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1 Microstructure characterization of oceanic 2 polyethylene debris

3

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21 ABSTRACT

22 Plastic pollution has become a worldwide concern. It was demonstrated that plastic breaks down
23 to nanoscale particles in the environment, forming so-called nanoplastics. It is important to
24 understand their ecological impact, but their structure is not elucidated. In this original work,
25 we characterize the microstructure of oceanic polyethylene debris and compare them to the non-
26 weathered objects. Cross-sections are analysed by several emergent mapping techniques. We
27 highlight deep modifications of the debris within a layer a few hundred microns thick. The most

28 intense modifications are macromolecule oxidation and a considerable decrease in the
29 molecular weight. The adsorption of organic pollutants and trace metals is also confined to this
30 outer layer. Fragmentation of the oxidized layer of the plastic debris is the most likely source
31 of nanoplastics. Consequently nanoplastic chemical nature differ greatly from plastics.

32 **Introduction**

33 The scientific community has defined plastic pollution as a major worldwide concern. Indeed,
34 since the introduction of plastic in the 1950s, 6 300 million tons of plastic waste has been
35 generated, a very large proportion of which has accumulated in landfills or the natural
36 environment¹. In addition to large microplastics (MPs, 1–5 mm), smaller plastic particles at the
37 micrometre (μ Ps)²⁻⁴ and nanometre (nanoplastics, NPs) scales⁵⁻⁷ in the environment have been
38 highlighted by recent studies. Because μ Ps and NPs exhibit very specific physico-chemical
39 properties and reactivities, the evaluation of their potential toxicological impact require specific
40 investigations⁸. Primary MPs and μ Ps are defined as particles purposely manufactured at this
41 scale, such as beads, fibres and pellets⁹. Secondary MPs and μ Ps result from the breaking down
42 or erosion of larger objects. These mechanisms already occur early in the life of the object¹⁰.
43 Primary NPs is still very anecdotic because there is no manufacturing at large scale, NPs mainly
44 result from the degradation of macroscopic plastic objects⁶. Under laboratory conditions, the
45 erosion of MPs presenting an advanced stage of weathering favours the formation of NPs¹¹. A
46 major source of plastic pollution is the mismanagement of municipal waste¹², and fragmentation
47 of these materials into micro- and nanosized particles is certainly a major degradation path¹³.
48 Plastic degradation involves hydrolysis, mechanical abrasion, thermal degradation,
49 biodegradation and/or photodegradation^{10, 14, 15}. Commonly used plastics are mostly prone to
50 photodegradation¹⁶. Plastic photodegradation leads to structural modification of the polymer

51 backbone, such as oxidation with the formation of carbonyl groups¹⁷, chain scission, radical
52 recombination and crosslinking¹⁸. Polymer photodegradation also leads to morphological
53 alterations; the macromolecules can reorganize, and the crystallinity of the plastic often
54 increases¹⁹. These physical transformations impact the mechanical properties of the material
55 and favour breakdown and embrittlement²⁰. Cracking, surface erosion and abrasion lead to the
56 formation of μ P and NPs. Changes in the bulk properties of plastic in the ocean have been
57 addressed²¹⁻²³, but the surface microstructure of plastic debris has not yet been thoroughly
58 investigated.

59 The aim of this work is to provide new insights into modifications of the polymer microstructure
60 upon weathering in the ocean and to elucidate the molecular structure of weathered plastics.
61 Two oceanic plastic debris in polyethylene (PE) were selected because PE is the most
62 commonly detected polymer in oceans^{29,35}. The methodology of this study could be extended
63 to investigate the microstructure of other weathered plastic such as polystyrene or
64 polypropylene. The physico-chemical properties of the debris were compared to those of the
65 original boxes, which allowed us to directly evaluate the impact of oceanic weathering. Cutting-
66 edge technologies were deployed to precisely describe cross-sections and transverse sections
67 of the material: micro-Fourier transform infrared (μ FTIR) spectroscopy, infrared spectroscopy
68 coupled to atomic force microscopy (nano-AFMIR) to measure the material oxidation,
69 fluorescence microscopy to monitor the adsorption of organic compounds and
70 scanning/transmission electron microscopies coupled with energy dispersive X-ray
71 spectroscopy (EDS-SEM/TEM) to monitor the adsorption of inorganic compounds. As μ P and
72 NPs are generated from weathered macroscopic plastic debris, this study provides essential
73 information for the comprehension of the physico-chemical nature of μ P and NPs.

74 **Materials and methods**

75 **Sample collection**

76 Plastic debris was collected by boat in the North Atlantic sub-tropical gyre in June 2015 during
77 the French 7th Continent Expedition sea campaign²¹. Two of eight plastic debris samples of PE
78 were selected here for the microstructure investigation. We selected a box of coffee and a box
79 of cocoa powder and purchased new boxes for comparison (Figure SI 1).

