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### **Title**

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

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### **Author**

Kroll, Jesse H.

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

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4 Jesse H. Kroll<sup>1,2\*</sup>, Neil M. Donahue<sup>3</sup>, Jose L. Jimenez<sup>4</sup>, Sean H. Kessler<sup>2</sup>, Manjula R.  
5 Canagaratna<sup>5</sup>, Kevin R. Wilson<sup>6</sup>, Katye E. Altieri<sup>7</sup>, Lynn R. Mazzoleni<sup>8</sup>, Andrew S. Wozniak<sup>9</sup>,  
6 Hendrik Bluhm<sup>6</sup>, Erin R. Mysak<sup>6,‡</sup>, Jared D. Smith<sup>6,‡</sup>, Charles E. Kolb<sup>5</sup>, and Douglas R.  
7 Worsnop<sup>5,10,11,12</sup>

8  
9 <sup>1</sup>*Department of Civil and Environmental Engineering, Massachusetts Institute of Technology,*  
10 *Cambridge MA*

11 <sup>2</sup>*Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge MA*

12 <sup>3</sup>*Center for Atmospheric Particle Studies, Carnegie Mellon University, Pittsburgh PA*

13 <sup>4</sup>*Cooperative Institute for Research in the Environmental Sciences and Department of Chemistry*  
14 *and Biochemistry, University of Colorado, Boulder, CO*

15 <sup>5</sup>*Center for Aerosol and Cloud Chemistry, Aerodyne Research, Inc., Billerica MA*

16 <sup>6</sup>*Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA*

17 <sup>7</sup>*Department of Geosciences, Princeton University, Princeton NJ*

18 <sup>8</sup>*Department of Chemistry, Michigan Technological University, Houghton MI*

19 <sup>9</sup>*Department of Chemistry and Biochemistry, Old Dominion University, Norfolk VA*

20 <sup>10</sup>*Department of Physics, University of Helsinki, Helsinki, Finland*

21 <sup>11</sup>*Finnish Meteorological Institute, Helsinki, Finland*

22 <sup>12</sup>*Department of Physics, University of Kuopio, Kuopio, Finland*

23  
24 *\* Corresponding author. E-mail: jhkroll@mit.edu*

25 *‡ present address: L.J. Smith and Associates, Rogers AR; ‡ present address: Straus Center for*  
26 *Conservation and Technical Studies, Harvard Art Museum, Cambridge MA*

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 ( $n_{\text{C}}$ ).

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## 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 mass<sup>1</sup>. A large fraction of organic particulate matter is secondary organic  
48 aerosol, formed from the oxidation of gas-phase organic species<sup>2,3</sup>.

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 CO<sub>2</sub><sup>4</sup>. However, the oxidation of larger  
54 organics associated with SOA involves a much larger number of reaction pathways,  
55 intermediates, and products, the detailed characterization of which is beyond the capabilities of  
56 most analytical techniques. This extreme chemical complexity has prevented the precise  
57 measurement and prediction of the oxidation dynamics associated with the formation and  
58 evolution of atmospheric organic aerosol.

59 Here we present 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 that is measurable using several modern analytical techniques. The general concept of  
62 average carbon oxidation state has been used previously in other contexts, such as in soil  
63 chemistry for the measurement of ecosystem oxidative ratios<sup>5</sup>, in botany for the estimation of

64 growth yields<sup>6</sup>, in wastewater treatment for the determination of degradation mechanisms<sup>7</sup>, and  
65 in atmospheric chemistry to describe individual oxidation products of methane<sup>8</sup> and  $\alpha$ -pinene<sup>9</sup>.  
66 To our knowledge  $\overline{\text{OS}}_{\text{C}}$  has never been used to describe the evolving composition of a complex  
67 mixture of organics undergoing dynamic oxidation processes.

68 Here we show that  $\overline{\text{OS}}_{\text{C}}$ , when coupled with carbon number ( $n_{\text{C}}$ ), 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.

73  
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 as chemically  
84 complex as secondary 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 are either important in the atmosphere or  
98 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 aerosol<sup>10-12</sup>. 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  $\text{CO}_2$  ( $\text{OS}_{\text{C}} = +4$ ). 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  $n_{\text{C}}$ ). 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 cases<sup>3</sup>, but even the high-molecular weight products of accretion reactions are susceptible  
126 to oxidative degradation<sup>13</sup> and ultimately will form  $\text{CO}_2$ .

