Supporting Information

Characterization of Highly Oxidized Molecules in Fresh and Aged Biogenic Secondary Organic Aerosol

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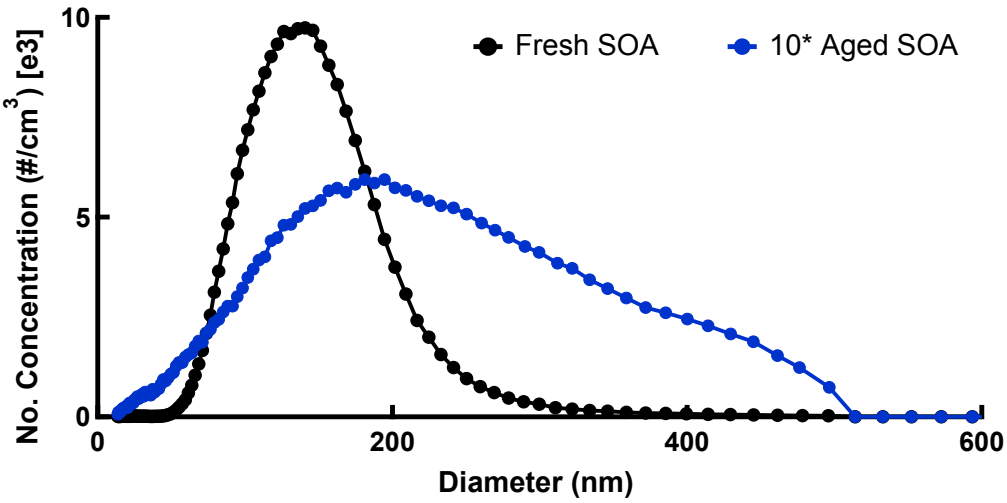

Figure S1. Example size distributions of fresh and aged SOA derived from β-pinene precursor measured with SMPS.

