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Spatial Heterogeneities

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## 1    **Organic Matter Oxidation of the Tégulines Clay formation, (Paris Basin,** 2       **France): Spatial Heterogeneities**

3  
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### 15    **Abstract**

16    Samples of Albian Tégulines Clay outcropping near Brienne-le-Château in the eastern part of the Paris  
17    Basin were subjected to a geochemical characterization of organic matter (OM), combining OM bulk  
18    Rock-Eval analysis (RE), organic petrography and molecular analysis. In this study, the objective was  
19    to investigate the oxidation of natural organic matter in critical zone developed in early reduced marine  
20    clay formation. For that purpose, core samples from three boreholes crosscutting the Tégulines Clay  
21    formation down to the Greensands were selected. Several meters of Brienne marls preserved Tégulines  
22    Clay from atmosphere and therefore from high weathering and high oxidation in AUB240 borehole,  
23    whereas Tégulines Clay were weathered in their upper part in AUB1010 and in AUB230 boreholes as  
24    a result to their vicinity to the surface. The results showed that the Total Organic Carbon (TOC) contents  
25    in all clays are very low, ranging between 0.3 and 0.7 wt.%. The RE bulk data and Tmax parameter of  
26    OM in preserved Tégulines Clay indicate that the OM is immature. The organic petrography shows a  
27    predominance of gel-like amorphous OM preserved by natural sulphurisation in anoxic environments.  
28    Organic matter in Tégulines Clay from the AUB230 and AUB1010 boreholes show similar  
29    characteristics. The OM at the top of Tégulines Clay contains large amounts of oxidized lignocellulosic  
30    debris and has high RE Oxygen-Index values. In the first upper 10 m of the clays, the RE bulk, organic  
31    petrography and molecular data revealed oxidative events (high OI and high oxidized debris contents).  
32    Below 10 m, the OM is almost preserved. The OM in the reduced marine Tégulines Clay formation is  
33    very little functionalized and seems to be slightly reactive but not negligibly with the inorganic fractions  
34    in presence of oxygen.

35    **Keywords:** Tégulines Clay formation, weathering profile, oxidation, Bulk organic characterization,  
36    Palynofacies, Molecular organic characterization

37

38

39

## 40 1 Introduction

41 Clay-rich geological formations are considered by many countries as natural barriers for radioactive  
42 waste isolation due to their low permeability and their sorption properties preventing the release of  
43 radioactive substances towards the biosphere. Most of previous investigations concerning clay-rich  
44 formations focus on deep systems (> 100 m) without direct interface with biosphere-atmosphere  
45 (Hendry and Wassenaar 2000; Hautevelle et al., 2007; Altmann et al. 2012). In the context of sub-surface  
46 waste repository, the vicinity of the surface can affect the solid-fluid equilibrium system of the  
47 geological formation due to weathering and oxidation phenomena involving in turn potential effects on  
48 solute transport properties with depth. Such phenomena in clay-rich formations are scarce and have been  
49 recently evidenced in the Lower Cretaceous Tégulines marine-clay formation (Tégulines Clay) near  
50 Brienne-Le-Chateau (Aube department, France) investigated for a decade in the context of sub-surface  
51 repository for low-level radioactive waste (Debure et al., 2020; Debure et al., 2018; Duffy et al., 2014;  
52 Lerouge et al., 2018, 2020). Like most of the marine clay-rich formations, Tégulines Clay evolved under  
53 reduced geochemical conditions during early diagenesis and its burial (Lerouge et al. 2018). In the  
54 studied area, weathering and oxidation phenomena including changes of mineralogy, chemistry, and  
55 petrophysical properties occur in Tégulines Clay at vicinity of the surface, due to interactions with  
56 oxygen and meteoric waters. A gradual oxidation profile developed in the clay formation and the  
57 resulting effects on pore water chemistry were evidenced based on several indicators as sulfur and iron  
58 oxidation states (Lerouge et al., 2018) and the changes of CO<sub>2</sub> partial pressure (Lerouge et al., 2020).  
59 Reactivity of Organic Matter (OM) with oxygen is suspected to play a role on CO<sub>2</sub> and redox regulation  
60 of the Tégulines Clay at vicinity of the surface.

61 In this study, we propose to investigate the reactivity of natural OM in Tégulines Clay as a marker of  
62 weathering and oxidation, using bulk and molecular techniques in the objective to better evaluate how  
63 atmosphere interacts with the rock and regulates its solid-fluid systems with depth. Organic Matter (OM)  
64 bulk analysis is firstly achieved by Rock-Eval analyses associated with palynofacies. This analytical  
65 approach allows determining the OM composition and its quality in term of maturity, refractory and  
66 redox state. Additional molecular organic geochemistry secondly completes the OM characterization,  
67 in term of origins (marine/terrestrial), maturity (saturated hydrocarbons) and oxidation (deposition mode

68 and weathering). Such type of approach was previously applied in deep clay-rich geological formation  
69 (Deniau et al., 2008; Elie et al. 2000; Elie and Mazurek, 2008; Hautevelle et al. 2007; Landais et al.  
70 1991; Landais and Elie, 1999) and is here challenged in a sub-surface context.

## 71 2 Materials and methods

### 72 2.1 Geological setting and mineralogy

73

74 The studied area is located near Brienne-le-Chateau in the eastern part of the Paris Basin (Aube  
75 department, Figure 1 (a,b)). The Gault clay formation (Gault Clay) consists of siliciclastic shales  
76 deposited in an open marine environment from Middle to Upper Albian (Lower Cretaceous) on the  
77 Greensands formation (Amedro et al., 2014). The stratotype of the Gault Clay defined in the Aube  
78 department consists of Tégulines Clay (82 m) overlaid by the Brienne marls (43 m). At the maximum  
79 burial of the Paris Basin, temperatures reached 30-36°C in the Gault Clay (Lerouge et al., 2018). In  
80 Early Miocene, the Paris Basin chalk formations were eroded. Nowadays the Gault Clay outcrops as an  
81 8-10 km wide and 80-km long band of terranes-oriented NE-SW through the Aube department. The  
82 Brienne marls only subsist in the western part of the studied area, elsewhere the Tégulines Clay outcrops.  
83 Its thickness increases from east to west between 60 and 120 m. Locally few meters of Quaternary  
84 surficial formations overly Gault Clay.

85 The unweathered Tégulines Clay essentially consists of clay minerals (47-72 %) associated with quartz-  
86 feldspar (28-43 %), carbonates (0-22%), and minor pyrite and phosphate nodules. Mineral variability in  
87 unweathered Tégulines Clay is mainly vertical (Fig. 1 (c)). The first 9-12 meters at the bottom of the  
88 clay formation is characterized as a clay-quartz rich unit (named UAQ), with the highest quartz –  
89 feldspar silty content (46 %) and the lowest carbonate content (3.5 %). The next 35-40 m constitutes a  
90 clay-rich unit (named UA) with a clay average content of 51 %, and intermediate carbonate and quartz-  
91 feldspar silty contents. The last 20-25 meters at the top of the clay formation constitutes a carbonate-  
92 clay rich unit (named UAC), characterized by the highest carbonate content (9-25 %) and the lowest  
93 quartz – feldspar silty content (30 %). The UAC unit constitutes a transitory term with the Brienne marls  
94 (Lerouge et al. 2018).

95

## 96 2.2 Materials, sampling campaigns

97 Fifty-three core samples of Tégulines Clay were selected among three boreholes for the study of organic  
98 matter: 7 from the AUB240 borehole (2018 drilling campaign), 31 from the AUB230 borehole (2017  
99 drilling campaign) and 15 from the AUB1010 borehole (2015 drilling campaign). Additional samples  
100 of soil and Quaternary surficial formations were collected in a trench (TPH 1-1) corresponding to the  
101 first meters of the AUB230 borehole, due to the difficulty to recover the first meters during the drilling.  
102 In the AUB240 borehole, surficial formations and ~12 meters of Brienne marls overlaid the Tégulines  
103 Clay, allowing a protection for the Tégulines Clay. Consequently, core samples collected in the  
104 Tégulines horizon from this borehole can be considered as the most representative of compacted pristine  
105 Tégulines Clay. The AUB230 borehole, located on a ridge top in cropland, crosscut ~ 30 cm of brown  
106 soil, ~ 5 m of surficial formations (sandy loam) and ~ 63 m of Tégulines Clay down to Greensands. The  
107 AUB1010, located down the valley, crosscut less than 2 m of surficial formations and ~ 33 m of  
108 Tégulines Clay down to Greensands (Fig. 3).