80 **Surface and bulk characterization**

81 Characterizations by ATR-FTIR and measurements by DSC and SEC results were published in
82 ter Halle et al. The PAH contents are presented in Bouhroum et al.²⁴, and the metal levels are
83 reported in Prunier et al²⁵.

84 **Fourier transform infrared (FTIR) spectroscopies**

85 The μ -FTIR mappings were obtained in transmission mode using a Hyperion 3000 (BRUKER)
86 equipped with a focal plan array (FPA) detector. Background and sample spectra were acquired
87 using 256 scans at a spectral resolution of 4 cm^{-1} . Ten-micrometre-thick cross-sections were
88 sealed in KBr pellets prior to observations. OPUS software allowed the CI maps to be drawn
89 with the integration of the carbonyl absorption bands in the 1780-1660 cm^{-1} region and the
90 methylene absorption band in the 1490 to 1420 cm^{-1} region. Spectra with high spectral and
91 spatial resolution were obtained by AFMIR using a spectroscope. The spectra were generated
92 with Analysis Studio software without any correction.

93 **AFM characterization**

94 Small-scale surface topographies were acquired by AFM using a Nanoscope V (Bruker) in
95 contact mode.

96 **Cross-section preparations**

97 Cross-sections of the plastic samples were cut using a microtome with a diamond blade.
98 Different thicknesses were obtained depending on the characterization technique. Cross-
99 sections of 10 μm were used for the μ -FTIR and light and fluorescence microscopies. EDS-
100 TEM required a thinner cut, and cross-sections of 150 nm were made specifically for this
101 analysis. For AFMIR, the surface of the section was basically flattened using the microtome,
102 and the measurements were performed directly on the plastic section. For EDS-MEB, the
103 section was obtained by cryofracture.

104 **Light and fluorescence microscopic observations**

105 Light and fluorescence microscopies were performed using a digital slide imager NanoZoomer
106 2.0R.S (HAMAMATSU) equipped with an LX2000 200 W Ultrahigh-pressure mercury lamp.
107 Observations were made at different excitation/emission wavelengths ($\lambda_{\text{em}}/\lambda_{\text{ex}}$): 359/461 nm,
108 495/519 nm, 552/578 nm 554/566 and 649/666 nm. The images were corrected with NDP view
109 software to obtain a gain of 1.8 for the fluorescence observation.

110 **EDS-SEM and EDS-TEM**

111 TEM and scanning transmission electron microscopy (STEM) studies were performed using a
112 JEOL cold-FEG JEM-ARM200F operated at 200 kV equipped with a probe Cs corrector
113 reaching a spatial resolution of 0.078 nm. EDX spectra were recorded on a JEOL CENTURIO
114 SDD detector.

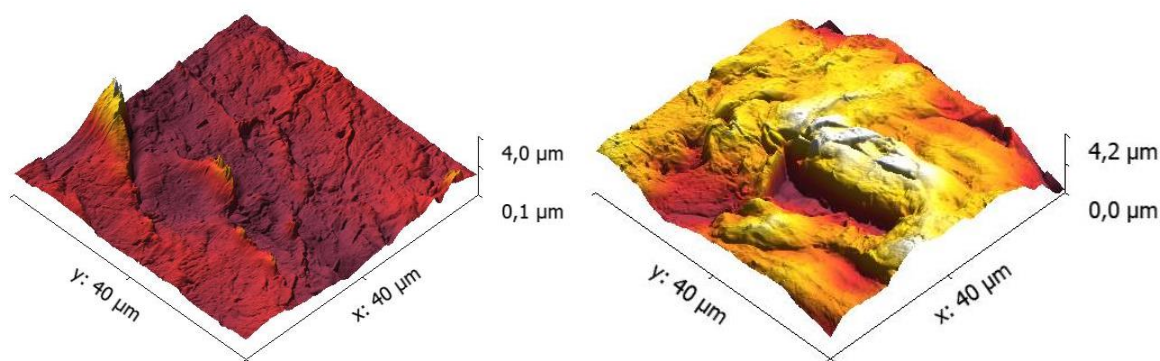
115 **Results and discussion**

116 Mesoplastics were collected in the North Atlantic sub-tropical gyre during the 7th Continent
117 Expedition. Two debris were easily identified as cocoa and coffee powder packaging items

118 named M_1 and M_2 , respectively (Figure S11). They were compared to two non-weathered
119 original items (named I_1 and I_2 , respectively). Most observations obtained for one pair of items
120 (new and weathered) followed the same trend as those obtained for the other pair. Therefore,
121 for clarity, we discuss the results for M_2 and I_2 in the text, and M_1 and I_1 data are presented in
122 the Supplementary Information files.

