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the chemistry of atmospheric organic aerosol*

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1 **Carbon oxidation state as a metric for describing the chemistry of atmospheric organic**
2 **aerosol**

3
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27
28 **Abstract**

29 A detailed understanding of the sources, transformations, and fates of organic species in the
30 environment is crucial because of the central roles that organics play in human health,
31 biogeochemical cycles, and Earth's climate. However, such an understanding is hindered by the
32 immense chemical complexity of environmental mixtures of organics; for example, atmospheric
33 organic aerosol consists of at least thousands of individual compounds, all of which likely evolve
34 chemically over their atmospheric lifetimes. Here we demonstrate the utility of describing
35 organic aerosol (and other complex organic mixtures) in terms of average carbon oxidation state
36 ($\overline{\text{OS}}_{\text{C}}$), a quantity that always increases with oxidation, and is readily measured using state-of-
37 the-art analytical techniques. Field and laboratory measurements of $\overline{\text{OS}}_{\text{C}}$, using several such
38 techniques, constrain the chemical properties of the organics and demonstrate that the formation
39 and evolution of organic aerosol involves simultaneous changes to both carbon oxidation state
40 and carbon number (n_{C}).

41 **Introduction**

42 The atmospheric oxidation of organic species is central to several key environmental chemical
43 processes that directly influence human health and global climate. These include the degradation
44 of pollutants, the production of ozone and other toxic species, and the formation and evolution of
45 fine particulate matter (aerosols). This last topic is inextricably linked to the oxidation of
46 atmospheric organics, since organic aerosol material makes up a substantial fraction (20%-90%)
47 of submicron aerosol mass¹. A large fraction of organic particulate matter is secondary organic
48 aerosol, formed from the oxidation of gas-phase organic species^{2,3}.

49 Current state-of-the art models have difficulty predicting the loadings, spatial and
50 temporal variability, and degree of oxidation of ambient organic aerosol, indicating a gap in our
51 understanding of atmospheric oxidation processes. The oxidation mechanisms of light volatile
52 organic compounds are relatively straightforward, with the canonical example being conversion
53 of methane into formaldehyde, CO, and ultimately CO₂⁴. However, the oxidation of larger
54 organics associated with secondary organic aerosol involves a much larger number of reaction
55 pathways, intermediates, and products, the detailed characterization of which is beyond the
56 capabilities of most analytical techniques. This extreme chemical complexity has prevented the
57 precise measurement and prediction of the oxidation dynamics associated with the formation and
58 evolution of atmospheric organic aerosol.

59 Here we describe a new metric for the degree of oxidation of atmospheric organic species,
60 the average carbon oxidation state ($\overline{\text{OS}}_{\text{C}}$), a quantity that necessarily increases upon oxidation
61 and is measurable using several modern analytical techniques. The general concept of average
62 carbon oxidation state has been used previously in other contexts, such as in soil chemistry for
63 the measurement of ecosystem oxidative ratios⁵, in botany for the estimation of growth yields⁶,

64 in wastewater treatment for the determination of degradation mechanisms⁷, and in atmospheric
65 chemistry to describe individual oxidation products of methane⁸ and α -pinene⁹. To our
66 knowledge $\overline{\text{OS}}_{\text{C}}$ has not been used to describe the evolving composition of a complex mixture of
67 organics undergoing dynamic oxidation processes.

68 Here we show that $\overline{\text{OS}}_{\text{C}}$, when coupled with carbon number (n_{C}), provides a framework
69 for describing the chemistry of organic species in the atmosphere, and in particular atmospheric
70 organic aerosol. These two fundamental quantities can be used to constrain the composition of
71 organic aerosol, and moreover to uniquely define key classes of atmospheric reactions, providing
72 insight into the oxidative evolution of atmospheric organics.

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74

75 **Results**

76 *Definition of $\overline{\text{OS}}_{\text{C}}$ and relationship with carbon number.* The oxidation state of carbon is defined
77 as the charge a carbon atom would take if it were to lose all electrons in bonds with more
78 electronegative atoms but gain all electrons in bonds with less electronegative atoms. This
79 quantity will necessarily increase in oxidizing environments such as Earth's atmosphere. The
80 oxidation states of individual carbon atoms within a molecule, or within a mixture of molecules,
81 may change differently upon oxidation, but the average oxidation state of the carbon ($\overline{\text{OS}}_{\text{C}}$) must
82 increase. Thus the quantity $\overline{\text{OS}}_{\text{C}}$ is an ideal metric of the degree of oxidation of organic species
83 in the atmosphere, and serves as a key quantity to describe organic mixtures that are as
84 chemically complex as organic aerosol.

85 In the atmosphere, the increase in carbon oxidation state arises from the formation of
86 bonds between carbon and oxygen (and other electronegative elements), and/or the breaking of
87 bonds between carbon and hydrogen (and other electropositive elements). This influence of both

88 electronegative and electropositive atoms has important implications for atmospheric oxidation.
89 First, metrics of oxidation that involve only one of these, such as the oxygen-to-carbon molar
90 ratio (O/C), may not accurately capture the degree of oxidation of the organics. For example, the
91 oxidation of an alcohol to a carbonyl involves no change in O/C; conversely, O/C may be
92 affected dramatically by non-oxidative processes such as hydration or dehydration. Second,
93 since the oxidation state of a carbon atom is not affected by bonds to other carbon atoms, the
94 number of carbons in a molecule (n_C) governs the range of possible values of $\overline{\text{OS}}_C$.

