Phase State and Physical Properties of Ambient and Laboratory Generated Secondary Organic Aerosol

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Supplemental Information

Laboratory generated samples

Experimental conditions for chamber experiments are given in Table S3 (the tables and figures are numbered in the order of appearance in the main manuscript). For the flow tube experiments, the flow tube was operated at low RH (< 2%), ambient temperature (~25 °C), with the lights turned off. The oxidant was ozone (30-50 ppm) produced by flowing oxygen gas through a commercial ozone generator. The residence time was ~5 min. In both cases (chamber and flow tube) samples were collected on stages 7 and 8 of a 10 stage rotating cascade impactor (MOUDI 110-R, MSP) using Si_3N_4 windows taped to aluminum substrates. Collection times were ~30-45 min for chamber experiments and ~1 min for flow tube experiments.

Data Collection/Analysis

Because of the weak signal to noise ratio, particles with average OD_{320} values < 0.03 were excluded from analysis. For I_o values of ~ 7,000 counts/ms, this cutoff corresponds to about 200 photons/ms. Since stray light in the STXM leads to approximately 100-200 photons/ms noise, the particles with the lowest average OD have the largest relative amount of noise.

Since some particles and particle components were non-spherical, the sizes reported are the area equivalent diameters (AED), defined as a diameter of a hemisphere required to cover the same area as the projection of the particles on the surface:

$$\text{AED} = 2\sqrt{\left(\frac{length_x \times length_y}{\pi}\right)} \qquad \text{Equation S1}$$

where $length_x$ and $length_y$ are the effective sizes of the particle in the x and y dimensions.

Absorption Coefficients

Organic material mass absorption coefficients μ (cm^2/g) were obtained from the sum of the absorption cross sections of the constituent atoms by:

$$\mu = \frac{N_A}{MW}\sum_i x_i \sigma_{ai} \qquad \text{Equation S2}$$

where MW is the molecular weight of the compound containing x_i atoms of type i, σ_a is the total atomic absorption cross section (cm^2/atom) for this type of atom, and N_A is the Avogadro's number. This approximation neglects interactions between the atoms in the material and is applicable at photon energies sufficiently far from absorption edges [*Henke et al.*, 1993; *Thomson et al.*, 2009]. Using the list of chemical formulas from negative mode high resolution mass spectrometry analysis of ambient particles (O'Brien el al., manuscript in preparation, 2014), the mass absorption coefficient was calculated and plotted as a function of the O/C value (Figure S3). An estimate for the average O/C value of 0.44 [*Setyan et al.*, 2012] leads to $\mu_{320} \cong$ 22,500 cm^2/g and $\mu_{278} \cong 1102$ cm^2/g.

Inorganic Contributions

The particles used in this analysis were identified as organic using algorithm detailed in [*Moffet et al.*, 2010b]. However, aerosol particles that are primarily organic can also have

inorganic components. To estimate the fraction of other elements in these particles we examined the OD at the carbon pre-edge (278 eV) and the post edge (320 eV) of a particle with inorganic and organic components via equations S3 and S4:

$$OD_{278} = \mu_{org,278}\rho_{org}d_{org} + \mu_{in,278}\rho_{in}d_{in} \qquad \text{Equation S3}$$

$$OD_{320} = \mu_{org,320}\rho_{org}d_{org} + \mu_{in,320}\rho_{in}d_{in} \qquad \text{Equation S4}$$

Where $\mu_{org,}\rho_{org}$ is the linear absorption coefficient of the organic species, $\mu_{in,}\rho_{in}$ is the linear absorption coefficient for the inorganic species, and d_{in} and d_{org} are the average sample thicknesses of the inorganic and organic, respectively. The thickness ratio [*Moffet et al.*, 2010b] can then be calculated by combining equations S3 and S4:

$$\frac{d_{org}}{d_{in}} = \frac{OD_{320}\mu_{in,278}\rho_{in} - OD_{278}\mu_{in,320}\rho_{in}}{OD_{278}\mu_{org,320}\rho_{org} - OD_{320}\mu_{org,278}\rho_{org}} \qquad \text{Equation S5}$$