123 **Characterization of plastic bulks and surfaces**

124 Table 1 summarizes the bulk and surface characteristics. For bulk characterization, we observed
125 no significant alteration of the melting points and crystallinity between the mesoplastics and
126 the original items. Polymer chain length is described by the number average molar mass (M_n)
127 and the weight average molar mass (M_w), which can be measured by size exclusion
128 chromatography (SEC). The M_n and M_w values were both significantly smaller for M_2
129 compared to I_2 : the M_n value was reduced by a factor 2.



130
131 Figure 1: AFM characterization of the new coffee box (I_2) and the corresponding weathered
132 object (M_2). The root mean square roughness values for the original box and the weathered
133 object were 323 nm and 623 nm, respectively.

134 For surface characterization, the mesoplastics presented a significantly higher carbonyl index
135 than the non-weathered item. Characterization of the plastic surface by atomic force microscopy

136 (AFM) shows that there is a significant increase in the root mean square (RMS) roughness by
137 at least a factor 2 (on $40 \times 40 \mu\text{m}^2$ areas, Figure 1 and Figure SI2). This roughening is induced
138 by the appearance of micro-sized peaks at a scale that is typical of semi-crystalline
139 arrangement²⁶. We also observe that the thickness of the mesoplastic is lower than that of the
140 original box (reduction of 15 to 20%, Figure 2 and 4). A reduction in material thickness during
141 production to save material resources may explain the difference in thickness but it can also be
142 envisaged that this thickness reduction is due to erosion; as it is observed upon polymer
143 photodegradation under controlled conditions²⁷.

144 The total level of polycyclic aromatic hydrocarbons (Σ PAHs) in the plastic samples were below
145 the detection limit for original items (Table 1), whereas mesoplastics contained measurable
146 levels of Σ PAHs in the range of ng/g. This finding is consistent with literature data²⁸. The level
147 in M_2 was seven times higher than that in M_1 . The important variations between Σ PAH levels
148 in plastic debris sampled in the same location have previously been noted²⁹.

149 For metal concentrations, the focus was made on four metals found in noticeable amounts: Fe,
150 Pb, Ti and Cr. A detailed analysis of metal concentrations in the sample collected during this
151 campaign is given elsewhere²⁵. The presence of metals in the original items is because some
152 metals are incorporated during the manufacturing process (such as Ti and Fe) to improve plastic
153 properties. All metal concentrations were systematically higher in the mesoplastics than in the
154 original items because of sorption phenomena. The most explicit results were observed for Pb
155 and Cr, as their quantities were 55 000 and 1 100 times higher in M_1 than in I_1 , respectively.
156 Large variability from one sample to another was also observed³⁰, and this variability is difficult
157 to rationalize.

158 Table 1: Characterizations of bulk material by ^{a)} attenuated total reflectance FTIR, ^{b)} calorimetry

159 (DSC), and ^{e)} SEC; ^{d)} total level of polycyclic aromatic hydrocarbons measured by HPLC-FLD
 160 (sum of eight PAH levels); and ^{e)} metal concentrations determined by ICP-MS

	I ₁	M ₁	I ₂	M ₂	
MATERIAL PARAMETERS	Carbonyl Index^{a)}	0.1	0.7	0	0.3
	Melting point^{b)} Endset (°C)	141.8	135.7	142	142.7
	Crystallinity^{b)} (%)	41	39	43	42
	M_n^{e)} (kg mol⁻¹)	21.0	10.9	12.3	7.1
	M_w^{e)} (kg mol⁻¹)	85.5	80.8	94.0	67.5
PAH/METAL CONCENTRATIONS	ΣPAHs^{d)} (ng g⁻¹)	ND	2.2	ND	15.3
	Fe (μg g⁻¹)	1.1	19.2	ND	58.1*
	Pb (μg g⁻¹)	0.05	2760.45	ND	0.02*
	Ti (μg g⁻¹)	42.5	78.5	ND	8.8*
	Cr (μg g⁻¹)	0.8	866.2	ND	3.0*

161 *Average of two values.
 162

163 To summarize, surface characterization were more sensitive than bulk characterization to
 164 highlights some structural modifications of the polymer upon weathering. While calorimetry
 165 does not allow us to measure differences in the melting point or the percentage of crystallinity,
 166 the molar masses (M_n and M_w) was more sensitive parameters. Both metals and organic
 167 pollutants can be sorbed by plastic debris in large amounts.