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 rapidly and routinely using state-of-the-art analytical techniques. Carbon oxidation state is  
131 determined by 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 state.

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:

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

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 content<sup>14</sup>  
147 allows for an accurate determination of  $\overline{OS}_C$  in secondary organic aerosol; however, even for  
148 such a peroxide-rich system, Eq. 2 yields an  $\overline{OS}_C$  that is within 0.1 of the exact value (from Eq.  
149 1). Similarly, the measurement of nitrogen-containing functional groups allows for N atoms to be  
150 explicitly included in the determination of  $\overline{OS}_C$ , though organic nitrogen is a sufficiently small  
151 fraction of organic particulate matter that this has a relatively minor effect on calculated  $\overline{OS}_C$   
152 (see Supporting Information). Nonetheless, in some cases these moieties might be present in  
153 relatively high abundances, and their effect on measured  $\overline{OS}_C$  is an important topic for future  
154 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)<sup>15-17</sup>, ultrahigh resolution mass spectrometry with electrospray  
159 ionization (ESI)<sup>14,18-22</sup>, nuclear magnetic resonance (NMR) spectroscopy<sup>23</sup>, Fourier transform  
160 infrared spectroscopy (FTIR)<sup>24</sup>, X-ray photoelectron spectroscopy (XPS)<sup>25</sup>, and high-resolution  
161 electron impact aerosol mass spectrometry (HR-AMS)<sup>26-31</sup>. 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.<sup>26</sup> 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 *Ambient 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  $\overline{\text{OS}}_C$  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  $\overline{\text{OS}}_C$  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.

187 Figure 2 shows the approximate area in  $\overline{\text{OS}}_C-n_C$  space corresponding to atmospheric  
188 organic aerosol, based upon the  $\overline{\text{OS}}_C$  measurements shown in Table 1, and determinations of  $n_C$   
189 from ultrahigh resolution ESI and/or known relationships between volatility and carbon  
190 number<sup>32</sup>. Results from AMS/volatility measurements and from ESI data are remarkably  
191 consistent, placing aerosol components in the areas of  $\overline{\text{OS}}_C-n_C$  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 ( $n_C \geq 5$ ,  $\overline{\text{OS}}_C < -1$ ) and the oxidative  
194 endpoint  $\text{CO}_2$ . 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 precursors<sup>3</sup>.  
202  
203 *Chemical Complexity.* Most points in  $\overline{\text{OS}}_c$ - $n_C$  space represent a multitude of compounds; for  
204 example, the point corresponding to  $n_C = 2$  and  $\overline{\text{OS}}_c = -1$  includes acetylene ( $\text{C}_2\text{H}_2$ ),  
205 acetaldehyde ( $\text{CH}_3\text{CHO}$ ), 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  $\text{H}_2\text{O}$ , which involves no change in  $\overline{\text{OS}}_c$  or  $n_C$ ). The  
207 number of possible chemical structures (chemical complexity) is a strong function of not only  
208  $n_C$ <sup>33</sup> 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  $\overline{\text{OS}}_c$  value. The number of possible structures then increases rapidly with  
212  $\overline{\text{OS}}_c$ , due to the combinatorial addition of different functional groups to different carbon atoms.  
213 The maximum in chemical complexity is located at  $\overline{\text{OS}}_c = 0$ ; for molecules in which the  
214 average carbon atom is oxidized ( $\overline{\text{OS}}_c > 0$ ), 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 ( $-1 \leq \overline{\text{OS}}_c \leq +1$ ) 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 OA indicates that a completely speciated approach is

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

226

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

237 For all systems studied (Fig. 4), oxidation leads to increased functionality on the carbon  
238 skeleton (higher  $\overline{\text{OS}}_{\text{C}}$ ), and, after only a few (1-4) generations of oxidation, a decrease in carbon  
239 number of the original carbon skeleton (lower  $n_{\text{C}}$ ). Fragmentation reactions are therefore key  
240 processes in the oxidative aging of atmospheric organics, particularly for oxidized species,  
241 whose oxygen-containing (electron-withdrawing) groups weaken adjacent carbon-carbon  
242 bonds<sup>34</sup>. This increase in  $\overline{\text{OS}}_{\text{C}}$  towards  $\text{CO}_2$  can occur via multiple reaction pathways, as  
243 illustrated by the numerous individual products of isoprene and  $\alpha$ -pinene oxidation (circles in