95 Figure 1 shows the possible combinations of $\overline{\text{OS}}_C$ and n_C for stable organic molecules
96 with a contiguous carbon skeleton, as governed by chemical valence rules. Also shown are the
97 locations in this two-dimensional space of organics that either are important in the atmosphere or
98 are commonly used as surrogates for atmospheric species. The vast majority of these species are
99 reduced ($\overline{\text{OS}}_C \leq 0$); most known compounds with higher average oxidation states are small, with
100 only 1-3 carbon atoms.

101 Reactions that govern the chemical transformation of atmospheric organics and the
102 evolution of organic aerosol involve movement in $\overline{\text{OS}}_C$ - n_C space. The oxidative transformation
103 of atmospheric organics can occur within a range of chemical environments, including in the gas
104 phase, at the gas-particle interface, or within the bulk organic or aqueous phase; non-oxidative
105 transformations (such as accretion reactions) may also occur. These chemistries can all be
106 described in terms of three key classes of reactions (Fig. 1 inset): functionalization (the oxidative
107 addition of polar functional groups to the carbon skeleton), fragmentation (the oxidative cleavage
108 of C-C bonds), and oligomerization (the association of two organic molecules). These reactions
109 are defined uniquely by the changes to $\overline{\text{OS}}_C$ and n_C of the organics; thus the $\overline{\text{OS}}_C$ - n_C space is an
110 ideal conceptual framework to describe the chemical changes that atmospheric organics undergo

111 upon oxidation. This fundamental chemical nature of the $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$ space distinguishes it from
112 other emerging two-dimensional treatments of organic aerosol¹⁰⁻¹². Such frameworks are
113 extremely useful for describing or modeling aerosol based on experimental measurements, but
114 they are based upon quantities that cannot be related to these general classes of chemical
115 reactions in a straightforward manner, and so they provide limited insight into the nature of
116 atmospheric chemical transformations (see Supporting Information for a more detailed
117 discussion).

118 In $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$ space, atmospheric oxidation has an inherent directionality: because carbon
119 oxidation state must increase upon oxidation, the ultimate end-product of the oxidation of
120 organic species (given enough time) is necessarily CO_2 ($\text{OS}_{\text{C}} = +4$). Reaching this oxidative end-
121 product requires both the addition of oxygen-containing moieties (increasing
122 $\overline{\text{OS}}_{\text{C}}$), and the breaking of C-C bonds (decreasing n_{C}). The oxidation of atmospheric organic
123 species therefore involves an overall movement towards the upper right of Fig. 1 (blue arrows).
124 Leftward movement towards larger carbon numbers (oligomer formation) certainly occurs in
125 many cases³, but even the high-molecular weight products of accretion reactions are susceptible
126 to oxidative degradation¹³ and ultimately will form CO_2 .

127

128 *Measurements of $\overline{\text{OS}}_{\text{C}}$.* A critical strength of $\overline{\text{OS}}_{\text{C}}$ as a metric of atmospheric processing of
129 organics, in addition to the fact that it must increase upon oxidation, is that it can be measured
130 routinely using state-of-the-art analytical techniques. Carbon oxidation state is determined by
131 the identity and abundance of non-carbon atoms in the organic compound(s):

132
$$\overline{\text{OS}}_{\text{C}} = -\sum_i \text{OS}_i \frac{n_i}{n_{\text{C}}} \quad (1)$$

133 in which the summation is over all non-carbon elements, OS_i is the oxidation state associated
134 with element i , and n_i/n_C is the molar ratio of element i to carbon. Thus the measurement of \overline{OS}_C
135 requires that all non-carbon elements in the sample be characterized, in terms of their relative
136 abundances and oxidation states.

137 Since atmospheric organics are primarily composed of carbon, hydrogen ($OS=+1$), and
138 reduced oxygen ($OS=-2$), Equation 1 can often be simplified to:

$$139 \quad \overline{OS}_C \approx 2 \text{ O/C} - \text{H/C} \quad (2)$$

140 This relation is exact for organics made up of only carbon, hydrogen, and most oxygen-
141 containing functional groups (alcohols, carbonyls, carboxylic acids, ethers, and esters). The
142 presence of peroxide groups (in which the O atoms have an oxidation state of -1) and
143 heteroatoms (which can have a range of oxidation states) introduces deviations from this relation.
144 These can be corrected for by measuring individual functional groups; however such moieties
145 generally represent a minor component of organic aerosol (on a per-carbon basis), so such errors
146 tend to be small. For example, the independent determination of O/C and peroxide content¹⁴
147 allows for an accurate determination of \overline{OS}_C in secondary organic aerosol formed from isoprene
148 ozonolysis; however, even for such a peroxide-rich system, Eq. 2 yields an \overline{OS}_C that is within 0.1
149 of the exact value (from Eq. 1). Similarly, the measurement of nitrogen-containing functional
150 groups allows for N atoms to be explicitly included in the determination of \overline{OS}_C , though organic
151 nitrogen is a sufficiently small fraction of organic particulate matter that this has a relatively
152 minor effect on calculated \overline{OS}_C (see Supporting Information). Nonetheless, in some cases these
153 moieties might be present in relatively high abundances, and their effect on measured \overline{OS}_C is an
154 important topic for future research.