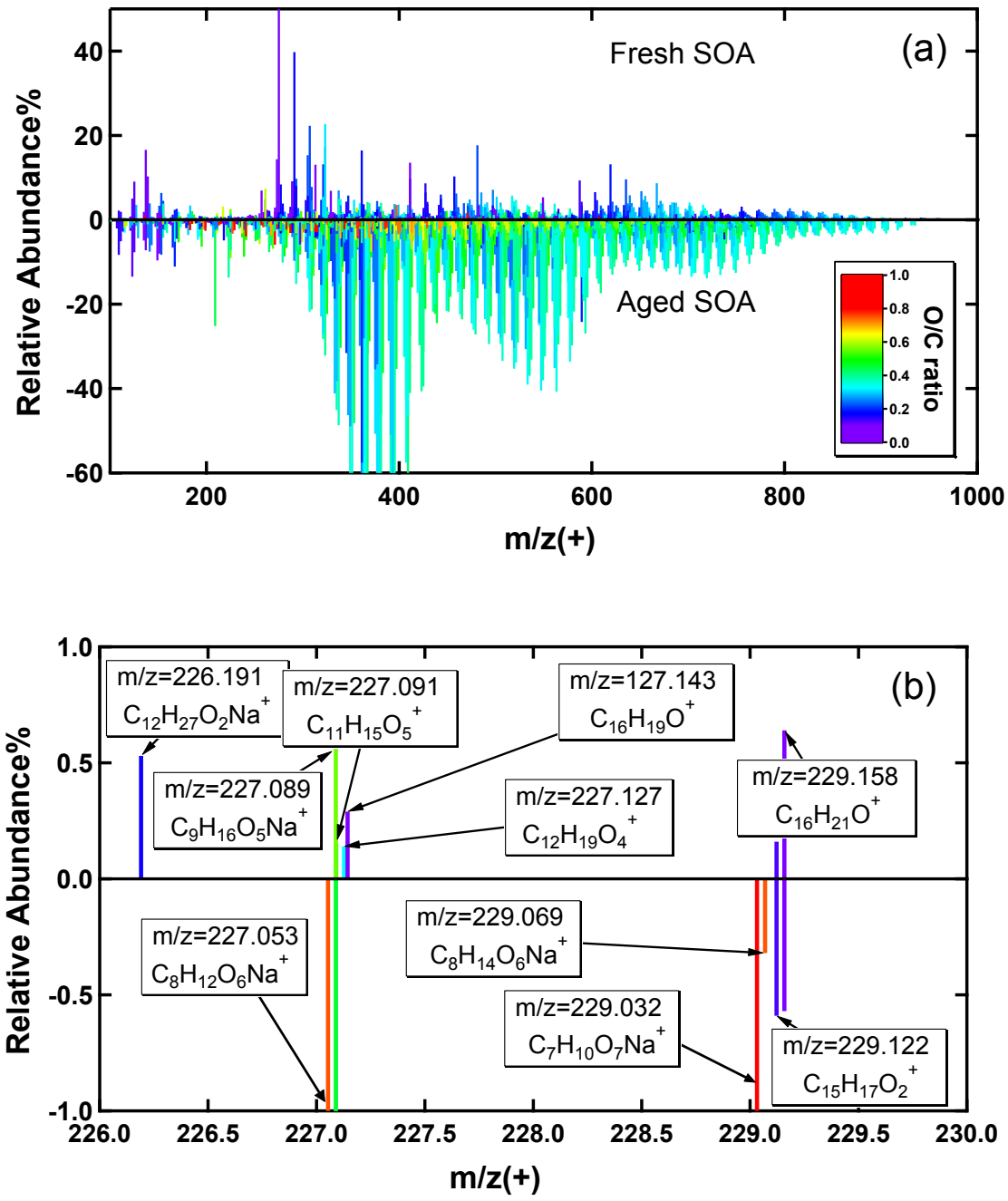

Figure S2. (a) Positive ion mode spectra comparison between fresh and aged SOA from β-pinene and (b) expanded spectra showing m/z 226-230 as an example. Abundance is plotted relative to the base peak.