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

246

## 247 **Discussion**

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

257         Nonetheless, it is known that the heterogeneous degradation of organic PM by gas-phase  
258 oxidants is generally substantially slower than of gas-phase organics<sup>35</sup>, since most particulate  
259 organics are shielded from gas-phase radicals interacting with the particle surface. Thus organic  
260 aerosol represents a “metastable state” in which partially oxidized organics can survive for a  
261 substantial period of time, even under highly oxidizing conditions. This view of organic aerosol  
262 as a chemically recalcitrant intermediate in the oxidation of organic species resembles the  
263 emerging view of the nature of humic materials in soils and aquatic systems<sup>36,37</sup>. In this sense  
264 the similarities between atmospheric particulate organics and humic materials may extend well  
265 beyond their chemical complexity and physicochemical properties<sup>23,38</sup>, to include their role as a  
266 “transition state” of organic matter<sup>37</sup>. While detailed chemical structures and transformations are

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

271         The description of the chemistry of organic species in terms of changes to their average  
272 carbon oxidation state (a universal, unambiguous metric for the degree of oxidation of carbon-  
273 containing species) and carbon number may thus be useful for describing not only atmospheric  
274 oxidation but also other complex reactive systems as well. This includes the formation and  
275 evolution of humic substances in soil or aquatic systems, the combustion of complex organic  
276 species, the formation or weathering of fossil fuels, and the chemical transformation of organics  
277 in oxygen-limited environments. Such systems can involve reactions other than the oxidative  
278 processes that govern atmospheric reactions, and therefore may exhibit trajectories in  $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$   
279 space different than those shown in Figure 4. For example, reduction moves organics downward  
280 and to the right (towards methane,  $\text{OS}_{\text{C}} = -4$  and  $n_{\text{C}} = 1$ ), whereas radical association reactions in  
281 low-oxygen environments (such as fuel-rich flames and some planetary atmospheres<sup>39</sup>), involve  
282 leftward movement, towards polycyclic aromatic hydrocarbons and eventually elemental carbon  
283 ( $\overline{\text{OS}}_{\text{C}} = 0$  and  $n_{\text{C}} \rightarrow \infty$ ). The measurement of  $\overline{\text{OS}}_{\text{C}}$  allows for the determination of these trajectories  
284 for entire mixtures, offering the potential for simple, predictive models of these exceedingly  
285 complex chemical systems.

286  
287

287 **Methods**

288

289 *Determination of average carbon oxidation state.*

290 All  $\overline{\text{OS}}_{\text{C}}$  values reported in Table 1 and illustrated in Figures 2 and 4 were determined using  
291 Equation 2. The one exception is the  $\overline{\text{OS}}_{\text{C}}$  of secondary organic aerosol formed from the  
292 photooxidation of alkenes<sup>15</sup>; the high contribution of organic nitrates (N/C=0.1) requires the  
293 explicit inclusion of nitrogen ( $\text{OS}_{\text{N}}=+5$ ). A discussion of the potential errors associated with  
294 neglecting heteroatoms in Eq. 2 is given in the Supplementary Information.

295 Ensemble (average) elemental ratios were taken mostly from previously reported  
296 measurements. For AMS<sup>26-31,40,41</sup> and CHNS data<sup>15-17</sup>, O/C and H/C ratios are taken directly  
297 from reported measurements. For ultrahigh resolution ESI data<sup>14,18-22</sup>, O/C and H/C are  
298 determined by averaging the elemental ratios of all measured CHO species, weighted by ion  
299 intensity<sup>20</sup>. For XPS data<sup>25</sup> (C1s spectra at 430 eV), all carbon was categorized as C=C, CH<sub>x</sub>, C-  
300 OH, C=O and C(O)OH based on its measured binding energy, allowing for the estimation of O/C  
301 and H/C ratios. Additional details of these measurements are provided in the Supporting  
302 Information.

