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Chemical Sinks of Organic Aerosol: Kinetics and Products of the Heterogeneous Oxidation of Erythritol and Levoglucosan

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1 **Chemical sinks of organic aerosol:**
2 **kinetics and products of the heterogeneous oxidation of erythritol and levoglucosan**

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14
15 **I. Abstract**

16 The heterogeneous oxidation of pure erythritol (C₄H₁₀O₄) and levoglucosan (C₆H₁₀O₅)
17 particles was studied in order to evaluate the effects of atmospheric aging on the mass and
18 chemical composition of atmospheric organic aerosol. In contrast to what is generally observed
19 for the heterogeneous oxidation of reduced organics, substantial volatilization is observed in both
20 systems. However, the ratio of the decrease in particle mass to the decrease in the concentration
21 of the parent species is about three times higher for erythritol than for levoglucosan, indicating
22 that details of chemical structure (such as carbon number, cyclic moieties, and oxygen-
23 containing functional groups) play a governing role in the importance of volatilization reactions.
24 The kinetics of the reaction indicate that while both compounds react at approximately the same
25 rate, reactions of their oxidation products appear to be slowed substantially. Estimates of
26 volatilities of organic species based on elemental composition measurements suggest that the

27 heterogeneous oxidation of oxygenated organics may be an important loss mechanism of organic
28 aerosol.

29 **II. Introduction**

30 Atmospheric organic aerosol (OA) is of special concern in considering the effects of
31 particulate matter on human health and global radiative forcing. Quantitative predictions of OA
32 loadings and properties often fail to match ambient measurements, in large part because of the
33 highly complex nature of organic mixtures and because the continuing oxidative aging of
34 organics during their atmospheric lifetimes (*1*). These oxidation reactions may occur either in the
35 vapor phase, as with volatile or semivolatile organics, or by heterogeneous reactions at the gas-
36 particle interface (*2,3,4,5,6*).

37 Recent laboratory work has focused on the heterogeneous oxidation of model condensed-
38 phase organic species, in order to understand the role of such reactions in aging mechanisms of
39 primary organic aerosol. Several studies (*2,3,5*) have found that substantial oxidation of reduced
40 organics, as well as loss of OA mass, occurs only at very high oxidant exposures, beyond what
41 most particles will experience in their atmospheric lifetimes. Nonetheless, this work suggests that
42 oxidized organics may be susceptible to volatilization reactions; these may be atmospherically
43 important given the abundance of oxidized compounds in OA (*1*).

44 In this study we investigate the kinetics and products of the heterogeneous oxidation of
45 oxygenated (polyhydroxylated) species by exposure to hydroxyl (OH) radicals. We focus on two
46 model organics, chosen both for their high degree of oxidation and for their importance as
47 surrogate or tracer species in OA. Erythritol, $C_4H_{10}O_4$, is an analog of 2-methyl erythritol, a
48 tracer species for isoprene secondary OA (SOA) (*7,8*). Levoglucosan, $C_6H_{10}O_5$, is a known
49 product of cellulose pyrolysis and is frequently used as a tracer for biomass burning OA (BBOA)

50 (9). Although the role of these compounds in atmospheric chemistry differs greatly, they are
51 functionally similar, with low carbon numbers, several hydroxyl groups, and a relatively high
52 degree of oxygenation (oxygen-to-carbon ratios of 0.8 to 1.0). The rates of oxidation of both
53 species may strongly affect their efficacy as tracers in determining relative amounts of SOA and
54 BBOA (10,11,12,13). More generally, the goal of this work is to investigate the possibility that
55 oxidative aging of organic aerosol may serve as a chemical sink of atmospheric particulate
56 matter (PM) via formation of volatile products (14).

57 **III. Experimental Methods**

58 The flow reactor used to study the heterogeneous oxidation of particles has been
59 described in detail previously (4,5) and will be discussed only briefly here. The reactor is made
60 up of type-219 quartz, with a length of 130 cm, inner diameter of 2.5 cm, and residence time of
61 ~37 s. Carrier flow consists of an O₂/N₂ mixture (in a 5/95 volume ratio), humidified to 30%
62 RH. Organic aerosol is generated by sending an aqueous solution of each organic through either
63 a constant-output atomizer (erythritol, >99% purity, Aldrich) (15) or a commercial nebulizer
64 (levoglucosan, 99% purity, Aldrich) (16), and the resulting particles (surface-weighted mean
65 diameter of ~270-305 nm) are drawn through a diffusion drier and into the flow reactor at
66 loadings of ~500-750 μg m⁻³. Such loadings are sufficiently high to ensure that >95% of the
67 erythritol and >99% of the levoglucosan is present in the condensed phase at equilibrium.