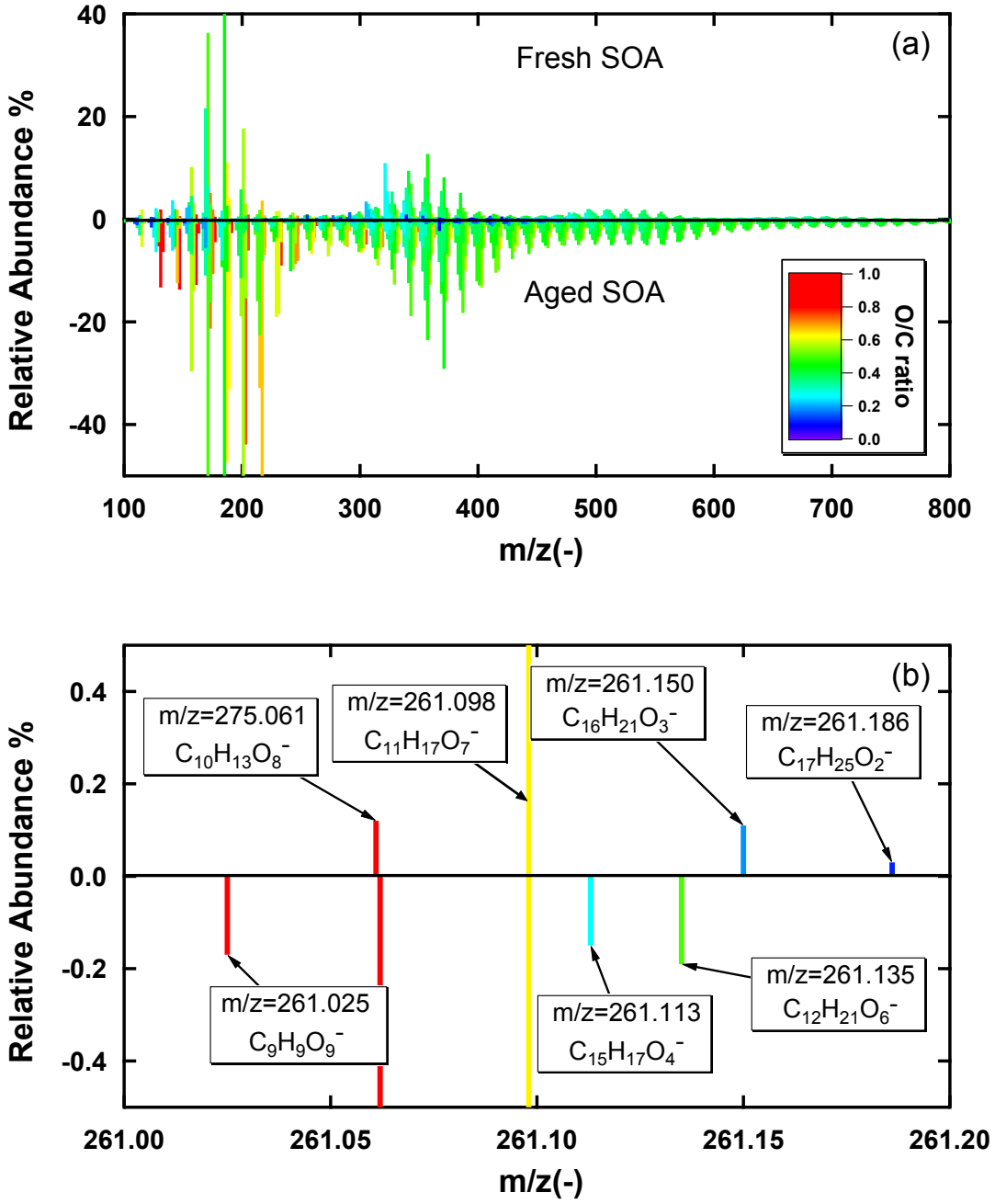

Figure S3. (a) Negative ion mode spectra comparison between fresh and aged SOA from β-pinene and (b) expanded spectra showing m/z 261.00-261.20 as an example. Abundance is plotted relative to the base peak.

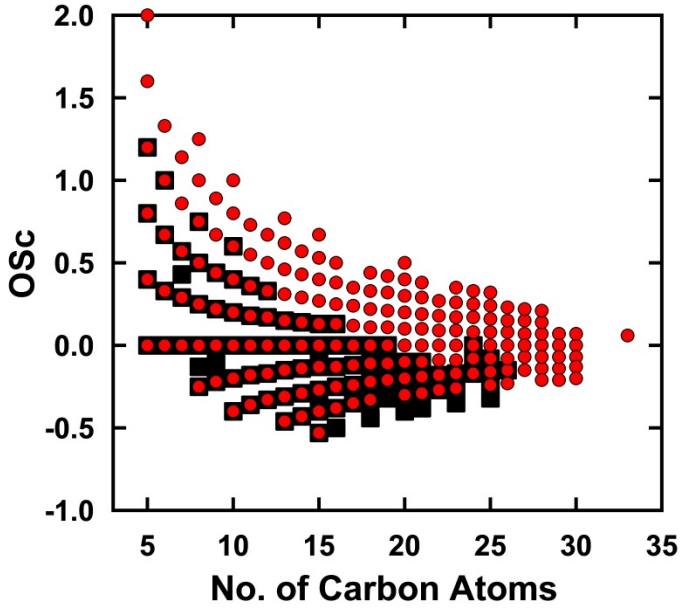

Figure S4. Carbon oxidation state vs. carbon number for the HOM assigned formulas from α-pinene SOA. Black squares represent assigned formulas observed in fresh SOA. Red circles represent assigned formulas observed in aged SOA.

