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## **Non-linear release dynamics for a CeO<sub>2</sub> nanomaterial embedded in a protective wood stain, due to matrix photo-degradation**

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1 Non-linear release dynamics for a CeO<sub>2</sub> nanomaterial  
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3 photo-degradation

4

5

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15 DECLARATION OF INTEREST: NONE

16

17

18 HIGHLIGHTS.

19 • Release of Ce due to matrix photo-degradation

20 • 2 distinct phases of release

21 • The release of 1 wt.% of the initial Ce mass appears as a realistic scenario for outdoor exposure of

22 ca. 3.5 years

23 • The presence of CeO<sub>2</sub> nanoparticles in the acrylic stain modifies the behavior of the matrix toward

24 weathering.

25 ABSTRACT.

26 The release of CeO<sub>2</sub>-bearing residues during the weathering of an acrylic stain enriched with CeO<sub>2</sub>  
27 nanomaterial designed for wood protection (Nanobyk brand additive) was studied under two different  
28 scenarios: (i) a standard 12-weeks weathering protocol in climate chamber, that combined condensation,  
29 water spraying and UV-visible irradiation and (ii) an alternative accelerated 2-weeks leaching batch  
30 assay relying on the same weathering factors (water and UV), but with a higher intensity of radiation  
31 and immersion phases. Similar Ce released amounts were evidenced for both scenarios following two  
32 phases: one related to the removal of loosely bound material with a relatively limited release, and the  
33 other resulting from the degradation of the stain, where major release occurred. A non-linear evolution  
34 of the release with the UV dose was evidenced for the second phase. No stabilization of Ce emissions  
35 was reached at the end of the experiments. The two weathering tests led to different estimates of long-  
36 term Ce releases, and different degradations of the stain. Finally, the photo-degradations of the  
37 nanocomposite, the pure acrylic stains and the Nanobyk additive were compared. The incorporation of  
38 Nanobyk into the acrylic matrix significantly modified the response of the acrylic stain to weathering.

39

40

41 KEYWORDS. Aging of nanomaterials, engineered nanomaterials (ENM) release, photo-degradation,  
42 polymer nanocomposites, acrylic stain.

43 CAPSULE.

44 The weathering of a nano-CeO<sub>2</sub>-enriched acrylic stain caused a multi-regime non-linear Ce release,  
45 accompanied by mutually dependent aging of both the matrix and the CeO<sub>2</sub>-nanomaterial.

46

47 MANUSCRIPT TEXT.

## 48 **Introduction**

49 The necessity to better estimate and characterize the release of engineered nanomaterials (ENMs) from  
50 products has been pointed out repeatedly these past years (Caballero-Guzman and Nowack, 2016;  
51 Mackevica and Foss Hansen, 2016; Reijnders, 2009; Som et al., 2010). Real exposure assessments are  
52 indeed still hampered by the difficulty to detect and quantify ENMs in complex natural environments  
53 (Szakal et al., 2014). While models have been developed to compensate the lack of direct  
54 measurements, they often have to rely on oversimplifications and extrapolations in order to estimate the  
55 exposure resulting from ENMs release (Caballero-Guzman and Nowack, 2016), which lowers their  
56 reliability. A more accurate determination of ENMs flows at all stages of the products lifecycle is then  
57 required.

58 The use phase is particularly challenging, as uncontrolled releases of ENMs can result from consumer  
59 handling or aging of the products. Such releases cannot be easily determined in the everyday life. Then  
60 the simulation of relevant aging scenarios under controlled conditions at the lab-scale appears as a good  
61 option.

62 The release of ENM during the use phase will depend on the nanoproduct category. For instance, the  
63 release from liquid suspensions is inherent to use and will be around 100%, while the release from solid  
64 nanocomposites is more difficult to predict. Solid nanocomposites are materials constituted with a solid

65 matrix and ENMs that can be either deposited at the solid surface or incorporated in the bulk as filling  
66 agents (nanofiller). The release of ENM from a solid nanocomposite can proceed from the leaching of  
67 ENMs by a liquid, via desorption from the surface, dissolution, or diffusion inside the matrix (Bossa et  
68 al., 2017; Duncan and Pillai, 2015). But it can also arise from the degradation of the solid matrix itself,  
69 caused by a mechanical action (Bressot et al., 2017) or (photo)chemical reactions (Duncan, 2015).

70 Products with an outdoor application will be especially exposed to photo-degradations due to  
71 weathering processes. The weathering of solid nanocomposites has been the focus of several studies  
72 since the release of TiO<sub>2</sub> nanoparticles from facades was evidenced for the first time by Kaegi *et al.*  
73 (Kaegi et al., 2008). Outdoor weathering setups with rain collectors were developed and allowed  
74 measuring the release of silver nanoparticles from an acrylic white paint (Kaegi et al., 2010) or from  
75 wood protective stains (Künniger et al., 2014) under natural conditions. However, such realistic  
76 scenarios required long-term exposures and many other groups preferred short-term lab-scale artificial  
77 weathering, that are pre-validated to correlate with material degradation CEN standards (Podgorski et  
78 al., 2003). In the past decade, short-term artificial weathering has been performed on paint (Wang and  
79 Nowack, 2018), stains (Shandilya et al., 2015), cement (Bossa et al., 2017; Wohlleben et al., 2011) and  
80 plastic nanocomposites (Fernández-Rosas et al., 2016; Neubauer et al., 2017; Nguyen et al., 2010;  
81 Wohlleben et al., 2017), either using homemade setups (Al-Kattan et al., 2013; Bernard et al., 2011;  
82 Olabarrieta et al., 2012; Pellegrin et al., 2009) or commercial climate chambers (Fiorentino et al., 2015;  
83 Hirth et al., 2013; Vilar et al., 2013; Zuin et al., 2013). Although a variety of weathering protocols have  
84 been tested, they most often included the exposure of the material to an artificial light source, simulating  
85 the full solar spectra (Busquets-Fité et al., 2013; Wohlleben et al., 2013), or restricted to its UV-part  
86 (Al-Kattan et al., 2013; Chin et al., 2004; Fiorentino et al., 2015). It was often combined with an  
87 exposure to water such as controlled relative humidity (Nguyen et al., 2010), periodic condensation  
88 (Fiorentino et al., 2015) or water spraying phases (Fernández-Rosas et al., 2016), representative for  
89 humidity, dew or rain, respectively. Depending on the groups, different methods were applied for  
90 release assessment. Some focused on quantifying the spontaneous release of ENMs during the

91 weathering assays, using collectors to gather particles detached by gravity (Nguyen et al., 2011), or run-  
92 off waters from spraying (Al-Kattan et al., 2015; Busquets-Fité et al., 2013). However, this involved  
93 large volumes of water (up to 5000L (Al-Kattan et al., 2013)). As an alternative, some authors  
94 implemented external release assessment, with (Hirth et al., 2013; Hsu and Chein, 2007) or without  
95 additional mechanical stress (Zuin et al., 2013) (e.g. shaking, sonication, abrasion). Although these  
96 different approaches were found successful, the diversity of protocols and setups made difficult the  
97 comparison between studies, the understanding of the mechanisms and laws governing ENMs release.

98 Recently, efforts were made towards harmonization of the experimental protocols, in the framework  
99 of large pilot interlaboratory studies (Wohlleben et al., 2017, 2014). They converged towards  
100 weathering procedures in climate chambers with or without periodic water spraying, and external  
101 release assessment. This harmonized protocol yielded contrasted results, depending on the nature on the  
102 material: UV-resistant polymers such as polyethylene led to minimal release, while epoxy resins  
103 experienced strong degradations under UV, entailing an accumulation of the ENMs at the surface, and  
104 eventually their release. A comparative study on a wide range of nanocomposites estimated that release  
105 rates from different matrices were spreading across 5 orders of magnitude while the impact of the  
106 nanofiller itself on the release rate was limited to one order of magnitude (Wohlleben and Neubauer,  
107 2016). It was then proposed that matrix degradability determined to a large extent the response of a  
108 nanocomposite to weathering and the ENMs release behavior.

109 In this study, we focused on a single polymer matrix and analyzed the impact of the addition of a  
110 nanomaterial to its weathering. We used an acrylic stain that offers a good resistance to UV (Chiantore  
111 et al., 2000; Forsthuber et al., 2013) and is commonly employed for wood protection. It was enriched  
112 with a CeO<sub>2</sub> nanomaterial, which acts as a UV-absorber and brings an additional protection to the stain.  
113 We studied the weathering of this nanocomposite to answer two questions: i) is there a potential for  
114 release of the nanomaterial upon aging of a UV-resistant matrix ? ii) is the weathering of the acrylic  
115 matrix modified in presence of the CeO<sub>2</sub> nanomaterial? In addition, we characterized a parameter rarely  
116 addressed in details i.e. the evolution of the release rate with the UV irradiation. Two artificial

117 weathering procedures were applied: a standard 12-weeks weathering protocol in a climate chamber,  
118 that combined condensation, water spraying and UV-visible irradiation, close to the harmonized  
119 protocol mentioned above; and an alternative accelerated 2-weeks batch assay applying the same  
120 weathering factors (water and UV), but with a higher intensity of radiation. In both experiments, the  
121 nanocomposite was weathered along with the reference stain without CeO<sub>2</sub> addition, in order to evaluate  
122 the impact of the nanomaterial on the aging. Surface degradations were monitored as an indicator for  
123 weathering. The release of Ce (as dissolved and/or particulate fraction) was quantified with short time  
124 steps (e.g. 24h to 72h), to analyze the release dynamics during weathering and relate it to the  
125 degradations of the stain surface. Finally the physico-chemical transformation of the nanomaterial  
126 within the stain with weathering duration was characterized to give an insight into aging mechanisms.

127

## 128 **Material and methods**

### 129 *Materials*

130 An acrylic stain commercialized by Castorama under one of its brand (Lasure Intérieur- Extérieur  
131 casto') was chosen for this study. It was deposited in three layers, on larch substrates, freshly sanded  
132 with 180 grain paper, observing 2-hours drying between successive layers and 24h final drying.

133 Two groups of samples were prepared. In the first group (called n-CeO<sub>2</sub>), the stain was enriched with  
134 citrate-coated CeO<sub>2</sub> nanoparticles, to improve UV filtering. For this, a commercial suspension  
135 (Nanobyk-3810) was added to the stain at 7wt.%, and this mix was applied to the upper face (*i.e.*  
136 exposed face) of the substrate sample (Figure 1). The characterization and aging of Nanobyk additive  
137 was done previously (Auffan et al., 2014). Lateral and lower faces were coated with the stain alone to  
138 protect the wood substrate during weathering.

139 In parallel, a second group of samples (called ACR) was painted on all faces with the Ce-free stain. It  
140 was used as a reference to evaluate the impact of ENM addition on the aging of the stain.

141 For the weathering experiments in the climate chamber (Suntest samples), larch blocks of 27 x 27 x  
 142 13 mm were cut. They were weighed before and immediately after the application of each layer of stain.  
 143 Taking into account a 18% CeO<sub>2</sub> content for Nanobyk additive (Tella et al., 2014), the amount of CeO<sub>2</sub>  
 144 deposited on each sample (upper face) was calculated, and is reported in Table 1.

145 For batch experiments, the stain deposit was made on a larger piece of wood (600 x 35 x 11 mm), cut  
 146 afterwards into 35 x 35 x 11 mm blocks. Lateral faces were covered with Ce-free stain after cutting.  
 147 This method resulted in a less accurate determination of CeO<sub>2</sub> content, as final samples could not be  
 148 weighed individually. CeO<sub>2</sub> surface concentration and stain density were then assessed based on the  
 149 assumption that batch samples exhibited the same final CeO<sub>2</sub> content (wt.%) as Suntest samples.

150

151 **Table 1.** Exposed surface, dry stain mass and density, mean CeO<sub>2</sub> mass deposited on samples, and resulting CeO<sub>2</sub> content  
 152 (wt.%) and surface concentration. Standard deviation is reported in parenthesis. On batch samples, no data was available  
 153 regarding the final mass of the stain. An equivalent CeO<sub>2</sub> final content (wt.%) to Suntest samples was assumed and CeO<sub>2</sub>  
 154 surface concentration, stain density and stain mass after drying were calculated based on this assumption (in italics).