68 Ozone is produced by either a mercury pen-ray lamp (1-10 ppm) or a commercial corona
69 discharge ozone generator (10-200 ppm, OzoneLab Instruments). O₃ concentrations, which
70 determine the level of OH exposure within are determined using an ozone monitor (2B
71 Technologies Inc.). Within the flow reactor (temperature: 35 °C), ozone is photolyzed by UV
72 light at 254 nm from two mercury lamps positioned immediately outside the quartz tube. O(¹D)

73 generated by ozone photolysis subsequently reacts with water vapor to form a pair of hydroxyl
74 radicals (OH), which initiate oxidation of the particles. The water vapor concentration is
75 maintained at a sufficiently high level to ensure that direct oxidation of organics by O(¹D) is
76 negligible, as determined previously (5). Hexane (~100 ppb) added to the tube is monitored by
77 GC-FID to quantify OH concentration. This technique has been used to correctly predict rate
78 constants in the reaction of OH with other selected gas-phase organics (4,5); OH concentrations,
79 which are changed by varying O₃, range from 10⁹ to 2 × 10¹¹ molecule cm⁻³. Such
80 concentrations correspond to approximate atmospheric exposures of 1 day to four weeks,
81 assuming an average ambient OH concentration of 3 × 10⁶ molecule cm⁻³. It should be
82 cautioned that these high OH concentrations may lead to significant secondary chemical effects,
83 which would make linear extrapolation to ambient levels highly uncertain. Examination of these
84 secondary effects by comparison of low- and high-concentration experiments at varying
85 residence times is therefore an important topic for future research.

86 Particles exiting the flow reactor are sampled into a scanning mobility particle sizer
87 (SMPS, TSI, Inc.), for the measurement of particle mobility diameters, and a high-resolution
88 time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research, Inc.), for the
89 measurement of particle composition (operating in “W-mode”) and vacuum aerodynamic
90 diameter (“V-mode”). Particle mass is obtained from combined SMPS measurements and AMS
91 particle-time-of-flight (PToF) data, by multiplying average particle volume (from the SMPS) by
92 the effective particle density (Figure S-2). Although this is strictly valid only for spherical
93 particles, minor variations in particle shape will result in only small errors in measured mass, less
94 than 10% (17).

95 Pure particles of levoglucosan and erythritol did not change in composition or mass
96 when the UV lights were turned on but no ozone was added, verifying both that the parent
97 organic compounds studied are not directly photolyzed, and that UV-generation of condensed-
98 phase oxidants is negligible. Significant gas-phase oxidation of the semivolatile compounds
99 studied here is also highly unlikely, due to their strong partitioning into the particle phase and the
100 short residence time in the flow reactor. Thus any changes to the mass or composition of the
101 particles result from heterogeneous oxidation of particulate species by gas-phase OH radicals.

102 The amount of starting compound (levoglucosan or erythritol) lost by reaction is
103 quantified by selecting a marker peak from the high-resolution mass spectrum and computing its
104 fractional contribution to total AMS mass:

$$105 \quad m_j = \frac{i_j}{i_{total}} m_{OA} \quad (1)$$

106 where i_j is the peak signal of the fragment ion selected to represent compound j, i_{total} is the sum
107 of all organic peak signals from the AMS, and m_{OA} is the OA mass, normalized by particle
108 number in order to account for wall losses, small atomizer fluctuations, and changes in collection
109 efficiency of the AMS. This method assumes that the chosen marker peak does not constitute a
110 significant portion of the individual mass spectra of the oxidation products, so that the peak
111 represents only the compound of interest. This approach has recently been shown to compare
112 very well with offline techniques for quantifying levoglucosan (10).

113 The peak used to track the mass loss of erythritol is chosen to be $C_4H_8O_3^+$ ($m/z = 104$),
114 which is formed by the neutral loss of H_2O from the molecular ion (M-18). Likewise, the
115 selected marker peak for levoglucosan is $C_6H_8O_4^+$ ($m/z=144$), also obtained by the loss of H_2O .
116 Both peaks were observed to be the fragments of highest mass in the pure compound spectra for

117 which the AMS signal-to-noise ratio was suitably large. It is unlikely that any oxidation products
118 would contribute significantly to the selected peaks, since they are expected to be of lower mass
119 (aside from oligomerization products, which are not strongly represented in these AMS spectra)
120 and have fewer hydrogen atoms than the parent compound.