303

304 *Estimation of carbon number.*

305 The number of carbon atoms per molecule ( $n_{\text{C}}$ ) in ambient organic aerosol (Figure 2) was either  
306 determined from speciated measurements (ESI data) or estimated based on measurements of  
307 particle volatility and OSc (AMS data). This latter approach utilizes the SIMPOL.1 structure-  
308 activity relationship<sup>42</sup> to relate saturation vapor pressure, degree of oxidation, and  $n_{\text{C}}$ .<sup>32</sup> Vapor  
309 pressures of organic aerosol classes are based on recent *in situ* thermodenuder measurements.<sup>43</sup>

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

317

### 318 *Multigenerational oxidation experiments.*

319 The oxidation trajectories in  $\overline{\text{OS}}_C$ - $n_C$  space (Figure 4) were determined from laboratory studies  
320 of the oxidation of individual organic species. Gas-phase and particle-phase (monomeric)  
321 products of the OH-initiated oxidation of isoprene and  $\alpha$ -pinene were measured by various  
322 speciated techniques.<sup>44-50</sup> The heterogeneous oxidation reactions of squalane, triacontane, and  
323 levoglucosan were carried out by sending nucleated particles into a flow reactor, where they  
324 were exposed to high concentrations of OH generated by ozone photolysis.<sup>40,41</sup> Changes to  
325 particle mass and elemental ratios upon oxidation were characterized using a scanning mobility  
326 particle sizer and an HR-AMS. For the oxidation of coronene,<sup>25</sup> vapor-deposited thin films of  
327 coronene (4-6 Å thickness) were exposed to varying levels of OH or O<sub>3</sub>, and the chemical  
328 changes measured using XPS at the Ambient Pressure Photoemission Spectrometer at beamline  
329 11.0.2 of the Advanced Light Source, (Berkeley, CA). The evolving abundance and type of  
330 carbon in the film was determined using C1s spectra at 430 eV. Experimental details are  
331 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.