	Suntest		Batch	
	n-CeO <sub>2</sub>	ACR	n-CeO <sub>2</sub>	ACR
Exposed surface (mm <sup>2</sup> )	729	729	1225	1225
Stain mass after drying (mg)	38 (18)	48 (36)	<i>40 (20)</i>	<i>27 (22)</i>
Stain density (g.m <sup>-2</sup> )	52 (24)	70 (47)	<i>33 (17)</i>	<i>22 (18)</i>
Deposited CeO <sub>2</sub> (mg)	1.5 (0.2)	-	1.8 (0.3)	-
Final CeO <sub>2</sub> content (wt.%)	4.5 (1.5)	-	<i>4.5 (1.5)</i>	-
<b>CeO<sub>2</sub> surface concentration (mg.m<sup>-2</sup>)</b>	2089 (273)	-	1481 (289)	-

155

### 156 *Artificial weathering*

157 Two artificial weathering procedures, based on a succession of dry irradiation and immersion or water  
 158 spraying phases, were tested. The two sets of experiments were both built on a cycle of 7 days  
 159 applying the same weathering factors but they were not designed to be compared in term of Ce release  
 160 and stain degradation. The first one was performed in a climate chamber Suntest XLS+ (Atlas



161 Material testing Solutions, Germany) for 12 weeks. It combined dry UV irradiation phases with water  
162 spraying events to simulate as much as possible a long-term “realistic” scenario. The weathering  
163 program was inspired from a standardized protocol (NF EN 927-6, 2006) specific to wood stains, but  
164 it was adapted to quantify in details Ce releases and release rates with the UV irradiation and to  
165 differentiate Ce release as dissolved Ce from particulate Ce.

166 A second simplified and accelerated protocol was developed for a 2-weeks batch experiment (batch  
167 test). It was designed to provide complementary information on the light effect by comparing release  
168 from illuminated samples and non-illuminated samples (dark samples). The purpose of this protocol  
169 was to determine whether the release behavior of a solid nanocomposite could be estimated with a  
170 short-term experiment.

171

#### 172 Weathering in the climate chamber Suntest XLS+:

173 As described in standard NF EN 927-6, the weathering program was based on weekly cycles repeated  
174 for 12 weeks. The weekly weathering cycle started with a 24h condensation, performed in a  
175 homemade setup outside the climate chamber (Figure S1, Supplementary Content). Then, ACR and n-  
176 CeO<sub>2</sub> samples were introduced inside the Suntest XLS+ and alternatively exposed to Xe lamp and  
177 Milli-Q water spraying for the rest of the week. Adaptations to the standard protocol were made, in  
178 order to quantify Ce releases and monitor their evolution during weathering. First of all, the volume of  
179 water sprayed was strongly reduced, by lowering the spraying frequency from 30 minutes every 180  
180 minutes (NF EN 927-6), to four 20 minutes events, distributed over the week as described by Figure  
181 1a. The water flowing at the surface of samples during spraying phases was collected in order to  
182 evaluate Ce releases induced by weathering. To do so, groups of 6 samples, representing a total  
183 exposed surface of 4374 mm<sup>2</sup>, were placed inside 800mL glass beakers. Raised and slanted PTFE  
184 holders were used, to avoid immersion and water stagnation at the sample surface. A total of five  
185 beakers (3 with n-CeO<sub>2</sub> and 2 with ACR) holding 6 samples were fitted inside the climate chamber,  
186 arranged on a rotating plate (PL SPP 2 with PMMA plate Ø 300mm, MG Industries, France) to ensure

187 homogenous spraying on all the samples (Figure 1c). Each beaker was weighed before and after each  
188 “rain” event to determine the exact volume of water received by the samples. In average 145 mL ± 42  
189 mL water were collected in one beaker during the 20 minutes spraying, which corresponded to a mean  
190 L/S ratio (rain volume/exposed stain mass) around 500 - 600 for each rain event. The cumulative L/S  
191 ratio at the end of the experiment was between 24000 and 30000 (depending on the beaker). Water  
192 sampling from these lixiviates was carried out 3 times a week as indicated by the asterisks in Figure  
193 1a for ICP-MS analysis. More details on the water sampling protocol can be found in Supplementary  
194 content.

195 During irradiation phases, the intensity of radiation was set to  $65\text{J.m}^{-2}.\text{s}^{-1}$  (300nm-400nm) at chamber  
196 floor, resulting in an effective UV intensity of  $91\text{J.m}^{-2}.\text{s}^{-1}$  at the elevated position of samples.  
197 Complementary with UV dose, irradiance in the 300 nm – 800nm range was measured once a week  
198 with an external radiometer MacSolar (SOLARC, Germany) and was found to be around  $500\text{J.m}^{-2}.\text{s}^{-1}$   
199 at the sample surface. The chamber temperature was around 30°C (max 36.6°C) during dry irradiation  
200 phases and 21°C (max 30.5°C) during water spraying, while black body temperature (BST panel) was  
201 measured respectively at 52°C (max 64.4°) and 21°C (max 32.9°C). An additional measurement of  
202 the temperature at sample surface during an irradiation phase indicated a value of *ca* 36°C.

203 At the end of each weekly cycle, one n-CeO<sub>2</sub> and one ACR sample were withdrawn from the  
204 experiment and replaced by fresh samples. The degradation of the stain could then be followed week  
205 after week. After 12 weeks, 1000 mm precipitations and a UV dose of  $513\text{MJ.m}^{-2}$  ( $2826\text{MJ.m}^{-2}$  in  
206 the 300 nm – 800 nm range) were accumulated by the oldest samples. In France, such precipitations  
207 and irradiance are usually reached in 8-12 months depending on the area (INES Education, n.d.;  
208 “Météo France - Météo et Climat,” n.d.)

#### 209 Batch weathering:

210 In this test, a higher intensity of radiation (i.e. radiant exposure in the 300-800 nm range) was used  
211 and full immersion of the sample was substituted to water spraying in order to accelerate weathering.

212 Immersion was also selected because it could be implemented more easily. The detailed experimental  
213 protocols are described below.

214 Batch weathering was based on a weekly cycle as during the Suntest experiments. It alternated dry  
215 irradiation phases with 5 immersions, distributed over the week as shown in Figure 2. During  
216 immersions, stained samples (ACR and n-CeO<sub>2</sub> samples, n=3 for each condition) of 35 x 35 x 11 mm,  
217 with an exposed surface of 1225 mm<sup>2</sup>, were placed in separate polypropylene (PP) beakers and  
218 submerged for 1.5h in 150mL Milli-Q water. One beaker without sample was also set up for blank.  
219 Constant magnetic stirring ensured a good homogenization of the leachate. pH and conductivity were  
220 measured before and after each immersion. At the end of immersion, a 20mL-aliquot was extracted  
221 for ICP-MS analysis. It was compensated with an equivalent volume of Milli-Q water to maintain a  
222 constant L/S ratio (immersion volume/stain mass) of 3750 during the whole experiment. Between two  
223 immersions, samples were withdrawn from the PP beakers and exposed to a 400W HPI-T Plus Metal  
224 Halide lamp (Philips, France, see Figure S2 for emission spectra). Beakers with leachate were covered  
225 and maintained in the dark to avoid leachate evolution until the next immersion. The distance of the  
226 sample to the lamp was adjusted to reach a high intensity of radiation. Mean irradiance at sample  
227 surface was measured at 105 J.m<sup>-2</sup>.s<sup>-1</sup> for UV range (290nm-390nm) and 1300 J.m<sup>-2</sup>.s<sup>-1</sup> for the 300nm-  
228 800 nm range, with a PCE-UV34 radiometer (PCE Ibérica S.L., Spain.) and MacSolar radiometer,  
229 respectively.

230 The experiment was reproduced for 2 consecutive weeks resulting in a UV dose of 97 MJ.m<sup>-2</sup> (1367  
231 MJ.m<sup>-2</sup> in the 300 nm-800 nm range) at the end of the assay. Sample temperature alternated between  
232 44°C during irradiation phase and 27°C during immersions.

233 The same weathering experiment of 2 weekly cycles was also performed in the dark (immersion step  
234 without irradiation) to investigate the influence of light on the degradation of the stain and  
235 nanomaterials release. The experimental setup and the weekly weathering cycle are detailed in Figure  
236 2.

237

### 238 *Quantification of Ce release*

239 Ce concentration in lixiviates of both experiments was analyzed by ICP-MS (Nexion 300, Perkin  
240 Elmer, France) after acidification at 2,5% HNO<sub>3</sub> (Ultrapure NORMATON 67%) following Ce isotope  
241 (<sup>140</sup>Ce). In the Suntest experiments, 20mL of sub-sample were filtrated at 10kDa (using Amicon 8050  
242 unit with cellulose membrane) before acidification in order to determine dissolved fraction of Ce in the  
243 lixiviates.

### 244 *Alteration of the nanocomposite due to weathering*

245 The degradation of the stains was estimated based on the detection of defects. Three phenomena  
246 defined in standard NF EN 927-6 were monitored: blistering, flaking and cracking. Blistering is defined  
247 as a lifting of the stain from the underlying surface, which appears as bubbles or blisters in the paint,  
248 usually caused by heat, moisture or a combination of both. It can eventually lead to peeling of the stain  
249 if not corrected. Cracking indicates splitting of the paint film through at least one coat, leading to failure  
250 of the paint. In its early stages, the problem appears as hairline cracks; in its later stages, flaking, i.e. a  
251 peeling of the paint from the underlying surface in the form of flake, can occur.

252 The observation of defects was made by optical microscopy at magnification x5 and x10, on a Leica  
253 DM RXP microscope. ISO standards 4628-1(2003) (ISO 4628-1, 2003), 4628-2(2003) (ISO 4628-2,  
254 2003), 4628-4(2003) (ISO 4628-4, 2003) and 4628-5(2003) (ISO 4628-5, 2003) were used as references  
255 to rate defect size and density. Grades for defects density and size are detailed in supporting information  
256 (tables S4 and S5).

257 Moreover, the oxidation state of Ce inside the stain was characterized before and after weathering, as an  
258 indicator for the alteration of CeO<sub>2</sub> nanomaterial. To this end, a thin laminate of the exposed face of  
259 Suntest samples was cut and analyzed by X-ray Absorption Near-Edge Spectroscopy (XANES) at the  
260 Ce-L<sub>3</sub> edge (5723 eV). Acquisition was made in the fluorescence mode (Canberra Ge-solid-state  
261 detector) on the CRG-FAME BM30B beamline at the ESRF (Grenoble, France). The beam size was  
262 100µm x 300µm. Ce<sup>III</sup>-oxalate and the commercial additive Nanobyk-3810, which contained only

263 Ce<sup>IV</sup>O<sub>2</sub> nanoparticles as determined previously (Auffan et al., 2014), were used as Ce<sup>III</sup> and Ce<sup>IV</sup>  
264 reference compounds, respectively. Each spectrum was at least the sum of two scans. XANES data were  
265 processed using an IFEFFIT software package (Ravel and Newville, 2005). Linear Combination Fits  
266 were performed in order to determine the relative Ce<sup>III</sup> and Ce<sup>IV</sup> contents.

267

## 268 **Results**

### 269 *Dynamics of Ce release*

270 Ce releases measured after water spraying events in the Suntest and immersions of batch experiments  
271 are reported in Figure 3a and Figure 4a. Data were plotted as a function of the UV dose. A table giving  
272 the equivalence between weathering time in weeks, UV dose and irradiation in the 300 nm – 800 nm  
273 range for both experiments is presented in Table S3.

274 For the Suntest experiments, Ce was detected in all lixiviates obtained from n-CeO<sub>2</sub> samples, while it  
275 was below the ICP-MS detection limit (DL < 0.1 ng.g<sup>-1</sup>) for the majority of ACR samples. Occasional  
276 levels above DL probably result from a contamination and cannot be considered as representative for a  
277 release of Ce from the stain matrix.

278 Besides the strong initial release ( $327 \pm 28 \mu\text{g.m}^{-2}$ ), the measured Ce releases varied from a few  $\mu\text{g.m}^{-2}$   
279 to  $\sim 200 \mu\text{g.m}^{-2}$ . This corresponded to Ce concentrations between 0.1 and 5  $\mu\text{g.L}^{-1}$  in “rain” waters. In  
280 Figure 3a, strong fluctuations are observed between consecutive time points. They are due to the  
281 modulations of the weekly weathering cycle in Suntest experiments, that imposed different irradiation  
282 times (22h, 44h or 72h) or number of water spraying events (1 or 2) between two sampling events  
283 (Figure 1a). In order to reduce this variation and better observe the general trend, Ce releases of Suntest  
284 experiment were integrated over the weekly cycle (Figure 3b). Two different regimes of emissions can  
285 be distinguished. During the four first weeks of weathering (total UV irradiation  $\leq 155 \text{ MJ.m}^{-2}$ ) Ce  
286 releases are erratic with a rather decreasing trend. After 5 weeks, weekly emissions start increasing.

287 Their magnitude increases with cumulative UV irradiation, and no stabilization is reached at the end of  
288 the experiment (12 weeks, 513 MJ.m<sup>-2</sup>).

289 The chemical analysis of the Suntest samples filtrated at 10kDa (Figure 3b, light blue) shows that Ce  
290 is released in the form of both particulate and dissolved species. The calculated Dissolved/Total Ce ratio  
291 varies strongly during the four first weeks of experiments, but after 155 MJ.m<sup>-2</sup> (4 weeks), it oscillates  
292 between 0.3 and 0.5 with a mean value of 0.4. CeO<sub>2</sub> nanoparticles in the additive initially consist in pure  
293 Ce<sup>IV</sup> (cerianite CeO<sub>2</sub>) (Auffan et al., 2014) and are considered to be poorly soluble in aquatic media  
294 (Söhnel and Garside, 1992) . The presence of dissolved Ce in the lixiviates indicates an alteration of the  
295 nanomaterial and implies the reduction of Ce<sup>IV</sup> to Ce<sup>III</sup> (more soluble at pH 6).