121 The effects of oxidation by OH exposure may vary widely, depending on the nature of
122 the organic compound being oxidized. It is therefore useful to introduce the mass loss ratio
123 (MLR), defined as the ratio of the change in particle mass to the change in mass of the reacting
124 species. For a given particle mass m_{OA} , reactive species mass m_R , and particles initially
125 composed of the pure reactive species, such that $m_{OA}(0) = m_R(0)$, one may write:

$$126 \quad \text{MLR} = \frac{\Delta m_{OA}}{\Delta m_R} = \frac{m_{OA} - m_{OA}(0)}{m_R - m_R(0)} = \frac{1 - \mu_{OA}}{1 - \mu_R} \quad (2)$$

127 where μ is the mass fraction remaining of either total aerosol or the reactive species. For our
128 purposes, we assume that $\mu_R = m_j / m_j(0)$, where m_j is the mass of the selected AMS peak as
129 computed in Equation 1. The MLR therefore describes the approximate yield of gas-phase
130 products upon oxidation. Values of the MLR are determined by averaging all data points for
131 which the total particle mass loss is greater than 20%, since values computed at low-oxidation
132 conditions are subject to substantial numerical errors.

133 We characterize the chemical changes to the reacting systems in terms of changes to the
134 overall elemental composition of organics in the condensed phase. In particular, the oxygen-to-
135 carbon ratio (O/C) and hydrogen-to-carbon ratio (H/C) are combined to estimate the overall
136 degree of oxidation of OA particles and the relative contributions of key functional groups. The
137 method for calculating elemental ratios from high-resolution AMS data is described in detail by
138 Aiken et al. (18,19). This approach requires a set of factors to correct measured values for biases

139 in ion fragmentation. Such factors are expected to be most accurate for complex mixtures or
140 organics, such as are found in ambient OA. As noted by Aiken et al. (18,19), these standard
141 correction factors (0.75 for O/C and 0.91 for H/C), are not as accurate for the measurement of
142 individual organics, such as those studied in the present experiments. We therefore use system-
143 specific correction factors for these studies in order to ensure that the elemental ratios of pure
144 compounds are reported as their known values. The correction factors used are 0.44 for O/C and
145 0.82 for H/C for erythritol, and 0.50 for O/C and 1.1 for H/C for levoglucosan, which is similar
146 to the correction for pure levoglucosan reported previously (18). Regardless of the correction
147 factor used, the overall conclusions reached with respect to the oxidative mechanism described
148 below remain unchanged.

149 **IV. Results**

150 Sample mass spectra of erythritol and levoglucosan particles at both low and high OH
151 exposures may be found in Figure S-6 and demonstrate significant changes in particle mass and
152 chemical characterization.

153 *(i) Erythritol*

154 Figure 1a depicts the decay rates of both erythritol and total particle mass for the
155 heterogeneous oxidation of pure erythritol particles (surface-weighted mean diameter: 270.5
156 nm). The exponential decay of erythritol is consistent with a pseudo-first-order approximation of
157 the second-order reaction of organic compounds with OH, although the chosen marker peak
158 ($C_4H_8O_3^+$) does not appear to decay to zero. Possible reasons for this apparent offset include
159 unreacted erythritol in the core of the particles (with a slow mass transfer rate) and signal
160 interference from product compounds at the marker peak. A fit to the first e-fold of the decay is
161 therefore used (Figure S-1) to obtain a rate constant of $(2.54 \pm 0.22) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

162 ¹. The mass loss ratio, a measure of the formation of gas- versus particle-phase reaction products
163 (Equation 2), is computed to be 0.75 ± 0.04 . Thus the heterogeneous oxidation of erythritol leads
164 primarily to the formation of volatile products (~75% yield), which escape into the gas phase.
165 Reported errors reflect uncertainty in the AMS peak calculation, SMPS mass, and fluctuations in
166 the atomizer flow and OH concentration within the reactor.

167 Heterogeneous oxidation kinetics can be described in terms of the effective uptake
168 coefficient $\gamma_{i,\text{OH}}$ defined as the ratio of the number of reactive collisions between OH and the
169 compound of interest to the total number of collisions (5). The uptake coefficient may be
170 calculated from the determined second-order rate constant according to

$$171 \quad \gamma_{i,\text{OH}} = \frac{2D_0 \cdot \rho_i \cdot N_A}{3\bar{c}_{\text{OH}} \cdot M_i} \cdot k_{i,\text{OH}} \quad (3)$$

172 where D_0 is the surface-weighted average particle diameter at the start of the experiment, ρ_i is
173 the density of the organic compound, N_A is Avogadro's number, \bar{c}_{OH} is the average speed of
174 hydroxyl radicals in the gas phase, and M_i is the molecular weight of the compound. The uptake
175 coefficient calculated by this method for erythritol, after correcting for diffusion limitations
176 (which account for approximately a 40% difference in the final value, using a diffusion constant
177 of OH in air of $0.217 \text{ cm}^2 \text{ s}^{-1}$) (5,20), is 0.85 ± 0.12 . Equation 3 is exact for spherical particles
178 and may slightly overestimate $\gamma_{i,\text{OH}}$ for particles with higher surface-area to volume ratios.