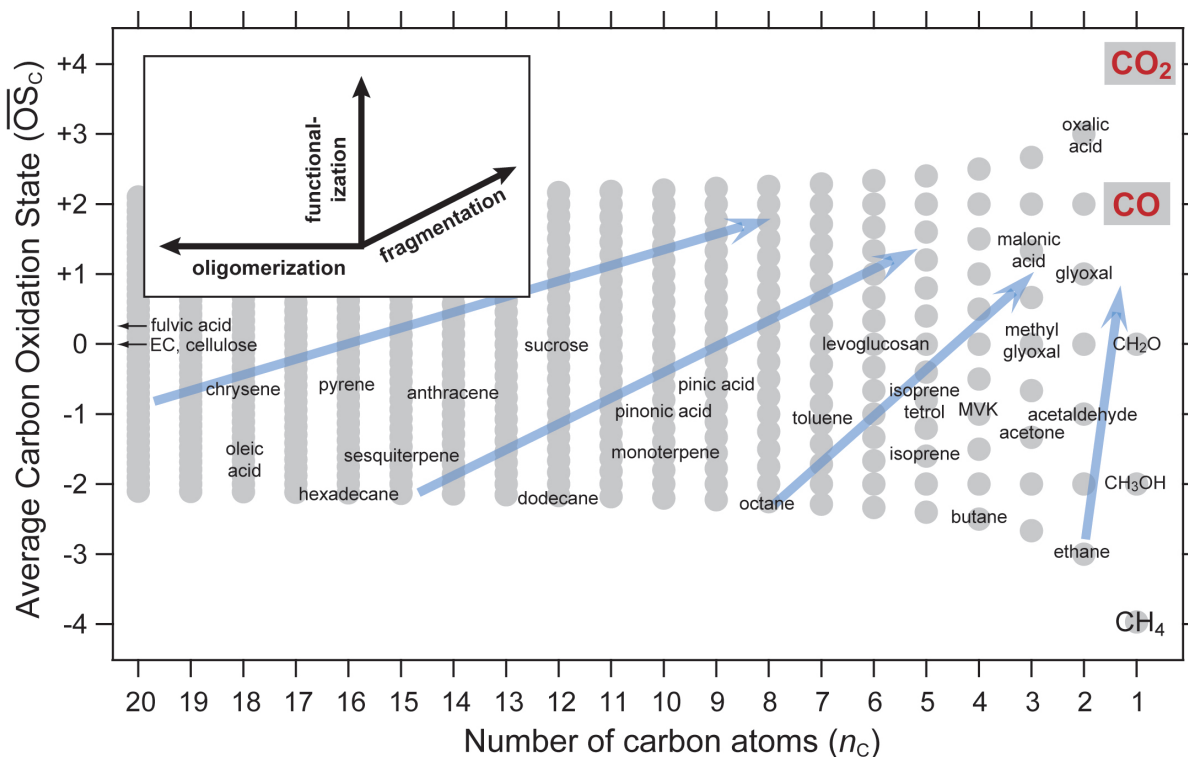
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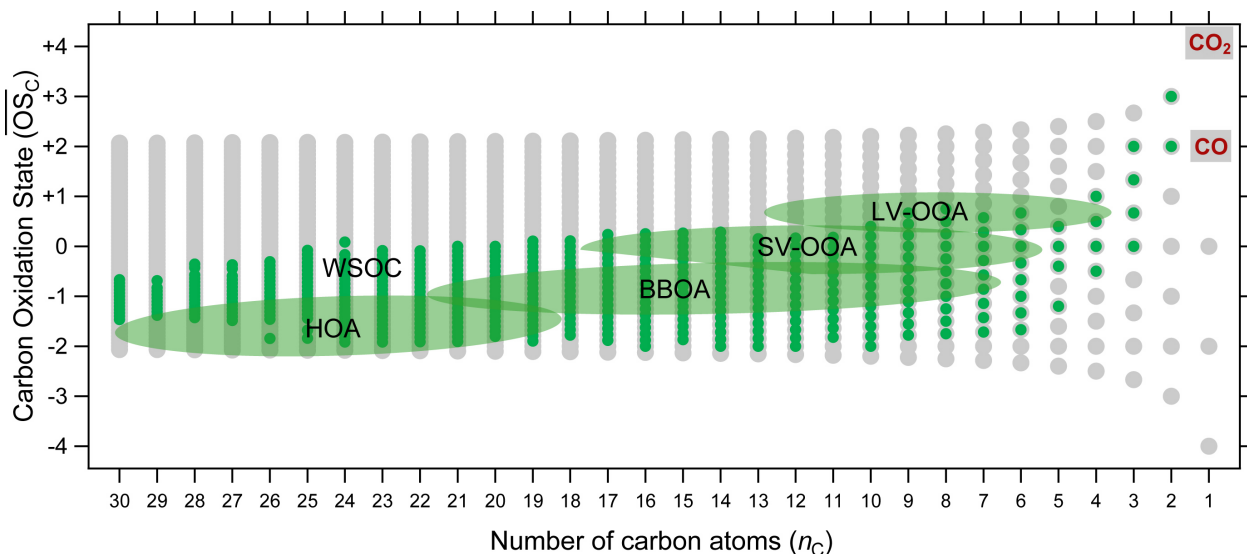
**Table 1.** Measurements of  $\overline{OS}_c$  of organic aerosol, using a range of analytical techniques: aerosol mass spectrometry (AMS), ultrahigh resolution mass spectrometry with electrospray ionization (ESI), and combustion techniques (CHNS). Values listed are the  $\overline{OS}_c$  ensemble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

<b><i>Ambient Organic Aerosol</i></b>	<b><math>OS_c</math></b>	<b>Technique</b>	<b>Ref.</b>
Urban/anthropogenic (Mexico City)	-1.6...+0.1	AMS	26
Remote/biogenic (Amazonian rainforest)	-0.9...-0.2	AMS	31
Aged (Whistler Mountain)	-0.6...+0.6	AMS	30
<b><i>Ambient Aerosol Fractions</i></b>			
Hydrocarbon-like organic aerosol (HOA)	-1.7...-1.6	AMS	26
Semivolatile oxygenated organic aerosol (SV-OOA)	-0.5...0.0	AMS	26
Low-volatility oxygenated organic aerosol (LV-OOA)	+0.5...+0.9	AMS	26
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	21
WSOC in fogwater	-0.7	ESI	22
<b><i>Primary Organic Aerosol</i></b>			
Vehicle exhaust (gasoline, diesel)	-2.0...-1.9	AMS	26
Biomass burning aerosol	-1.0...-0.7	AMS	26
<b><i>Secondary Organic Aerosol</i></b>			
Monoterpene + O <sub>3</sub>	-1.1...-0.5	AMS, ESI	20,26,27,29
Isoprene + OH or O <sub>3</sub>	-0.8...-0.2	AMS, ESI	14,26,29
Monoaromatics + OH	-0.9...+0.1	AMS	26,29
Alkane/alkene photooxidation	-0.7...-0.4	AMS, CHNS	15,28
Methylglyoxal aqueous oxidation	-0.3	ESI	18