168 **Oxidation profile**

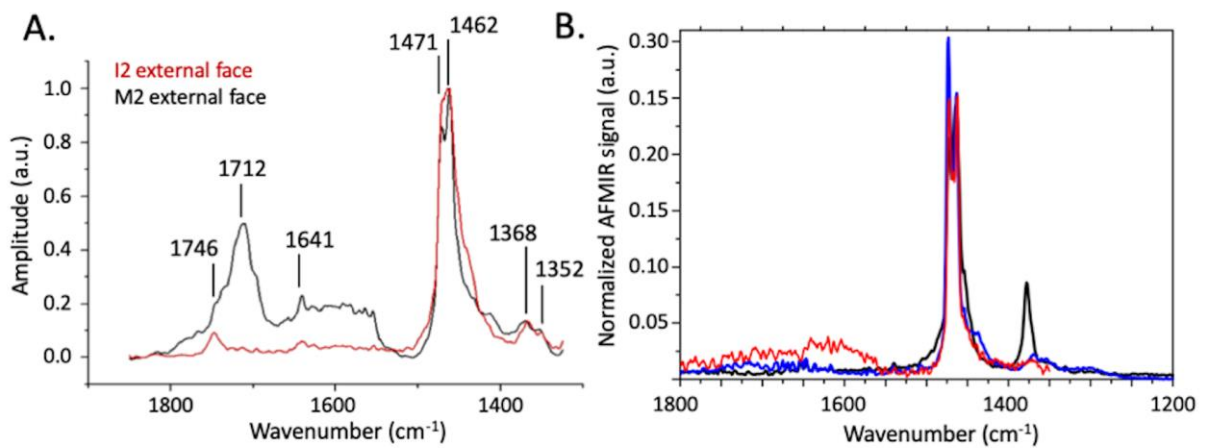
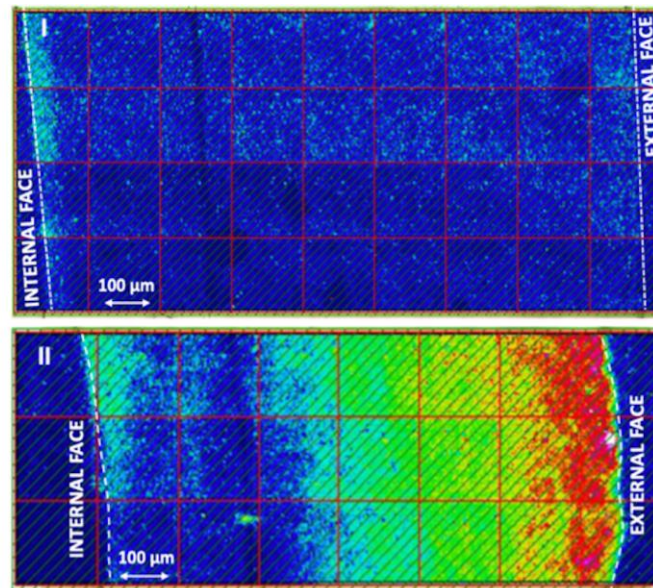
169 For the microstructure investigation, cross-sections were obtained using different methods to

170 produce samples with thicknesses adapted to each characterization technique (Figure SI 3). μ -
171 FTIR mapping of the cross-sections allowed us to obtain a cartography of the carbonyl index
172 (Figure 2). The coffee box sample I₂ exhibited a low and uniform carbonyl index across the
173 whole cross-section (upper mapping in Figure 2). I₂ is not oxidized on its surfaces or at its
174 centre. In contrast, cross-section mapping of M₂ highlights a highly oxidized external face, with
175 a deep oxidation gradient from the edge towards the centre. Oxidation was observed at depths
176 of up to 500-600 μm within the material; one can note that the oxidation layer is heterogeneous
177 at the micrometre scale. The internal face appeared much less oxidized. The rate of oxygen
178 diffusion into the material presumably evolves with the material aging. With aging the surface
179 becomes more porous and could facilitate oxygen transport and further deep oxidation of the
180 debris.

181 AFMIR is a recently developed cutting-edge technique that combines the high spatial resolution
182 of an AFM and the chemical characterization offered by IR spectroscopy³¹. AFMIR presents a
183 high spatial resolution of ten nanometres. Spectra were acquired between 900 or 1350 cm^{-1} and
184 1900 cm^{-1} . Punctual measurements (30 x 30 nm) were performed at three different locations
185 along the cross-section (external and internal faces and centre).