109 Major mineralogy of the Tégulines Clay core samples from the AUB230 and AUB1010 deduced from  
110 XRD data treatment are consistent (Lerouge et al., 2018, 2020) (fig. 1 (c)).

111 At the top of Tégulines Clay from the AUB230 and AUB1010 boreholes, claystone is sticky and grey  
112 with iron oxi-hydroxides. Interactions between Tégulines Clay and surficial oxidizing waters induce  
113 mineralogical changes such as pyrite oxidation, calcite dissolution and precipitation of iron hydroxides  
114 and gypsum between the top of the formation down to ~11 m. Detailed mineralogical, geochemical and  
115 petrophysical work on Tégulines Clay of the AUB1010 and AUB230 boreholes rather indicated an  
116 extension of the oxidation front down to ~20 m depth (Lerouge et al., 2018, 2020). Current investigations  
117 provide evidence of ancient root network development down to ~12 m depth at least.

118

## 119 2.3 Methodology

### 120 2.3.1 Rock-Eval analysis (RE)

121 The type, quality and amount of OM preserved in TCF samples before and after thermal maturation  
122 were determined using new Rock-Eval 6® pyrolysis (Vinci Technologies, Rueil Malmaison). About 50  
123 to 60 mg of powdered and dried samples were used for the analysis depending on the estimated OM

124 contents. The pyrolysis program involved an isothermal stage at 200 °C, held 2 min under inert gas  
125 (helium); the temperature was then raised to 650 °C (30 °C.min<sup>-1</sup>) and held for 3 min. The oxidation  
126 phase started with an isothermal stage at 400 °C under purified air. Then, the oven temperature was  
127 raised to 750 °C (at 30 °C.min<sup>-1</sup>) and held for 5 min. New Rock-Eval 6® classical parameters and their  
128 significance were explained by Espitalie et al. (1985a,b) and Lafargue et al. (1998). 4 parameters were  
129 used in the present study: (i) the total organic carbon content (TOC, wt %), which accounts for the  
130 quantity of OM calculated from the integration of the amount of thermo-evaporated free hydrocarbons  
131 (S1 peak), hydrocarbons produced by kerogen pyrolysis (S2), S3CO and S3CO<sub>2</sub> produced by the  
132 breakdown of kerogen under inert gas and S4CO and S4CO<sub>2</sub> produced by the oxidation and the  
133 pyrolysis of residual carbon under purified air; (ii) the oxygen index (OI, mg CO<sub>2</sub>.g<sup>-1</sup> TOC), which is  
134 the oxygenated quality of OM calculated from the S3 peak; (iii) the hydrogen index (HI, mg HC.g<sup>-1</sup>  
135 TOC), which represents the amount of HC quality produced during pyrolysis (calculated from the S2  
136 peak); (iv) the T<sub>max</sub>, which is deduced from the T<sub>pic</sub> of Rock-Eval VI. T<sub>pic</sub> is the temperature of the  
137 peak oil production during pyrolysis. T<sub>max</sub> is often used as an OM maturity indicator (Espitalie et al.,  
138 1985a,b). The Total Organic Carbon (TOC), the Hydrogen Index (HI) and the Oxygen Index (OI) are  
139 the 3 main parameters used in environmental science (Di-Giovanni et al. 1998, Boussafir et al. 2012).  
140 T<sub>peak</sub> deduced from S2 spectra is also used in environmental science. It is the temperature of the oven  
141 for the maximum hydrocarbon released.

142 Thanks to the deconvolution of the S2 pyrolysis spectra using Peakfit software (SPSS®), we were able  
143 to show the presence of 5 elemental Gaussian distributions describing the release of the different  
144 pyrolytic molecular families at T<sub>peak</sub> temperatures (+- 20°C) of 260 °C, 310 °C, 370 °C, 460 °C and 560  
145 °C. The relative contribution of these different pyrolytic molecular compounds to the signal was also  
146 semi-quantified by the calculation of peak surfaces of the corresponding Gaussians plotted to those of  
147 the entire S2 signal surface.

### 148 2.3.2 Microscopic investigations

149 Initially developed by Combaz (1964), the quantitative organic petrography is a method that consists to  
150 study thin slides under a microscope that permit the identification and the quantification of the organic

151 compounds present in a constant amount of sediments (1 cm<sup>3</sup> or 1 gram) after the elimination of  
152 carbonate and silicate by hydrochloric and hydrofluoric treatments (Graz et al. 2010). Optical  
153 investigations were performed with a DMR XP Leica microscope by using the transmitted light mode.  
154 The approach is based on the distinction of different categories of petrographic components  
155 characterized by their optical, form properties and, origins (Combaz 1980; Tyson 1995). This  
156 quantification was carried out on a minimum of 500 particles with a 50x magnification objective (Di-  
157 Giovanni et al. 1998, Sebag et al. 2006 a,b, Graz et al. 2010). To achieve absolute quantification of  
158 palynofacies, a pollen standard of precise concentration has been introduced in the samples. (Battarbee  
159 and Kneen 1982; Vernal et al. 1987) In this study, the standard chosen is *Cupressus sp.* Because of its  
160 strong reaction under UV excitation thus eliminating any confusion. Three main classes were  
161 distinguished in the different samples: the amorphous organic matter, without any biological apparent  
162 structures, lignocellulosic debris inherited from higher plant and other particles distinguished by their  
163 easily recognizable morphology. Different categories were observed in these three main classes and are  
164 detailed in Table 1 and Figure 2.

### 165 2.3.3 Lipid molecular analysis

166 Lipids were extracted from ca. 5 g of dried sediment using a Dionex ASE 200 with a dichloromethane  
167 (DCM): methanol (MeOH) mixture (9:1 v/v; at 100 °C and 1000 psi for 5 min in 3 cycles). After solvent  
168 evaporation, the total extract was then separated into neutral, acid and polar fractions using liquid  
169 chromatography with aminopropyl bonded silica as solid phase (Jacob et al., 2005). 5 $\alpha$ (H)-cholestane  
170 was added as an internal standard to the neutral and acid fractions and dried under N<sub>2</sub> flux. The acid  
171 fraction samples were then methylated by adding a mixture of anhydrous MeOH and acetyl chloride  
172 kept at 60 °C for 1 h. The obtained methyl ester and neutral fractions were then derivatized by reacting  
173 40  $\mu$ l *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) in 60  $\mu$ l pyridine at 60 °C for 1 h. and analyzed  
174 by GC-MS.

175 GC-MS analyses were performed on a Trace GC coupled to a TSQ Quantum XLS mass spectrometer  
176 (both from Thermo Scientific). Gas chromatograph (GC) was fitted with a Trace Gold TG-5MS capillary  
177 column (60 m x 0.25 mm id, 0.25  $\mu$ m film thickness). The sample was dissolved in toluene and injected



178 with a splitless mode in a 2  $\mu$ l volume. The injector temperature set at 280 °C. Helium was the carrier  
179 gas at a flow rate of 1 ml.min<sup>-1</sup>. The GC operating conditions were as follows: temperature increase from  
180 40 to 120 °C at 30 °C/ min and 120 to 310 °C at 3 °C/min with a final isothermal hold at 310 °C for 68  
181 min. The mass spectrometer was operated in the electron ionization (EI) mode at 70 eV and scanned  
182 from 50 to 650 Daltons. The identifications of the different peaks were based on a comparison of mass  
183 spectra with published data. Lipids concentration was estimated by the comparison of TIC area of each  
184 lipid with that of the internal standard and normalized to the weight of the extracted sample.

185

## 186 3. Results and discussion

### 187 3.1 Rock Eval data

#### 188 3.1.1 Quantitative and qualitative characterization of the OM

189 For all the analyzed samples, the results obtained by Rock-Eval analysis are presented in Figure 3 and  
190 Supplementary data 1. While, the TOC values indicates an organic content below 1 wt.% for the  
191 Tégulines Clay, the content is varying with the depth with an increase from 0.36 to 0.59 wt.% in the first  
192 10 meters and with a small variation around a 0.53 mean value in the deeper part. The Hydrogen Index  
193 (HI) and the Oxygen Index (OI) were reported both in the Figure 3 as a function of depth and in a Pseudo  
194 van Krevelen diagram to characterize the OM type (Fig. 4). Again, as detailed hereafter the first 10 m  
195 show a different behavior with a decrease of HI and OI while below 10 m OI and HI are homogeneous  
196 and showed almost no variation with depth

#### 197 *Soil and Quaternary formation*

198 Soil and Quaternary formation are available only for AUB230. The soil at the top of the AUB230  
199 borehole (TPH1-1 0-30 cm) has a TOC of 1.45 wt.%, and is characterized by high HI and OI values,  
200 revealing oxygenated immature OM. These data are in good agreement with soil data of the literature  
201 (Copard et al. 2006).