296 For batch experiment (Figure 4a), a release of 75-250 µg.m<sup>-2</sup> of Ce was detected directly after  
297 immersion 1 regardless of the irradiation regime (dark or light). Cerium release did not exceed  
298 background levels from 32 MJ.m<sup>-2</sup> to 46 MJ.m<sup>-2</sup> (immersion 4), then increased for n-CeO<sub>2</sub> samples  
299 exposed to light, while they remained below the DL for samples kept in the dark. The first measurable  
300 releases at 46 MJ.m<sup>-2</sup> were around 0.08 mg.m<sup>-2</sup> of Ce, then kept increasing to reach 1.3 ± 0.4 mg.m<sup>-2</sup> of  
301 Ce at 97 MJ.m<sup>-2</sup>. This trend was disturbed only by a strong release event at 77 MJ.m<sup>-2</sup> (2.9 ± 1.8 mg.m<sup>-2</sup>  
302 of Ce, immersion 1, week 2), which is probably the result of the longer irradiation period of 72h at the  
303 beginning of the new cycle. Combined with the absence of Ce release from dark samples after  
304 immersion 1, this shows a clear correlation between exposure to sunlight and Ce emissions. Once again,  
305 no stabilization in Ce release was observed at the end of the experiment, which is consistent with the  
306 trend measured for the Suntest experiments at higher cumulated UV doses.

307 The two aging scenarios express a very similar behavior, with two distinct phases for Ce release. The  
308 initial phase (phase I) showed an overall decreasing trend with time and no clear dependency on light. In  
309 the second phase (phase II) emissions increased with weathering and are light-dependent. No plateau in  
310 Ce release was observed at the end of both assays.

311 Ce releases cumulated over the duration of the experiments were plotted in Figure 3c and Figure 4b.  
312 They confirmed the similar trends observed for both experiments. At the end of the aging experiments,

313 the total Ce release reached  $2.8 \pm 0.3 \text{ mg.m}^{-2}$  for the Suntest and  $6.0 \pm 2.4 \text{ mg.m}^{-2}$  for the batch assay. In  
 314 both cases, this represented less than 1wt.% of the initial Ce mass ( $\sim 0.16\text{wt.}\%$  for Suntest samples,  
 315  $\sim 0.5\text{wt.}\%$  for batch samples). A strong initial release was measured during the first rain event of the  
 316 Suntest experiments ( $327 \pm 28 \text{ }\mu\text{g.m}^{-2}$  of Ce) accounting for 12% of total Ce emissions. The initial  
 317 release was much lower in batch test, ( $< 0.1 \text{ }\mu\text{g}$  of Ce) accounting for only 1.3% of the total Ce  
 318 emissions. For the two tests, most of the Ce release took place in the second part of the experiment  
 319 (phase II), representing 73% and 98% of Ce emissions, for the Suntest protocol (after  $155 \text{ MJ.m}^{-2}$ ) and  
 320 batch experiment (after  $46 \text{ MJ.m}^{-2}$ ), respectively.

321 In order to get an insight on Ce release for longer weathering durations, release curves obtained in the  
 322 two experiments were fitted by a second order polynomial law. Fitting parameters are reported in Table  
 323 2. Fits were extrapolated to assess the irradiation necessary to reach the release of 1%, 10% or 100%  
 324 release of the initial Ce mass in our specific experimental conditions (i.e. for a given type and thickness  
 325 of stain). For the Suntest protocol, 1wt.% of the initial Ce amount is predicted to be released after  $1250$   
 326  $\text{MJ.m}^{-2}$ , 10% after  $3800 \text{ MJ.m}^{-2}$  and 100% after  $11800 \text{ kWh.m}^{-2}$ . According to the Solar Radiation Data  
 327 (“SoDa - Web Services,” n.d.), the annual UV dose corresponding to the area of Marseille in France is  
 328 around  $350 \text{ MJ.m}^{-2}$ . Based on this data, the release of 1% of the initial Ce mass corresponds to 3.5 years  
 329 of aging of the stain. However, the release of 10wt.% or 100wt.% of the Ce present in the stain would  
 330 require 10 and 33 years, respectively. The fit of batch data leads to very different values, with 1% of  
 331 total Ce mass being released after  $130 \text{ MJ.m}^{-2}$ , 10% after  $355 \text{ MJ.m}^{-2}$  and 100% after  $1070 \text{ MJ.m}^{-2}$ .  
 332 These values correspond to outdoor exposures of 4 months, 1 year and 3 years in the south of France.

333

334 **Table 2.** Parameters of the polynomial fit of release curves.  $y = m_0 + m_1*x + m_2*x^2$ .

<b>Experiment</b>	<b><math>m_0</math></b>	<b><math>m_1</math></b>	<b><math>m_2</math></b>	<b><math>R^2</math></b>
<b>Suntest</b>	0.8171	- 0.0024	$1 \times 10^{-5}$	0.997
<b>Batch</b>	- 0.158	- 0.0479	$1.1 \times 10^{-3}$	0.995

335

336

337 Figure 5 shows the evolution of defect density and size for ACR and n-CeO<sub>2</sub> stains observed for the two  
338 aging scenarios. Before weathering, the samples were generally free of defects. Isolated flakes were  
339 present on a few samples but cracking and blistering were not observed. The samples that were  
340 weathered in the dark did not develop any defect (not shown). On the contrary, defects appeared at the  
341 surface of samples that were exposed to light (Figure S4). The batch aging protocol induced blistering  
342 for both Ce-enriched or Ce-free stain, but no cracking nor flaking was observed (Figure 5c and d).  
343 Similar blisters sizes and densities were measured for ACR and n-CeO<sub>2</sub> samples, with a growing  
344 magnitude as aging proceeded. For ACR samples weathered in Suntest XLS+, defects mainly took the  
345 shape of flakes and cracks (Figure 5a). Blistering was rarely observed. Defects appeared at a very early  
346 stage of the experiments. However their density remained rather low (mainly grade 1, as defined in ISO  
347 4628-2, 4628-4 and 4628-5) and their size ranked mostly S1 (*i.e.* = only visible under magnification  
348 x10) or S2 (*i.e.* = incipiently visible with normal and corrected vision) on some occasions (indicated by  
349 a star symbol). Neither defect density nor size showed a significant evolution with the UV dose,  
350 confirming the good resistance of this material to weathering.

351 A totally different pattern emerged for n-CeO<sub>2</sub> samples. Their surface remained rather free of defects  
352 during the four first weeks of experiment, showing a good initial resistance to weathering. Nevertheless,  
353 after 155 MJ.m<sup>-2</sup> (dotted line in Figure 5b), defects started multiplying. As ACR samples, n-CeO<sub>2</sub>  
354 samples displayed cracks under microscopic magnification (x10) but their density reached higher  
355 grades. Flaking was absent from the nanocomposite surface after weathering, but contrary to the  
356 reference material, dense and large blisters became visible. No significant variations in defect sizes were  
357 observed with aging, but the density was clearly higher after 4 weeks weathering (155 MJ.m<sup>-2</sup>),  
358 correlated with the change in Ce release regime (Figure 3b).

359 Cracks are the defects most frequently reported for acrylic stains weathered under both artificial (Aloui,  
360 2006; Irmouli et al., 2012; Kielmann and Mai, 2016; Olsson et al., 2014; Popescu and Simionescu,  
361 2013) and natural conditions (De Windt et al., 2014; Olsson et al., 2014). They can sometimes lead to



362 flaking, but blistering is usually not expected. This scenario matches well the observations made on  
363 ACR samples of our Suntest experiment but deviates from what was observed for the rest of samples.  
364 During batch testing, blistering was developed in a similar way for Ce-enriched or Ce-free stain. This  
365 effect could then find an origin in the experimental protocol itself, where repeated immersions could  
366 favor water penetration and entrapment at the wood/stain interface. After Suntest weathering (and  
367 periodic condensation phases), n-CeO<sub>2</sub> samples showed a significant blistering, which was absent from  
368 the surface of ACR samples (Ce-free stain);

369 In addition to wood stain degradation, the oxidation state of Ce inside the stain was monitored as an  
370 indicator for the alteration of the CeO<sub>2</sub> nanomaterial. XANES spectra of the Nanobyk additive and the  
371 non-weathered n-CeO<sub>2</sub> sample are given in Figure 6. They exhibit two peaks (double white line) at ~  
372 5728 eV and ~ 5735 eV, corresponding respectively to the final states 2p4f<sup>15</sup>d<sup>1</sup>L and 2p4f<sup>05</sup>d<sup>2</sup> of Ce<sup>IV</sup>  
373 (Dexpert et al., 1987; Finkelstein et al., 1992) . Both match perfectly showing that CeO<sub>2</sub> nanoparticles  
374 were not altered by their incorporation into the stain and its deposition onto a wood substrate. After 12  
375 weeks of weathering following the Suntest protocol (513 MJ. m<sup>-2</sup> UV dose), the double white line  
376 characteristic of Ce<sup>IV</sup> states is still visible on the XANES spectra. However a third peak appeared at  
377 ~5724 eV that is the absorption energy of the Ce<sup>III</sup> reference compound. Cerium<sup>III</sup> oxalate is also plotted  
378 in Figure 6 and presents a single white line, corresponding to the 2p<sub>3/2</sub> / 4f<sup>15</sup>d electronic transition  
379 (Takahashi et al., 2002), at ~5724 eV. Consequently, we assume that part of the Ce initially present in  
380 the stain as Ce<sup>IV</sup> was then reduced to Ce<sup>III</sup> during weathering. Linear Combination Fits (LCF) were  
381 performed on the derivatives of XANES spectra to determine the relative Ce<sup>IV</sup> and Ce<sup>III</sup> contents. The  
382 results are reported in Table 3 for three different locations on the sample. On average, a Ce<sup>III</sup> content of  
383 38% ± 4% was found.

384

385 **Table 3.** Results of the Linear Combination Fits (LCF) performed on the derivatives of XANES spectra measured at three  
 386 different spots of an n-CeO<sub>2</sub> sample weathered for 12 weeks in Suntest XLS+ (513 MJ.m<sup>-2</sup>). The error on the calculated Ce<sup>IV</sup>  
 387 and Ce<sup>III</sup> content is ± 10%

n-CeO <sub>2</sub> 12 weeks	Ce <sup>IV</sup>	Ce <sup>III</sup>	R	chi <sup>2</sup>
<b>Spot 1</b>	73%	42%	0.012981	0.03407
<b>Spot 2</b>	79%	33%	0.010084	0.02433
<b>Spot 3</b>	75%	38%	0.015139	0.03815

388

389

## 390 Discussion

### 391 *Release of Ce*

392 The release of Ce from an acrylic matrix enriched with a CeO<sub>2</sub> nanomaterial (Nanobyk additive) was  
 393 evidenced with our two weathering protocols. Far from being a negligible phenomenon, Ce emissions  
 394 from 2 to 200 µg.m<sup>-2</sup> were measured for each rain event from the beginning of the Suntest experiment.  
 395 After 46 MJ.m<sup>-2</sup>, Ce release ranging from 0.08 to 2.9 mg.m<sup>-2</sup> was also systematically observed during  
 396 the immersions of the batch test. The residual release detected for samples maintained in the dark in  
 397 batch experiment indicates that the exposure to UV (and visible) irradiation is the driving force of the  
 398 release. Water certainly acts as a vector removing degradation debris from the sample surface, but did  
 399 not induce weathering in the absence of UV. Combined to UV, it very likely contributed to accentuate  
 400 the weathering via hydrolytic reactions, as suggested by Wohlleben et al. in the case of polyamide  
 401 (Wohlleben et al., 2014). Cumulated over the experiment, Ce release caused by water spraying events  
 402 during Suntest testing reached *ca.* 3 mg.m<sup>-2</sup>. Recently, harmonized weathering protocols have been  
 403 proposed, using external release measurements (Wohlleben et al., 2017) that would exclude such  
 404 spontaneous release from their assessment, resulting in an inaccurate determination of the released  
 405 mass.