To calculate the linear absorption coefficients for the organic terms, the μ_{320} and μ_{278} estimates from above and a density of 1.3 g/cm^3 [*Setyan et al.*, 2012] were used. For the inorganic terms, three cases were considered. In the first case, the linear absorption coefficients were calculated for elements with atomic numbers between 6 (carbon) and 26 (Iron) that have been observed in atmospheric aerosols [*Moffet et al.*, 2010a]. Elements with higher linear absorption coefficients will absorb more photons and at 278 eV Al, Si, P, S, Cr, Mg, and Fe all have higher linear absorption coefficients in the range of 7-13 μm^{-1} (Figure S4a). At 320 eV the elements Si, P, S, Cl, Cr, Mn, and Fe all have coefficients between 5.6-10 μm^{-1} (Figure S4b). Given these ranges, values of 10 μm^{-1} at 278 eV and 8 μm^{-1} at 320 eV were used. In the second case, the linear

absorption coefficients for NaCl were used (8.1 μm^{-1} at 278 eV and 6.3μm^{-1} at 320 eV). In the last case, values for ammonium sulfate were used (3.2 μm^{-1} at 278 eV and 2.4 μm^{-1} at 320 eV). Using these estimates and the measured OD_{278} and OD_{320} values, the average thickness ratio for each data set was calculated and is shown in Table S4. All of the data sets range from ~10-30% inorganic with higher percentages when all of the inorganic is assumed to be ammonium sulfate as the inorganic. Thus, for these campaigns, approximately 11-30% of the thickness for the organic particles is likely due to the absorption cross section contribution from non-organic molecules or atoms.

References

Henke, B. L., et al. (1993), X-Ray Interactions - Photoabsorption, Scattering, Transmission And Reflection at E=50-30,000 EV, Z=1-92 (VOL 54, PG 181, 1993). *Atom. Data Nucl. Data Tables 55*(2): 349-349.

Moffet, R. C., et al. (2010a), Microscopic characterization of carbonaceous aerosol particle aging in the outflow from Mexico City, *Atmospheric Chemistry and Physics 10*(3): 961-976.

Moffet, R. C., et al. (2010b), Automated Chemical Analysis of Internally Mixed Aerosol Particles Using X-ray Spectromicroscopy at the Carbon K-Edge, *Anal Chem 82*(19): 7906-7914.

Setyan, A., et al. (2012), Characterization of submicron particles influenced by mixed biogenic and anthropogenic emissions using high-resolution aerosol mass spectrometry: results from CARES, *Atmospheric Chemistry and Physics 12*(17): 8131-8156.

Thomson, A., et al. (2009). *Center for X-Ray Optics and Advanced Light Source X-Ray Data Booklet*. Lawrence Berkeley National Laboratory, Lawrence Berkeley National Laboratory.

