Response to RC1

Review of “Ice nucleation on surrogates of boreal forest SOA particles: effect of water content and oxidative age”

We thank the reviewer for their comments and helpful suggestions. Our answers are in blue below. The tracked changes version of the manuscript has been posted as an Author Comment.

I have general comments on the abstract below. Generally, I think the paper is well written and a nice study that adds to the body literature. I also have a comment on figure 2, which is fairly trivial.

1. Abstract is a little longer than it needs to be. I feel like the first paragraph could be removed to add a bit more focus.

   As suggested, the first paragraph has been removed.

2. Was the core-shell formation observed in the measurements – could this be said explicitly in the abstract?
   Unfortunately, the core-shell formation can not be directly observed from the ice nucleation measurements. However, our observations constitute indirect evidence for the core-shell formation. In order to clarify this, the abstract has been modified as follows:

   Modified paragraph:
   “The measurements suggest that at low temperatures, water diffusion into dry SOA particles is slow enough to form a core-shell morphology. The liquid outer layer can equilibrate within the timescale of the experiment and freeze homogeneously. On SOA particles with higher water content, water diffuses faster into the particle, delaying equilibration at the particle surface and preventing the formation of a diluted shell, which can delay homogeneous freezing. We propose that the partial water vapour pressure to which the particles are exposed prior to an experiment can serve as an indicator of whether a core-shell structure is developing”.

3. You clearly show the results of preconditioning the SOA at different humidities in figure 2. This is a key figure for the paper and well-presented. For those not well versed with the CFDCs I think it is necessary to explain what the steps in the plots are (scans). There is also a typo in the legend, which refers to 4% RH instead of 40%.
   - The typo in the legend has been corrected.
   - Added to Fig. caption:

     “The color code indicates activated fraction”

- The following sentences have been added to explain further how the measurements were performed:

  > *"The activated fraction is measured along RH scans at several temperatures."*

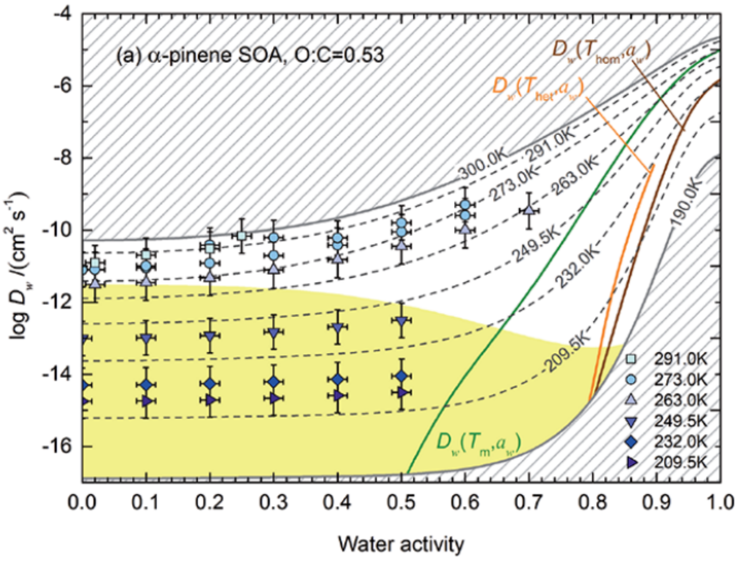
That said, upon detailed reading I am confused about how it works.

The observations seem clear:

4. preconditioning the aerosol at 40% RH allows the aerosol to take on more water at room temperature. When you then transfer the aerosol to the CFDC these aerosol particles nucleate ice close to the threshold for homogeneous nucleation of pure water.

   In the 40% RH case, we did not observe ice formation in the covered RH range up to 100% water saturation (according to Murphy & Koop, 2005).

5. When you precondition the aerosol at lower RH (10 and 1%) the aerosol nucleate ice close to the 'Koop line'. I would like to better understand these findings because I am not sure I fully understand them. The figure below is taken from Lienhardt et al. (2015) for alpha-pinene aerosol. The yellow area is where the aerosol is in a 'glassy' state.



Preconditioning at 40% RH at room temperature should mean the aerosol are not in a glassy state (they are above the yellow area in the Lienhardt plot) and take on water as we expect according to Koehler theory. However, if the aerosol are then cooled to low temperature in the CFDC they should enter a glassy state with liquid water 'trapped' due to low diffusivity.

On the other hand, preconditioning at low RH means that the aerosol will start in (or very close to) the glassy state at room temperature, and cooling further will lead to aerosol particles that have low water content in a glassy state.

Let us now consider what would happen to these particles in the CFDC. Both wet and dry particles have water contents below the threshold for homogeneous nucleation at these temperatures so should not nucleate ice at the start of the scan. The 'Koop' line sits around 85 to 90% RH, and the maximum preconditioned RH is 40%, so ice should not be nucleated, initially.

My understanding is that you then increase the RH in the CFDC during RH-scans. As mentioned above your data show that the "dry particles" nucleate ice on the 'koop line' whereas the "wet particles" nucleate ice close to the homogeneous freezing line for pure water.

The question I have is why do we see this different behaviour?

How do the "wet particles" get all the way to the homogeneous freezing line for pure water without nucleating ice, whereas the "dry particles" nucleate ice sooner?

The theory above suggests that the "dry particles" should have lower diffusion coefficients and therefore would struggle to increase their water content as the RH increases in the CFDC – it is more difficult for water to diffuse through the dry aerosol particles (according to the Lienhardt plot).

My feeling is that the difference in size between the "wet" and "dry" preconditioned particles could be very important. As part of this review I did some back of the envelope calculations (assuming dry density is 1500 kg/m3 and dry molecular weight is 200 g / mole).
These calculations suggest that under equilibrium conditions the preconditioned sizes are around 173 nm; 361 nm; and 652 nm respectively. Could it be that the water is able to diffuse into the smaller particles and dilute them sufficiently (so they nucleate on the 'koop line'), but not the largest particle size?