202 Quaternary surficial formation at the top of the Tégulines Clay in the AUB230 borehole does not contain  
203 any analyzable OM, except the samples at 4 and 5 m, that corresponds to the transition with Tégulines

204 Clay. The latter show low but valid TOC, and a hydrogenated quality (HI) and oxygenated (OI) average  
205 ranging respectively between 100 and 286 mg HC. g<sup>-1</sup> TOC and 268 and 307 mg CO<sub>2</sub>. g<sup>-1</sup> TOC.

#### 206 *Tégulines Clay*

207 Tégulines Clay in the AUB240 borehole (Fig. 3) shows homogenous RE parameters (TOC, HI, OI)  
208 suggesting stable OM and can be considered as a reference in term of types and preservation of OM in  
209 the clay formation for this study. TOC values are extremely low, ranging between 0.4 and 0.7 wt.%. The  
210 HI through the clay formation varies between 17 mg HC. g<sup>-1</sup> TOC and 30 mg HC. g<sup>-1</sup> TOC. The OI is  
211 ranging between 122 and 176 mg CO<sub>2</sub>.g<sup>-1</sup> TOC.

212 TOC values of Tégulines Clay in the AUB230 borehole (AUB230 6.10 - 68.45 m) range between 0.4 –  
213 and 0.7 % and are almost similar to that of Tégulines Clay in borehole AUB240. At the top of the clay  
214 formation at 6.00-6.10 m, TOC value of 0.4 is low compared to the soil (TPH1-1 0-30) and remains  
215 almost homogeneous until 45 m. In the deepest part (>45 m), the TOC increases slightly to reach 0.8  
216 wt. %. At 70 m toward the transition with Greensands, the TOC decreases to 0.5 wt.% (Supplementary  
217 data 1). The HI decreases between 6 and 9 m (98 – 25 mg HC. g<sup>-1</sup> TOC) and remains stable, until 55 m  
218 where the HI increases again to reach 118 mg HC g<sup>-1</sup> TOC at 68 m. The OI is relatively high (mean  
219 around 180 mg O<sub>2</sub> g<sup>-1</sup> TOC) between 6 and 9 m and remains stable until the depth of 45.84 m (around a  
220 mean of 76 mg O<sub>2</sub> g<sup>-1</sup> TOC). However, one pulse of OI can be observed at 21.3 m (117 mg CO<sub>2</sub> g<sup>-1</sup>  
221 TOC). Below 45.84 m the OI values decrease (37 to 48 mg O<sub>2</sub> g<sup>-1</sup> TOC). The RE parameters measured  
222 in Tégulines Clay of the AUB230 borehole allow discriminating three main parts corresponding to the  
223 top (6 – 9 m), the center (10 – 45 m) and the bottom of the borehole (55 – 68 m). At the top of Tégulines  
224 Clay, the HI/OI relationship is quite classical with an obvious anti-correlation: the HI decreases and OI  
225 increases in this section demonstrating a classical oxidation profile (Marchand et al. 2008).

226 Tégulines Clay of the AUB1010 borehole (Fig. 3) are characterized by low TOC content at the surface  
227 and then remains homogenous with values comprised between 0.3 % and 0.6 %. The HI is high at the  
228 top (192 mg HC. g<sup>-1</sup> TOC) and decreases rapidly at 3.31 m (81 mg HC. g<sup>-1</sup> TOC). Deeper, the HI remains  
229 homogenous (17 – 29 mg HC g<sup>-1</sup> TOC). The HI value at 1.88 m is high (192 mg HC. g<sup>-1</sup> TOC) as for  
230 the soil sample (TPH1-1 0-30) revealing more immature well-preserved OM. The OI values are

231 extremely high at the surface (883 mg CO<sub>2</sub>.g<sup>-1</sup> TOC and 912 mg CO<sub>2</sub>.g<sup>-1</sup> TOC at 1.88 m and 3.31 m  
232 respectively) due to low TOC content and probably the input of surficial pedogenetic OM. Deeper, the  
233 OI decreases rapidly and remains relatively stable along with the profile (122 – 241 mg CO<sub>2</sub>.g<sup>-1</sup> TOC).  
234 The trends of the HI/OI ratios in Tégulines Clay of the AUB1010 and the AUB230 boreholes are similar.  
235 Tégulines Clay OM of the three boreholes plot in type III OM field, revealing the terrestrial origin and/or  
236 well-oxidized type II OM. Tégulines Clay OM of the borehole AUB240 shows intermediate OI and HI  
237 values indicating the most preserved conditions of OM. Tégulines Clay OM of the AUB230 borehole is  
238 a mixture of type II- and type III- OM, revealing 1) either the ratio of inherited marine OM (type II) and  
239 terrestrial input (type III) or 2) a degradation process of marine OM allowing a shift from type II- OM  
240 to an intermediate type with a decrease in the HI and a slight increase in the OI compared to the original  
241 quality of the OM at the time of its deposition. Tégulines Clay of borehole AUB1010 shows oxygenated  
242 OM revealing more oxic conditions resulting in a shift from type II or more terrestrial oxidized (Fig. 4).

### 243 3.1.2 T<sub>max</sub> and shape of the pyrolysis S2 peak

244 The S2 signal delivered by the Rock-Eval pyrolysis is a spectrum that allows defining the rate of  
245 pyrolysate hydrocarbons expressed as a function of temperature (Copard et al. 2006). Deconvoluting the  
246 S2 signal permits us to better understand the evolution of the pyrolysis Temperature (T<sub>peak</sub>) to unravel  
247 the composition of the natural organic matter, which is generally composed of a complex mixture of  
248 organic compounds. The S2 peak is non-Gaussian and is accompanied by shoulders for the immature  
249 samples. The different peaks and shoulders correspond to the cracking of the different organic  
250 compounds (Disnar 1982; Disnard & Trichet 1984; Disnar et al., 2003). The literature concerning the  
251 shape of the pyrolysis S2 peak is mainly focused on soils samples. In this study, the different peaks of  
252 OM in the soil sample (TPH1-1 0-30 cm) can be attributed to specific compounds. The S2 peak shows  
253 a broad shape and two T<sub>peak</sub> at 370 °C and 460 °C (C3 and C4) (Fig. 5a), typical of a soil sample and in  
254 agreement with the bulk RE results. The cluster C3, at 370 °C can be attributed to the thermal breakdown  
255 of biological constituents such as polysaccharides and lignin (Disnar et al. 2003). The C4 cluster shows  
256 more preserved OM. For this sample, cluster C1 is absent. In their study, Copard et al. (2006) showed

257 that the C1 cluster (260 °C) is more labile and easily mineralized and could be easily absent in the most  
258 diagenetically or pedogenetically evolved samples.

259 For OM in Tégulines Clay, the shape of the pyrolysis S2 peak does not permit to attribute a specific  
260 compound but will permit to interpret the results in term of preservation. The mathematical  
261 deconvolution of S2 peak show five molecular RE pyrolytic families named C1 to C5 with 260, 310,  
262 370, 460 and 560 °C  $T_{\text{peak}}$  respectively (Fig. 5, 6 and supplementary data 2).

263 Tégulines Clay OM in AUB240 borehole shows very homogeneous cluster contribution with depth (Fig.  
264 5b; Fig. 6a). C4 is the major cluster encountered (80 %), followed by C3 and C5. The distribution of  
265 these contributions reveals preserved conditions with diagenetically well stabilized OM and are in  
266 accordance with the bulk RE values (Copard et al. 2006).

267 Tégulines Clay OM in AUB230 and AUB1010 boreholes show variations of the cluster distribution with  
268 depth. In AUB230 borehole, OM between 9 and 55 m show a high contribution of the C4 cluster (Fig.  
269 5d, Fig. 6b supplementary data 2) that is almost similar to Tégulines Clay OM in AUB240 borehole,,  
270 revealing stable OM input in probably good preserved conditions. At 21 m, the C2 cluster is more  
271 represented indicating the presence of labile OM. At the top of the clay formation (6.10 m), OM is  
272 particular with a high contribution of the C1 cluster (Fig. 5c). This could be due to the presence of light  
273 recycled OM composed of a small molecular structure easily thermopyrolysable. At the bottom of the  
274 clay formation (67 and 68 m) (Fig. 5e), the higher contribution changes to C3 cluster also revealing  
275 stable and preserved OM (Copard et al. 2006).