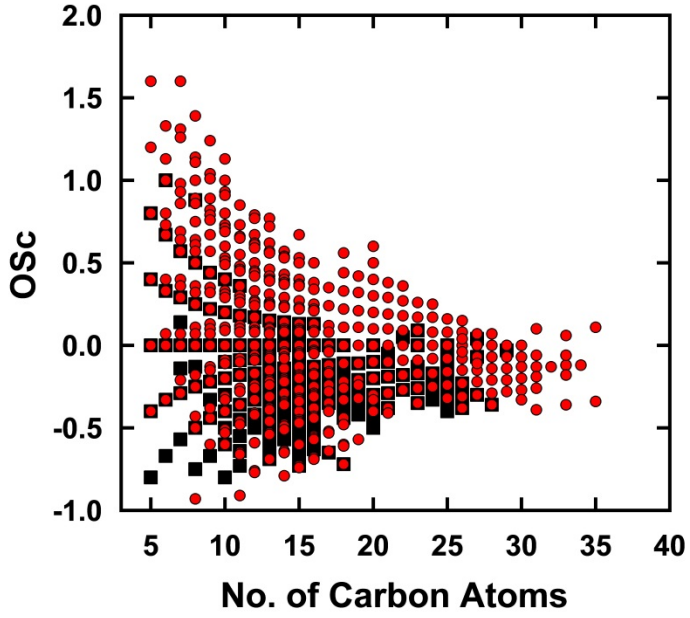

Figure S5. Carbon oxidation state vs. carbon number for the HOM assigned formulas from limonene SOA. Black squares represent assigned formulas observed in fresh SOA. Red circles represent assigned formulas observed in aged SOA.

Table S1. Experimental conditions and concentrations of particles measured by SMPS. Five replicate experiments (two at 25% RH and three at 75% RH) were carried out for generating fresh and aged SOA from β-pinene. Three replicates (one at 25% RH and two at 75% RH) were performed for fresh and aged SOA from limonene.

Precursor (ppmv)	$[O_3]$ (ppmv)	Exp. No.	Relative Humidity	[OH] (molecules cm^{-3})	Number Concentration (# cm^{-3})	Mass Concentration (μg m^{-3})
β-Pinene (≤1)	>20	1	25%	N/A	2.2E+05	4.9E+02
		2	75%	N/A	2.0E+05	5.1E+02
		3	25%	2.9E+09	2.5E+04	2.2E+02
		4	75%	8.9E+09	2.4E+04	3.1E+02
Limonene (≤1)	>20	1	25%	N/A	4.7E+05	7.9E+02
		2	75%	N/A	6.2E+05	7.6E+02
		3	25%	2.6E+09	5.2E+04	5.0E+02
		4	75%	9.2E+09	4.6E+04	4.2E+02

Table S2. Peaks and assigned formulas in SOA samples from β-pinene and limonene. Shown are average numbers and standard deviations for replicate measurements (5 for β-pinene and 3 for limonene). Approximately 70% of the assigned peaks in the positive ion spectra contained sodium.

Precursor	Sample Type	Ion Mode	Peaks Detected	Peaks Analyzed	Ions Assigned and the Percentage	Unique Molecular Formulas[a]
β-Pinene	Fresh	(+)	5473 ± 466	2767 ± 180	2654 ± 108 (95.9%)	1293 ± 83
	Aged	(+)	4037 ± 157	1921 ± 106	1808 ± 87 (94.1%)	1089 ± 75
	Fresh	(-)	3725 ± 317	2074 ± 248	1918 ± 119 (92.5%)	1096 ± 82
	Aged	(-)	4939 ± 326	2615 ± 242	2500 ± 235 (95.6%)	1517 ± 156
Limonene	Fresh	(+)	5308 ± 231	4577 ± 145	4261 ± 68 (93.1%)	1864 ± 78
	Aged	(+)	5964 ± 289	4191 ± 101	3617 ± 45 (86.3%)	2559 ± 50
	Fresh	(-)	3750 ± 223	2390 ± 65	2295 ± 66 (96.0%)	1408 ± 77
	Aged	(-)	5273 ± 381	1320 ± 85	2218 ± 71 (95.6%)	1805 ± 98

[a]After accounting for ionization and isotopic substitutions. Approximately 70% of the assigned peaks in the positive ion spectra contained sodium. None contained potassium.