179 Figure 1b shows the evolution of three selected fragment ion signals from the AMS (each
180 normalized to its maximum value) with increasing oxidant exposure. As in Figure 1a, the amount
181 of erythritol remaining is represented by its marker ion, $\text{C}_4\text{H}_8\text{O}_3^+$. Additionally, we use
182 $\text{C}_4\text{H}_7\text{O}_3^+$ ($m/z = 103$, M-19) as a marker for first-generation oxidation products; the signal from

183 this ion is negligible for pure erythritol compared with its observed rise in the reacting system.
184 While the choice of marker peak is determined on a largely empirical basis, it should be noted
185 that if we assume that each oxidation reaction involves the formation of a carbonyl, either by
186 addition or by conversion of a hydroxyl group and requiring the loss of two hydrogen atoms (as
187 discussed in the next section), higher-generation products would necessarily have 6 or fewer
188 hydrogen atoms and would therefore be unable to form the $C_4H_7O_3^+$ fragment ion. We are
189 therefore confident that the selected ion peak serves as a useful metric for the formation of first-
190 generation products.

191 The rate coefficient computed for the decay of erythritol is combined with a simplified
192 two-step oxidation model (described in detail in the Supporting Information) in order to estimate
193 a rate coefficient for the decay of first-generation products, with the fit trace shown in Figure 1b.
194 The resulting effective uptake coefficient is calculated by equation 3 as 0.28 ± 0.03 , significantly
195 less than that of its parent compound, erythritol. Lastly, CO_2^+ ($m/z = 44$) is taken to be
196 representative of the most highly oxidized compounds present in the mixture, likely indicating
197 the presence of carboxylic acid groups in product molecules; additional discussion of changes in
198 the CO_2^+ presence may be found in the Supporting Information. The calculated decay of first-
199 generation products and apparent subsequent growth of more oxidized compounds together
200 indicate that heterogeneous oxidation is a multigenerational process, in accord with previous
201 results (5), and points to the continually evolving chemical nature of OA, which is consistent
202 with a recent study of the heterogeneous oxidation of SOA (21).

203 Figure 1c shows the elemental ratios O/C and H/C for the particulate products of OH +
204 erythritol. Although the relative amount of oxygen in erythritol particles rises only slightly, the
205 hydrogen content drops by a significant degree over the course of the reaction, suggesting that

206 the dominant reactions that yield condensed-phase products are likely to involve the conversion
207 of hydroxyl groups to carbonyl groups. The slight increase in O/C can be accounted for in part
208 by the growing CO_2^+ signal (to a maximum of ~6% of the AMS organic signal), which suggests
209 the increased importance of carboxylic acid functional groups as well.

210 *(ii.) Levoglucosan*

211 The levoglucosan oxidation experiments were analyzed using the same approach as used
212 for erythritol, described above; results are presented in the right half of Figure 1. Figure 1d
213 depicts the decay rates of both levoglucosan mass and total particle mass in a system initially
214 containing pure levoglucosan particles (surface-weighted mean diameter: 304.3 nm). The
215 exponential decay is again consistent with a second-order reaction model and has a
216 corresponding rate constant of $(3.09 \pm 0.18) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with a diffusion-
217 corrected effective uptake coefficient of 1.05 ± 0.11 . Although this computed value is greater
218 than unity, errors caused by under-estimating the average particle surface area using the mobility
219 diameter may lower the actual value. The mass loss ratio, determined by equation 2, is $0.23 \pm$
220 0.04 , significantly lower than what was observed for erythritol. This indicates that the majority
221 of the products of levoglucosan oxidation remain in the particle phase. Hennigan et al. have
222 reported a similar effect, whereby mass loss of biomass-burning organic aerosol upon oxidation
223 is much slower than the loss rate of levoglucosan (10).

224 Figure 1e depicts the progression of selected marker ion peaks with increasing oxidant
225 exposure. Levoglucosan is represented by $\text{C}_6\text{H}_8\text{O}_4^+$, first-generation products are denoted by
226 $\text{C}_6\text{H}_7\text{O}_4^+$ ($m/z = 143$, M-19), and the most highly oxidized compounds are monitored by CO_2^+ .
227 The selection of these three ion peaks follows the same process as described for erythritol in

228 Figure 1b. Again, the growth and subsequent decay of first-generation products, coupled with the
229 later rise in CO_2^+ signal, presents evidence of significant multigenerational chemistry on
230 atmospherically relevant oxidation timescales. The effective uptake coefficient for product decay
231 is calculated to be 0.39 ± 0.05 , a similar effect to the one observed in the erythritol oxidation
232 system, and fit traces for both levoglucosan and its products are indicated in Figure 1e as well.