276 Tégulines Clay OM in AUB1010 borehole (Fig. 5; Fig. 6c) shows an S2 deconvolution similar to that  
277 in AUB230 borehole. The most upper sample (AUB1010 1.88, Fig. 5f) is characterized by the  
278 contribution of C1, C3 and C4 (35, 45 and 20% respectively) clusters. The C1 cluster reveals the  
279 presence of thermally labile biological compounds and shows more immature OM that could be, as for  
280 the AUB230 6.10 m, a similar light recycled OM. Between 3 and 16 m, the major cluster is C4 (Fig. 5g,  
281 h): stable OM with a variable contribution of the other clusters. Between 17 and 34 m (Fig. 5i), the major  
282 cluster is C4, followed by C3 and C5. These conditions are similar to the AUB240 borehole and suggest  
283 more stabilized and preserved OM.

284

285 The R400 parameter (proportion of the S2 peak integrated before 400°C, Disnar et al. 2003) and  
286 depending on the proportion of labile and probably more diagenetically reactive biomolecules was also  
287 calculated (supplementary data 1). This parameter varied between 0.1 and 0.6 and was higher for surface  
288 samples (0.6 at 0-30 cm) indicating the presence of 60 % of labile OM in the surface. This parameter  
289 was low in the AUB240 borehole (0.10 – 0.14) which is related to the 90 % of more stable OM (10 %  
290 of labile OM) with highly refractory character.

291  $T_{\max}$  is also largely used in the literature in order to characterize the maturity of the OM. A general  
292 overview of the samples reveal that the  $T_{\max}$  is lower than 430 °C, suggesting that the OM is considered  
293 immature.

### 294 3.2 Quantitative palynofacies investigations

295 The particles observed in the different samples were identified following the different morphological  
296 and textural criteria presented in Fig. 2 and table 1. All the acronyms cited in the next section are detailed  
297 in the table 1.

298 The quantitative palynofacies results for TPH1-1 are presented in Fig.7a. As expected from the Rock-  
299 Eval results, the sample collected in the first 30 cm (0-30 cm) reveals a predominance of preserved  
300 lignocellulosic fragments (plc), slightly degraded lignocellulosic fragments (slc) plc+slc (4.41 mg. g<sup>-1</sup>)  
301 and divers particles (div) (1.70 mg.g<sup>-1</sup>). The pyrite is absent at this depth. These lignocellulosic  
302 compounds are, in their majority under gel-like forms, suggesting the sequestration of these particles in  
303 an anoxic hydromorphic environment permitting protection artificially the OM (Boussafir et al 2012).  
304 These parameters are in accordance with the RE data (high TOC, HI) and S2 deconvolution are typical  
305 of a soil sample. The samples from the trench collected below 30 cm (30 cm to 5 m) did not permit to  
306 perform any quantitative analysis due to the too-small number of residual particles in the palynofacies.  
307 Tégulines Clay OM in AUB240 borehole (Fig. 7b) shows a homogeneous palynofacies content with  
308 depth. The major particles encountered are the grAOM (1.11 – 2.31 mg.g<sup>-1</sup>) followed by the OgrAOM  
309 (0.06 – 0.69 mg.g<sup>-1</sup>) and do (0.26 – 0.51 mg.g<sup>-1</sup>). OgrAOM content increases between 29 and 80 m (0.06  
310 mg.g<sup>-1</sup> – 0.69 mg.g<sup>-1</sup>) and pyrite is observed in inclusion. All these features suggest preserved anoxic  
311 conditions of the initial deposit and agree with the RE and deconvolution results.

312 For the borehole AUB230 (Fig. 7c), at 6.10 m, the palynofacies is dominated by grAOM (1.03 mg.g<sup>-1</sup>).  
313 There is also the presence of pyrite (0.59 mg.g<sup>-1</sup>) and od (0.27 mg.g<sup>-1</sup>) with small particles (between 10  
314 and 20 µm). In addition, the div category decreases in comparison with the surface. At 9.36 m, the  
315 palynofacies is characterized by small particles (around 1 µm) and pyrite is absent. The presence of  
316 small black particles as opaque-debris and/or oxidized Lignocellulosic particles suggests more oxidative  
317 conditions. Between 10 and 18 m the grAOM is present in a higher proportion (between 1.47 and 4.51  
318 mg.g<sup>-1</sup>). The proportion of OgAOM is higher than the 9.36 m sample (between 0.090 and 0.24 mg.g<sup>-1</sup>).  
319 The od proportion is homogeneous in this depth range. At 25 m, the proportion of OgAOM increases  
320 (0.35 mg.g<sup>-1</sup>) and the pyrite content also increases (0.49 mg.g<sup>-1</sup>). Between 30 and 55 m, the proportion  
321 of grAOM is higher than the other samples (between 1.99 and 4.83 mg.g<sup>-1</sup>) there is also the presence of  
322 pyrite and the od category detains bigger size (~100 µm). At the end of the borehole, (55-68 m), the  
323 proportion of grAOM is the highest (4.83-6.83 mg.g<sup>-1</sup>), the OgAOM proportion is also high (0.57-0.84  
324 mg.g<sup>-1</sup>) with bigger size and pyrite in inclusion. The palynofacies show a higher contribution of grAOM  
325 and OgAOM with pyrite inclusion. This feature also shows more preserved conditions. The increase of  
326 the AOM particles is correlated with the increase of HI and the principal contribution of C3 cluster  
327 suggesting that this AOM is the principal component of kerogen and suggest more preserved conditions  
328 of the formation.

329 The palynofacies for the AUB1010 borehole was difficult to interpret because the particles were present  
330 in very low proportion and could not permit any quantitative work. The particles were mainly composed  
331 of very small (around 1 µm) OgAOM and od particles. The samples of the AUB1010 borehole are  
332 similar to the AUB230 (6.10 m) sample and suggest more oxidative conditions.

333 The palynofacies is representative of the organic matter composition after the sedimentation and the  
334 organic diagenesis (Tyson 1993, Zhang et al. 2015). The different assemblages of refractory particulate  
335 organic matter permit to record environmental evolution and depositional characteristics. In particular,  
336 the different distributions can reflect the conditions of the oxygenation (Tyson 1993, Disnar et al. 2003,  
337 Di-Giovanni et al. 1999a). As mentioned in the geological setting, the Gault Clay was deposited in an  
338 open marine environment (Lerouge et al. 2018). Indeed, the presence of Glauconie, Siderite and Pyrite  
339 are characteristic of an anoxic marine deposition at shallow depth. In our study, AUB230 (at 55-68 m)

340 and the AUB240 samples present the well-preserved palynofacies assemblage. These samples show the  
341 presence of AOM with pyrite in inclusion (Fig. 7b, c). (Tyson 1993, Boussafir et al 1995a, b) showed  
342 that the presence of gel-like AOM is generally associated with high preservation rates and low energy  
343 environments and result to anoxic deposits. This OM is similar to that observed in Kimmeridgian clays  
344 Formation (Boussafir et al, 1995, a, b, Boussafir et al. 1997) and has an ultrafine monoscopically  
345 amorphous structure derived from the preservation by natural sulfuration in an anoxic environment. The  
346 H<sub>2</sub>S produced during the sulphate-reduction process allows the formation of pyrite in association with  
347 the iron present in the sediments and preserve a part of the initially metabolizable OM and therefore  
348 becomes resistant to degradation and oxidation. This process is at the origin of the highly stabilized  
349 nature of the OM of these clays. Consequently, the OM of Tégulines Clay is insensitive to  
350 physicochemical conditions and would probably not have a direct action on the redox system of this  
351 clay formation.

352

### 353 3.3 Molecular investigation in Tégulines Clay OM

#### 354 3.3.1 Total lipids extract

355 Tégulines Clay samples from the AUB230 borehole were selected for the molecular investigation of  
356 organic matter, based on S1 (> 0) and TOC values (~0.2) of the RE results.