155 Here we focus on the simplified determination of $\overline{\text{OS}}_{\text{C}}$ from Equation 2, based on
156 measurements of O/C and H/C only. A number of analytical techniques can be used to
157 determine elemental ratios, and therefore $\overline{\text{OS}}_{\text{C}}$, of atmospheric particulate matter. These include
158 combustion analysis (CHNS)¹⁵⁻¹⁷, ultrahigh resolution mass spectrometry with electrospray
159 ionization (ESI)^{14,18-21}, nuclear magnetic resonance (NMR) spectroscopy²², Fourier transform
160 infrared spectroscopy (FTIR)²³, X-ray photoelectron spectroscopy (XPS)²⁴, and high-resolution
161 electron impact aerosol mass spectrometry (HR-AMS)²⁵⁻³⁰. Each technique has its own strengths
162 and weaknesses for characterizing organic aerosol. For example, CHNS analysis is accurate and
163 universal, but requires large amounts of collected organics, and oxygen content is usually
164 determined only by subtraction. ESI can provide exact elemental ratios of individual compounds
165 within a complex mixture, and requires very little sample volume; however it is a selective
166 ionization technique, with response factors that may vary widely among different species. HR-
167 AMS is a sensitive, online technique for measuring elemental ratios in real time, but is not as
168 accurate as other techniques, since it requires uncertain empirical corrections to account for
169 biases during ion fragmentation.²⁵ Because of the uncertainties associated with each technique, it
170 is useful to examine results from a range of elemental analysis approaches in order to obtain an
171 accurate, complete picture of the carbon oxidation state of organic aerosol.

172

173 *Atmospheric organic aerosol and $\overline{\text{OS}}_{\text{C}}$.* Table 1 presents compiled measurements of the mean
174 carbon oxidation state of organic aerosol, taken from measurements of O/C and H/C using the
175 three most widely-used elemental analysis techniques (CHNS, ESI, and HR-AMS). These
176 include measurements of ambient organic aerosol, ambient aerosol fractions (by physical
177 extraction or factor analysis), and laboratory-generated primary or secondary organic aerosol.

178 A consistent picture emerges from these results: the $\overline{\text{OS}}_{\text{C}}$ of organic aerosol ranges from -2 to
179 +1, depending on the level of atmospheric aging. Individual species in organic aerosol, such as
180 oxalate and other highly oxidized species, may have oxidation states greater than +1, but all
181 available data suggest that the average carbon oxidation state of organic aerosol rarely exceeds
182 this value. Even classes of organics that are generally considered to be highly oxidized, such as
183 humic-like substances (HULIS) and oxygenated organic aerosol (OOA), have an $\overline{\text{OS}}_{\text{C}}$ below +1.
184 It appears that more highly oxidized carbon is found predominantly in the gas phase,
185 presumably because species with several (>3) adjacent carbonyl groups are thermodynamically
186 or photochemically unstable, and will rapidly decompose to smaller species.

187 Figure 2 shows the approximate area in $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$ space corresponding to atmospheric
188 organic aerosol, based upon the $\overline{\text{OS}}_{\text{C}}$ measurements shown in Table 1, and determinations of n_{C}
189 from ultrahigh resolution ESI and/or known relationships between volatility and carbon
190 number³¹. Results from AMS/volatility measurements and from ESI data are remarkably
191 consistent, placing aerosol components in the areas of $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$ space corresponding to large
192 and/or polar organics. Particle-phase organics, specifically the most oxidized fraction (HULIS,
193 OOA, etc.), lie in between the large, reduced species ($n_{\text{C}} \geq 5$, $\overline{\text{OS}}_{\text{C}} < -1$) and the oxidative
194 endpoint CO_2 . Thus secondary organic aerosol is not the product of only a few select
195 hydrocarbons but rather is formed in the oxidation of most organic species. The only reduced
196 organic species unlikely to contribute to aerosol formation upon oxidation are small (four
197 carbons or fewer), though even those might form organic aerosol via oligomerization reactions.
198 The potential formation of aerosol from such a wide variety of organic species is a likely
199 contributor to underestimates of secondary organic aerosol concentrations, since models (and

200 the experiments on which they are based) typically focus on only a few select aerosol
201 precursors³.
202
203 *Chemical Complexity.* Most points in $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$ space represent a multitude of compounds; for
204 example, the point corresponding to $n_{\text{C}} = 2$ and $\overline{\text{OS}}_{\text{C}} = -1$ includes acetylene (C_2H_2),
205 acetaldehyde (CH_3CHO), and ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) (these compounds are related to
206 each other by the nominal gain/loss of H_2O , which involves no change in $\overline{\text{OS}}_{\text{C}}$ or n_{C}). The
207 number of possible chemical structures (chemical complexity) is a strong function of not only
208 n_{C} ³² but also oxidation state. Figure 3 shows the number of possible structures for just a single
209 carbon skeleton (an unbranched, acyclic carbon chain), with carbonyl, alcohol, and/or
210 carboxylic acid groups. For a given carbon number, only one structure (the n -alkane) is
211 possible at the lowest $\overline{\text{OS}}_{\text{C}}$ value. The number of possible structures then increases rapidly with
212 $\overline{\text{OS}}_{\text{C}}$, due to the combinatorial addition of different functional groups to different carbon atoms.
213 The maximum in chemical complexity is located at $\overline{\text{OS}}_{\text{C}} = 0$; for molecules in which the
214 average carbon atom is oxidized ($\overline{\text{OS}}_{\text{C}} > 0$), the number of possible chemical structures then
215 decreases with increasing oxidation state.

