Organic Coating of Aerosol Particles Observed during ACTIVATE and its Potential Impact

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Two aerosol samples collected during three flights

RF156 (5/18/22, AM)

RF157 (5/18/22, PM)

RF174 (6/13/22)
Aerosols collected using cascade impactor for chemical imaging analysis

- Cascade impactor with 4 stages and decreasing cutoff diameters collecting particles on 5x7mm silicon wafers (F. Mei)
- Used for Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) surface analysis (Z. Zhu)
ToF-SIMS surface spectrometry and imaging

- ToF-SIMS is used to obtain elemental composition and molecular information on a surface and in-depth (i.e., 3-D chemical composition)
- Localized information with a beam spot size of about 100 nm and sputtering depth of 5-10 nm
How does SIMS detect thin organic coating layer?

- SIMS is different from TEM (transmission electron microscopy) for particle imaging
- TEM beams pass through the thin coating layer
- SIMS has shallow information depth and controllable sputtering (removing 5-10 nm layer at a time)

(Y. Li et al., 2023 EST)
ToF-SIMS surface imaging of RF156/157 sample

Original surface

10 nm removed

Overall

OA

Chloride

Nitrate

Sulfate

<table>
<thead>
<tr>
<th>Original surface</th>
<th>OA</th>
<th>Chloride</th>
<th>Nitrate</th>
<th>Sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total: 700; TC: 5.713e+006</td>
<td>C2H-: MC: 12; TC: 4.630e+004</td>
<td>Cl-: MC: 60; TC: 1.865e+005</td>
<td>NO3-: MC: 60; TC: 2.027e+005</td>
<td>HSIO4-: MC: 25; TC: 1.100e+004</td>
</tr>
<tr>
<td>10 nm removed</td>
<td>C2H-: MC: 12; TC: 5.679e+003</td>
<td>Cl-: MC: 60; TC: 1.640e+005</td>
<td>NO3-: MC: 60; TC: 1.623e+005</td>
<td>HSIO4-: MC: 25; TC: 1.100e+004</td>
</tr>
</tbody>
</table>
SIMS surface imaging of Bermuda (RF174) sample

Original surface

10 nm removed
Impact of surface chemistry on aerosol activation

- Inorganic aerosol has a larger kappa ($k_i$) and smaller critical size ($d_i$) than organic aerosols ($k_o$, $d_o$) for activation at a certain SS
- A mean $k_m$ between $k_i$ and $k_o$ is used in ESMs with internal mixing assumption
- Particles in zone 1 and zone 2 are activated, but with organic-shell-inorganic-core structure only zone 1 is activated

(Y. Li et al., 2023 EST)
CCN closure analysis based on ACTIVATE measurements

• **Hypothesis**: most aerosol particles are coated with organics, having smaller kappa
  - Kappa derived from chemical composition mass fractions is greater than measured
  - Analyzing CCN closure instead due to large uncertainties in estimating kappa from CN and CCN

• **ACTIVATE data**: mass of aerosol components (AMS, PILS), CN size distribution (LAS, SMPS) and CCN (@0.1-1%, 0.37% SS)

• **Method**: Calculating CCN number from CN size distribution and kappa derived from chemical composition and comparing with measured CCN at the same SS

• **Expectation**: Calculated CCN > Measured CCN
ACTIVATE measurements for the two cases

Size distribution

Particle Size Distribution (dN/dlogDp, cm$^{-3}$)

Mass concentration

Kappa

Kappa=0.108 (HSRL-2, 532nm)  
0.195 (PM), 0.32 (AM), 0.15 (in situ)
CCN closure for the two cases

05/18/2022 (two RFs)

06/13/2022

✓ calculated CCN > Measured CCN
Changes in $k_o$ make a difference to LES simulated cloud properties

- About 50% of organic components in a CAO case (2/28/2020)
- $k_o$ (mean=0.1, max=0.229), leading to $k_m = 0.31$ and $k_{max} = 0.39$
- A significant impact on Nc, $r_e$, LWP and SW cloud forcing
- Even strong impact when $k = k_{min}$

(X. Li et al., 2023 JAS)
Sensitivity of clouds to aerosol chemistry at ARM SGP site

- LWP and cloud top are not sensitive to kappa \( k_m = 0.33 \) versus \( k_{min} = 0.04 \), compared well with ARM measurements
- \( N_c (r_e) \) is much smaller (larger) when \( k = k_{min} \), closer to ARM measurements
- 12-h mean SW cooling is 1.2 W m\(^{-2}\) weaker (instant as large as 10 W m\(^{-2}\))

(Mei et al., in review for BAMS)
- Cold air outbreak case (March 1, 2020)
- CCN (0.5% ss), $N_d$ and $r_e$ are sensitive to the kappa values from assumed aerosol composition
- Much smaller impact on LWC, except for the lowest $k$
- The lowest $k$ pushes $N_d$ to an artificial lower bound (10 cm$^3$), having an impact on precipitation
Summary

• Chemical analysis reveals organic coating structure of ACTIVATE aerosols

• Hygroscopicity (kappa) and CCN closure analysis shows an important impact of the organic coating
  o Kappa estimation is subject to large uncertainty and algorithm limitation
  o Estimated CCN from aerosol composition and size distribution measurements are compared to CCN measurements
  o The 5-18-2022 case shows clear overestimation of CCN, while the 6-13-2022 case shows the opposite, likely due to too small organic fraction and/or too clean condition
  o 2020-2022 flights overall show an overestimation of CCN during some legs (Takeoff/Landing, Ascent, ACT, ABL and BBL)
  o Results are sensitive to supersaturation (larger discrepancy in CCN at lower SS)

• LES, SCM and GCM show sensitivities of clouds to kappa changes