233 Levoglucosan undergoes a drop in H/C similar to erythritol, as shown in Figure 1f, but
234 the larger rise in O/C suggests that oxidation reactions also involve the addition of new
235 functional groups, such as hydroxyl, carbonyl, and carboxylic acid groups (CO_2^+ signal reaches
236 ~8% of the total AMS organic signal), instead of solely the conversion of alcohols to carbonyls.
237 As oxidant exposure increases, the values of O/C of both systems begin to converge to an
238 apparent upper bound of ~1.1.

239 **V. Discussion**

240 *(i.) Oxidative mechanisms & Structural effects*

241 In marked contrast to the heterogeneous oxidation of reduced particulate organics (2,3,5),
242 the heterogeneous oxidation of erythritol and levoglucosan leads to a substantial loss of OA mass
243 via volatilization reactions. The differences in the mass loss plots of erythritol and levoglucosan
244 (Figures 1a and 1d, respectively) indicate that the effects of oxidation on aerosol loadings are
245 highly dependent on the chemical structure of the organic species in the aerosol. Although the
246 two compounds decay at very similar rates—the effective uptake coefficients γ agree to within
247 approximate experimental uncertainty—the total particle mass follows this decay much more
248 closely for erythritol than it does for levoglucosan. This discrepancy likely arises from
249 differences in the chemical mechanisms leading to volatility changes.

250 These differences can be understood in terms of the mechanism of the oxidation of
251 polyols, depicted in Figure 2 (22). In pathway A, abstraction of a hydrogen atom from a carbon
252 bonded to a hydroxyl group, followed by reaction with O₂, leads to the direct formation of a
253 carbonyl without the cleavage of a C-C bond. In pathway B, the hydrogen atom is instead
254 abstracted from the hydroxyl group directly. The resulting α -hydroxy alkoxy radical rapidly
255 decomposes by C-C bond scission. While the former case raises product vapor pressure by
256 approximately one order of magnitude (23), the latter may raise volatility by a much larger
257 degree by decreasing the carbon number of each product molecule. However, in the case of
258 cyclic molecules, “tethering” of the R groups allow for the cleavage of a C-C bond with no
259 change to the carbon number. Levoglucosan, which has two cyclic moieties, can therefore
260 undergo two cleavage reactions without dissociating to two separate molecules and so will not
261 experience as dramatic an increase in vapor pressure as erythritol. The rate of mass loss relative
262 to oxidation is therefore lower, suggesting that compounds with ring structures and higher
263 molecular weights are likely to contribute to longer-lived organic aerosol.

264 Because both compounds are polyhydroxylated, similar pathways to those discussed
265 above are possible for successive generations of oxidative reactions. The low decay rate of first-
266 generation products in both systems—relative to the decay rate of initial compound—indicates,
267 however, that the reaction process is demonstrably slowed, in part by the loss of hydrogen atoms
268 needed for abstraction in the first step of oxidation. Although some degree of the difference in
269 reaction rates can be explained by the changing sphericity of particles with increasing oxidation,
270 conservative estimates of the uptake coefficient still yield significant discrepancies between the
271 decay rates of initial compounds and the decay of first-generation products. Additionally, the
272 growing presence of the CO₂⁺ ion in both systems points to the likely production of carboxylic

273 acid groups upon later generations of oxidation; this is consistent with our recent evidence that
274 carboxylic acid addition becomes increasingly important with fragmentation reactions (4),
275 although the detailed mechanisms are not yet well understood.

276 *(ii.) Van Krevelen Analysis*

277 The direct comparison of elemental ratios, independent of time or oxidant exposure, is
278 made in Figure 3, using a “van Krevelen diagram” (a plot of H/C vs O/C) (24,25). Heald et al.
279 recently showed that for many ambient measurements of OA, as well as for several laboratory
280 oxidation studies, elemental ratio data tend to fall along a line passing through (0,2) and with a
281 slope of about -1 in this space, consistent with a mixture of carbonyl- and hydroxyl-forming
282 reactions during oxidative aging (24). As shown in Figure 3, erythritol and levoglucosan are
283 located at points far away from this line. As the particles are exposed to larger amounts of OH,
284 the particulate organics tend strongly downwards, with an approximate slope of -4.6 for
285 erythritol and -1.3 for levoglucosan. The steeper slope for erythritol is a result of the conversion
286 of hydroxyl groups to carbonyl groups. Both systems are moving towards similar C/H/O
287 relationships, consistent with previous observations that oxidative aging of widely varying
288 organics tends to form products with similar chemical properties (1).