216 Many of the compounds that make up organic aerosol (Figure 2) lie in the region of
217 maximum chemical complexity (Figure 3). This underscores the enormous experimental and
218 theoretical challenges associated with describing aerosol in terms of its individual molecular
219 components. The number of oxidized organics ($-1 \leq \overline{\text{OS}}_{\text{C}} \leq +1$) is far greater than can
220 reasonably be constrained by measurements of ambient species, laboratory studies of reaction
221 rates and products, or explicit models of the fate of individual atmospheric compounds. The
222 sheer number of possible species in organic aerosol indicates that a completely speciated

223 approach is probably not feasible for a generalized description of organic aerosol. This is
224 especially true for regional or global air-quality and climate models, which instead require
225 concise descriptions of atmospheric organic mixtures in terms of measurable ensemble
226 quantities such as $\overline{\text{OS}}_C$.

227

228 *Oxidative transformations of atmospheric organics.* In order to be accurate, such concise
229 descriptions must properly capture the oxidation mechanisms of atmospheric organic species.
230 This underscores the critical importance of the measurement of selected individual species
231 within organic aerosol to characterize reaction pathways, as well as to identify aerosol sources
232 and toxic species. Insight into oxidation mechanisms can be obtained from experimental studies
233 of the multigenerational oxidation products of individual organics; results from several such
234 studies, mapped onto $\overline{\text{OS}}_C$ - n_C space, are shown in Figure 4. These results were obtained using
235 a range of analytical techniques, including ensemble measurements of condensed-phase
236 organics (HR-AMS and XPS) and speciated measurements of gas- and particle-phase organics
237 (various mass spectrometric techniques).

238 For all systems studied (Fig. 4), oxidation leads to increased functionality on the carbon
239 skeleton (higher $\overline{\text{OS}}_C$), and, after only a few (1-4) generations of oxidation, a decrease in carbon
240 number of the original carbon skeleton (lower n_C). Fragmentation reactions are therefore key
241 processes in the oxidative aging of atmospheric organics, particularly for oxidized species,
242 whose oxygen-containing (electron-withdrawing) groups weaken adjacent carbon-carbon
243 bonds³³. This increase in $\overline{\text{OS}}_C$ towards CO_2 can occur via multiple reaction pathways, as
244 illustrated by the numerous individual products of isoprene and α -pinene oxidation (circles in

245 Fig. 4). The ensemble measurements (lines in Fig. 4) constrain the mean values of \overline{OS}_C , with
246 individual compounds spanning a range in oxidation state, carbon number, and volatility.

247

248 **Discussion**

249 Oxidation of organics has long been viewed as a source of atmospheric organic aerosol, via
250 secondary organic aerosol formation. However the ultimate dominance of fragmentation
251 reactions (movement to the top right of \overline{OS}_C-n_C space) means that oxidation may also serve as a
252 organic aerosol sink, since oxidized organics may fragment and volatilize upon further oxidation.
253 The effects of such oxidative degradation reactions on atmospheric aerosol are governed by
254 reaction rates, given the relatively short lifetime of atmospheric PM via physical deposition (~1
255 week). This implies that better constraints on the kinetics of key organic “aging” reactions are
256 needed for the accurate prediction of the loadings, properties, and effects of atmospheric organic
257 aerosol.

258 Nonetheless, it is known that the heterogeneous degradation of organic PM by gas-phase
259 oxidants is generally substantially slower than of gas-phase organics³⁴, since most particulate
260 organics are shielded from gas-phase radicals interacting with the particle surface. Thus organic
261 aerosol represents a “metastable state” in which partially oxidized organics can survive for a
262 substantial period of time, even under highly oxidizing conditions. This view of organic aerosol
263 as a chemically recalcitrant intermediate in the oxidation of organic species resembles the
264 emerging view of the nature of humic materials in soils and aquatic systems^{35,36}. In this sense
265 the similarities between atmospheric particulate organics and humic materials may extend well
266 beyond their chemical complexity and physicochemical properties^{22,37}, to include their role as a
267 “transition state” of organic matter³⁶. While detailed chemical structures and transformations are

268 likely to be quite different (for example, biological processes do not affect atmospheric organics
269 to the extent that they do for humic substances), the similarities suggest strong commonalities in
270 the description and experimental studies of such highly complex environmental organic
271 mixtures.

272 The description of the chemistry of organic species in terms of changes to their average
273 carbon oxidation state (a universal, unambiguous metric for the degree of oxidation of carbon-
274 containing species) and carbon number may thus be useful for describing not only atmospheric
275 oxidation but also other complex reactive systems as well. This includes the formation and
276 evolution of humic substances in soil or aquatic systems, the combustion of complex organic
277 species, the formation or weathering of fossil fuels, and the chemical transformation of organics
278 in oxygen-limited environments. Such systems can involve reactions other than the oxidative
279 processes that govern atmospheric reactions, and therefore may exhibit trajectories in $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$
280 space different than those shown in Figure 4. For example, reduction moves organics downward
281 and to the right (towards methane, $\text{OS}_{\text{C}} = -4$ and $n_{\text{C}} = 1$), whereas radical association reactions in
282 low-oxygen environments (such as fuel-rich flames and some planetary atmospheres³⁸), involve
283 leftward movement, towards polycyclic aromatic hydrocarbons and eventually elemental carbon
284 ($\overline{\text{OS}}_{\text{C}} = 0$ and $n_{\text{C}} \rightarrow \infty$). The measurement of $\overline{\text{OS}}_{\text{C}}$ allows for the determination of these trajectories
285 for entire mixtures, offering the potential for simple, predictive models of these exceedingly
286 complex chemical systems.