406

### 407 *Dynamics of Ce release*

408 The evolution of release as a function of the UV irradiation was thoroughly analyzed in our two  
409 weathering scenarios. They revealed dynamic release processes that could similarly be divided in two  
410 distinct phases and presented common features in both experiments. The first phase (phase I) showed a  
411 decreasing trend with time, similarly to what was described by other authors for paints (Al-Kattan et al.,  
412 2013; Kaegi et al., 2010). As no clear dependency on light exposure was found, the release mechanism  
413 is certainly a wash off of loosely bound material from the surface. Unlike in the above-cited studies, in  
414 this experiment, the initial phase was followed by a second one, where Ce emissions increased for  
415 irradiated samples and kept growing until the end of the tests. The exposure to UV-visible radiation and  
416 the dose received by the samples appeared as key parameters in that phase. In particular, phase II  
417 showed a significant accentuation of Ce release with increasing exposure to UV radiation. We postulate  
418 then, that release was a consequence of the photo-degradation of the stain, as already witnessed for  
419 epoxy (Nguyen et al., 2011) or polyamide (Fernández-Rosas et al., 2016). In both experiments, it was  
420 found that the release measured in the second phase accounted for more than 70% of the total Ce release  
421 (73% in Suntest and 98% in batch test). Therefore the release due to photo-degradation largely  
422 predominates over the release of loose material in this study. No stabilization of Ce release was reached  
423 at the end of our experiments. Increased Ce emissions are expected, if weathering proceeds on the same  
424 trend, but they could also accentuate and accelerate if matrix aging gets worse. Indeed, previous work  
425 already showed that strong damages occurred on commercial photocatalytic stains after 7 months lab  
426 weathering, with a direct impact on the amount and the form of TiO<sub>2</sub> nanoparticles released during  
427 abrasion processes (Shandilya et al., 2015). Prolonged laboratory tests or higher radiant exposures are  
428 necessary to determine the long-term release behavior.

429 It is interesting to highlight that the release rates determined in phase II did not follow a linear trend,  
430 and were fitted instead by a 2<sup>nd</sup> order function. Until now, release studies often provided as result a  
431 single value of release rate. This is appropriate when release observes a constant or linear trend, as  
432 reported for nano-SiO<sub>2</sub> in acrylic paints (Al-Kattan et al., 2015) or epoxy (Nguyen et al., 2010).  
433 However, a recent review (Koivisto et al., 2017) pointed out that release may not always be linearly

434 proportional to the UV dose. The authors introduced a relation to describe the release due to UV  
435 radiation as follow:

$$436 \quad R = a \times D^b$$

437 Where  $R$  is the release rate in  $\text{mg.m}^{-2}$ ,  $D$  the UV irradiation energy in  $\text{MJ.m}^{-2}$ , and  $a$  and  $b$  are fitting  
438 parameters. A  $b$  factor around 1, implying linearity between the release rate and UV dose, was  
439 determined on four occasions for release data found in the literature, but values of  $b \neq 1$  were  
440 predominant. Our results support a non-linear release function in the case of the n-CeO<sub>2</sub> nanocomposite,  
441 but could not be fitted satisfactorily by a power law. This may be due to the fact that the release function  
442 proposed by Koivisto *et al.* is analogous to the Schwarzschild's law, and describes photo responses  
443 resulting from irradiation (Martin et al., 2003). In our experiments an additional factor of degradation  
444 was present in the form of water, which may cause a divergence from the power law. Besides, we  
445 identified two distinct regimens of Ce release, similarly to what was observed for Si release from 5 wt.  
446 % nano-SiO<sub>2</sub> epoxy composite (Sung et al., 2015) and polyurethane nanocomposite (Jacobs et al.,  
447 2016).

448 It suggests that different processes may be at stake in ENM release and emphasizes the need for  
449 investigating the dynamics of release more carefully.

450

#### 451 *Long-term release estimates*

452 Surprisingly, despite very different weathering conditions, our experimental aging protocols displayed a  
453 very good agreement in their overall release tendencies (i.e. stain degradation and Ce release). However,  
454 significant deviations appeared with a more quantitative analysis Extrapolation of the data indeed led to  
455 totally different estimates of the UV doses necessary to reach 1wt.%, 10wt.% or 100wt.% release of the  
456 Ce initially present in the material. In the Suntest experiment, the release of 1% of the initial Ce mass  
457 appeared as a realistic scenario for an outdoor exposure of *ca.*3.5 years. The release of 10% of the initial  
458 Ce puts the aging well beyond the typical recommended 5 year lifetime of an outdoor wood stain, and  
459 the 100% release of Ce would even take 33 years. On the other hand the extrapolation of batch data (i.e.

460 implying repeated full immersion of the samples) concluded that 1% release should be achieved after a  
461 few months, 10% short after 1 year and 100% after about 3 years. All these durations lied within the  
462 lifetime of the stain (ca. 5 years) and a 100% release could then be expected based on this experiment.

463

#### 464 *Stain degradation due to weathering*

465 In addition to release quantification, the alteration of the stain caused by weathering was  
466 characterized, based on the occurrence of defects (blisters, flakes or cracks) at the sample surface. It  
467 unveiled another divergence between the two weathering protocols, in the defects produced on the  
468 stains. Blistering was predominant on both ACR and n-CeO<sub>2</sub> samples of the batch testing, while it was  
469 rarely observed under natural circumstances. This suggested that the applied weathering conditions may  
470 be unrealistic and questioned the reliability of the release assessment in that case. On the contrary, the  
471 weathering of ACR stains in the Suntest XLS+, showing slight cracking and flaking, was consistent  
472 with what is usually observed under natural conditions (De Windt et al., 2014; Olsson et al., 2014). This  
473 confirmed both the good resistance of acrylic stains to weathering and the realistic character of the  
474 Suntest experiment.

475 Contrary to ACR samples, the n-CeO<sub>2</sub> samples weathered with the Suntest protocol showed a  
476 densification of their defects after 155 MJ.m<sup>-2</sup>. It coincided with the increase of Ce release, reinforcing  
477 the hypothesis that Ce emissions of phase II resulted from a degradation of the stain. It also suggested  
478 that there is a relationship between defect formation and release. A high density of defects was observed  
479 on the Suntest samples and the release rate at 110 MJ.m<sup>-2</sup> was around 0.7 mg.m<sup>-2</sup>. For the batch samples,  
480 the density and size of surface defects remained lower, but they displayed an almost ten times higher  
481 release rate at 97 MJ.m<sup>-2</sup> : 6 mg.m<sup>-2</sup>. Therefore we conclude that Ce release was not a direct  
482 consequence of the formation of cracks or blisters. We rather think that these are two outcomes of the  
483 same degradation phenomenon. If the correlation between the formation of defects and release can be  
484 confirmed on other systems, defects could however serve as an indicator for release in the future.

485 The higher cracking density measured for n-CeO<sub>2</sub> samples with respect to the pure acrylic stain, may  
486 result from a stiffening of the film, due to dense Ce. The n-CeO<sub>2</sub> samples also developed blisters that  
487 were not observed on the ACR samples (CeO<sub>2</sub>-free stain). This suggests that the incorporation of CeO<sub>2</sub>  
488 nanoparticles to the acrylic matrix modified its response to weathering.

489

#### 490 *Aging of CeO<sub>2</sub> nanomaterial inside the stain*

491 Finally the presence of dissolved Ce was evidenced in lixiviates. X-ray absorption spectroscopy proved  
492 that the reductive dissolution of the CeO<sub>2</sub> nanomaterial started in the stain, leading to the release of  
493 dissolved Ce<sup>III</sup> in the lixiviates. The initial CeO<sub>2</sub> nanoparticles experienced a transformation during the  
494 weathering of the nanocomposite, resulting in the release of a material significantly different from the  
495 pristine CeO<sub>2</sub> nanoparticles. In the past years, literature reviews established that ENM release from a  
496 solid nanocomposite often took the form of nanomaterial embedded in matrix fragments (Froggett et al.,  
497 2014) behaving differently than the pristine ENM (Al-Kattan et al., 2014). Here, we bring new elements  
498 suggesting that even if free ENMs were released, they may have experienced transformations during the  
499 weathering process, affecting their fate, their transport, their interactions with organisms and thus  
500 modify their behavior in the environment compared to pristine material. Strikingly, the aging of the  
501 Nanobyk additive in water under UV radiation brought into light an alteration of the CeO<sub>2</sub> nanoparticles  
502 (Auffan et al., 2014). However it consisted in a reorganization of Ce atoms at the nanoparticle surface  
503 and in that case, no reduction of Ce<sup>IV</sup> to Ce<sup>III</sup> was detected. In this study, a different response to aging  
504 was observed for the Nanobyk additive incorporated to the acrylic stain. On the other hand the acrylic  
505 stain also displayed a different weathering behavior with or without embedded nanomaterial. This  
506 advocates for the need of studying nanocomposites as novel materials, with potentially different  
507 responses than their separate compounds.

#### 508 **Conclusions**

509 The dynamics of Ce release from a CeO<sub>2</sub>-acrylic nanocomposite designed for wood protection was  
510 investigated under short- and middle-term assays. It revealed two different regimes of release, as well as  
511 a non-linear relationship between the release rate and UV irradiation, highlighting that release  
512 phenomena cannot always be properly described by a single release rate value. Efforts should then be  
513 made to better characterize the dynamics of release from nanocomposites and help to improve the  
514 accuracy of ENM flow models (Wang and Nowack, 2018).

515 In this work, two weathering scenarios (a realistic middle-term experiment in climate chamber and a  
516 simplified short-term batch test), specifically designed to monitor the evolution of the release rates with  
517 time and UV doses were tested. They displayed a good agreement regarding the occurrence of dual  
518 release regimes. In absence of a release plateau during the experiments, polynomial fits of the release  
519 curves were used to provide estimates of long-term release. The similarity in general release trends  
520 between the two tests showed here some limits, as they led to very different estimates of Ce releases.  
521 Indeed, calculations indicate that after 3.5 years, 100 wt.% of the initial Ce will be released based on the  
522 batch experiment vs 1 wt.% in the Suntest experiment).

523 The two protocols also produced different surface defects on the stains. In particular the defects  
524 observed on batch samples were pointed out as unrealistic, while the Suntest protocol mimicked natural  
525 weathering more faithfully. This supports the reliability of the release rates determined with this  
526 procedure and makes it a good candidate for standardized tests. The good agreement of batch  
527 experiment on the overall release tendency, suggests that it could rather serve as a screening test, to  
528 evaluate the release behavior of a nanocomposite. Systematic testing on a range of materials is  
529 necessary before such a use could be validated.

530 Based on the Suntest experiment the release of 1% of the initial Ce mass during the lifetime of the  
531 stain appears as realistic. However longer experiments are needed to confirm this estimate. An  
532 intensification of the matrix degradations could indeed induce the loss of the acrylic polymer structure,  
533 resulting in a third phase of release.

534 Finally, the incorporation of CeO<sub>2</sub> nanoparticles into the acrylic matrix has been shown to modify the  
535 response of the stain to weathering while the CeO<sub>2</sub> nanomaterial experienced a transformation that was  
536 not expected based on previous weathering experiments. The weathering of a nanocomposite cannot be  
537 decomposed as the weathering of two isolated parts. Synergistic effects can arise between the matrix  
538 and its nanomaterial, making the study of the weathering of nanocomposites necessary.