357 The extract concentrations in Tégulines Clay are characterized by low content in labile compounds (0.3  
358 to 1.0 mg.g<sup>-1</sup> of dry sediment), and are consistent with the Rock-Eval quantitative (TOC) and qualitative  
359 (HI and OI) parameters and the palynofaciès composition (supplementary data 1), indicating the  
360 immaturity of OM (low free HC) and preserved insoluble kerogen. The extract concentrations in  
361 Tégulines Clay samples from the AUB240 and AUB1010 boreholes are very low and close to 0 mg/g  
362 (Rock-Eval ,S1, supplementary data 1), giving evidence of refractory and residual OM essentially.

363

#### 364 3.3.2 Chromatograms patterns: n-alkanes

365 The molecular composition of the Tégulines Clay samples for the AUB230 borehole was investigated.  
366 Three chromatograms patterns are presented in Figure 8 (sample at 6.10 m representing the oxidized  
367 area, sample at 25 m and, sample at 66 m representing preserved area). Very few compounds are present



368 in the different samples. Phthalates compounds were found in the samples (55 – 60 min retention time).  
369 the origin of these phthalates is unknown and could be the result of the extremely low concentration of  
370 natural organic compounds in the samples that could exacerbate the phthalates peaks and are not related  
371 to laboratory contamination. Several steroids were also encountered. In the biosphere, sterols contain  
372 essentially 27, 28 and 29 C atoms. C<sub>27</sub>-sterols produced by animals and C<sub>28</sub>-sterols produced by  
373 microalgae and fungi, C<sub>29</sub>-sterols are synthesized by land plants (Huang and Meinschein 1979; Volkman  
374 1986). The samples from the top and intermediate depths (6.10 m to 45 m) are composed of sitosterol,  
375 sitostanol, cholesterol, cholestanol coprostanol and epi-coprostanol. These sterols have a terrigenous  
376 origin. The end of the borehole is exempt from sterols.

377 This study mainly focuses on the alkanes composition in the different samples as they are more abundant  
378 and can lead to several calculations such as the Carbon Preference Index (CPI). The n-Alkanes are  
379 ubiquitous in the environment and are directly synthesized by living organisms or derived from straight-  
380 chain biolipids (Eglinton and Hamilton, 1967). They can be used to discriminate the sources and the  
381 preservation of the sedimentary immature OM (Brocks and Summons, 2003).

382 The total abundance of n-Alkanes varies between 0.29 and 9.14 µg/g sed, and increases from the bottom  
383 to the top of the clay formation (Table 4). In the AUB230 borehole, n-alkanes were dominated by n-  
384 C<sub>29</sub> to n-C<sub>33</sub> (Fig. 8) rather typical of terrestrial OM. The CPI defined by Bray and Evans, (1961) was  
385 determined with the following equation:  $CPI = 2(\text{odd } n\text{-C}_{23} \text{ to } n\text{-C}_{31}) / (\text{even } n\text{-C}_{22} \text{ to } n\text{-C}_{30} + \text{even}$   
386  $n\text{-C}_{24} \text{ to } n\text{-C}_{32})$ . The n-alkanes CPI index is generally interpreted in terms of the origin. A CPI ~ 1  
387 indicates marine origin, whereas a CPI > 1 reflects more terrestrial contribution. Between 9.36 and 45  
388 m, the CPI value is ~1.0 suggesting more marine contribution, however, this value could also reflect the  
389 oxidation of the OM. At the end of the borehole, the CPI is higher than 1, reflecting a mixture of marine  
390 and terrestrial organic compounds, more representative of the sedimentation conditions. CPI can also be  
391 used in order to characterize the degree of preservation of the n-alkanes in the sediments (Xie et al. 2004,  
392 Zheng et al. 2007, Jansen and Nierop, 2009 Zhou et al. 2010; Garel et al., 2013). CPI values between 3  
393 and 10 refer to preserved OM. Values between 1 to 3 are the first signs of early degradation. Values  
394 close to 1 indicate more bacterial activity or recycled OM. At the start of the diagenesis, the molecular  
395 compounds are mainly composed of oxygen functional groups. During the diagenesis, the



396 defunctionalization of the compounds leads at the end to the formation of hydrocarbons. The lipids that  
397 are stocked in the sediments lead to the loss of many compounds and short chains molecules are more  
398 degraded than the long chains ones.

399 The CPI values, calculated from the n-alkanes concentrations showed variations with depth. The CPI  
400 was high for the trench sample and decreased after to values around 1 (9.36 – 21.30 meter deep). At the  
401 end of the borehole, the CPI values increased again. These features suggest more preserved OM at the  
402 top, in relation to the immature state of the OM, more degraded conditions between 9.36 and 21.30 m  
403 and again, more preserved conditions (or slightly degraded) at the end of the borehole. These results are  
404 in accordance with the RE and palynofacies results. The top of the AUB230 borehole is oxidized and  
405 after 21 m, more preserved OM is observed. However, the CPI ratio shows oxidized conditions until 21  
406 m whereas the palynofacies and at a lesser extent, the RE data shows an oxidation profile until 10 m.  
407 The CPI ratio is in accordance with the mineralogical data (Lerouge et al. 2018) where the oxidation  
408 profile is observed until 21 m.

409

#### 410 3.4 Comparison with other marine clay formations – Impact of the oxidation

411

412 From a general overview, the TOC values show that the Tégulines Clay are very poor in organic content.  
413 Guo et al. (2021) also studied the Tégulines clay in order to investigate the mobility of organic  
414 compounds in this formation. Despite a low TOC content (as observed in this study), they observed the  
415 retention of certain compounds such as lipophilic compounds. Other marine clay-rich formations that  
416 have experimented low temperature such as Tégulines Clay have been extensively investigated in the  
417 literature concerning their organic matter composition and variations. The Opalinus Clay from northern  
418 Switzerland did not display a higher temperature of burial than 85 °C (Elie and Mazurek, 2008). They  
419 also display quite low C contents from 0.1 to 1 wt% (Todorof et al. 1993; Nagra, 2002). Callovo-  
420 Oxfordian claystones is another formation, located in the Eastern part of the Paris basin, that experienced  
421 low temperature (50 °C) (Landais and Elie, 1999). Their total organic C content is also generally low  
422 (<1 wt.% of the bulk rock). The  $T_{\max}$  recorded for the Tégulines Clays is essentially < 430 °C. This  
423 temperature is revealing immature OM. The RE  $T_{\max}$  of the Opalinus Clay also displays temperatures

424  $\leq 435$  °C in accordance with low thermal maturity. The thermal immaturity of the Callovo-Oxfordian  
425 formations was demonstrated by the predominance of odd/even long-chain n-alkanes with CPI higher  
426 than 2 (Hautevelle et al. 2007). In the case of the Tégulines Clay, the CPI cannot estimate the immaturity  
427 as most of the formation is under oxidation. However, CPI can be used for the estimation of the  
428 preservation. Our study emphasizes that the RE technique is suited to be used for oxidized formations.  
429 The HI versus OI plot (pseudo Van Krevelen plot, Fig. 4) is usually employed to separate the marine  
430 and terrestrial contributions in preserved conditions. In Elie and Mazurek (2008), the Opalinus Clay  
431 falls into the Type III kerogen area, revealing more terrestrial contribution. The Callovo-Oxfordian  
432 formations van Krevelen diagram indicate type II and III OM mixture, showing a marine origin, with a  
433 contribution of terrestrial-derived materials (Disnar et al. 1996; Hautevelle et al. 2006). For the  
434 Tégulines Clay, no conclusion permits to settle between marine or terrestrial contribution because the  
435 HI and OI values can also suggest the presence of oxidized marine contribution, leading to the transfer  
436 to the type III kerogen area.

437 The molecular investigation of the Tégulines Clay seems also to be perturbed by the oxidation profile.  
438 The yields of OM extract in Tégulines Clay are low 0.3 to 1.0 mg. g<sup>-1</sup> of dry sediment. By comparison,  
439 the extract yield for Opalinus Clay is comprised of 0.9 and 48 mg. g<sup>-1</sup> (Elie and Mazurek 2008). The  
440 yield fractions of soluble OM ranges between 0.01 and 0.65 mg of organic extract/g of rock for the  
441 Callovo-Oxfordian formations (Hautevelle et al. 2007). Despite the low yield of soluble OM, Callovo-  
442 Oxfordian formations displayed a large variety of compounds deciphered by GCMS (n-alkanes, steroids,  
443 hopanoids among others), permitting to get information on the OM maturity and origin. In contrast, the  
444 chromatograms patterns of the different samples from the AUB230 borehole show the presence of a low  
445 number of peaks, revealing a low number of molecular compounds (Fig. 8). Only n-alkanes could be  
446 easily deciphered. However, the results concerning the n-alkanes distribution and the CPI are  
447 questionable. Indeed, the predominant n-alkanes are ranging between C<sub>29</sub> and C<sub>33</sub>, revealing terrestrial  
448 origin such as for the Opalinus Clay (Odd/Even predominance of C<sub>25</sub>-C<sub>35</sub> range (Elie and Mazurek,  
449 2008)). By contrast, the Tegulines CPI is ~ 1 revealing marine origin. These opposite results could stem  
450 from an artifact caused by the oxidation of the OM, shifting the short-chain of n-alkanes. These results  
451 can question the use of certain techniques when dealing with oxidized OM.