287
288

289 **Methods**

290

291 *Determination of average carbon oxidation state.*

292 All $\overline{\text{OS}}_{\text{C}}$ values reported in Table 1 and illustrated in Figures 2 and 4 were determined using
293 Equation 2. The one exception is the $\overline{\text{OS}}_{\text{C}}$ of secondary organic aerosol formed from the
294 photooxidation of alkenes¹⁵; the high contribution of organic nitrates (N/C=0.1) requires the
295 explicit inclusion of nitrogen ($\text{OS}_{\text{N}}=+5$). A discussion of the potential errors associated with
296 neglecting heteroatoms in Eq. 2 is given in the Supplementary Information.

297 Ensemble (average) elemental ratios were taken mostly from previously reported
298 measurements. For AMS^{25-30,39,40} and CHNS data¹⁵⁻¹⁷, O/C and H/C ratios are taken directly
299 from reported measurements. For ultrahigh resolution ESI data^{14,18-21}, O/C and H/C are
300 determined by averaging the elemental ratios of all measured CHO species, weighted by ion
301 intensity¹⁹. For XPS data²⁴ (C1s spectra at 430 eV), all carbon was categorized as C=C, CH_x, C-
302 OH, C=O or C(O)OH based on its measured binding energy, allowing for the estimation of O/C
303 and H/C ratios. Additional details of these measurements are provided in the Supporting
304 Information.

305

306 *Estimation of carbon number.*

307 The number of carbon atoms per molecule (n_{C}) in ambient organic aerosol (Figure 2) was either
308 determined from speciated measurements (ESI data) or estimated based on measurements of
309 particle volatility and OSc (AMS data). This latter approach utilizes the SIMPOL.1 structure-
310 activity relationship⁴¹ to relate saturation vapor pressure, degree of oxidation, and n_{C} .³¹ Vapor
311 pressures of organic aerosol classes are based on recent *in situ* thermodenuder measurements.⁴²

312 The effects of functional groups on vapor pressure is estimated by assuming that each oxygen
313 atom decreases the volatility of an organic molecule by a factor of 0.06 (consistent with the
314 addition of carboxylic acids to the carbon skeleton), with oxygen content calculated from \overline{OS}_C
315 using an empirical relationship that relates elemental ratios ($O/C+H/C=2$).¹² In the
316 multigenerational oxidation experiments (AMS and XPS traces in Figure 4), ensemble values of
317 n_C were determined by assuming that fractional changes in carbon number are equal to the
318 fraction of carbon remaining in the particle phase after oxidation.

319

320 *Multigenerational oxidation experiments.*

321 The oxidation trajectories in \overline{OS}_C-n_C space (Figure 4) were determined from laboratory studies
322 of the oxidation of individual organic species. Gas-phase and particle-phase (monomeric)
323 products of the OH-initiated oxidation of isoprene and α -pinene were measured by various
324 speciated techniques.⁴³⁻⁴⁹ The heterogeneous oxidation reactions of squalane, triacontane, and
325 levoglucosan were carried out by sending nucleated particles into a flow reactor, where they
326 were exposed to high concentrations of OH generated by ozone photolysis.^{39,40} Changes to
327 particle mass and elemental ratios upon oxidation were characterized using a scanning mobility
328 particle sizer and an HR-AMS. For the oxidation of coronene,²⁴ vapor-deposited thin films of
329 coronene (4-6 Å thickness) were exposed to varying levels of OH or O₃, and the chemical
330 changes measured by XPS using the Ambient Pressure Photoemission Spectrometer at beamline
331 11.0.2 of the Advanced Light Source (Berkeley, CA). The evolving abundance and type of
332 carbon in the film was determined using C1s spectra at 430 eV. Experimental details are
333 provided in the Supporting Information.

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Author Contributions: The work described here was originally conceived by J.H.K. with C.E.K. and D.R.W., with substantial input by N.M.D., J.L.J., M.R.C, S.H.K, and K.R.W. K.E.A., L.R.M., and A.S.W. provided the ESI data (Table 1 and Figure 2). S.H.K. carried out the combinatorial calculations to produce Fig. 3. Data on the aging of organics (Figure 4) were collected by J.D.S, S.H.K., J.H.K., and K.R.W. (squalane, triacontane, and levoglucosan) and E.R.M., J.D.S, K.R.W., and H.B. (coronene). J.H.K. wrote the paper with input from all co-authors, especially N.M.D., J.L.J, M.R.C., and C.E.K.; J.H.K., N.M.D., H.B. and E.R.M. wrote the Supporting Information.