539

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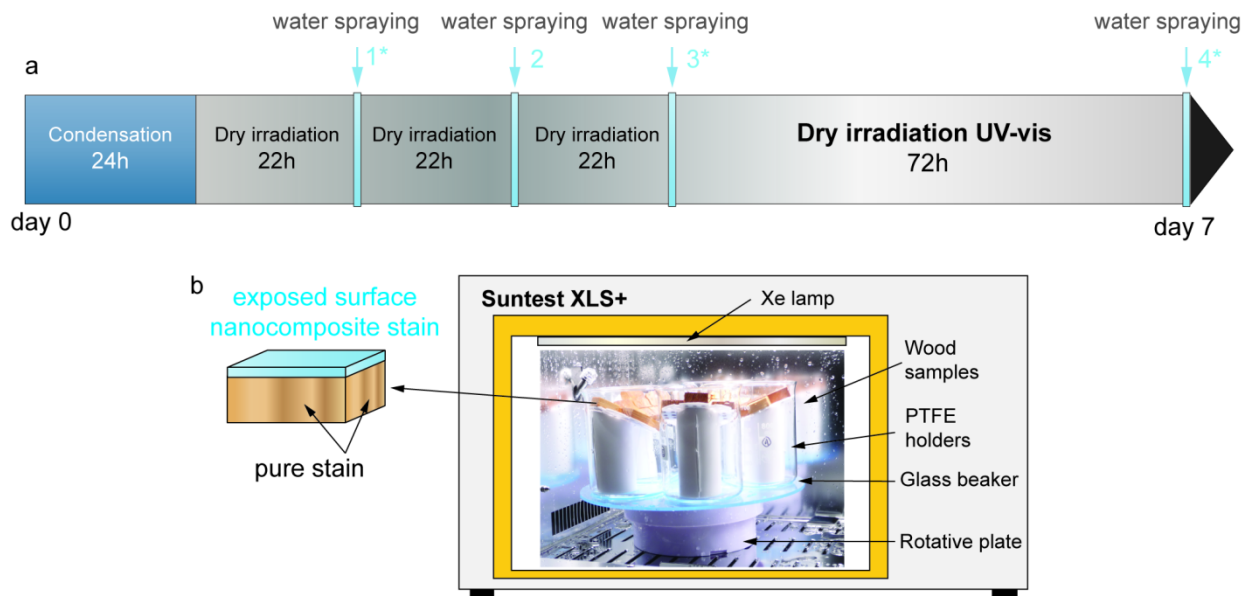
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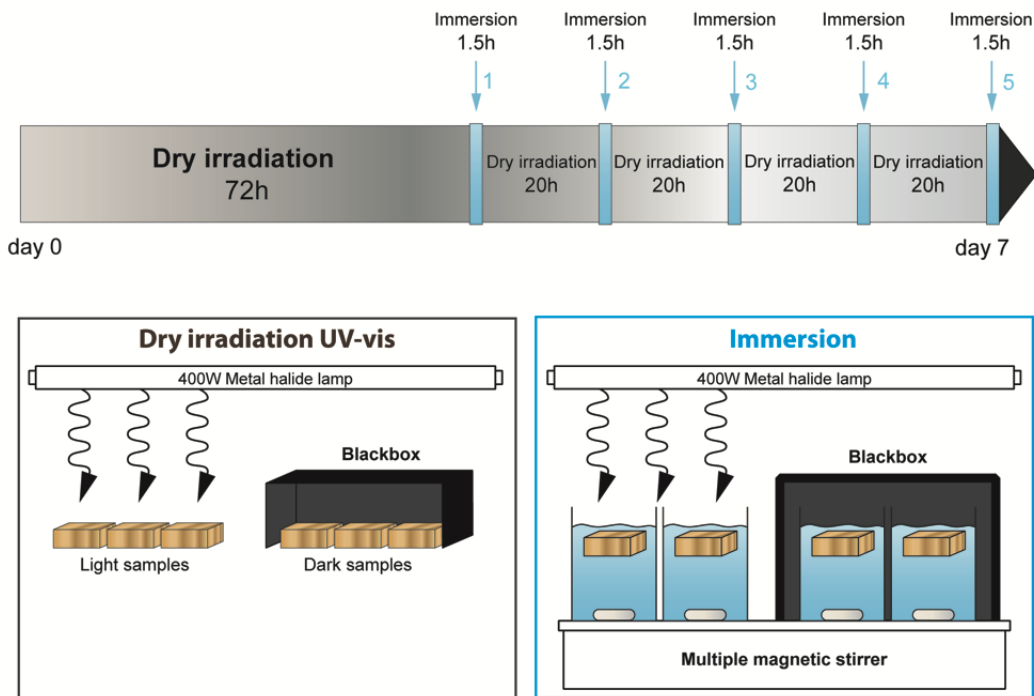
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**Figure 1. Experimental setup and procedure for weathering in climate chamber.** **a** Weekly weathering cycle. Gray areas correspond to dry irradiation (UV-vis) phases while 20 minutes spraying events (MilliQ-water) appear in light blue. Water sampling is notified by an asterisk whenever the case. **b** Experimental setup inside Suntest XLS+ (right). Irradiation under Xe lamp and water spraying phases were applied alternatively. n-CeO<sub>2</sub> wood samples were coated with stain enriched with CeO<sub>2</sub> additive on their exposed face (= upper face), and Ce-free stain on the remaining faces, as illustrated by the left scheme. ACR samples were coated with Ce-free acrylic stain on all 6 faces.

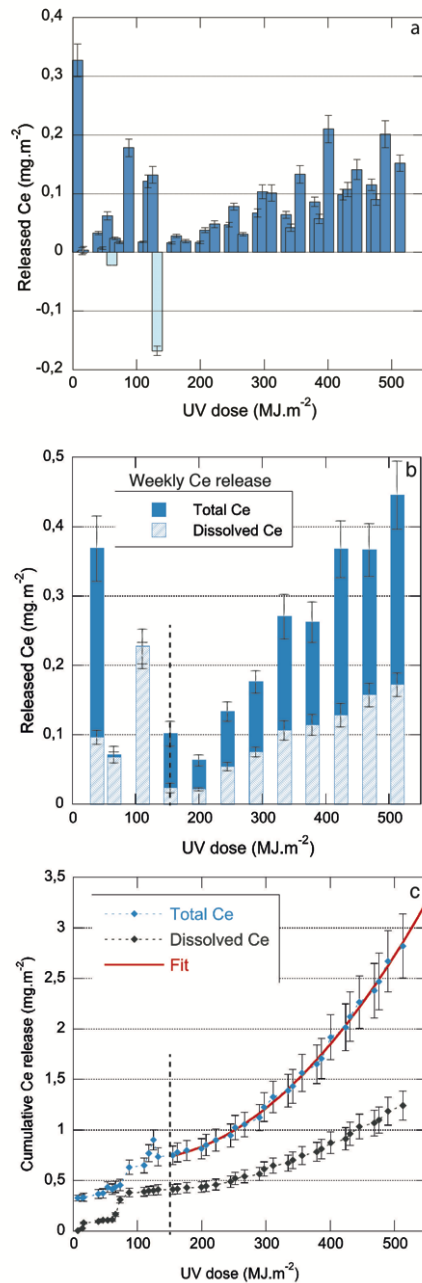


**Figure 2. Experimental setup for batch weathering composed of successive dry irradiation and immersion phases.** Left: Dry irradiation phases. Right: immersion phases. The weekly weathering cycle is described by the timeline. Gray areas correspond to dry irradiation phases while immersions (1.5h) appear in light blue. The same cycle was carried out in parallel under light exposure (irradiation + immersion) and in the dark (immersions only) for ACR and n-CeO<sub>2</sub> samples (n=3 for each condition). The setups for dry irradiation phases and immersion phases are illustrated in gray and blue frames respectively.

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**Figure 3. Ce releases taking place during water spraying of Suntest experiment.** **a** Ce release measured between two sampling events (not cumulated). Negative releases were isolated from the series as they represent artifacts of measurement due to the sampling method. **b** Ce releases integrated over the weekly cycles of Suntest experiment. Dissolved Ce determined on samples filtrated at 10kDa is represented in light blue. The dotted line marks a change in release regime after 4 weeks weathering (155  $\text{MJ.m}^{-2}$  UV dose). **c** Cumulative release of total and dissolved Ce calculated for Suntest experiment. Ce background measured on ACR samples was included in the error bars. Ce releases of phase II were fitted by a polynomial law of the second order (in red). Fit parameters are given in Table 2.

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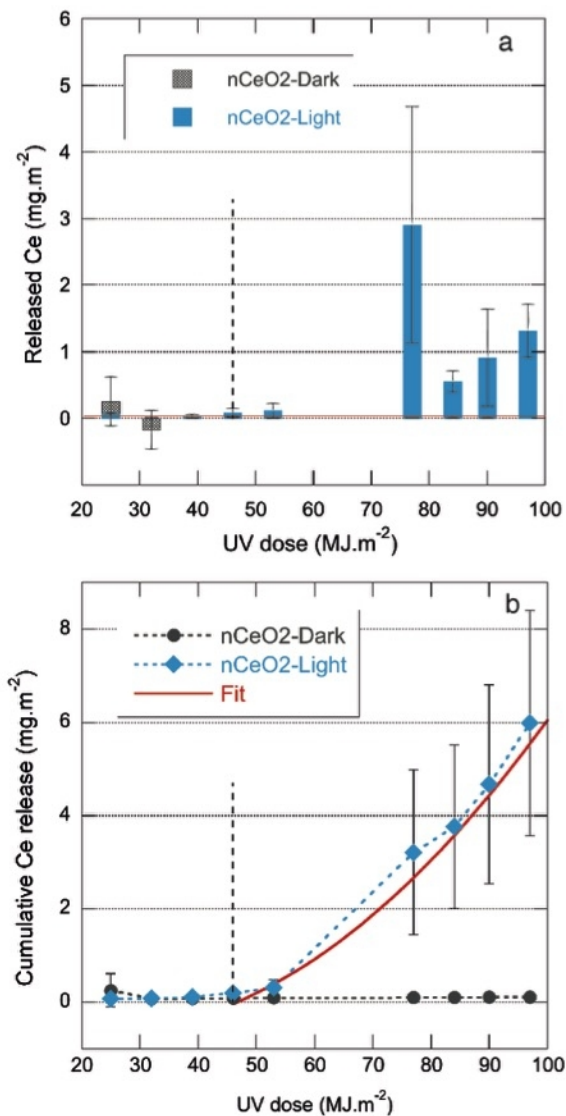
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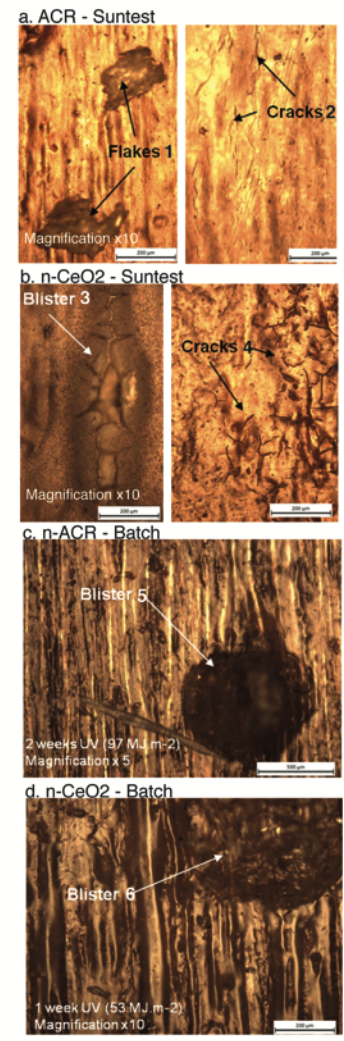
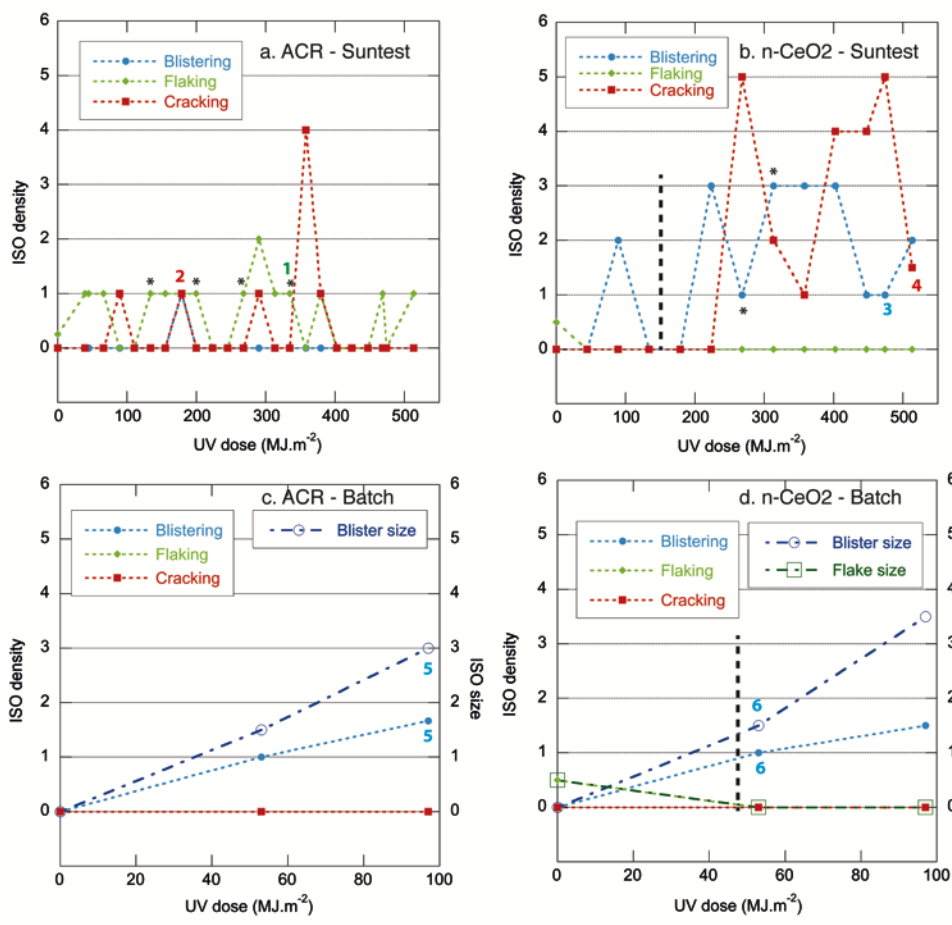