289 The chemical information supplied by a system’s coordinates on a van Krevelen diagram
290 is sufficient to estimate the minimum number of carbon atoms that a compound must have to be
291 found predominantly in the particle phase at a given loading. These are determined by assuming
292 that compounds are composed solely of contiguous saturated carbon chains and have only
293 hydroxyl and carbonyl (and, by extension, carboxylic acid) functional groups. Volatilities are
294 calculated using the group contribution method of Pankow and Asher (23), and the carbon

295 number represents the minimum number of carbon atoms required to ensure that the compound
296 will partition by at least one-half into the condensed phase (26).

297 The shaded regions in Figure 3a represent the minimum carbon number calculated over
298 the entire range of realistic O/C and H/C values for a system in which the aerosol loading is 700
299 $\mu\text{g m}^{-3}$, the approximate loading in the present experiments. The data for both erythritol (four
300 carbons) and levoglucosan (six carbons) remain within the prescribed limits for condensed-phase
301 elemental composition, indicating consistency between the estimated volatilities of organic
302 compounds and the present measurements. However, because each point on the diagram
303 represents an average in terms of the elemental composition of the system, individual products
304 may be further removed from the observed data, leading to significant phase partitioning of some
305 highly oxidized compounds.

306 *(iii.) Atmospheric Implications*

307 Although Figure 3a is sufficient to describe the phase partitioning behavior of compounds
308 in the present experiments, the aerosol loadings studied are 1-3 orders of magnitude greater than
309 typical ambient loadings (1). We correct for this in Figure 3b, which adjusts the contours to
310 correspond to a loading of $10 \mu\text{g m}^{-3}$. In this case, levoglucosan and its immediate oxidation
311 products are still expected to remain largely within the condensed phase during aging. The
312 erythritol system, however, moves rapidly into a region for which four carbon units is
313 insufficient to ensure that oxidation products will be present primarily in the particle phase.
314 Many of the condensed-phase products observed in this experiment are therefore likely to
315 become even more strongly volatilized in the atmosphere, so that the mass loss ratio is likely to
316 increase as the atmospheric OA loading becomes more dilute; this observation underscores the

317 importance of volatility changes arising from interconversion of functional groups upon
318 oxidation.

319 The effective uptake coefficient can be combined with estimates of particle size and
320 atmospheric oxidant concentration in order to determine a pseudo-first-order rate coefficient for
321 the compound of interest and, by extension, the compound's atmospheric lifetime. Assuming a
322 mean diameter of ~200 nm and OH concentration of 3×10^6 molecules cm^{-3} , erythritol would
323 have a heterogeneous oxidation lifetime of about 12.7 days, while levoglucosan would have a
324 lifetime of about 9.6 days, both of which are very near the estimated depositional lifetimes (~10
325 days) of similarly-sized particles (27). Whereas previous studies have suggested that
326 heterogeneous oxidation of reduced organics (hydrocarbons) (2,3,5) and some SOA systems (21)
327 does not significantly affect aerosol mass on atmospherically relevant timescales, the much
328 lower lifetimes determined here for levoglucosan and erythritol suggest that mass changes from
329 heterogeneous reactions may be more significant for compounds that are already more heavily
330 oxidized and have low molecular weights, which is consistent with our recent results (4).
331 Additional studies have shown that in aqueous droplets and environments with high relative
332 humidity, the lifetimes of both compounds are decreased to less than a day (10,11,12). It should
333 also be noted that because erythritol is semi-volatile, gas-phase oxidation reactions are likely to
334 represent an even larger atmospheric sink for the compound in regions with low-to-moderate OA
335 loadings; this may partially explain previous observations of a decrease in isoprene SOA mass by
336 further aging (28).

337 The chemical lifetimes of OA mass contributed by these compounds—comprising the
338 initial compound and its condensed-phase oxidation products—may be estimated approximately
339 by dividing the product lifetime by its mass loss ratio. Since the mass loss ratio of erythritol