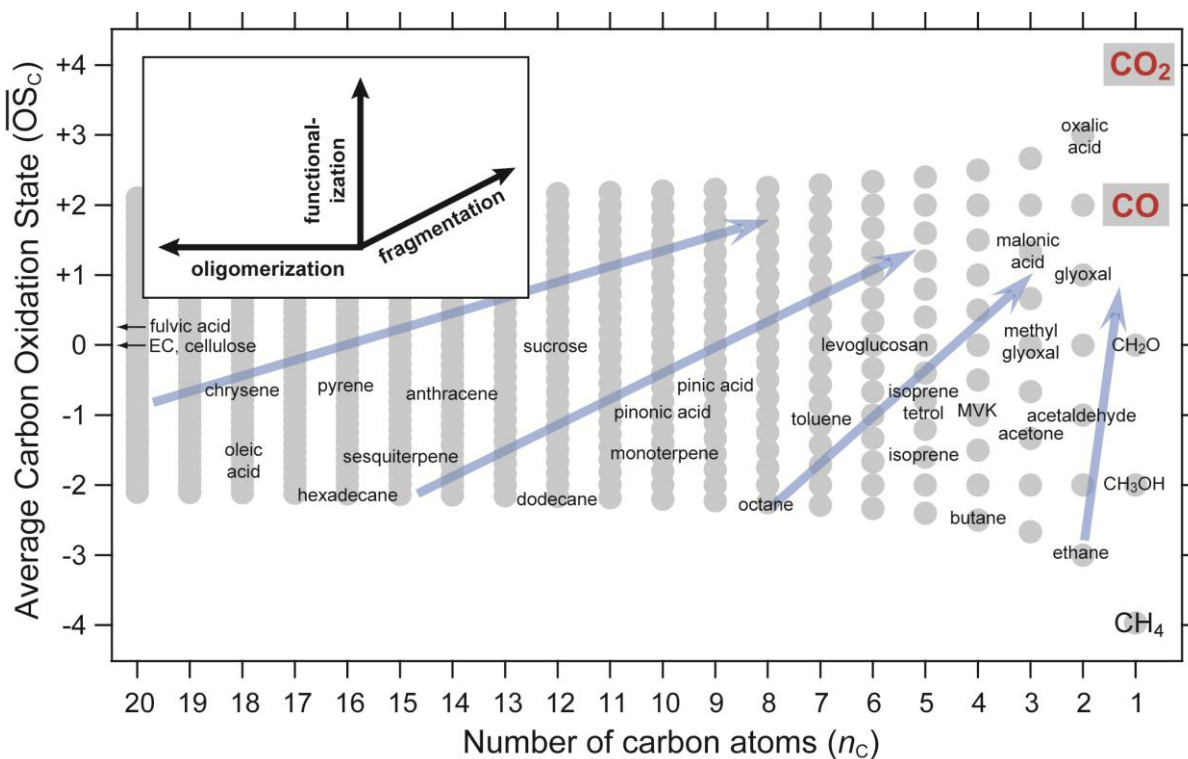
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359 **Table 1.** Measurements of $\overline{\text{OS}}_{\text{C}}$ of organic aerosol, using various analytical techniques: aerosol
 360 mass spectrometry (AMS), ultrahigh resolution mass spectrometry with electrospray ionization
 361 (ESI), and combustion techniques (CHNS). Values listed are the $\overline{\text{OS}}_{\text{C}}$ ensemble averages for a
 362 given sample, with “...” denoting a range of reported values; $\overline{\text{OS}}_{\text{C}}$ values of individual
 363 molecules within a sample may be distributed around these averages, as illustrated in Figure 2.
 364
 365

| <i>Ambient Organic Aerosol</i> | $\overline{\text{OS}}_{\text{C}}$ | Technique | Ref. |
|--|-----------------------------------|------------------|-------------|
| Urban/anthropogenic (Mexico City) | -1.6...+0.1 | AMS | 25 |
| Remote/biogenic (Amazonian rainforest) | -0.9...-0.2 | AMS | 30 |
| Aged (Whistler Mountain) | -0.6...+0.6 | AMS | 29 |
| | | | |
| <i>Ambient Aerosol Fractions</i> | | | |
| Hydrocarbon-like organic aerosol (HOA) | -1.7...-1.6 | AMS | 25 |
| Semivolatile oxygenated organic aerosol (SV-OOA) | -0.5...0.0 | AMS | 25 |
| Low-volatility oxygenated organic aerosol (LV-OOA) | +0.5...+0.9 | AMS | 25 |
| Humic-Like Substances (HULIS) | -0.4...-0.3 | CHNS | 16,17 |
| Water-soluble organic carbon (WSOC) in rainwater | -0.9...-0.7 | ESI | 18 |
| WSOC in aerosol | -1.0 | ESI | 20 |
| WSOC in fogwater | -0.7 | ESI | 21 |
| | | | |
| <i>Primary Organic Aerosol</i> | | | |
| Vehicle exhaust (gasoline, diesel) | -2.0...-1.9 | AMS | 25 |
| Biomass burning aerosol | -1.0...-0.7 | AMS | 25 |
| | | | |
| <i>Secondary Organic Aerosol</i> | | | |
| Monoterpene + O ₃ | -1.1...-0.5 | AMS, ESI | 19,25,26,28 |
| Isoprene + OH or O ₃ | -0.8...-0.2 | AMS, ESI | 14,25,28 |
| Monoaromatics + OH | -0.9...+0.1 | AMS | 25,28 |
| Alkane/alkene photooxidation | -0.7...-0.4 | AMS, CHNS | 15,27 |
| | | | |