452 3.5. Comparison of the TCF OM with mineralogical and dissolved inorganic carbon  
453 (DIC) changes through the TCF weathering profile

454 In this study, the AUB230 borehole enabled to evidence the three main facies (from the bottom to the  
455 top: UAQ, UA, and UAC units, see §2.1.) that can be encountered in the TCF, whereas the AUB1010  
456 borehole only crosscut the UAQ and UA units (Lerouge et al., 2018). In the both boreholes, the oxidation  
457 profile was observed between the sub-surface and ~21 m depth (Lerouge et al., 2018, 2020) (Fig. 9).

458 The brown and granulous textures, the bulk and molecular characteristics of the OM at the surface (0-  
459 30 cm borehole AUB230) revealed high amounts of organic matter showing typical oxidative  
460 degradation in soil, according to the following reaction:  $\text{CH}_2\text{O} + \text{O}_2 = \text{H}_2\text{O} + \text{CO}_2$ . These observations  
461 are in good agreement with the DIC of 1.4 mEq/L measured in soil pore waters, the high  $\text{CO}_2$  soil  
462 degassing and the low  $\delta^{13}\text{C}$  value of degassed  $\text{CO}_2$  (-25.5 ‰ PDB) (Lerouge et al., 2020).

463 Between 30 cm and 5 m deep in the AUB230 borehole, in ocher carbonate-free sandy clay loams  
464 overlying TCF, the bulk and OI index of the OM gave evidence of extremely low TOC contents and  
465 high oxidative conditions consistent with the altered pedogenetic OM surficial bring (Fig. 4). These  
466 observations are in good agreement with the low DIC (<0.9 mEq/L) measured in pore waters and the  
467 low  $\delta^{13}\text{C}$  values of DIC (~ -21 ‰ PDB) (Lerouge et al., 2020).

468 Below ~5 m in the AUB 230 borehole and ~2-3 m in AUB1010 borehole, the top of TCF is ocher, plastic  
469 and marked by an intense and visible oxidation of pyrite and other iron-bearing minerals (iron-rich clays,  
470 ankerite) that decreases down to 11 m depth. Pyrite oxidation leads to iron oxyhydroxide and gypsum  
471 precipitation, but also to a small calcite dissolution due to slight acid pH. Ankerite oxidation leads to  
472 iron oxyhydroxide precipitation. The clay fraction in TCF is quite homogeneous and composed by  
473 ~16±5 % of detrital kaolinite, ~16±4 % of illite-smectite, ~12±5 % of illite-mica, and minor chlorite (<2  
474 %), and ~8±6 % of diagenetic glauconite. The study of clay minerals in the 5-10 m zone, based on  
475 microscopic observations, XRD and electron microprobe gave evidence of a change of color from  
476 greenish to ocher due to oxidation of iron, a loss of iron to form iron oxides and an increase of the  
477 smectite component, in particular concerning chlorite and glauconite (Lerouge et al. 2018, 2020). In the  
478 same way, the OI of the OM is high and confirms oxidative conditions. Combined mineralogical and  
479 OM data are consistent with the high DIC values (up to 8.5-8.6 mEq/L) measured in Tegulines Clay

480 pore waters in the 5-10 m zone of the both AUB230 and AUB1010 borehole. The  $\delta^{13}\text{C}$  values of  
481 degassed  $\text{CO}_2$  (-19.5 to -12.9 ‰ PDB) corresponds to a mixing between OM matter degradation and  
482  $\text{CO}_2$  due to calcite dissolution (Lerouge et al., 2020). The OM study gave a supplementary information  
483 with the OI index, which is consistent with a mixing of the altered pedogenetic OM surficial supply and  
484 the oxidation of original organo-clays fraction of the initial marine sediments (Fig. 4). The identification  
485 of OM surficial supply down to ~9-10 m is in good agreement with the rare presence of small roots  
486 down to 10-12 m in boreholes (Lerouge et al., 2020). The oxidation of pristine marine OM down to ~9-  
487 10 m in the weathering profile is also an important point, which is a subject of debate for chemical  
488 modelling of weathering profile in marine clay formations (Bao et al., 2017).

489 Between 9-10 m and 55 m, the OM oxidation state was homogenous and low, whereas changes of  
490 consistency from plastic to hard and of mineralogy (slight oxidation of glauconite marked by yellowish  
491 color) were still observed at ~ 20-25 m (Debure et al. 2018; Lerouge et al. 2018). The variation between  
492 plastic/non plastic behavior of the TCF seems to not play a role for OM preservation.

493 The bottom of the TCF evolved under reducing conditions, and are characterized by an enrichment in  
494 clay minerals, including glauconite and smectite (Lerouge et al., 2018). The OM data also showed more  
495 preserved OM with higher HI, the microscopic data also show more preserved conditions with higher  
496 grAOM and O<sub>g</sub>AOM contents with the inclusion of pyrite suggesting the role of bacterial sulphate  
497 reduction in an anoxic sedimentary environment. Indeed, the association of pyrite with the amorphous  
498 orange gel-like organic matter is interpreted as a non-biodegradable and stable organic matter preserved  
499 by incorporation of sulfur by natural sulfurization (Boussafir et al. 1994, 1995, 1997).

500 At interface with the Greensand, TCF shows a drop of the TOC, S<sub>1</sub>, S<sub>2</sub> and an increase of OI  
501 (Supplementary data 1). The green sand detains coarser particles than the Tégulines Clay and could store  
502 and/or preserve less OM.

503 Overall, the OM characterization (RE, palynofacies) of TCF in the different boreholes supports a well-  
504 developed oxidation profile in the ~ 0-10 m and preservation of reduced conditions in the deeper parts,  
505 in agreement with the previous mineralogical and geochemical studies. As for sulfur and iron oxidation  
506 states, the oxidized or preserved state of the OM will finally help to redox regulation with depth in the  
507 Tégulines Clay. Indeed, despite a similar TOC content all along the investigated boreholes, the

508 preservation of the organic matter and especially its reducing capacity will be one of the parameters that  
509 might influence the mobility of sensitive-redox chemical elements (Debure et al. 2018, 2020). The small  
510 amount of preserved, very little functionalized and unreactive OM and the refractoriness and stability  
511 of OM of almost all the borehole samples studied plead for a slight influence of OM in the Tégulines in  
512 a redox system.

513 Clay minerals, and particularly smectite, can physically protect the OM in these sediments (Hedges and  
514 Oades 1997; Nelson et al. 1999, Drouin et al. 2010; Mahamat et al. 2016). The comparison with the  
515 organic data (TOC, HI, OI) shows that we have, at the bottom of the borehole an increase of clay  
516 minerals, including smectite / smectite-illite and glauconite, and an IH increase. Bruun et al. (2010)  
517 stated that smectite have higher capacity to stabilize organic matter than illite due to higher specific  
518 surface area and cation exchange capacity. All these information permits to state that the protection  
519 of the organic matter at the bottom of the AUB230 borehole (66 – 68 m) can be the presence of  
520 smectite in higher proportion.

521 The OM is preserved in the AUB240 borehole while it was more oxidized in the AUB1010 at least  
522 between 3 and 16 m and also observed from mineral characterizations. The OM preservation is higher  
523 in the AUB240 borehole, as a 12 m layer of Brienne Marls overlies it themselves covered by 8 m of  
524 surficial layers (loess, clay sediments and carbonated alluvium). By contrast, the surficial layer in the  
525 AUB230 borehole represents only 5 m and even less (3 m) in the AUB1010 borehole. Therefore,  
526 meteoric water reaches faster the Tégulines in the AUB1010 and AUB230 boreholes. Finally, the  
527 difference between the AUB230 and the AUB1010 borehole relies on their position in the valley. The  
528 AUB230 borehole is located at the hilltop while the AUB1010 is located at the bottom where the water  
529 can stream from the hills. The position of the AUB1010 borehole is therefore favorable to a higher  
530 alteration compared to the other boreholes and all these characteristics explain the higher oxidation depth  
531 observed for organic matter in that borehole.