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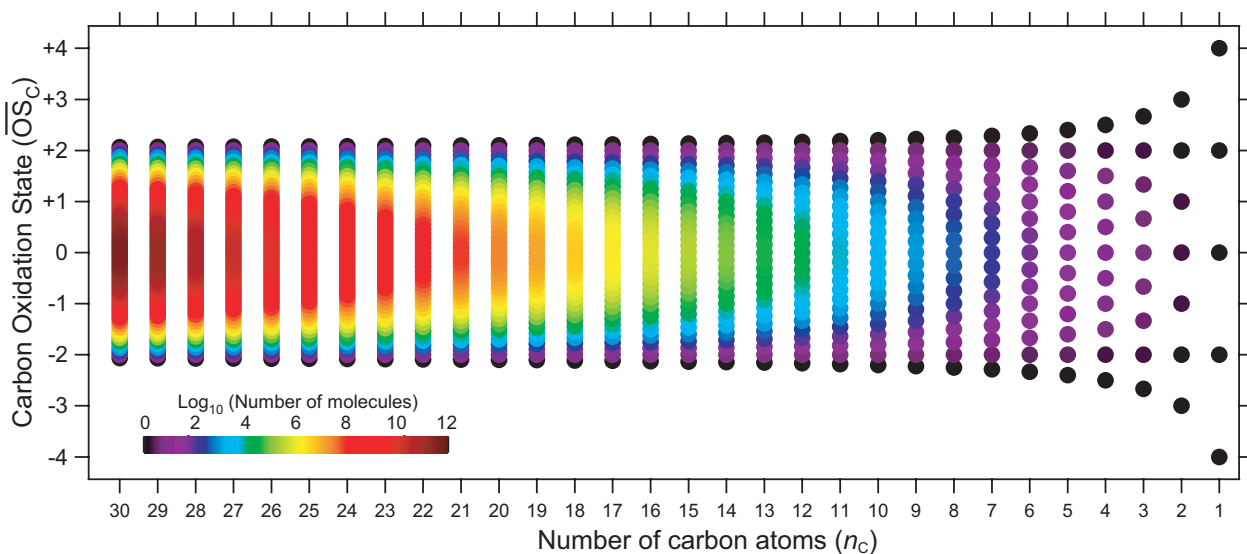
369 **Figure 1.** Possible combinations of average carbon oxidation state ( $\overline{OS}_C$ ) and number of carbon  
 370 atoms ( $n_C$ ) for stable organic molecules. Any organic species can be placed in this two-  
 371 dimensional space; the locations of key atmospheric organics (and common surrogate species)  
 372 are shown. The vast majority of known atmospheric species are reduced ( $\overline{OS}_C \leq 0$ ), with only the  
 373 smallest compounds having higher oxidation states. Inset: vectors corresponding to key classes  
 374 of reactions of atmospheric organics, functionalization (addition of polar functional groups),  
 375 fragmentation (cleavage of C-C bonds), and oligomerization (covalent association of two organic  
 376 species). The combination of these reaction types leads to complex movement through  $\overline{OS}_C$ - $n_C$   
 377 space; however, the inevitable increase in  $\overline{OS}_C$  with atmospheric oxidation implies that, given  
 378 enough time, organics will generally move up and to the right (blue arrows), towards CO<sub>2</sub>.



