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Interactive comment on “Studies of propane flame soot acting as heterogeneous ice nuclei in conjunction with single particle soot photometer measurements” by I. Crawford et al.

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Received and published: 15 August 2011

We thank the referee for the comments and suggestions. Our responses to the comments are given below.

This manuscript describes the measurement of a series of controlled experiments in which the ice nucleation efficiencies of soot particles of varying composition (organic and sulphuric acid content) are investigated using a combination of particle generation, freezing chamber, and sampling instrumentation. The authors report a decrease in IN activity with increasing organic aerosol content, and the approach of IN activity to that comparable to homogeneous nucleation of sulphuric acid with the addition of

Full Screen / Esc

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Interactive Discussion

Discussion Paper



Interactive
Comment

this acid to the soot+OC mixtures. The results of this work are relevant for the atmospheric/climate community, and the measurements are technically credible. The manuscript is recommended for publication in ACP after the comments below are addressed.

It is unclear how the authors arrived at the nominal organic carbon contents of 5, 30, and 70% (mass basis?).

Response: An OC of 5% means that 95% of the carbon mass is classified as EC as detected as CO₂ by the thermographic method detailed in Schnaiter et al. 2006 in section 3, page 2984. We accept that the definition of OC is not sufficiently discussed in the section detailing the soot production and this section will be expanded to include a description of the thermographic method.

Inserted text: “The organic carbon (OC) content of the soot was determined using an off-line thermographic technique. Combustion aerosol samples were deposited onto quartz fibre filters which were then analysed over three temperature stages; in the first stage low volatility OC compounds were volatilised in 350°C helium flow and then catalytically oxidised. The carbon fraction was determined as CO₂ by NDIR spectrometry; in the second stage the remaining OC compounds were volatilised in a 650°C helium flow; in the final stage the remainder of the sample was burned in a 650°C oxygen flow and the detected carbon fraction was classified as Elemental Carbon (EC), allowing the EC/OC ratio to be calculated. Further details can be found in Schnaiter et al. 2006.

Also, can the authors make statements about the composition in the organic fraction of the aerosol and its relevance? Are the non-incandescing particles possibly purely OC? Given the size range over which the SP2 can measure scattering particles, would it be faithful to say that these fractions represent the number fraction of all particles generated by the CAST burner, or could there be smaller or larger particles outside of this range that may also be influencing the results?

Response: The composition of the organic fraction of the mini-CAST soot was mea-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

sured using an HR-ToF-AMS where polycyclic aromatic hydrocarbons (PAH) were found in the OC fraction. It was observed that the addition of sulphuric acid reduced the PAH content. A paper is in preparation on the topic of the hygroscopic growth and activation of this soot which will include more information about the nature of the OC.

This is highly dependant on the analysis method used and the corresponding definition of OC. If we use the SP2 analysis of the OC30 soot we find 1 purely scattering particle in every 21 detected which may be used to indicate the amount of pure OC in the aerosol. However, the absence of incandescence does not mean that the particles would be classified as OC using a thermographic method. From our recent SP2 intercomparison campaign we found that the rBC mass as measured with the SP2 to be lower than the EC mass measured using the thermographic method, i.e. there are carbon compounds in the aerosol which do not contribute to incandescence but do oxidise at 650°C. The most likely explanation is that the particles evaporate in the SP2 laser beam before reaching incandescent temperatures. There may be a small influence from particles outside the detection range of the SP2. However, the mode of the size distribution of the interstitial and residual aerosol is observed to be within in the detection range and these particles are the ones of significance.

How comparable is the (sulphuric-acid) coated to non-coated case as there is an additional "pre-treatment" (heating) of the soot+OC aerosol prior to sulphuric acid coating? Could this not evaporate organics or modify the morphology of the soot? Why were the temperature treatments different for the OC5 and OC70 case?

Response: The referee is correct that the heating of the soot aerosol before and during coating could partly evaporate organics. However, it can be assumed that the majority or of the organics re-condense in the cooling section of the coating tube. The Soot aerosol was heated to the same temperature as the sulphuric acid saturated air, and the short mixing region containing the two airflows was set to be 20°C higher to avoid quick and uncontrolled cooling before the two airflows were well mixed. The aerosol flow was not heated to "pretreat" the soot but to suppress nucleation of sulphuric acid

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

particles and to also initiate controlled cooling in the flow tube. We did not use different “treatments” for the cases; for the OC70 soot the sulphuric acid saturator was set to a lower temperature because this aerosol had a lower surface area and the nucleation of sulphuric acid particles occurred at a higher saturator temperature of 55°C. We optimized the coating parameters so that a maximum sulphuric acid coating was achieved without the formation or nucleation of new particles in the coating flow tube.

