Aging induced changes in ice nucleation activity of combustion aerosol as determined by near edge X-ray absorption fine structure (NEXAFS) spectroscopy

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S1 DVS

S1.1 Hydroxyl accessibility measurements

DVS measurements allow quantifying the accessibility of OH functional groups present on the soot through protium-deuterium exchange measurements. We largely followed the protocol of Thybring et al. (2017), who used the same technique on wood

5 samples. The soot sample is initially dried for 6 h at T = 333 K and $RH_w = 0$ %, yielding the sample dry mass, $m_{0,dry}$. The dried sample is then deuterated at T = 298 K and $RH_w = 95$ % by exposure to deuterated water vapor (99.9 % D atom purity, SigmaAldrich), over a course of 10 h:

$$R - OH + D_2 O \to R - OD + HDO, \tag{SR1}$$

where R – OH and R – OD denote the initial and the deuterated adsorbent respectively. The exchange of protium by deuterium atoms will take place at the hydroxyl sites that are accessible for the D₂O vapor and cause a weight increase in the soot sample. Subsequently, the deuterated soot sample is again dried at T = 333 K and RH_w = 0 % over the course of 6 h, yielding the deuterated dry adsorbent mass m_{d,dry}.

Through exchange of D with H from the OH groups, the OH group accessibility is then calculated from the gravimetric data as:

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$$OH_{access} = \frac{m_{d,dry} - m_{0,dry}}{m_{0,dry}(M_D - M_H)}.$$
 (S1)

Here, OH_{access} denotes the number of available OH groups per gram of adsorbent and M_D and M_H the molar masses of deuterium ($M_D = 2.014 \text{ gmol}^{-1}$) and protium ($M_H = 1.007 \text{ gmol}^{-1}$), respectively. All OH accessibility experiments were performed using 6.0 grade N₂ (PanGas, H₂O < 0.5 ppm) in order to avoid depreciation induced measurement errors.

The hydroxyl accessibility of the soot samples is shown in Table S1. The determined amount of OH groups on the soot sample

- 5 is very low compared to the OH amount found for instance on wood samples, which is typically on the oder of 10 mmolg^{-1} (Grönquist et al., 2019). Contrary to the sorption isotherms, the protium-deuterium exchange measurements take place at a fixed *RH*. Consequently, the uncertainties in the OH-accessibility measurements are dominated by the mass sensitivity and the mass drift of the scale. We have observed a maximum mass drift of the scale of 0.003 mg over the course of 24 h, covering the time period of protium-deuterium exchange experiment. Considering this mass drift within Eq. (S1) and using a typical
- 10 sample mass of 10 mg, we derived a maximum uncertainty in our protium-deuterium exchange measurements, purley resulting from mass drift of 0.3 mmolg⁻¹. However, we point out that this represents an upper limit, and we estimate the uncertainty in accessible OH groups to be more likely around 0.1 mmolg⁻¹ for sample masses of 10 mg based on previous experiments, where multiple measurements were performed on the same sample. Here, all values reported in Table S1 correspond to single experimental runs only. We used samples masses between 3 - 17 mg. The exception was unaged mCASTbr, where a sample
- 15 mass below 3 mg was used, which was likely too low to detect hydroxyl groups on this soot sample.

Table S1. The amount of accessible hydroxyl groups for different soot types as determined by DVS is given in units of $[\text{mmolg}^{-1}]$ (single runs) and the degree of graphitization given by the peak height ratio $r = \frac{I_{\pi^*}}{I_{\sigma^*}} = \frac{OD_{285\text{eV}}}{OD_{292\text{eV}}}$, as defined by di Stasio and Braun (2006), and calculated from the mean NEXAFS spectra shown in Fig. 3.