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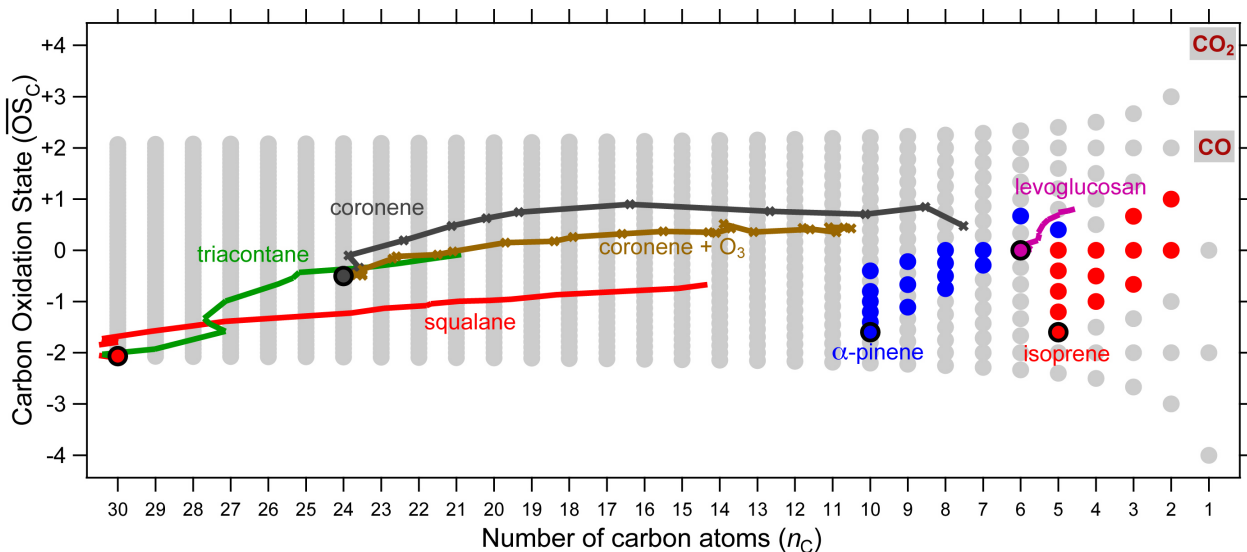
381 **Figure 2.** Location in  $\overline{OS}_C$ - $n_C$  space of organic aerosol, based upon  $\overline{OS}_C$  measurements of  
 382 organic aerosol (Table 1). Green circles: locations of individual components of water-soluble  
 383 organic compounds (WSOC), as measured by ultrahigh resolution mass spectrometry with  
 384 electrospray ionization.<sup>21,22</sup> Green ovals: locations of different organic aerosol classes, as  
 385 determined from factor analysis of AMS data<sup>26</sup> and volatility measurements to determine  $n_C$ <sup>32</sup>.  
 386 Hydrocarbon-like organic aerosol (HOA) and biomass burning organic aerosol (BBOA)  
 387 correspond to primary particulate matter directly emitted into the atmosphere. Semivolatile and  
 388 low-volatility oxidized organic aerosol (SV-OOA and LV-OOA) correspond to “fresh” and  
 389 “aged” secondary aerosol produced by multi-step oxidation of gas phase precursors<sup>11</sup>. These  
 390 aerosol species and types fall along the rough oxidation trajectories shown in Fig. 1, according to  
 391 their degree of oxidation. The apparent absence of large ( $n_C \geq 5$ ), highly oxidized ( $\overline{OS}_C > 1$ )  
 392 organics in organic aerosol is likely due to the thermodynamic and photochemical instability of  
 393 such species.

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**Figure 3.** Chemical complexity of organics as a function of oxidation state and carbon number. Points are colored by the logarithm (base 10) of the number of possible compounds at a given  $\overline{OS}_C$  and  $n_C$ , assuming an unbranched, acyclic carbon skeleton, and the addition of carbonyl, alcohol, and acid groups only. Including a wider range of carbon skeletons or functional groups will lead to a dramatically steeper increase in chemical complexity with  $\overline{OS}_C$  and  $n_C$ <sup>33</sup>.



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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)<sup>40,41</sup>; the heterogeneous oxidation of thin films, measured by XPS (crossed lines)<sup>25</sup>; and the gas-phase oxidation of hydrocarbons, measured by various techniques to speciate gas- and particle-phase organics (solid circles)<sup>44-50</sup>. 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.

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