186 The AFMIR spectra of M₂ (Figure 2 A and SI4) indicated that the oxidation band was more
187 intense and broader than that of I₂ and was shifted to 1712 cm^{-1} . The broadening of the oxidation
188 band is explained by the presence of various oxidation products. As frequently reported in the
189 literature, photooxidation of PE generates ketones (peak at 1720 cm^{-1}) in the initial step. In
190 addition, secondary processes lead to the formation of carboxylic acids (1713 cm^{-1}), esters
191 (1735 cm^{-1}) and lactones (1780 cm^{-1})³². The absorption band at 1641 cm^{-1} is attributed to the
192 formation of double bonds during PE photodegradation. Both the oxidation and double bond
193 bands were detected in the three scanned regions of the macrodebris. Thus, even within the

194 material, the products of photodegradation are detected. This finding is in agreement with the
195 μ FTIR mapping that indicated a deep oxidation gradient from the edge towards the centre of
196 the material section. Those local IR absorption spectra also gives an information about the
197 crystallinity of the sample. The relative intensity of the 1473-1464 cm^{-1} peak may vary from
198 point to another. This might be an orientation effect generated during item production.
199 Furthermore, M₂ shows a shoulder at 1438 cm^{-1} and several weak absorption bands at 1370-
200 1354 and 1303 cm^{-1} . Generally, in pure crystalline product, 1354 and 1303 cm^{-1} (also called
201 amorphous bands³³) weak bands are absent³⁴ and the wagging mode of CH₂ at 1370 cm^{-1} is
202 more intense. Figure 2 B. shows the IR response of crystalline hentriacontane for whom the
203 intensity the wagging mode at 1370 cm^{-1} is largely higher than the two other bands (1354 and
204 1303 cm^{-1}). When comparing the AFMIR spectra of M2 internal and external face we cannot
205 establish if one face is more crystalline than another.



206

207 Figure 2: On the top: profile of oxidation obtained by μ -FTIR with a representation of the
 208 carbonyl index mapping of the new coffee box I₂ (I) and the mesoplastic M₂ (II). At the bottom :
 209 A) local AFMIR spectra at the external face of the original coffee box (black) and the
 210 mesoplastic (red) B) local AFMIR spectra of hentriacontane (black), internal face of the
 211 mesoplastic (blue) and external face (red). The internal face appears less oxidized than the
 212 external face.

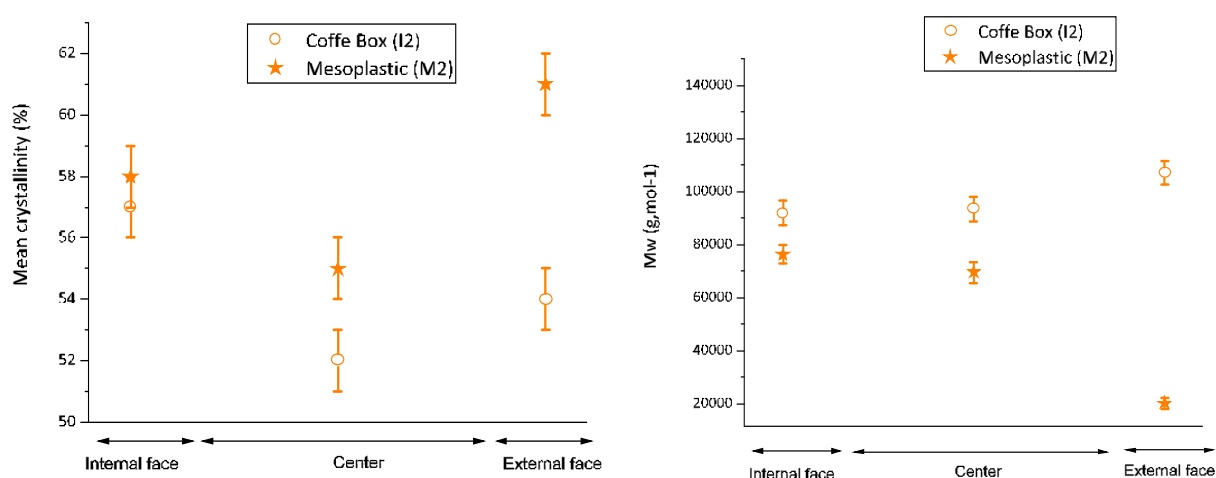
213 Calorimetric characterization of the transverse section

