganic core coated by organic material.

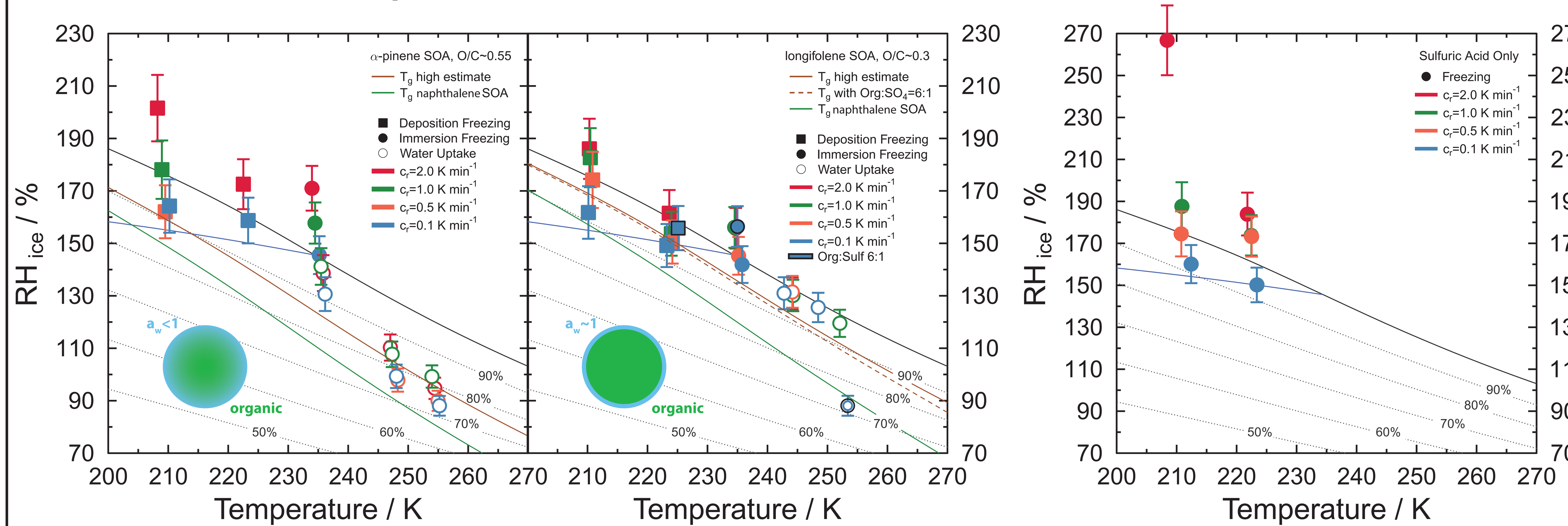
Panels to the right:
Scanning electron microscope images of SOA particles from different precursor gases
A) isoprene
B) isoprene + SO_2
C) α-pinene
D) α-pinene + SO_2





STXM/NEXAFS analysis for longifolene SOA with and without sulfate seed aerosol particles in panels, A-C and D-F, respectively. (A and D) False color X-ray image of particles. Green and blue shaded regions indicate the dominance of either organic or inorganic material, respectively, from singular value decomposition analysis. (B and E) The average component spectra corresponding to the components in panels A and D. (C and F) Scanning electron microscope images of SOA particles collected with a nano-MOUDI II cascade impactor. Single particle diameters range from 180-300 nm.