532

## 533 Conclusion

534 This study investigated the OM composition of the Tégulines Clay formation using bulk, microscopic  
535 and molecular techniques. All the profiles studied show that Tégulines Clay are poor in organic content  
536 in general. The bulk results using RE analyses revealed that the OM of all clays studied samples was  
537 immature. The RE parameters, deconvolution of S2 peak, R400, palynofacies and molecular  
538 investigations were all positively correlated. Indeed, at the surface (TPH1-1 0-30), the OM showed  
539 relatively high HI and TOC with a large amount of preserved particles revealing typical soil litter OM.  
540 The deconvolution of the S2 peak curve showed a dominant contribution of the C3 cluster that is typical  
541 of the breakdown of polysaccharides and lignin in the surface part of the studied profile. The other trench  
542 samples collected below 30 cm showed very oxidized conditions (low TOC and high OI). The AUB240  
543 borehole, from the bulk and microscopic investigation, revealed more preserved conditions, mainly due  
544 to the overlaying of the Brienne marls and is presented as a reference borehole in term of OM  
545 preservation. The investigation of the AUB230 borehole clearly showed an oxidation profile at the top  
546 and more pristine, preserved and reductive conditions deeper. The AUB1010 borehole showed similar  
547 conditions to the AUB230 borehole but a higher oxidation depth. These different oxidation depths could  
548 be explained by the different spatial topological location of the boreholes. This study showed that the  
549 Tégulines Clay OM is: very low in amount, stable in its preserved section, essentially residual and little-  
550 sensitive to the biotic and abiotic degradation and thus would be very weakly reactive. The OM influence  
551 would also be limited in a redox system supporting previous results obtained on the behavior of  
552 sensitive-redox chemical elements. Finally, this is supported on the one hand by the small amount of  
553 preserved, very little functionalized and unreactive OM and on the other hand, by the refractoriness and  
554 stability of OM of almost all the borehole samples studied. This study also shows that a good set of  
555 techniques permit to deal with the complex atmosphere / Geological formations interactions in the  
556 critical zone.

557

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1 Table 1 *Characteristics of the different particles encountered in the different samples*

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Classes	Categories	Characteristics
<b>Amorphous particles</b>	GrAOM: granular Amorphous Organic Matter	Diffuse limits, grey to yellow in transmitted light, opaque or slight orange in reflected light, size: 10-100 µm
	gAOM: Gelified Amorphous Organic Matter	Particle entirely gelified, no internal structure, orange to red in transmitted light, dark orange in reflected light, size: can reach very large size over 100 µm
	Gd: Gelified debris	Sharp contours, high reflectance, size: 10 µm
	Od: Opaque debris	Sharp contours, high reflectance, dark in transmitted light, size: 10 µm
	Plc: Preserved lignocellulosic	Elongated particles with visible internal structures, yellow in transmitted light (10-100 µm)
<b>Ligno cellulosic de bris</b>	Salc: Slightly amorphised lignocellulosic	Elongated particles with visible internal structures, yellow to orange in transmitted light (10-100 µm), trace of gelification
	Glc: Gelified lignocellulosic	Elongated particles with visible internal structures, yellow to orange in transmitted light (10-100 µm), higher state of gelification
	Olc: Opaque lignocellulosic	No internal structure visible, elongated, show high reflectance (10-100 µm)
<b>Other organic particles</b>	Div: divers	Mycelium fragments: elongated particles, brown color; Cuticular fragments: particles with homogeneous limits, brown, with typical botanic structures, size variable and can exceed several hundred µm; Spores and pollens: particles from the terrestrial and aquatic flora, translucent or yellow for fresh particles and brown-orange for preserved particles; acritarchs, foraminifera
	pyrite	framboidal, opaque, with geometrical forms under transmitted light

3 Table 2 Distributions, abundances and ratios of *n*-alkanes in the Trench TPH1-1 (0 – 30 cm sample) and AUB230 borehole.  
 4 <sup>a</sup>Major *n*-alkanes in core samples, <sup>b</sup>Total = total abundance of *n*-alkanes ( $\mu\text{g/g}$  sediment), <sup>c</sup> odd/even ratio (odd/even =  
 5  $\sum \text{conc. odd alkanes} / \sum \text{conc. even n-alkanes}$ ) <sup>d</sup>*n*-alkanes carbon preference index CPI =  $2(\text{odd } n\text{-C23 to } n\text{-C31}) / (\text{even } n\text{-C22 to}$   
 6  $n\text{-C30+ even } n\text{-C24 to } n\text{-C32})$ .

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	Major alkanes <sup>a</sup>	Total of alkanes ( $\mu\text{g/g}$ sed) <sup>b</sup>	odd/even <sup>c</sup>	CPI <sup>d</sup>
TPH1-1 0- 30cm	n-C29, n-C31, n-C33	5.08	2.97	4.95
AUB230 9.36m	n-C29, n-C31, n-C33	9.14	1.26	1.08
AUB230 21.30m	n-C29, n-C31, n-C33	0.95	1.06	0.97
AUB230 25.32m	n-C29, n-C29, n-C31	0.61	1.37	1.19
AUB230 45.84m	n-C29, n-C31, n-C33	0.56	1.34	1.15
AUB230 66.35m	n-C29, n-C31, n-C33	0.47	0.97	1.57
AUB230 67.45m	n-C25, n-C31, n-C31	0.29	1.27	1.74