214 For the microstructure investigation, the materials were sectioned transversally with a thickness

215 of 100 μm for DSC analysis (Supplementary Table 1). Bulk DSC measurements did not
216 highlight differences between the original items and the mesoplastics. While I_2 edges were only
217 slightly more crystalline than the core material (1 to 2% \pm 1%). The heterogeneity of I_2 may be
218 a result of the manufacturing process (during injection moulding) or may be because the box
219 was exposed to light and already underwent slight photodegradation during storage. On the
220 contrary M_2 external face was significantly different from the core material, while the internal
221 face presented fewer differences (Figure 3). The degree of crystallinity of the external face
222 increased by 6% compared to that of the core material, and the melting point decreased by 3°C.
223 The increase in crystallinity of plastics debris is explained by two parameters²¹. First
224 explanation is that amorphous regions are more easily degraded. The second is that polymer
225 degradation increases the mobility of the macromolecules, which can form new crystals. Due
226 to degradation, the molar mass of the chains is decreased, and therefore, the lamellae of the
227 folded chain are shorter. The shorter macromolecules are more mobile and this allow them to
228 crystalize³⁵. Consequently weathered polyethylene are more crystalline than pristine. The
229 resultant crystals obtained with a shorter folding length are smaller than the original crystals;
230 therefore, they exhibit a lower melting point (the lower the folding length is, the lower the
231 corresponding melting point)³⁶⁻³⁸. The observed lower melting point of the resulting materiel
232 indicates that the new crystals are of a lesser quality compare to the pristine ones. This can be
233 linked either to the lower molecular weight of the polymer chains involved or to a very slow
234 crystallization process. Since it is not possible to evaluate the aging time of the samples, we
235 cannot discriminate between these two possibilities. We also noticed a significant narrowing of
236 the melting curves for the external faces compared to the rest of the material (Figure SI 5 and
237 6).

238 **SEC of the transverse section**

239 The transverse sections were analysed by SEC (details in Supplementary Table 1). Generally
 240 speaking, polymer photodegradation has a greater effect on the longer macromolecular chains,
 241 and M_w is more sensitive than M_n to polymer chain scission. M_w data is presented here and M_n
 242 in supplementary material (Table SI 1). I_2 presented an inhomogeneity in the molar mass, but
 243 the variations in M_2 were much greater. Again, the external face of the mesoplastics presented
 244 the most intense modifications (Figure 3) with a M_w value decreased by 80%. M_2 external face
 245 presents a molecular weight of only 20 000 g/mol.



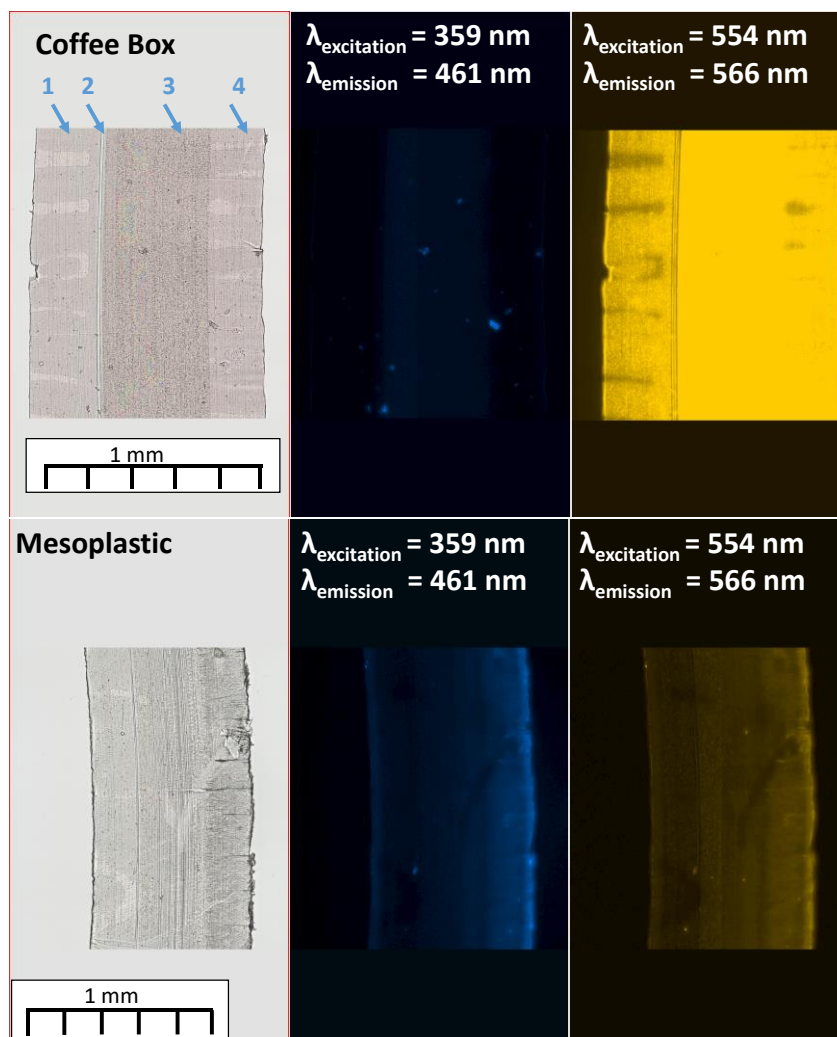
246 Figure 3: On the left, percentage of crystallinity and on the right weight average molar mass
 247 (M_w). Data measured for the transverse sections (internal and external with a thickness of 100
 248 μm) and the core material (thickness of 1 mm).