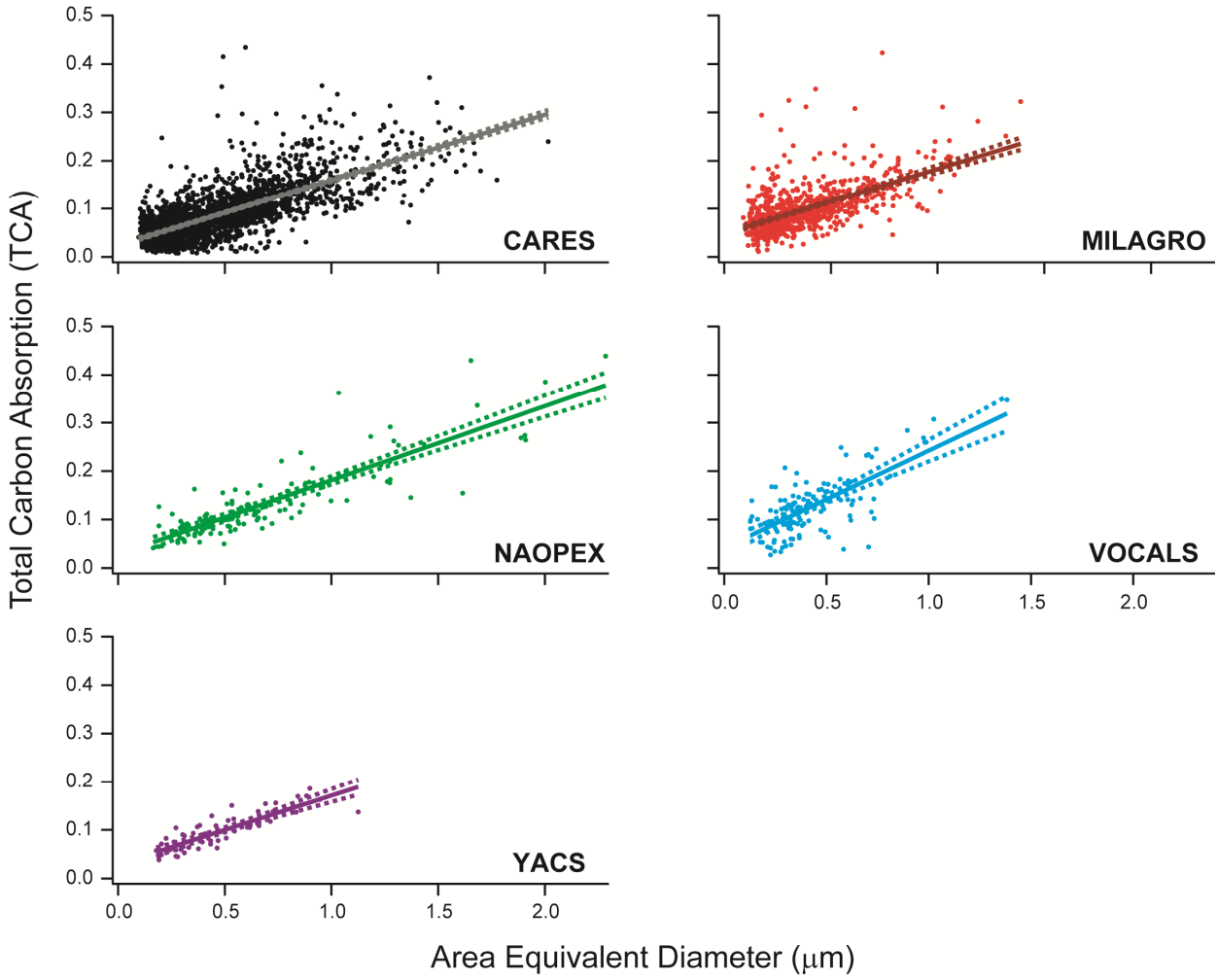


Figure S1. Optical thickness of carbon (total carbon absorption = OD_{320}-OD_{278}) as a function of size of impacted organic particles for each ambient data set. Solid lines are best fit lines for each data set and dashed lines are ±95% confidence intervals. The thick fitted lines are reproduced in Figure 2 of the main text, and the slopes, intercepts, and confidence intervals are listed in Table 1.