What is the estimated mass fraction or coating thickness of sulphuric acid on the particles? Were there any TEM images taken for sulphuric acid-coated BC particles? Were there noticeable differences in size (either through mass addition or collapsing of fractal aggregates of BC) as measured by the SMPS? From this work, is it possible to speculate whether another acid species can play a similar role in the atmosphere, or are the effect effects specific to the molecular properties of sulphuric acid (based on a mechanistic interpretation of the observations)?

Response: The coating thickness cannot be derived from SMPS size distributions as the particles shrink due to restructuring and then also grow due to the coating and the conflicting effects cannot be disentangle as was seen by Schnaiter et al. 2005. We do not have any TEM images from this series of experiments. A sulphuric acid coating was added to spark generator soot in a previous study (Möhler et al. 2005) using a similar procedure which resulted in a sulphuric acid volume fraction of ~10%, so we can expect the CAST particles to have a similarly thick coating. We would expect other acid species to play a similar role as the coating acts to change the freezing mechanism from deposition freezing of the IN to homogeneous freezing of the coating.

It is a notable conclusion that the coating of sulphuric acid draws the required ice nucleation supersaturations toward that of homogeneous sulphuric acid, but how is it that homogeneous freezing of sulphuric acid becomes the dominant mechanism even while they are internally mixed with particles shown to form ice nuclei at lower saturation ratios (OC5 case)? It would seem that the nucleation rate should be governed by the fastest mechanism in the system. Also, some statement of sulphuric acid content on

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a mass or coverage basis would be helpful to interpret the magnitude of influence of sulphuric acid coatings for the OC30, OC70 cases.

Response: Presumably the sulphuric acid coating acts to suppress the active sites for deposition freezing found on the OC5 soot, making it inactive as a deposition and also an immersion nucleus. This allows the sulphuric acid coating to freeze via the homogeneous freezing pathway. In this study we were only able to qualitatively assess the coating effect and no estimate of the acid coating thickness is given. The question about the sulphuric acid content has been answered earlier.

p.11014, sentence beginning on line 5 – not sure if this sentence is structured as intended.

Response: Sentence is as intended.

p.11016. Can you discuss the relevance of the reference expansion measurements?

Response: The reference expansions are made to quantify the error resulting from the nucleation in any background aerosol which may still be present in the chamber after evacuation. This is to be taken as the detection limit when determining the onset of nucleation.

p.11018 – this "coating" is due to the remaining ice, or it is due to the enriched fraction of organics in activated particles? Is it possible to detect the difference in the mass size distributions in the interstitial particles?

Response: We don't believe the coating thickness for the OC5 soot to be significantly affected by the incomplete evaporation of the ice as this would displace the modal value of τ_d which is not observed.

Figures 5 and 7 – which work does ACP 2003 refer to? Also, shading areas corresponding to atmospherically-relevant ranges of supersaturations in these figures would be helpful to place the work in appropriate context.

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Response: ACP 2003 refers to Mohler et al. (2003). We accept that the caption is not clear and will be revised to:

“For comparison the homogeneous freezing of pure sulphuric acid droplets are shown from previous AIDA studies Mohler et al. (2003, labelled ACP 2003)”

The figure includes the homogeneous freezing threshold according to Koop et al. (2000) for $\Delta a = 0.303$ (solid line) and water saturation (dashed line). We don't believe it is necessary to add the requested shading to the figures but we will modify the final paragraph of section 3.1 to clarify the relevance of the efficiency of the different test aerosols as follows:

The above experiments on the uncoated soot are summarised in Fig. 5 where the onset of freezing is shown as a function of temperature and ice saturation ratio. It can clearly be seen that the OC5 soot became ice active as deposition nuclei below water saturated conditions whereas the OC30 and OC70 soots required water saturation for ice nucleation to occur. soot types with IN thresholds above the water saturation line can be considered as completely unimportant for heterogeneous ice nucleation in the atmosphere.

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ACPD

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