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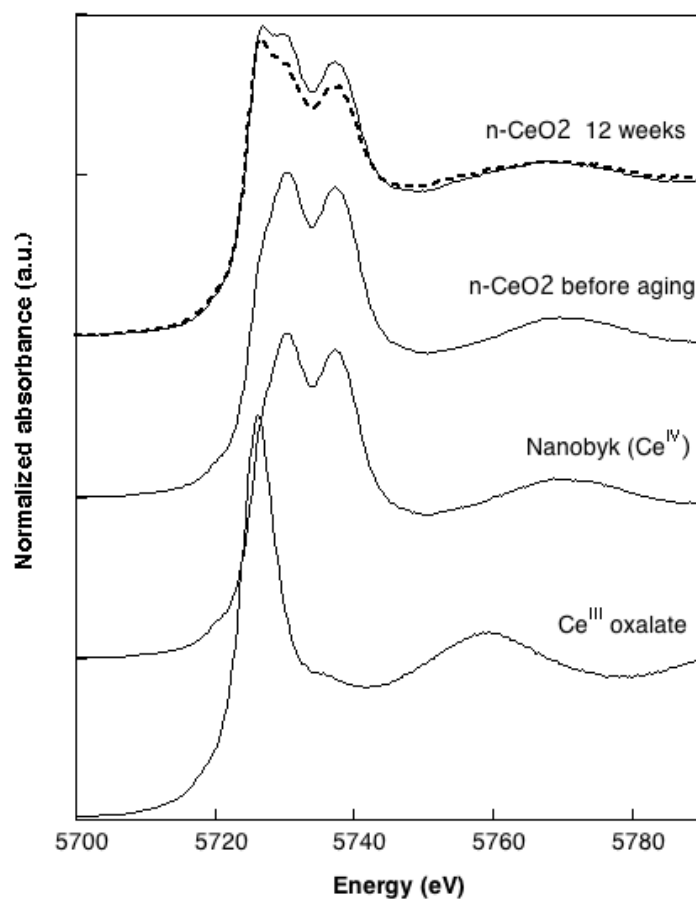
**Figure 4. Ce releases taking place immersions of batch experiment.** The data was averaged over three replicates. Standard deviation is represented in error bars. **a** Ce release measured for n-CeO<sub>2</sub> samples maintained in the dark (grey) or exposed to light (blue), during each immersion. A mean Ce background of 0.04 mg.m<sup>-2</sup> was estimated based on Ce level in the blank beaker (no sample) and is indicated by the red horizontal line on the graph. **b** Cumulative Ce releases calculated for batch experiment, for n-CeO<sub>2</sub> samples maintained in the dark (grey) and exposed to light (blue). Ce releases of phase II were fitted by a polynomial law of the second order (in red). Fit parameters are given in Table 2.

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**Figure 5. Assessment of stain degradation according to blistering, flaking and cracking criteria.** **a** Defect density observed on ACR samples of Suntest experiment as a function of the UV dose. Crack size ranked S1 (only visible with magnification x10 – marked Cracks 2) for all non-zero values. For flaking most samples displayed an S1 except for the 4 points marked with a star where larger defects could be observed (marked Flakes 1) (S2, incipiently visible with normal and corrected vision). **b** Defect density observed on n-CeO<sub>2</sub> samples of Suntest experiment as a function of the UV dose. For blistering, most samples displayed an S3 ranking (clearly visible with normal corrected vision) (marked Blister 3), except for points indicated by a star (S2). The crack size was S1 on all samples (marked Cracks 4). **c, d** Evolution of defect density and size for **c** ACR and **d** n-CeO<sub>2</sub> samples exposed to light in batch experiment. The blister size was S3 (marked Blister 5 and Blister 6). No defects were observed on samples that were maintained in the dark. On **b** and **d** the dotted lines mark the onset of phase II determined from release curves. Numbers (1-6) refer to defects (cracks, flake, and blister) observed by optical microscopy (magnifications x5 and x10) and shown as example.

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**Figure 6.** XANES spectra measured at the Ce L3-edge on an n-CeO<sub>2</sub> sample, before and after 12 weeks weathering under Suntest protocol (513 MJ.m<sup>-2</sup> UV dose). The spectra obtained on the initial and weathered nanocomposite (n-CeO<sub>2</sub> before aging and n-CeO<sub>2</sub> 12 weeks, respectively) are compared to those of a Ce<sup>III</sup> reference (Ce<sup>III</sup>-oxalate) and Nanobyk additive, serving here as Ce<sup>IV</sup> reference. For the 12 weeks weathered n-CeO<sub>2</sub> sample, Linear Combination Fits based on Ce<sup>III</sup> and Ce<sup>IV</sup> reference spectra were computed (dotted line). The corresponding Ce<sup>III</sup> and Ce<sup>IV</sup> relative contents are reported in Table 3.