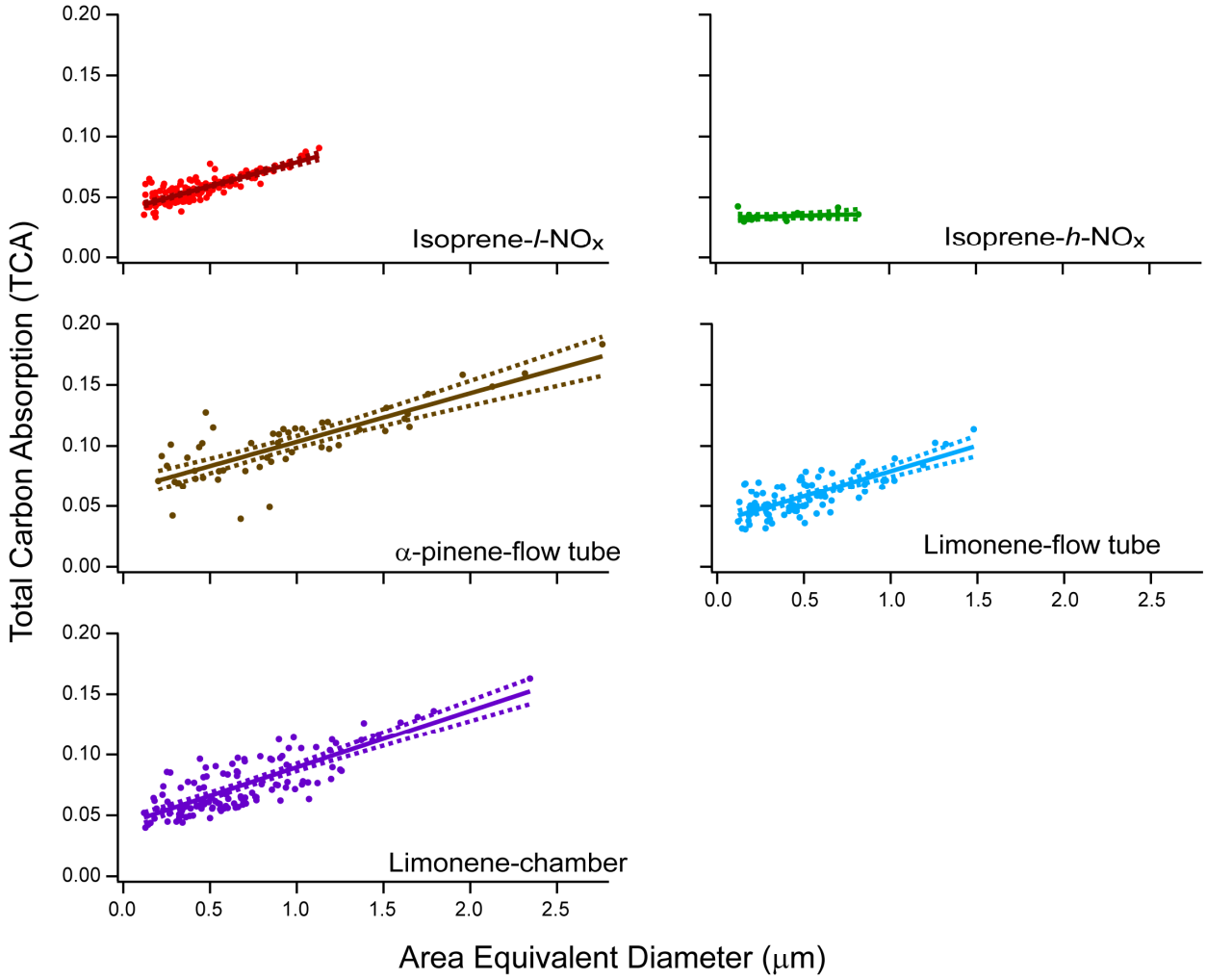


Figure S2. Optical thickness of carbon (total carbon absorption = OD_{320}-OD_{278}) as a function of size of impacted organic particles for each laboratory data set. Solid lines are best fit lines for each data set; the same lines are reproduced in Figure 2 of the main text. The slopes are listed in Table 1.