249 **Fluorescence and electronic microscopy of cross-sections**

250 When excited, I_2 emitted an intense fluorescence, particularly at an excitation wavelength of
 251 554 nm (Figure 4). The initial fluorescence of I_2 is attributed to additives, probably dyes of the
 252 quinacridone family³⁹. The fluorescence emitted by M_2 at this excitation wavelength was much
 253 less intense, which may be because a result of the additive either migrating out of the materials⁴⁰
 254 or being degraded⁴¹. Although typical results for plastic additive desorption under normal

255 conditions of use are generally known^{42, 43}, the desorption of additives under weathering
256 conditions has been less described.

257 At 359 nm, although I₁ and I₂ were not fluorescent M₁ and M₂ (Figure 4 and SI 7) exhibited a
258 fluorescence gradient from the external face towards the centre in the range of 200 to 400 µm.
259 This fluorescence indicates the presence of new aromatic compounds in the material and could
260 be attributed to PAHs that present characteristic fluorescence⁴⁴⁻⁴⁶ with an excitation wavelength
261 between 255 and 365 nm. This signal could also be attributed to marine dissolved organic
262 matter⁴⁷ or the products of degradation of additives within the plastic. It is important to note
263 that these fluorescent chemicals are sorbed within the first hundred microns of the materials
264 and could easily leach, for example, in the case of ingestion, where the pH conditions could
265 favour transfer to the organisms.

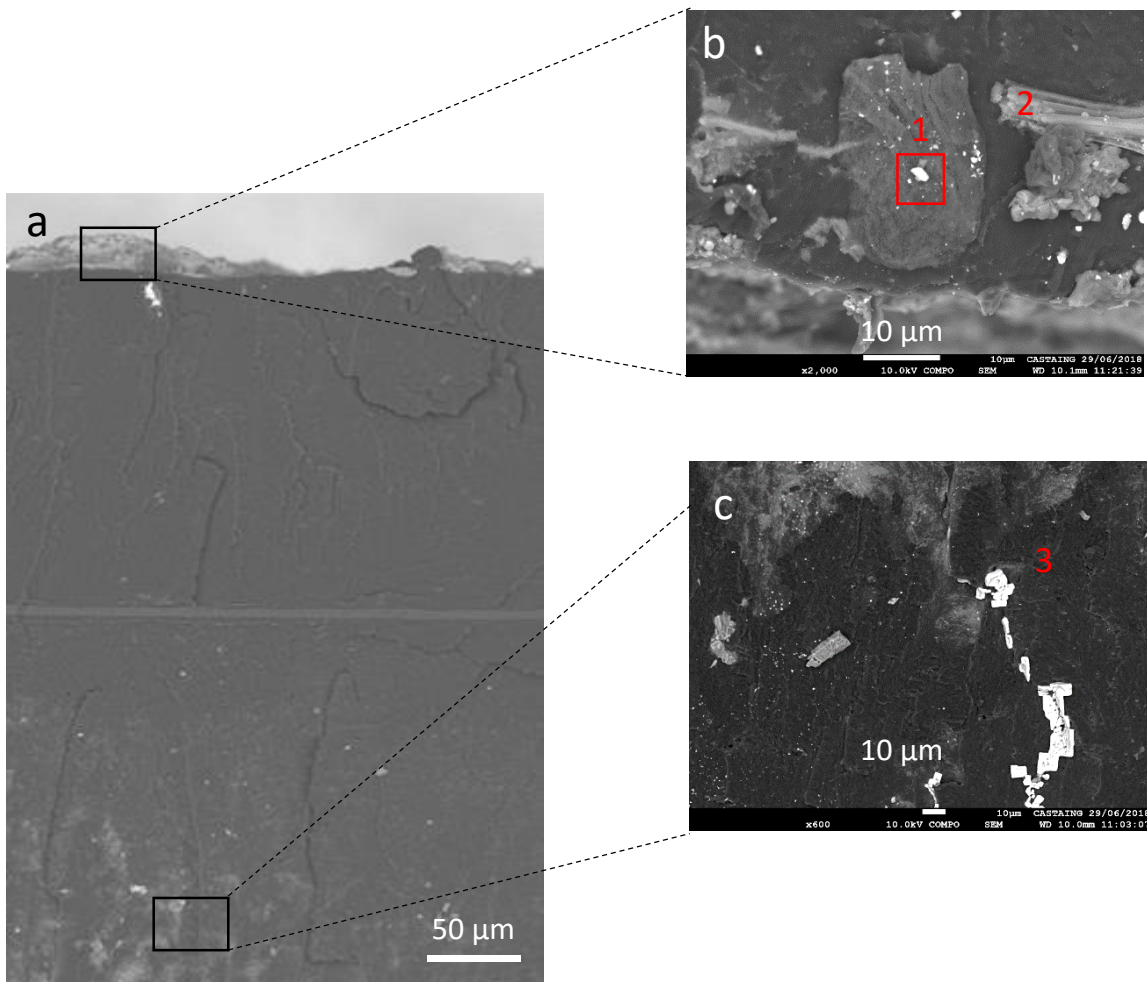


266

267 Figure 4: Microscopic observations of the new item (I₂) and the mesoplastic (M₂). On the left
 268 is a bright field image, and on the right are fluorescence images.