	Sample ID	Soot type	OH_{access}	$r = \frac{I_{\pi^*}}{I_{\sigma^*}}$
	S 1	mCASTbl unaged	0.304	0.48
	S4	mCASTbl water	0.172	0.52
•	S8	mCASTbl [H ₂ SO ₄] $5 \cdot 10^{-5}$ M	0.137	0.60
	S5	mCASTbr unaged	N/A	0.73
	S12	mCASTbr water	0.358	0.75
	S9	mCASTbr [H ₂ SO ₄] $5 \cdot 10^{-5}$ M	0.206	0.78

S2 STXM/NEXAFS

S2.1 Beam damage and carbon deposition assessment

In Fig. S1, we show the conditions where beam damage due to X-ray exposure occurred and how it was avoided. As an example, we report beam damage on the mCASTbr soot sample here. Two NEXAFS spectra over the same soot aggregate were acquired

5 one after another and any changes were identified. The total number of incident photons per pixel was approximately $I_0 \approx 2700$ and similar at all energies. Although the X-ray photon flux typically changes as a function of energy, we changed the time at which the X-ray beam irradiates a pixel (t_{dwell} , on the order of milliseconds) to ensure a roughly uniform I_0 .

The blue spectra in Fig. S1 were acquired first and the red spectra were acquired second. In Fig. S1a, the red particle spectrum has a slightly larger signal across the entire carbon energy scale, which we attribute to carbon deposition. We decreased t_{dwell}

by half over all energies, and thus I₀ also decreased by half. We then irradiated another particle twice and the result is shown in Fig. S1b. The incident photon count is I₀ ≈ 1130 (Fig. S1b), so that the red spectrum in Fig. S1b has a comparable exposure (photon count) to the blue spectrum in Fig. S1a. Comparison of peak heights of the graphitic and exciton peak for the spectra depicted in Fig. S1b reveals a change of approximately 3 and 6 % respectively. Overall, we conclude that an irradiation of I₀ ≈ 2700 was optimal for the spectra required here, to maximize the absorption signal and at the same time minimize X-ray beam damage of the soot samples.



Figure S1. Assessment of sample damage resulting from X-ray exposure for unaged mCASTbr particles. Blue and red NEXAFS spectra were acquired on the same particle after each other, representing increasing beam damage of the sample. (a) Complete spectra where each pixel was irradiated with approximately 2700 photons. (b) Same as in (a) but using only half the t_{dwell} time. In both (a) and (b) spectra are not rescaled.

S2.2 O K-edge spectra

Consideration of the oxygen spectra, shown in Fig. S3, can be used to confirm assignment of functional groups in the corresponding carbon spectra. The dominant absorption feature in the O K-edge spectra of mCASTbr is the peak centered around 538 eV, which is attributed to $1s \rightarrow \sigma^*$ transitions of oxygen associated within ketones, carboxyl and alcohol functional groups

- 5 (Zelenay et al., 2011). Carboxyl and ketone functionalities also show a O1s → π^{*}_{R(C*=O)} transition at 532 eV and 531 eV, respectively (Hopkins et al., 2007), with the latter being more pronounced in both unaged soot types. A small absorption peak at 531 eV and a larger transition at 538 eV usually implies acidic functionalities. However, in the case of unaged mCASTbl the absorption feature around 531 eV is very weak (almost absent) compared to the unaged mCASTbr. This suggests that unaged mCASTbl contains mainly C O and only weak absorption due to C = O bonds. In turn this indicates that the 287.5
- 10 eV peak is likely not due to ketone functionalities (see Fig. 3). A $1s \rightarrow \pi^*$ transition from oxygen associated with carbonyl groups at 529.9 eV would support the assignment of benzoquinone in the carbon spectra, but O K-edge spectra are noisy, due to the generally little oxygen present. Overall, measurements at the oxygen edge were noisy and/or not possible in some soot particles due to the low oxygen content, which is further supported by the negligible amounts of accessible OH groups found by gravimetric protium-deuterium exchange measurements (see Section S1.1).