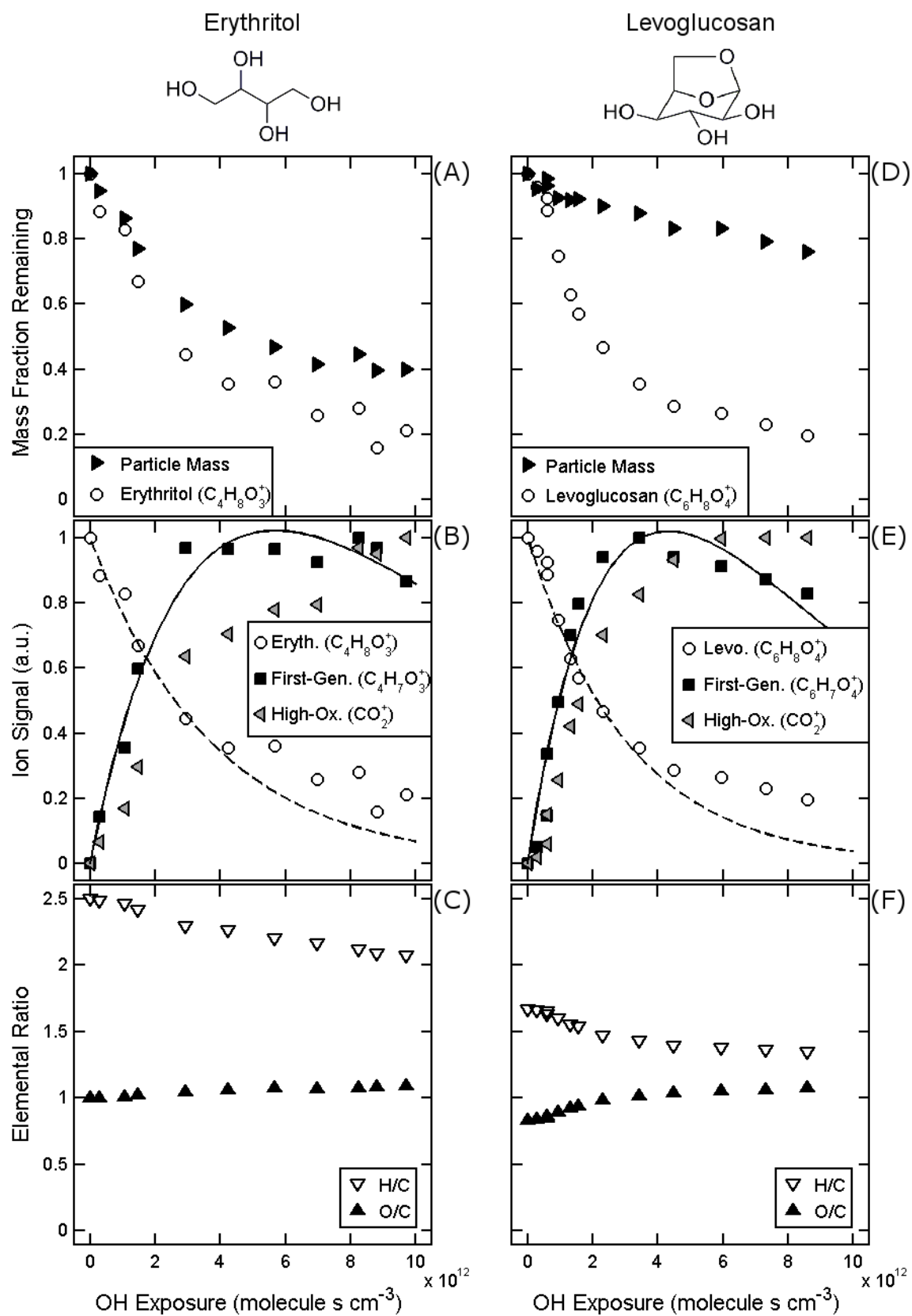
340 approaches unity at atmospheric conditions, its OA lifetime will be about the same as that of
341 erythritol (~12.7 days), suggesting oxidative aging could in fact be an important sink of
342 polyhydroxylated (and possibly other oxidized) components of OA, though the secondary effects
343 of more complex aerosol mixtures on oxidation remains an important topic for further research.
344 The low observed MLR of levoglucosan, by contrast, implies longer-lived particle-phase
345 products, on the order of several weeks, although OA continues to be slowly volatilized during
346 this time. We therefore demonstrate that oxidized organic compounds found in both SOA and
347 BBOA—which make up a large fraction of total aerosol loading (*I*)—are susceptible to further
348 heterogeneous oxidation reactions and that these reactions are capable of significantly altering
349 both the chemical composition and the mass of the oxidized OA.

350

351 **VI. References**

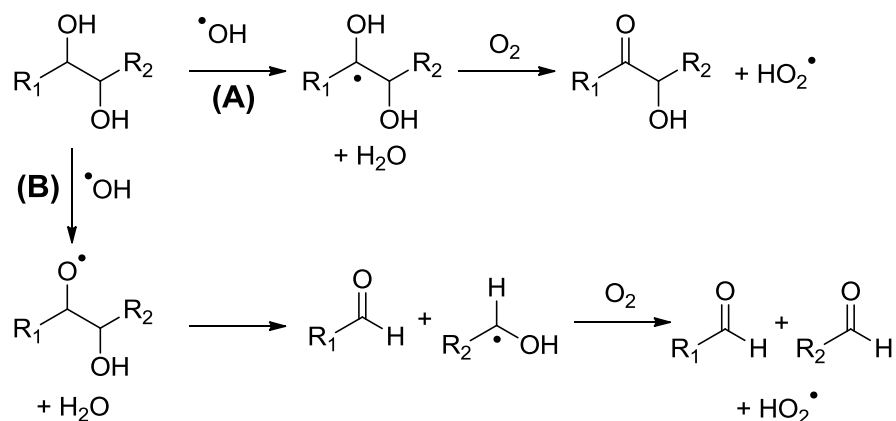
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436 **Figure 1.** (A) Decay curves of pure erythritol (open circles) and total particle mass (filled
437 triangles) over increasing oxidant exposures. (B) Mass contributions of selected marker peaks,
438 used to represent erythritol (circles), first-generation products (squares), and heavily-oxidized
439 products (triangles). Solid and dashed curves denote non-linear fits to kinetic expressions. (C)
440 Hydrogen-to-carbon (H/C, open triangles) and oxygen-to-carbon (O/C, filled triangles) ratios of
441 reacted erythritol system. (D-F) Structure and evolving characteristics of levoglucosan system, as
442 compared to erythritol.
443