According to Figure 4 I think you may be suggesting that the wet preconditioned SOA forms an outer shell and traps the water inside, whereas the dry preconditioned SOA does not – This would explain your data, and so the idea about particle size might not be needed, but how does this happen? How and why is the dry shell formed on the outside of the wet preconditioned particles?

We think that the difference in ice nucleation between the "wet" and "dry" preconditioned particles cannot be attributed to a size difference of the particles, as the particles were size-selected. According to the parametrization by Varutbangkul et al. (2006), the growth factors (d_{wet}/d_{dry}) for α-pinene SOA at 1%, 10% and 40% RH are 1.00000, 1.00008, and 1.007176 respectively, indicating that the preconditioned particle sizes barely differ from the dry size.

Regarding the suggested mechanism, our hypothesis is that the dry preconditioned SOA (Fig 1.a, below) forms an outer shell as a result of water uptake and slow diffusion into the particle. Even if the amount of uptaken water is small, the slow diffusion of the water into the particle (that takes place at low T inside SPIN) enables the formation of a liquid layer in equilibrium with the CFDC conditions. This outer liquid layer in equilibrium with the surrounding RH allows homogeneous freezing at the conditions marked by the "Koop line".

In the case of a "wet" particle, the water diffusion (Fig. 1.b, below) is faster, removing water from the surface.Assuming a comparable amount of water is taken up by the "wet" and "dry" particles during their 10 s residence time in the CFDC, the "wet" particle can not reach equilibrium and ends up more concentrated, too concentrated to freeze homogeneously. Equilibration with the surrounding humidity conditions would take more time. As equilibration time scales can be on the order of minutes and longer (Price et al., 2015), we think what we observed could also be happening in high updrafts in the atmosphere.

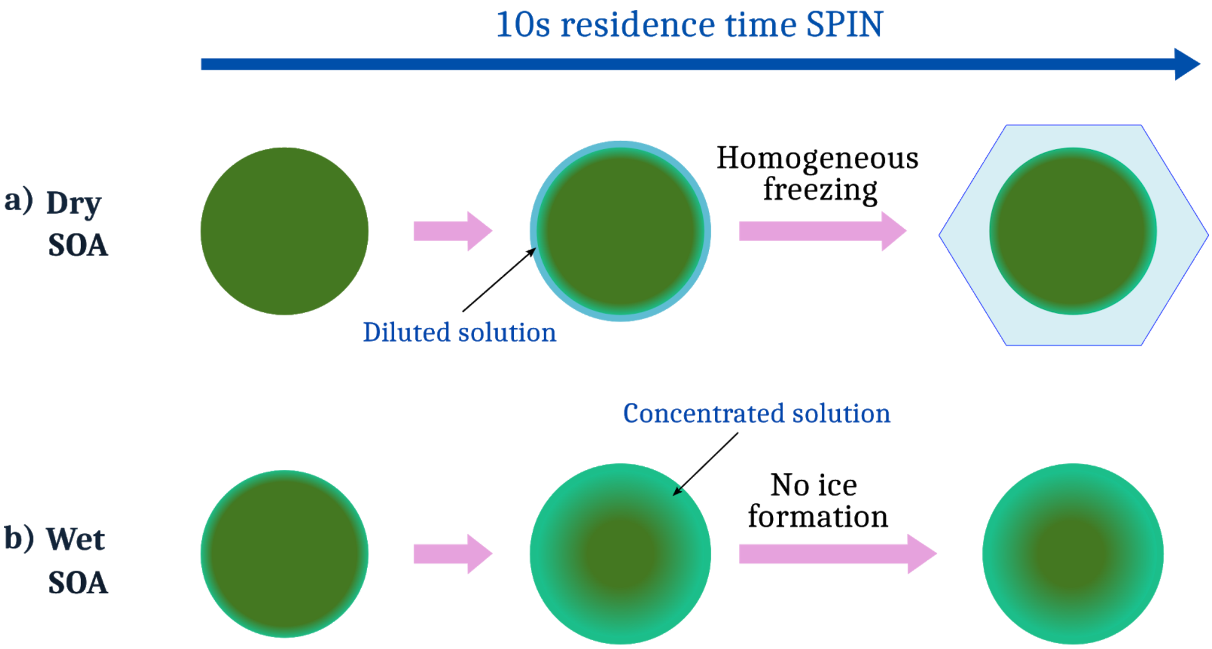


Fig 1. Suggested freezing mechanism for SOA particles with different water content.

If this can be made clear in the manuscript I am happy to recommend publication.
The discussion in section 3.1. has been modified:

"When dry SOA particles (Fig. 4a) take up water at low temperature inside SPIN, water diffusion towards the particle core is slow enough to enable the formation of a liquid layer in

equilibrium with the CFDC conditions. This outer liquid layer in equilibrium with the surrounding RH freezes at the homogeneous freezing conditions (Koop et al. 2000). This mechanism is similar to the one suggested by Fowler et al. (2020).

For SOA particles with higher water content (Fig. 4b), water diffuses faster into the particle, removing water from the surface. Assuming a comparable amount of water taken up by the wet- and dry- conditioned SOA during their 10 s residence time in SPIN, wet-conditioned particles can not reach equilibrium, resulting in a more concentrated state, too concentrated to freeze homogeneously. Longer residence times could restore the homogeneous freezing of the particles by the equilibration with the surrounding RH. However, as equilibration time scales can be on the order of minutes and longer (Price et al., 2015), we believe that the observed inhibition of homogeneous freezing could also happen in fast updrafts in the atmosphere.”