Figure S2. Near edge absorption fine structure (NEXAFS) spectra of (a) unaged mCASTbl, (b) water aged mCASTbl, (c) acid aged mCASTbl, (d) unaged mCASTbr, (e) water aged mCASTbr and (f) acid aged mCASTbr soot particles, measured at the oxygen K-edge. All spectra have been corrected for pre-edge background intensities by subtracting the mean intensity between 523 - 527 eV from each spectrum and normalized to the oxygen K-edge absorbency (mean value between 540 - 550 eV) and are shifted vertically for clarity and comparability. Solid colored lines denote averaged spectra and dotted lines spectra of individual particles of a given soot type.



Figure S3. Same as in main text Fig. 3 without vertical offset between spectra.

S2.4 O:C ratios of soot samples

In Table S2 we report the O:C ratio for both the unaged and acid aged mCASTbl and mCASTbr. In order to derive the O:C ratio we first calculate the atomic photo absorption cross section, μ_a as:

$$\mu_a = 2r_e \lambda n_i,\tag{S2}$$

5 where, r_e is the classical electron radius, λ is the X-ray wavelength and n_i denotes the complex part of the atomic scattering factor that has previously been tabulated as a function of X-ray energy (see $http: //henke.lbl.gov/optical_constants/index.html$). Using the relation between optical density and photon intensity given in Eq. 2, we arrive at:

$$\frac{I}{I_0} = e^{-OD} = e^{-N\mu_a l}.$$
(S3)

It follows that $OD = N\mu_a d$, where N is the number of atoms per unit volume and l is the path length of X-rays through the 10 particle (equivalent to the particle diameter for a spherical particle). The total amount of C and O is given by the difference in post and pre-edge absorption, so that the contribution of OD attributable to either C or O can be written as:

$$\Delta OD = OD_{post} - OC_{pre}.$$
(S4)

The pre and post-edge absorption is defined at 278-320 eV for carbon and 525-550 eV for oxygen. We acquired OD images at these four discrete energies to derive the O:C ratios. The time required for four OD images is significantly less than to

15 acquire an entire spectra (50-100 *OD* images), and so much larger images encompassing more particles could be obtained. This ensured a statistical significance of the average O:C ratio for the sample. Assuming that X-ray absorption is only due to these elements, the O:C ratio can then be calculated by relating the total amount of O and C derived from the NEXAFS spectra:

$$\frac{\Delta OD_C}{\Delta OD_O} = \frac{OD_{C,pos} - OD_{C,pre}}{OD_{O,pos} - OD_{O,pre}}$$
(S5)

$$= \frac{N_C d(\mu_{a,C,pos} - \mu_{a,C,pre})}{N_O d(\mu_{a,O,pos} - \mu_{a,O,pre})}.$$
(S6)

20 Upon simplification we arrive at the expression for the O:C ratio, $\frac{N_O}{N_C}$, given by:

$$\frac{N_O}{N_C} = \frac{\Delta OD_O}{\Delta OD_C} \cdot \frac{\mu_{a,C,pos} - \mu_{a,C,pre}}{\mu_{a,O,pos} - \mu_{a,O,pre}}.$$
(S7)

Some particles had very little or no detectable oxygen signal and thus, it was not uncommon for $\frac{\Delta OD_C}{\Delta OD_O}$ to be negative. Although negative O:C ratios are physically not feasible, we also included this data to reveal the full variability within our samples. Table S2 shows the median O:C ratio, the median absolute deviation, and the standard error.

Table S2. Median (\tilde{X}) O:C ratios for unaged and acid aged soot samples, MAD denotes the median absolute deviation of O:C, σ is the standard deviation after removing outliers, defined when the O:C of a particle deviates from the median by more than 3·MAD, and # denotes the number of particles imaged for each soot type. The number of particles considered as outlier is indicated in parenthesis.

Sample ID	Soot type	\tilde{X}	$\pm MAD$	σ	#
S1	mCASTbl unaged	0.00	0.05	0.06	119(20)
S8	mCASTbl [H_2SO_4] $5 \cdot 10^{-5}$ M	0.04	0.94	1.18	185(38)
S5	mCASTbr unaged	0.05	0.04	0.08	128(16)
S9	mCASTbr [H_2SO_4] $5 \cdot 10^{-5}$ M	0.08	0.04	0.10	101(11)

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