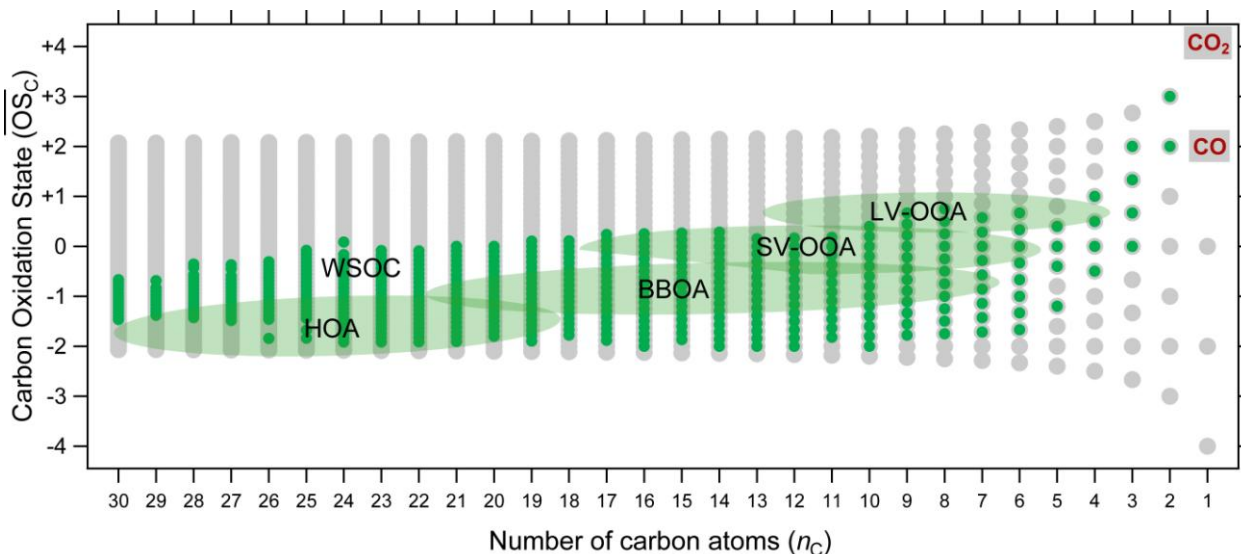
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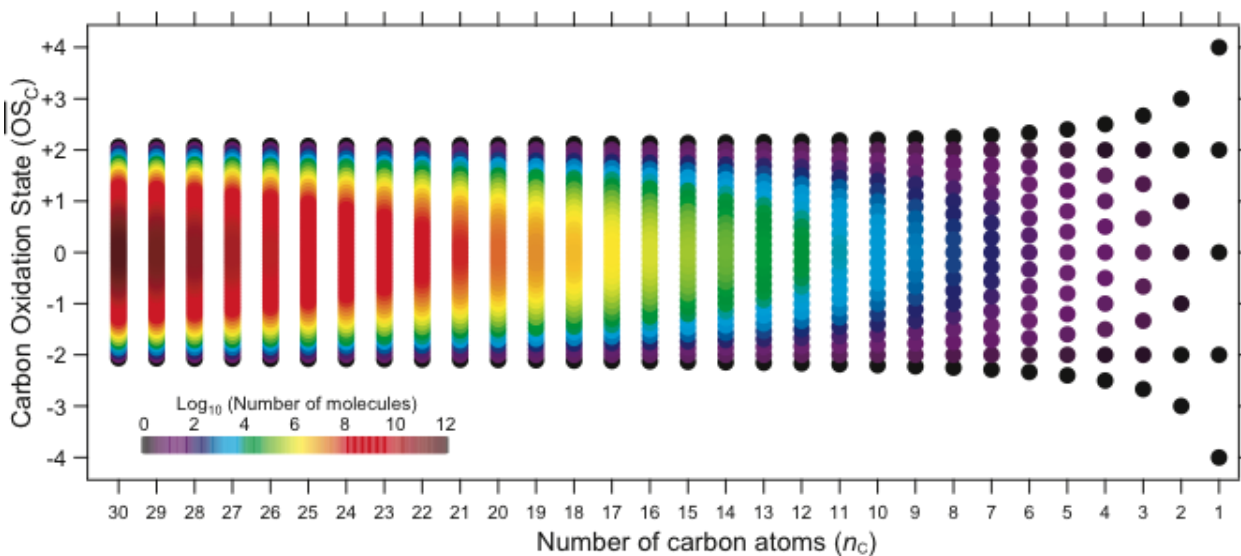
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370 **Figure 1.** Possible combinations of average carbon oxidation state (\overline{OS}_c) and number of carbon
 371 atoms (n_c) for stable organic molecules. Any organic species can be placed in this two-
 372 dimensional space; the locations of key atmospheric organics (and common surrogate species)
 373 are shown. The vast majority of known atmospheric species are reduced ($\overline{OS}_c \leq 0$), with only the
 374 smallest compounds having higher oxidation states. Inset: vectors corresponding to key classes
 375 of reactions of atmospheric organics, functionalization (addition of polar functional groups),
 376 fragmentation (cleavage of C-C bonds), and oligomerization (covalent association of two organic
 377 species). The combination of these reaction types leads to complex movement through \overline{OS}_c - n_c
 378 space; however, the inevitable increase in \overline{OS}_c with atmospheric oxidation implies that, given
 379 enough time, organics will generally move up and to the right (blue arrows), towards CO_2 .