269 The atomic composition of the cross-sections was characterized by EDS-TEM. Numerous Ca
 270 and Ti ion-based particles were found in all four materials (Figure SI 8 to 10). Particles
 271 containing calcium were between 5 and 10 μm, and Ti ion-based particles were larger (200 to
 272 500 nm). Inorganic compounds are included in the plastic formulation as additives to improve
 273 some of the material properties like CaCO₃ particles that are used as plastic fillers. These
 274 particles were randomly distributed in the carbon matrix and were also found in the
 275 mesoplastics, so there is no evidence for their leaching upon weathering. Some deep cracks

276 were observed, filled with sea salt crystals (Figure 5c and SI 11) Numerous nanoparticles were
277 detected on M₂ external face (Figure 5a). The nanoparticles contained high amounts of Fe. Iron
278 was systematically present with Mn, Ni and Zn (Figure SI 12 and 13). These observations
279 confirm the occurrence of a recently described process²⁵: the formation of Fe or Mn precipitated
280 minerals on plastic debris surfaces in the ocean. It was also demonstrated that polymer oxidation
281 promotes metal sorption²⁵. It is noticeable to mention that high amounts of Pb was detected in
282 bulk M₁ and EDS-TEM revealed the presence of elongated Pb particles with a size between 100
283 and 200 nm (Figure SI 14 and 15).



284

285 Figure 5: EDS-SEM observations of M₂. a: view of the whole transverse section, b:
286 magnification of a part of the external face, c: magnification of deep cracks filled with sea salt

287 crystals. The multilayer structure of the polymer is elucidated by EDX-SEM (Figure SI 16) and
288 is composed of ethylene vinyl alcohol copolymer.

289 As a conclusion, the microstructure investigation of ocean-weathered mesoplastics compared
290 to original items has highlighted strong morphological, structural and molecular modifications
291 of the outer layer of the material. We also could observe that the outer side was more altered
292 certainly because more exposed to UV. Whereas bulk characterization did not allow to detect
293 deep modifications. The microstructure investigation showed that the outer layers of the debris
294 were remarkably more crystalline than the rest of the material. This outer layer consisted also
295 of very shorten and highly oxidized polyethylene macromolecules. All these modifications are
296 expected to eventually affect the mechanical properties of the polymer and lead to
297 embrittlement⁴⁸⁻⁵⁰. Embrittlement, fragmentation and delamination of the affected surface layer
298 are most likely linked with the non-homogeneous erosion of the surface layer, leading to a
299 strong increase in the surface roughness. The spatial distributions of oxidation and roughening
300 are on the same scale as the polymer semi-crystalline microstructure (micrometre). This process
301 mainly involves fragmentation into μ Pes and NPs, which explains the significant thickness
302 decrease of the mesoplastics. The generation of NPs from microplastics was observed by
303 Gigault et al.¹¹. This study also demonstrated the strong sorption of organic and inorganic
304 chemicals, mostly localized on the outer layer. The field of NP investigation is new, and there
305 is no description of the molecular structure of nanoplastics. What are NPs are made of? How
306 are the macromolecules organized in NPs? As μ Pes and NPs result from fragmentation of the
307 outer layer of macrodebris, their structure is certainly similar to that of the outer layer. The
308 present study provides insight into the structure of μ Pes and NPs. We conclude that μ Pes and NPs
309 are certainly composed of macromolecules that differ greatly from those composing plastics;
310 these macromolecules are highly oxidized and significantly shorter. We also conclude that NPs

311 interact with species like trace metals or organic compounds originating from sorption on
312 plastic debris surfaces. Overall, NP structural investigations must be conducted, or it will not
313 be possible to understand their fate in oceans or their potential impact on ecosystem and human
314 health.

315 ASSOCIATED CONTENT

316 **Supporting Information** Additional experimental details, including a photo of the
317 macrodebris and the GPS coordinates where they have been collected. The characterization of
318 M₁ and I₁ by AFM, AFMIR, calorimetry, GPC and fluorescence microscopy. Additional SEM,
319 EDX-SEM and EDX-TEM data are also presented in the Supplementary Information in Figure
320 SI 1 to 15 and Table SI 1

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325

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