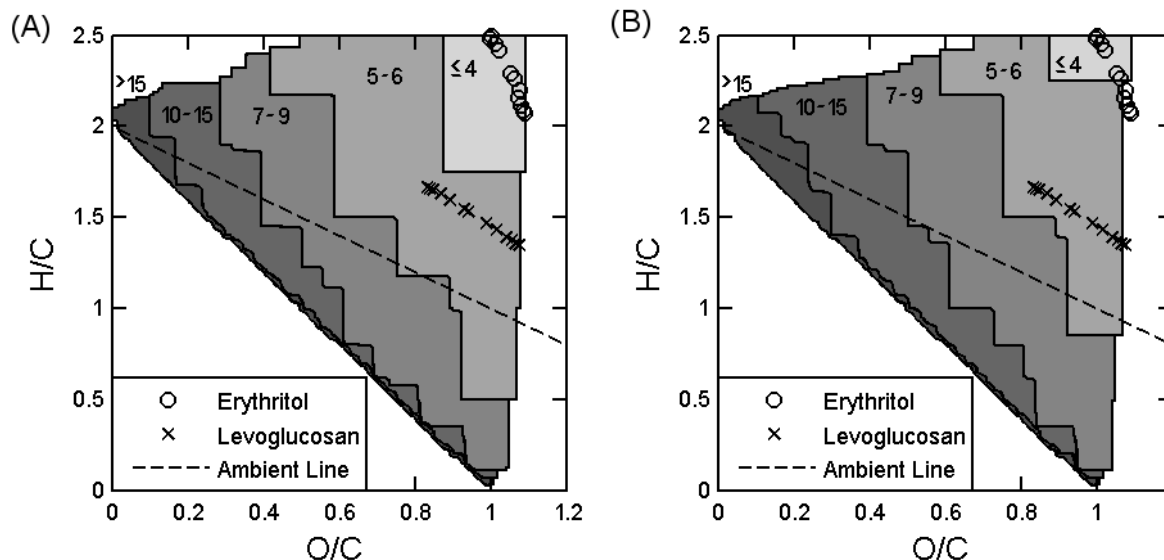
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447 **Figure 2.** Two possible reaction pathways in the oxidation of erythritol and levoglucosan,
448 adapted from Bethel et al. (22). The functionalization pathway (A) leads to a higher degree of
449 oxidation without resulting in the loss of carbon, but the conversion of a hydroxyl group to a
450 carbonyl group results in a product of higher volatility. The fragmentation pathway (B) leads to
451 degradation of C-C bonds and strongly increases overall particle volatility. If the two R groups
452 are connected to each other, however, the molecular backbone will remain intact, and
453 volatilization will be suppressed.

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456 **Figure 3.** (A) Van Krevelen plot of H/C versus O/C for the erythritol (circles) and levoglucosan
 457 ('x') reacting systems. The direction of oxidation is downward and to the right for each system.
 458 Dashed line depicts the "ambient" line ($H/C = 2 - O/C$), which is the average of many
 459 measurements. Shaded regions represent the approximate minimum number of carbon atoms per
 460 molecule required in order for the compounds to have a saturation concentration less than $700 \mu\text{g}$
 461 m^{-3} , the approximate mass loading of the systems considered herein. Blank spaces represent
 462 regions for which the calculated minimum carbon number, along with the represented hydrogen
 463 and oxygen numbers, result in chemically infeasible combinations in the absence of carbon-
 464 carbon double bonds. (B) The same Van Krevelen plot, with shaded regions adjusted to the more
 465 atmospherically-relevant loading of $10 \mu\text{g} \text{m}^{-3}$. The erythritol system average moves out of the
 466 "4-carbon" region at an OH exposure of $4 \times 10^{12} \text{ molecule s cm}^{-3}$, corresponding to ~ 15.4 days
 467 of oxidation in the atmosphere.