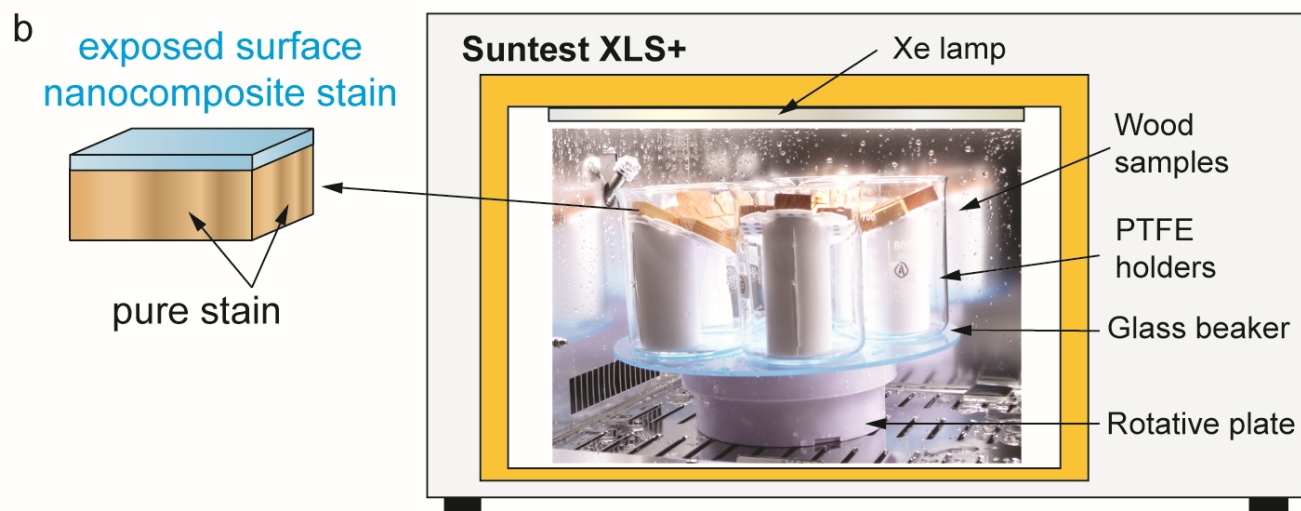
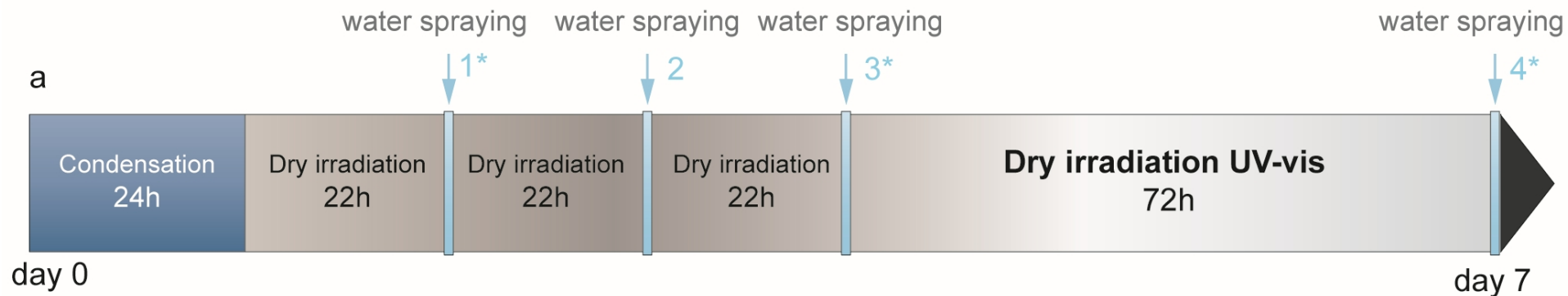
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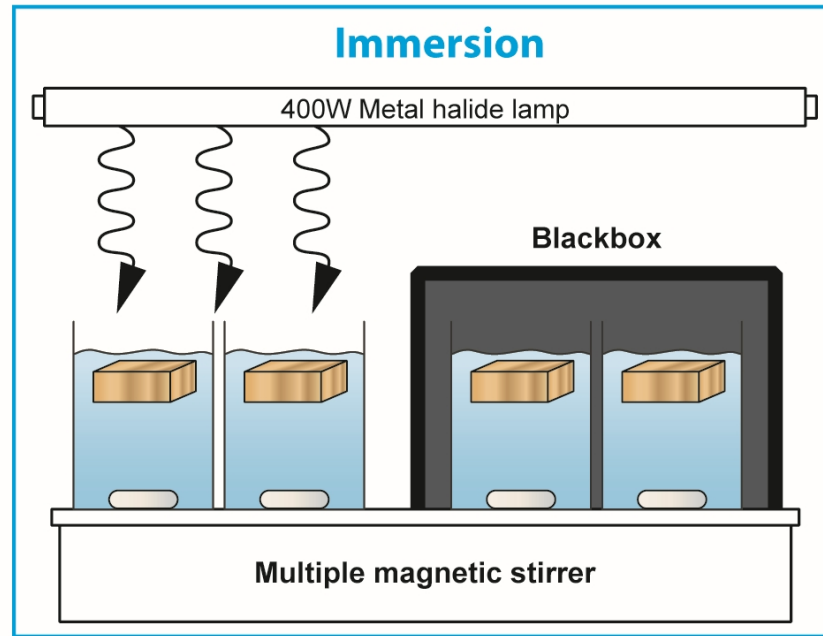
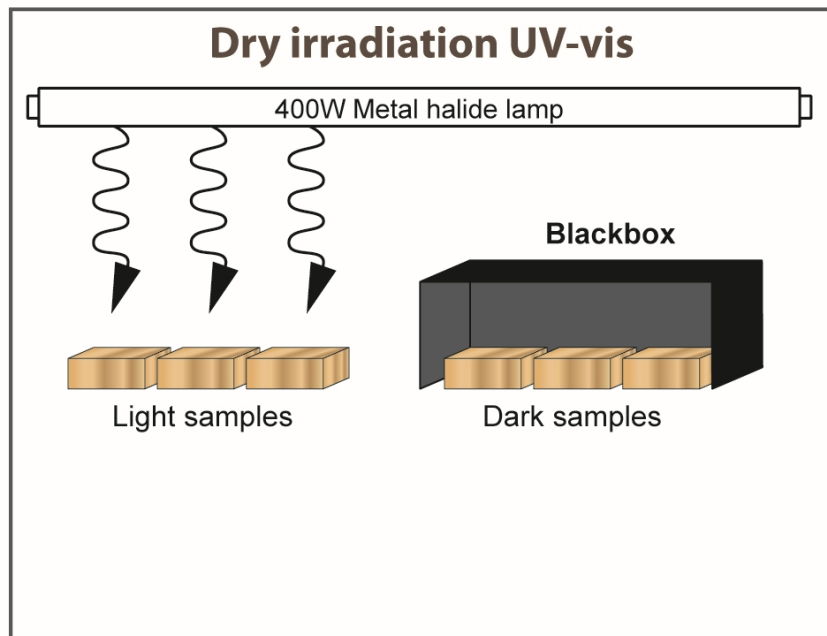
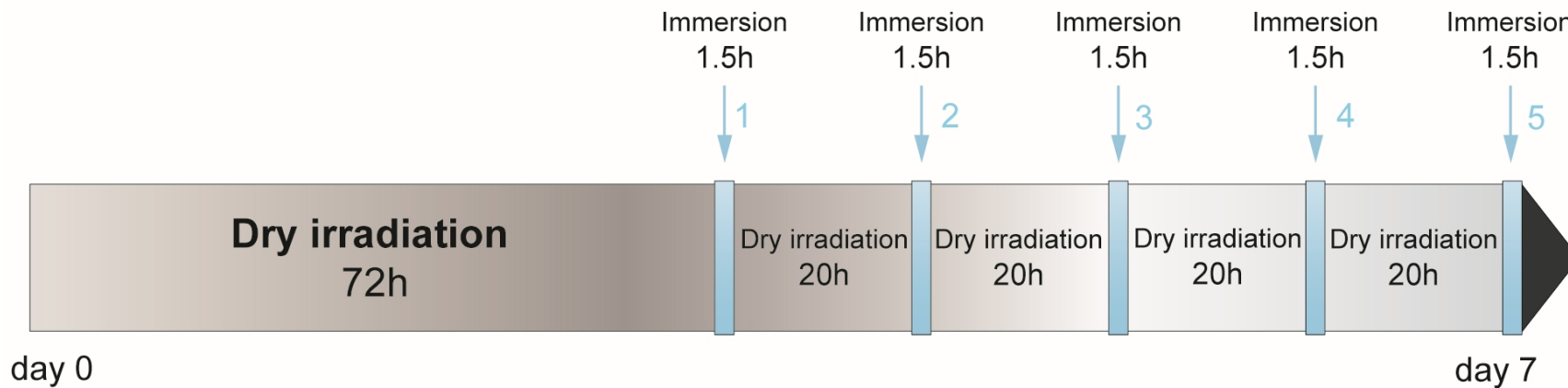
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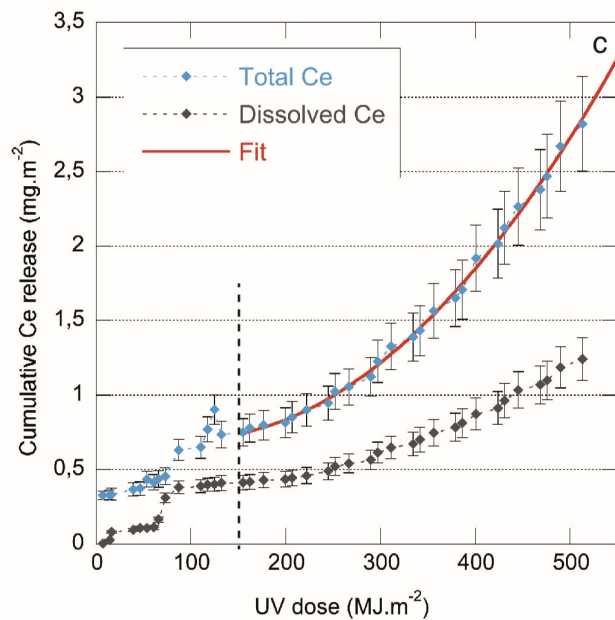
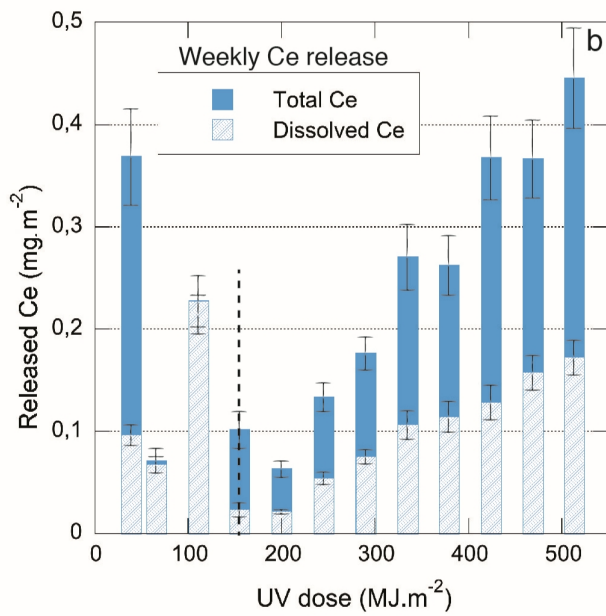
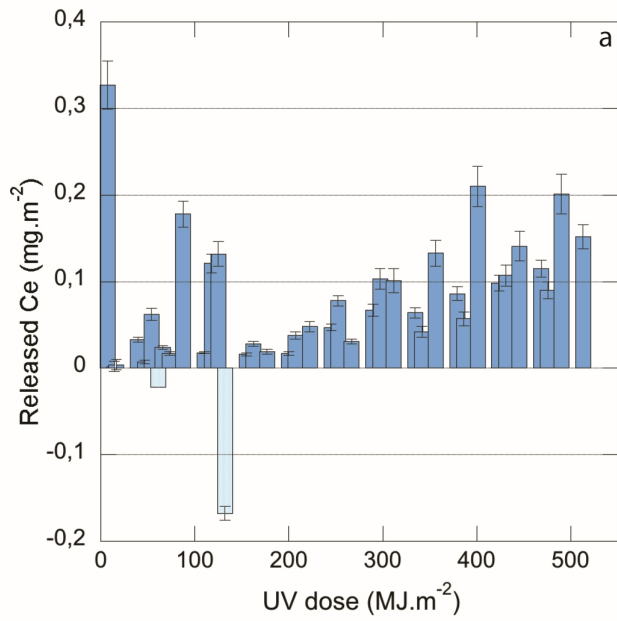
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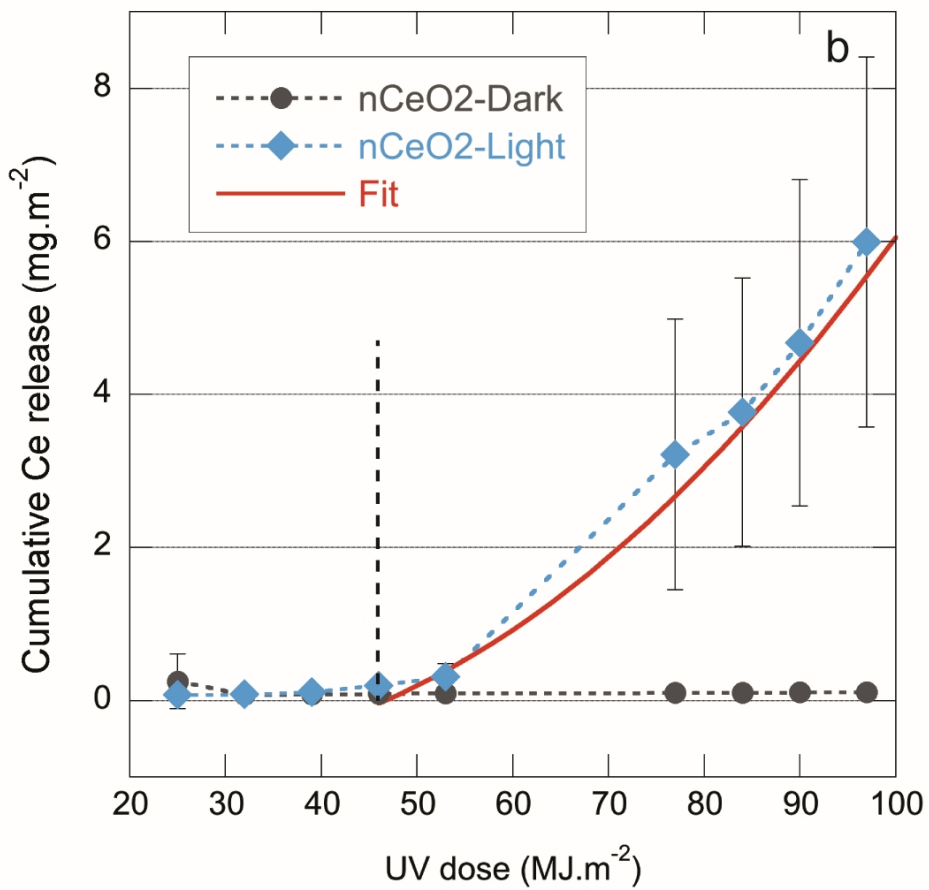
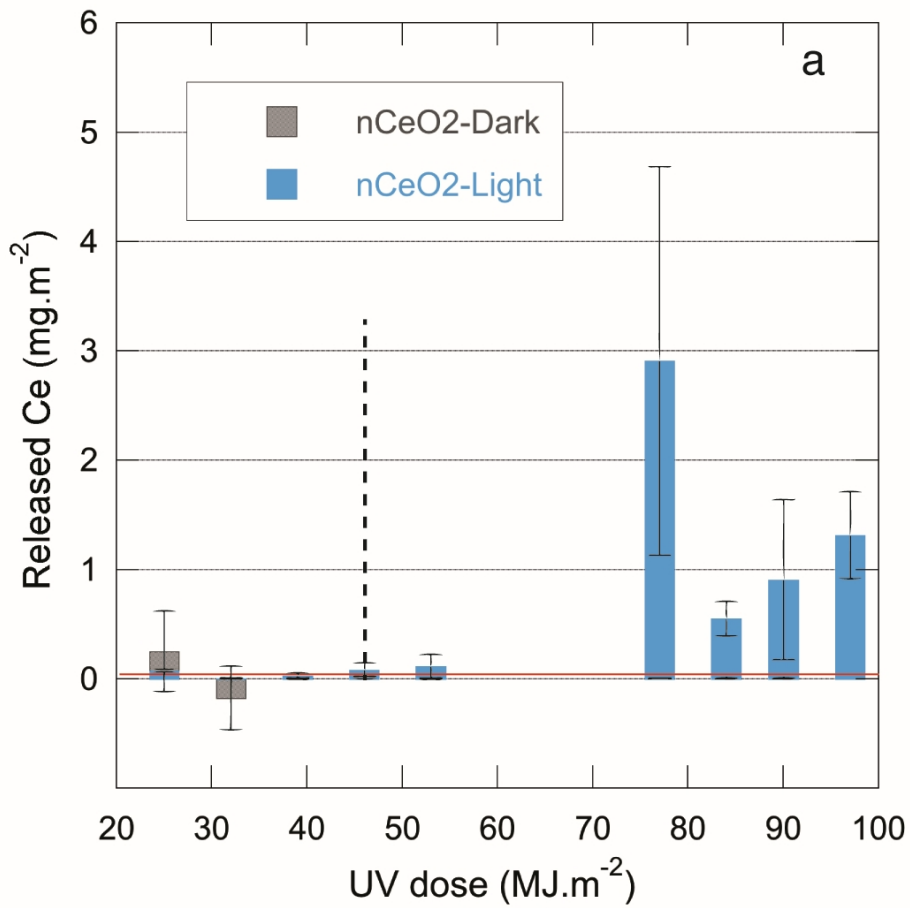
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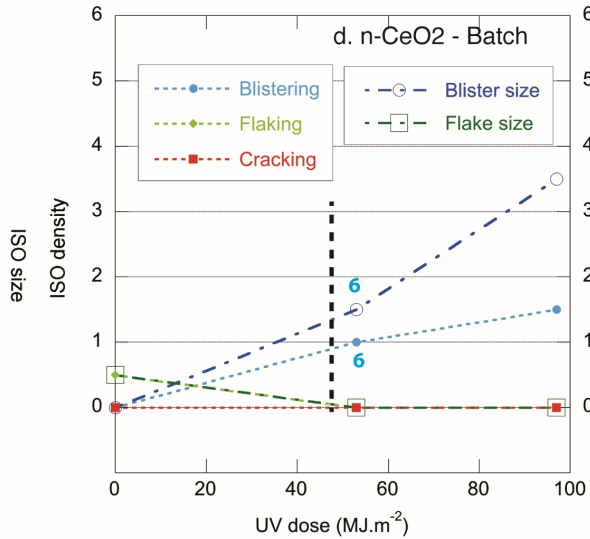
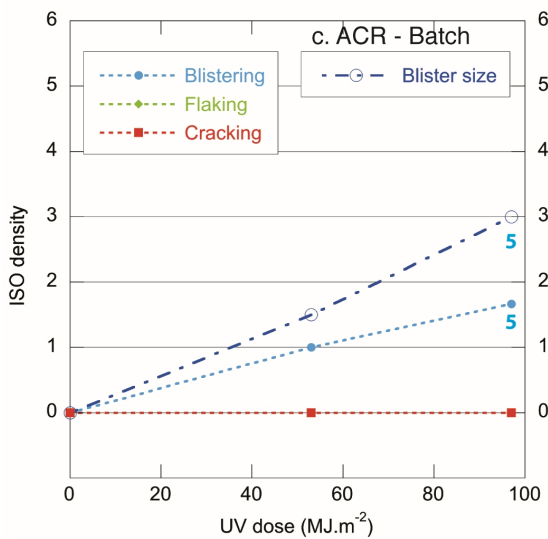
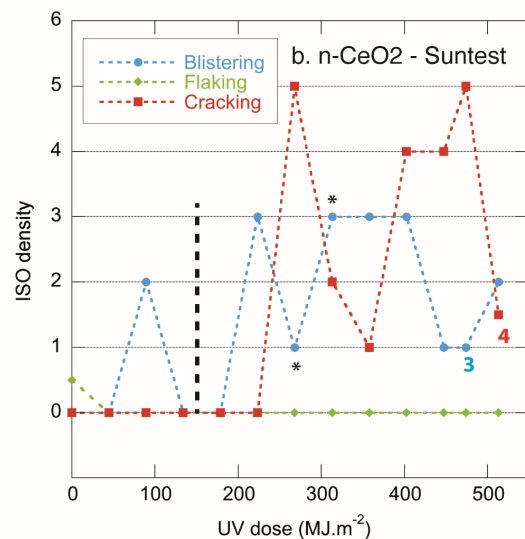
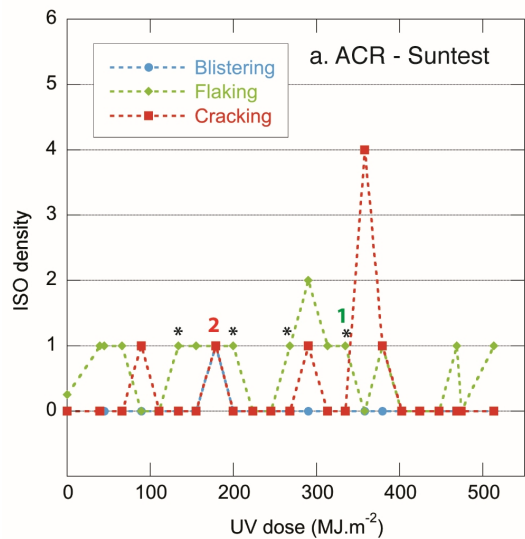