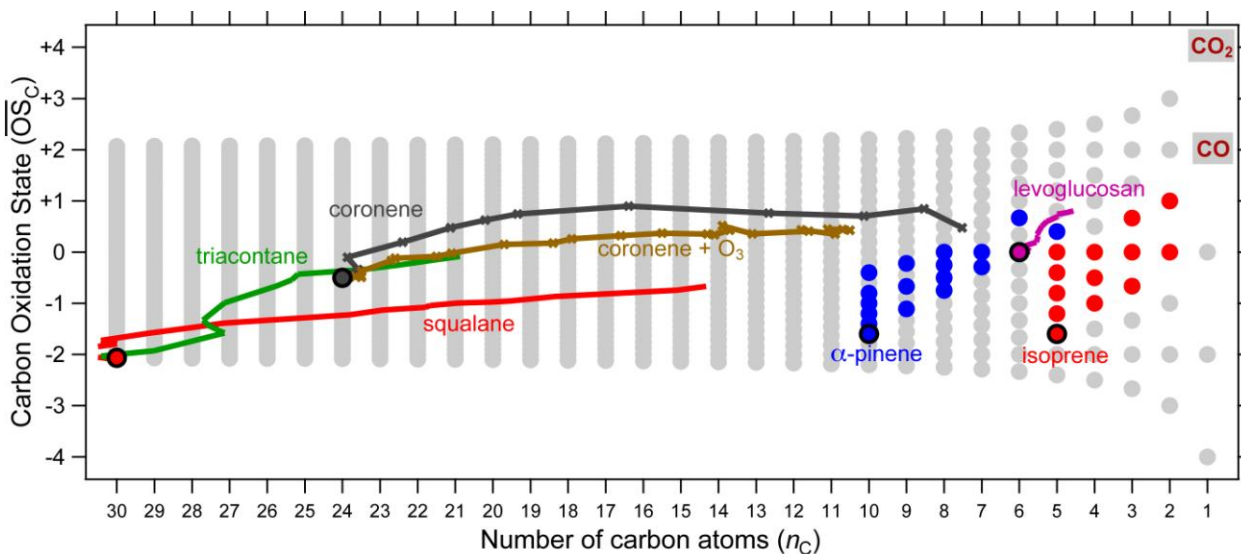
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382 **Figure 2.** Location in \overline{OS}_C - n_C space of organic aerosol, based upon \overline{OS}_C measurements of
 383 organic aerosol (Table 1). Green circles: locations of individual components of water-soluble
 384 organic compounds (WSOC), as measured by ultrahigh resolution mass spectrometry with
 385 electrospray ionization.^{20,21} Green ovals: locations of different organic aerosol classes, as
 386 determined from factor analysis of AMS data²⁵ and estimation of n_C from volatility
 387 measurements.³¹ Hydrocarbon-like organic aerosol (HOA) and biomass burning organic aerosol
 388 (BBOA) correspond to primary particulate matter directly emitted into the atmosphere.
 389 Semivolatile and low-volatility oxidized organic aerosol (SV-OOA and LV-OOA) correspond to
 390 “fresh” and “aged” secondary aerosol produced by multi-step oxidation reactions.¹¹ These
 391 aerosol species and types fall along the rough oxidation trajectories shown in Fig. 1, according to
 392 their degree of oxidation. The apparent absence of large ($n_C \geq 5$), highly oxidized ($\overline{OS}_C > 1$)
 393 organics in organic aerosol is likely due to the thermodynamic and photochemical instability of
 394 such species.
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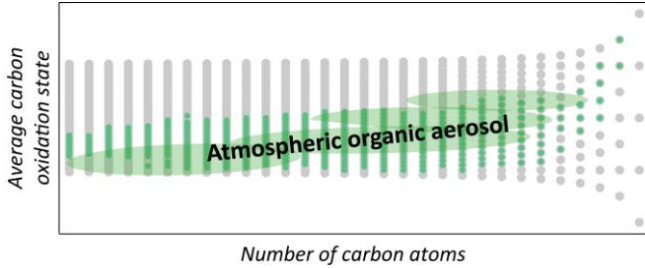
398 **Figure 3.** Chemical complexity of organics as a function of oxidation state and carbon number.
399 Points are colored by the logarithm (base 10) of the number of possible compounds at a given
400 \overline{OS}_C and n_C , assuming an unbranched, acyclic carbon skeleton, and the addition of carbonyl,
401 alcohol, and acid groups only. Including a wider range of carbon skeletons or functional groups
402 will lead to a dramatically steeper increase in chemical complexity with \overline{OS}_C and n_C .³²
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Figure 4. Oxidation trajectories in \overline{OS}_C - n_C space, as determined from laboratory studies of oxidation reactions. OH is used as the oxidant except as noted. Results from three independent experimental and analytical approaches are shown: the heterogeneous oxidation of pure organic particles, measured with HR-AMS (solid lines)^{39,40}; the heterogeneous oxidation of thin films, measured by XPS (crossed lines)²⁴; and the gas-phase oxidation of hydrocarbons, measured by various techniques to speciate gas- and particle-phase organics (solid circles)⁴³⁻⁴⁹. In most cases, oxidation initially adds functional groups to the carbon skeleton (upwards movement), but later oxidation steps involve a decrease in n_C via the breaking of carbon-carbon bonds (movement upwards and to the right), indicating the crucial role of fragmentation reactions in photochemical aging and aerosol evolution. For clarity, only monomeric products are shown; the formation of oligomers also entails initial movement to the left, but since these oligomeric species are composed of monomeric subunits, they will display the same general trajectories upon oxidation.

421 **Table of Contents Graphic**
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424

425 **Table of Contents Summary**

426 Organic aerosol particles are centrally important to climate and human health, but remain poorly
427 characterized on account of their immense chemical complexity. Here, using both field and
428 laboratory measurements of organic aerosol, we demonstrate the use of average carbon oxidation
429 state (\overline{OS}_C) for describing aerosol chemical properties and atmospheric transformations.
430

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