Ice Nucleation and Water Uptake Results



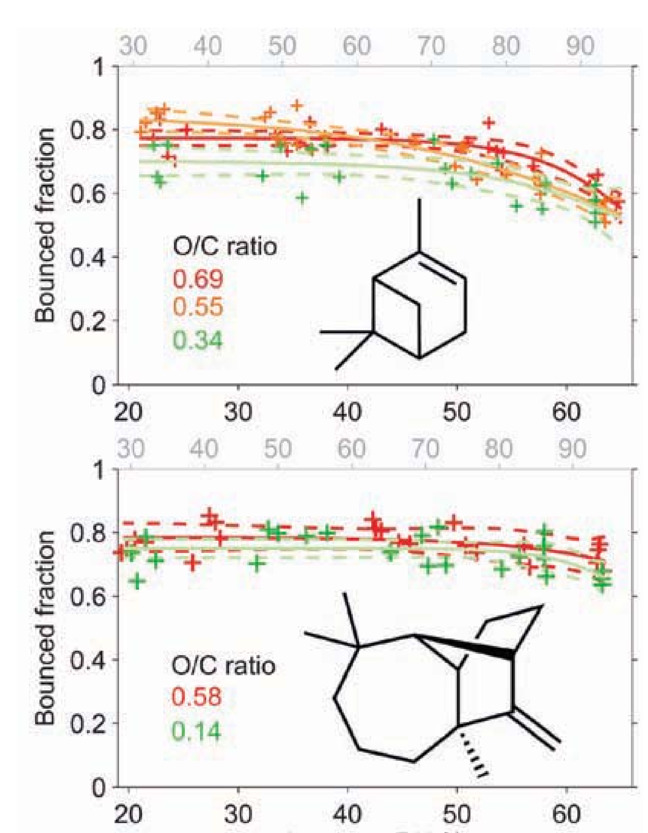
Ice nucleation and water uptake onsets as a function of the relative humidity with respect to ice, RH_{ice}, and temperature for deposition ice nucleation and immersion freezing. Relative humidity with respect to water are plotted as dotted lines. The homogeneous ice nucleation limit is shown as a solid blue line following Koop and Zobrist, PCCP (2009) using Δa_w=0.313. The estimated glass transition curves are derived from a formulation given by Koop et al., PCCP (2011) using observations by Saukko et al., ACP (2012). The green glass transition line is valid for anthropogenic derived SOA particles from naphthalene precursor gas (Wang et al., JGR, 2012).

In general, ice nucleation efficiency of SOA particles is close to the homogeneous freezing for slow rates.

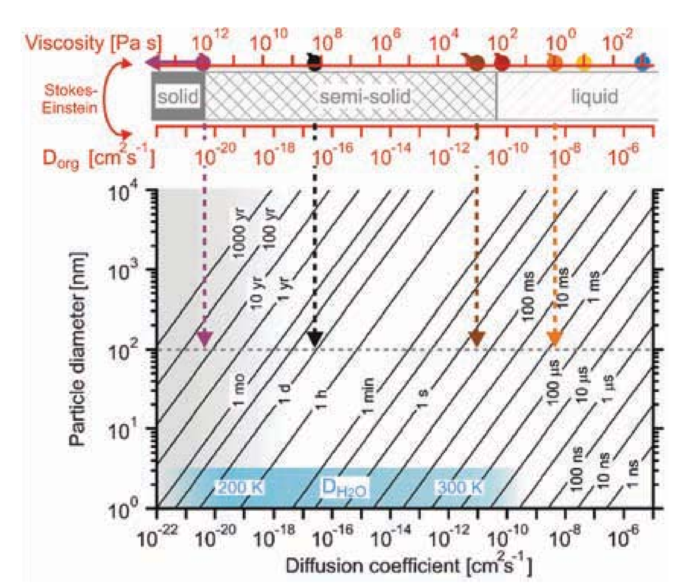
The faster the cooling rate, the RH_{ice} onset increases. This is likely due to the viscosity dependent plasticizing effect of water on the amorphous phase.

Water uptake follows closely glass transition point estimates similar to previous study (Wang et al., JGR, 2012).

Discussion on SOA Phase State



Bounce behavior of SOA from photo-oxidation experiments of biogenic precursors, where solid lines are fits to guide the eye, dashed lines give the 95% confidence bounds for the fits. Upper panel: α-pinene SOA, lower panel: longifolene SOA (Saukko et al., ACP, 2012).



Viscosity and diffusion coefficient for solid, semi-solid, and liquid organic pahse states. e-folding times of equilibration for various particle diameters (Koop et al., PCCP, 2011).

Conclusions

- **Multi-model approach including optical-, electron-, and X-ray microscopy on various substrates allows to characterize physicochemical particle properties in relation to the particles' cold cloud formation potential.**
- **These methods extend room temperature measurements of amorphous organic particles to temperatures as low as 200 K.**
- **SEM provides support for liquid or solid amorphous organic phase state**
- **STXM/NEXAFS reveals particle internal microstructure. Seed aerosol from SO_2 vapors are coated with SOA, demonstrating a 2 phase separation.**
- **SOA from biogenic precursor gases take up water around estimated glass transition points.**
- **Biogenic SOA nucleate ice at conditions similar to homogeneous freezing.**
- **RH_{ice} rate dependent ice nucleation experiments reveal a viscosity dependent plasticizing effect of water. This results in different RH_{ice} onsets for different RH_{ice} rates and SOA types. This suggests that the time scales for glassy α-pinene SOA to (partially) dissolve is shorter than for glassy longifolene particles. In other words, the viscosity of longifolene may be larger than for α-pinene. As a result, the time scales to achieve equilibrium between an aqueous particle phase with sufficient volume to homogeneously nucleate ice and surrounding water partial pressure are different.**

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