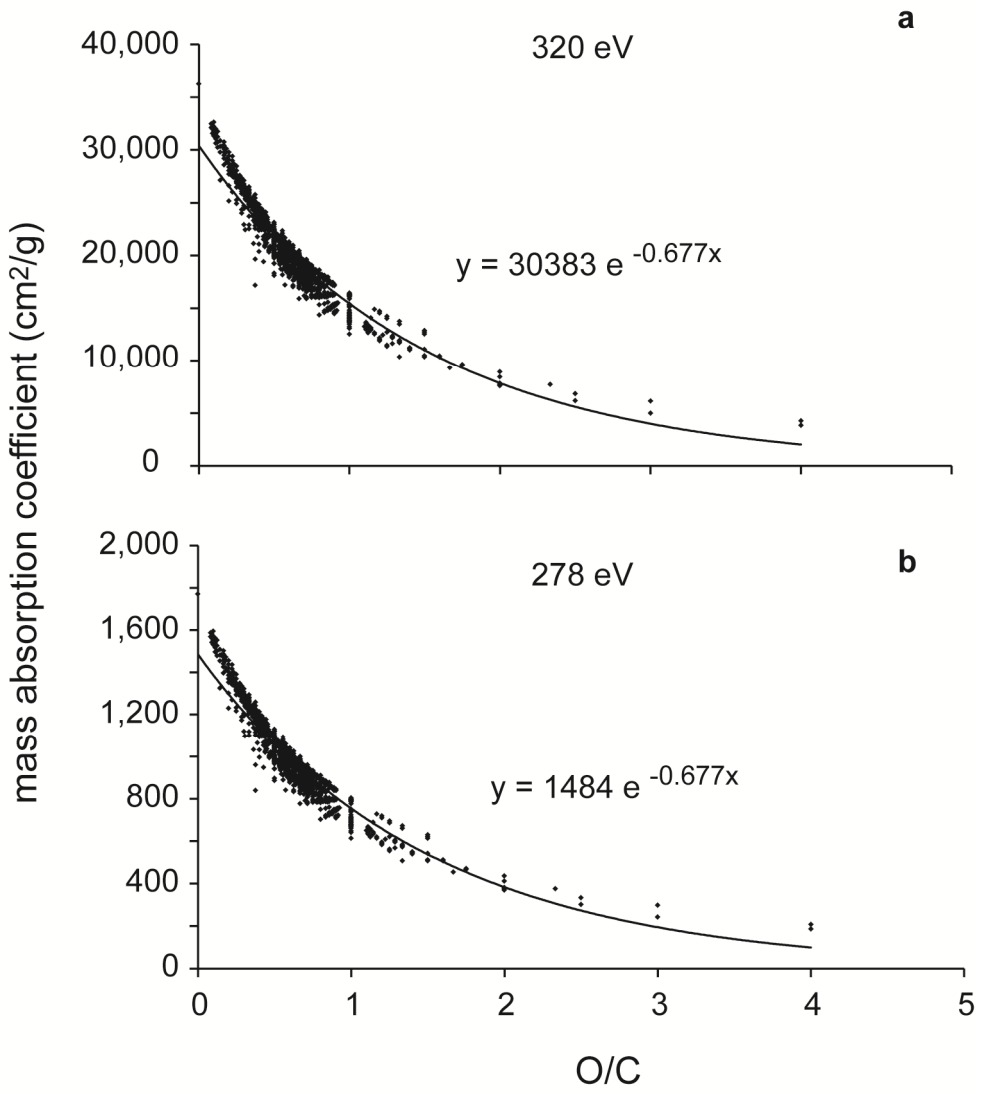
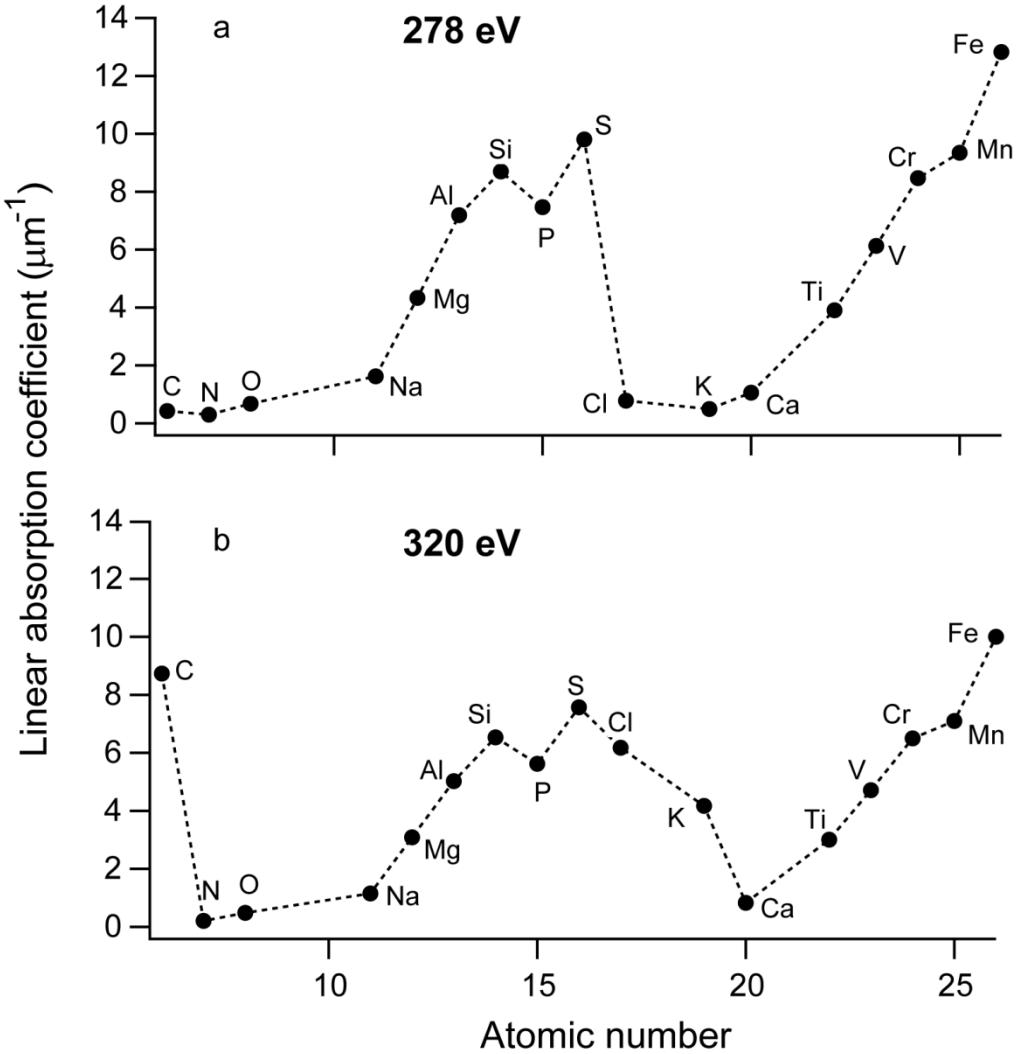