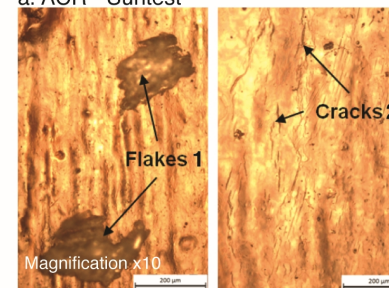




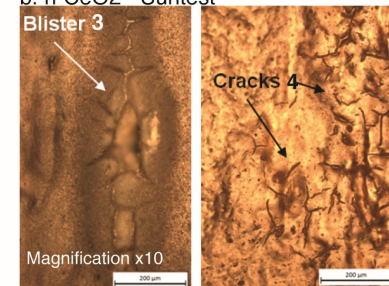




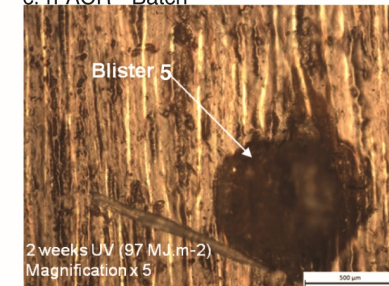
a. ACR - Suntest



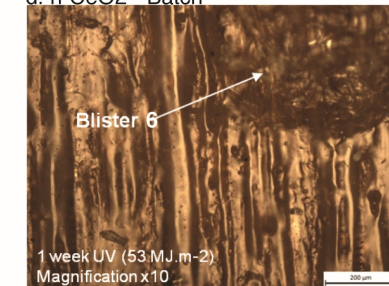
b. n-CeO<sub>2</sub> - Suntest

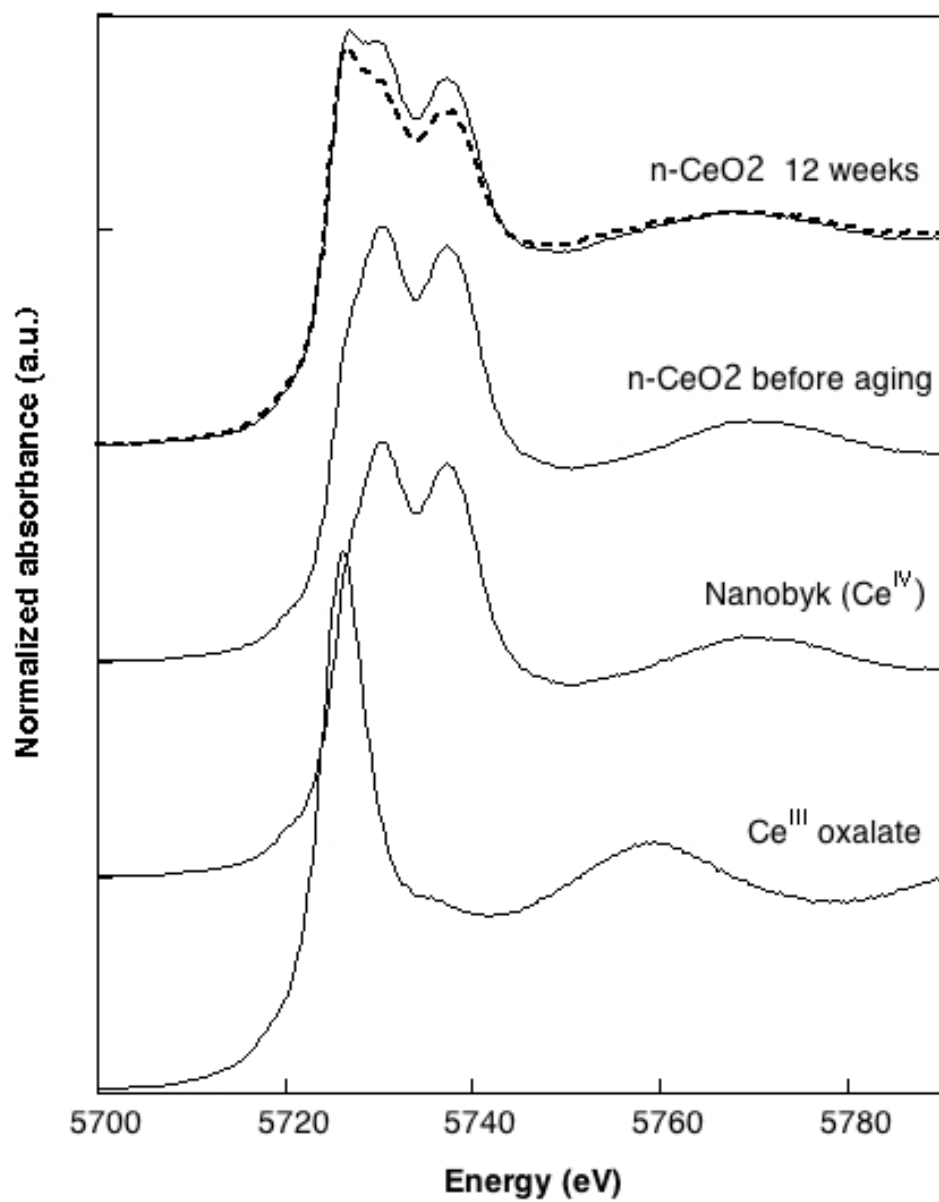


c. n-ACR - Batch



d. n-CeO<sub>2</sub> - Batch





1 Supporting Information for:

2 Non-linear release dynamics for a CeO<sub>2</sub> nanomaterial embedded in a  
3 protective wood stain, due to matrix photo-degradation

4 *Lorette Scifo*<sup>a,b</sup>, *Perrine Chaurand*<sup>b</sup>, *Nathan Bossa*<sup>b</sup>, *Astrid Avellan*<sup>b</sup>, *Mélanie Auffan*<sup>b</sup>, *Armand*  
5 *Masion*<sup>b</sup>, *Bernard Angeletti*<sup>b</sup>, *Isabelle Kieffer*<sup>d</sup>, *Jérôme Labille*<sup>b</sup>, *Jean-Yves Bottero*<sup>b</sup> and *Jérôme Rose*  
6 *b.*

7 AFFILIATION.

8 <sup>a</sup> *Tecnalia-France, Montpellier, France.*

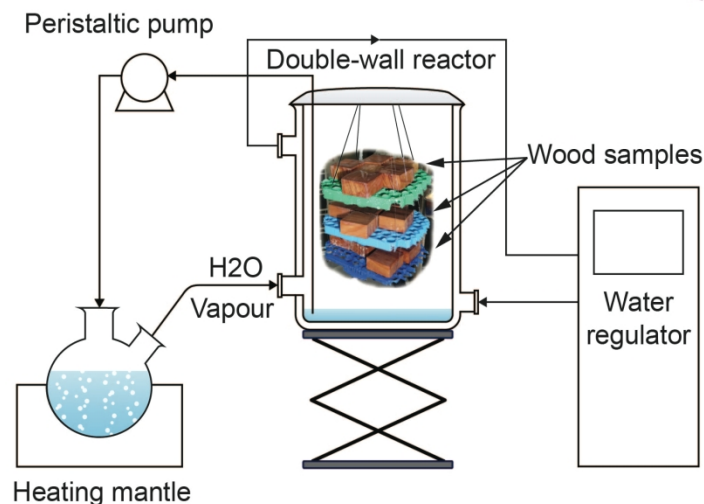
9 <sup>b</sup> *Aix Marseille Univ, CNRS, IRD, INRA, Coll France, CEREGE, Aix-en-Provence, France.*

10 <sup>d</sup> *OSUG-FAME, UMS 832 CNRS-Univ. Grenoble Alpes, F-38041, Grenoble, France*

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**Figure S1.** Homemade setup used for condensation phases in Suntest weathering (outside climate chamber). Ultrapure water is boiled in a flask. Vapor is directed towards a double-wall reactor where it is chilled and condenses at the surface of wood samples.

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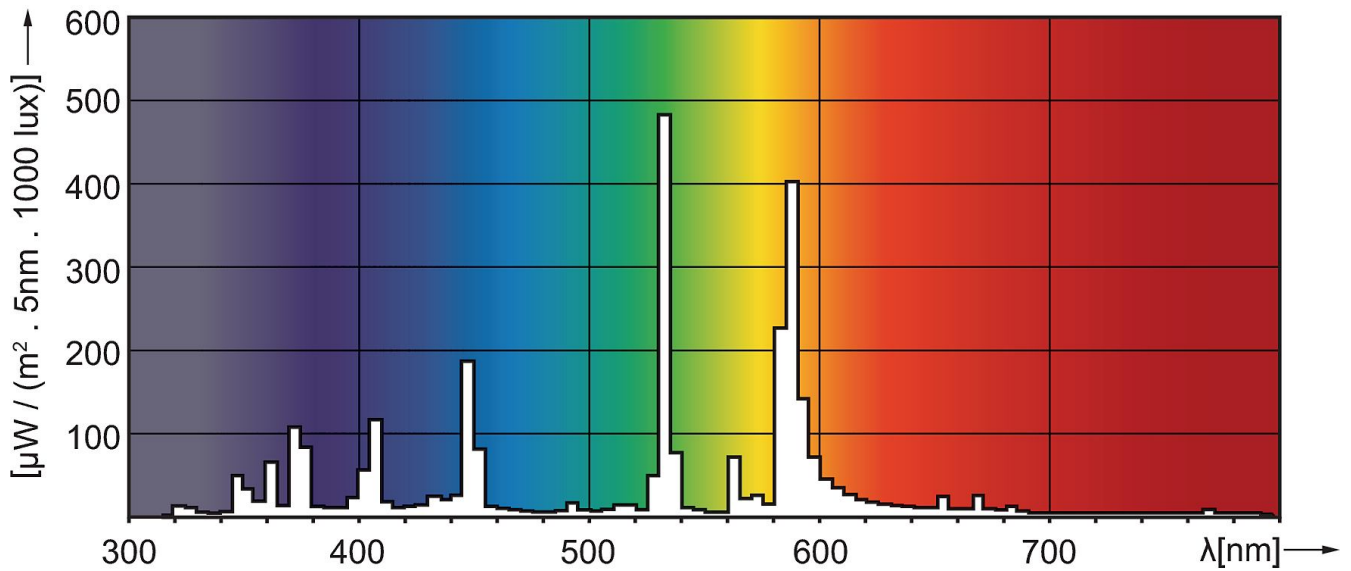
15 **Sampling and physico-chemical characterization of “rain” waters in Suntest experiment.**

16

17 40mL-aliquots of the water collected in beakers were taken after rain events #1 and #4 (Figure 1a) for  
 18 further analyses. The beakers were then re-introduced in Suntest XLS+ with the remaining water  
 19 volume. Whenever necessary, controlled amounts of Milli-Q water were added to the beakers to  
 20 compensate for evaporation and prevent drying out. After spraying event #3 the whole water volume  
 21 was collected and empty beakers were returned to the climate chamber for the longest 72h irradiation  
 22 phase. pH and conductivity of all the aliquots were measured immediately after sampling. Redox  
 23 potential was also measured once a week, on aliquots taken after rain event #3. Short sonication (15s)  
 24 was applied before, but no stirring was maintained during the measurement of physico-chemical  
 25 parameters.

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**Figure S2.** Emission spectra of Philips HPI-T Plus Metal Halide lamp. Downloaded from <http://www.lighting.philips.fr/>.

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**Table S3.** Equivalence between weathering time in weeks, UV dose and radiant exposure in the 300nm - 800nm range for Suntest and batch experiments.

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Weathering time (weeks)	Suntest experiment		Batch experiment	
	UV dose (MJ.m <sup>-2</sup> )	Radiant exposure 300nm-800nm (MJ.m <sup>-2</sup> )	UV dose (MJ.m <sup>-2</sup> )	Radiant exposure 300nm-800nm (MJ.m <sup>-2</sup> )
1	40	218	53	707
2	66	360	97	1367
3	111	607		
4	155	856		
5	199	1102		
6	245	1353		
7	290	1606		
8	335	1844		
9	379	2089		
10	424	2335		
11	469	2580		
12	513	2826		

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36 **Table S4.** Defect density

<b>Grade</b>	<b>Defect density</b>
0	No defects, i.e undetected
1	Very little, i.e defects are rarely observed and are not significant
2	Few defects, i.e a small but significant amount of defects is observed
3	Moderate number of defects
4	Considerable number of defects
5	Dense concentration of defects

37

38 **Table S5.** Defect size

<b>Grade</b>	<b>Defect size</b>
0	Not visible at magnification x10
1	Only visible with optical magnification up to x10
2	Incipiently visible with normal or corrected vision
3	Clearly visible with normal or corrected vision (up to 0.5mm)
4	From 0.5mm to 5mm
5	Above 5 mm

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