Figure S3. Calculated mass absorption coefficients as a function of O/C at a) 320 eV and b) 278 eV for chemical formulas from organic molecules found in atmospheric aerosols.



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136 **Figure S4.** Linear absorption coefficients at (a) 278 eV and (b) 320 eV for elements found in

137 atmospheric aerosols [*Henke et al.*, 1993].

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144 **Table S1.** Ambient sample collection information and fitting results for OD_{320} and OD_{278} vs.

145 area equivalent diameter[a]

			320 eV		278 eV	
Campaign	**Year**	**Number of particles**	**Slope**	**Intercept**	**Slope**	**Intercept**
CARES	2010	2428	0.18±0.007	0.041±0.004	0.045±0.002	0.016±0.001
MILAGRO	2006	798	0.19±0.015	0.068±0.006	0.057±0.005	0.019±0.002
NAOPEX	2001	123	0.22±0.022	0.036±0.018	0.069±0.007	0.008±0.006
VOCALS	2008	125	0.30±0.056	0.065±0.027	0.098±0.02	0.023±0.01
YACS	2002	56	0.17±0.028	0.056±0.015	0.027±0.01	0.025±0.006

146 [a]The ±95% confidence intervals for the slope and intercept are given.

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161 **Table S2.** Laboratory sample fitting results for OD_{320} and OD_{287} vs. area equivalent diameter[a]

Sample	MOUDI stage	Number of particles	320 eV Slope	320 eV Intercept	278 eV Slope	278 eV Intercept
Isoprene-*l*-NO_x	7	137	0.048±0.004	0.054±0.002	0.0083±0.002	0.014±0.001
Isoprene-*h*-NO_x	7	16	0.018±0.010	0.044±0.004	0.015±0.007	0.011±0.003
α-pinene-flow tube	7	51	0.044±0.009	0.079±0.010	0.0042±0.001	0.015±0.001
Limonene-flow tube	7	87	0.045±0.009	0.051±0.005	0.0027±0.002	0.014±0.001
Limonene-chamber	8	122	0.052±0.007	0.057±0.006	0.0049±0.002	0.015±0.001

162 [a]The ±95% confidence intervals for the slope and intercept are given. *l*-NO_x and *h*-NO_x refer to
163 low-NO_x and high-NO_x oxidation by OH; ozone is used as the oxidant for the remaining
164 samples.

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178 **Table S3.** Summary of experimental conditions for the chamber experiments[a]

Sample	[HC] ppm	Oxidant precursor	[NO] ppb	[NO_y] ppb	[O_3] ppb	T (°C)	Concentration (μg/m^3)	Average Size (nm)
Isoprene-*l*-NO_x	1.0	H_2O_2	<1	5	3	25	40.8	326
Isoprene-*h*-NO_x	1.1	H_2O_2	430	530	4	24	192	174
Limonene[b]	0.30	Ozone	<1	6	590	24	1251	177

179 [a]The [HC] are the initial mixing ratios after injection of the liquid precursor, the remaining
180 values were measured at the start of the sample collection.
181 [b]The Limonene chamber experiment was done in the dark.
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198 **Table S4.** Average organic to inorganic thickness ratios for each campaign

Campaign	d_{org}/d_{in} (% of thickness that is inorganic)		
	In = S, metals, etc.	**In=NaCl**	**In=$(NH_4)_2SO_4$**
CARES	12 (10%)	9.4 (12%)	3.2 (28%)
MILAGRO	9.7 (9%)	7.9 (11%)	2.7 (26%)
NAOPEX	12 (9%)	9.6 (10%)	3.2 (25%)
VOCALS	9.5 (11%)	7.7 (13%)	2.6 (30%)
YACS	12 (9%)	10 (10%)	3.4 (25%)

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