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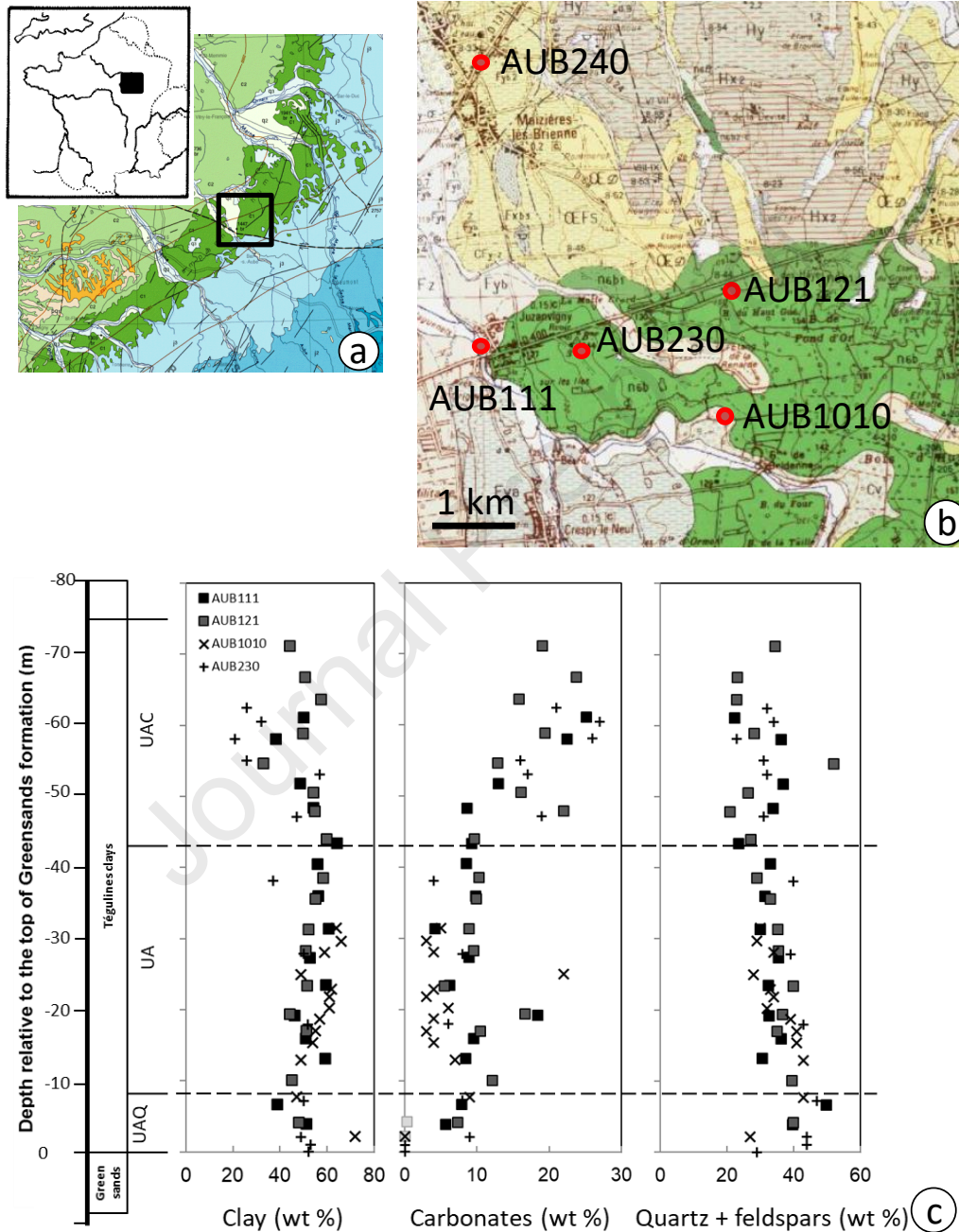
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1 Fig. 1 (a) Geological map of the east part of the Paris Basin showing the studied area; (b) Geological map of the studied area  
 2 showing the location of the AUB240, AUB230 and AUB1010 boreholes selected for the organic matter study; (c) Major  
 3 mineralogy of the Tégulines clay from the AUB230 and AUB1010 boreholes deduced from XRD data treatment, compared  
 4 with previous data of AUB111 and AUB121 boreholes (Lerouge et al., 2018); UA: clay rich unit; UAC: carbonate-clay rich  
 5 unit; UAQ: clay-quartz rich unit  
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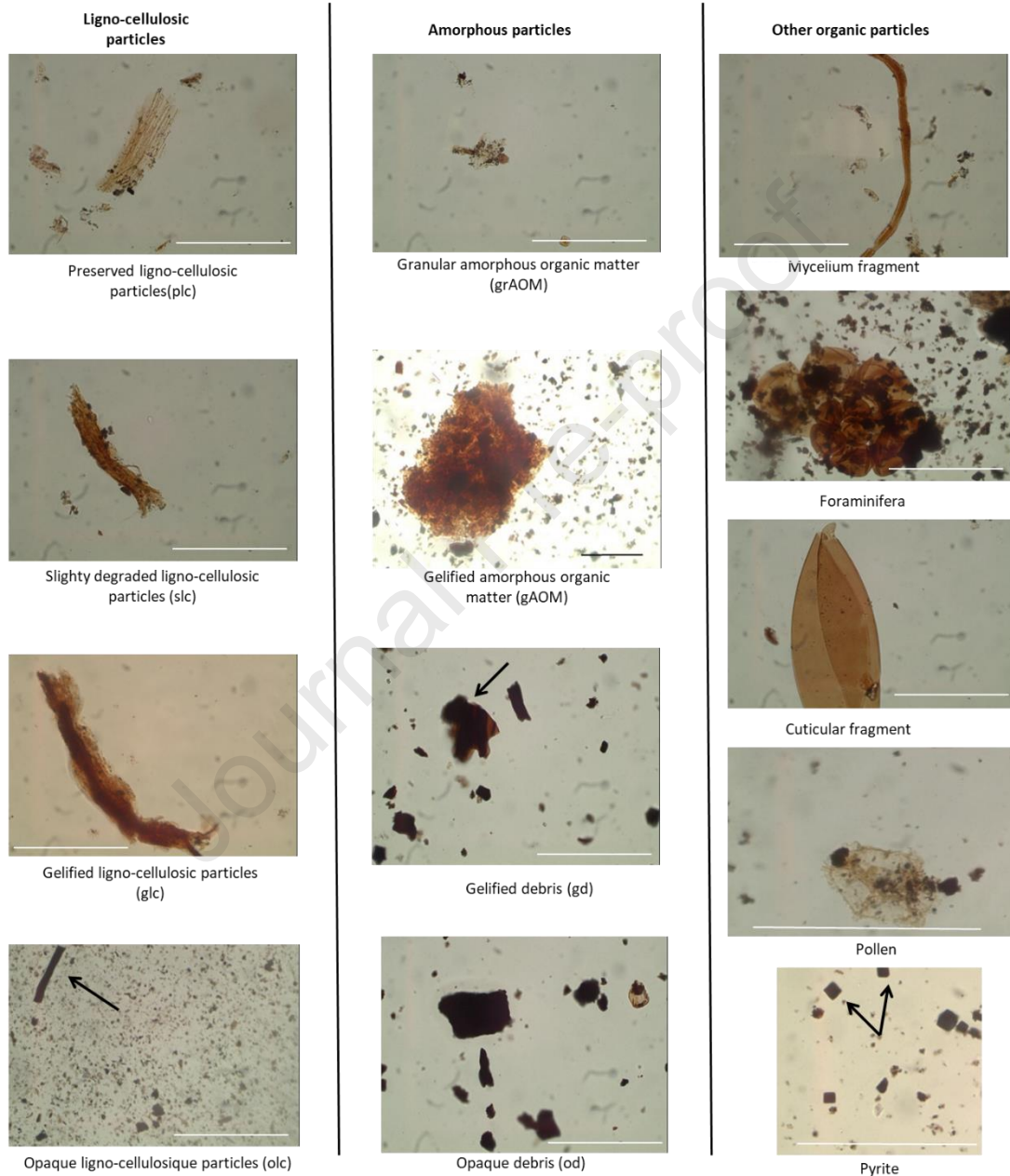
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13 Fig. 2 The different categories of particulate organic matter distinguished from their morphology, the scale of the white bars  
 14 corresponds to 100  $\mu\text{m}$ ; **Ligno-cellulosic fragments**: - preserved ligno-cellulosic fragments (plc),- slightly degraded ligno-  
 15 cellulosic fragments (slc), - gelified ligno-cellulosic fragments (glc),- opaque ligno-cellulosic fragments (olc); **amorphous**  
 16 **particles**: - granular amorphous organic matter (grAOM),- gelified amorphous organic matter (gAOM),- gelified debris  
 17 (gd),- opaque debris (od); **Others organic particles**: - mycelium fragments (Myc); - foraminifera, - cuticular fragments  
 18 (Cut), - Spores and pollens (sp), - (c) Pyrite.  
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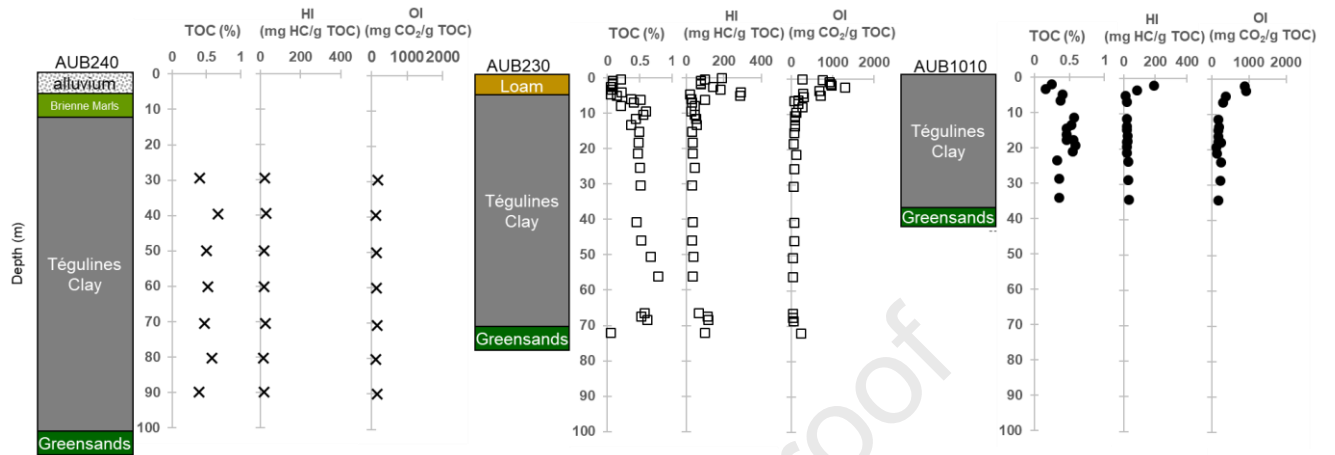
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26 Fig. 3 Total Organic Carbon (TOC, %), Hydrogen Index (HI,  $mg\ HC.g^{-1}TOC$ ), and Oxygen Index (OI,  $mg\ CO_2.g^{-1}TOC$ ) in  
 27 relation with depth for the AUB240, AUB230 and AUB1010 boreholes.  
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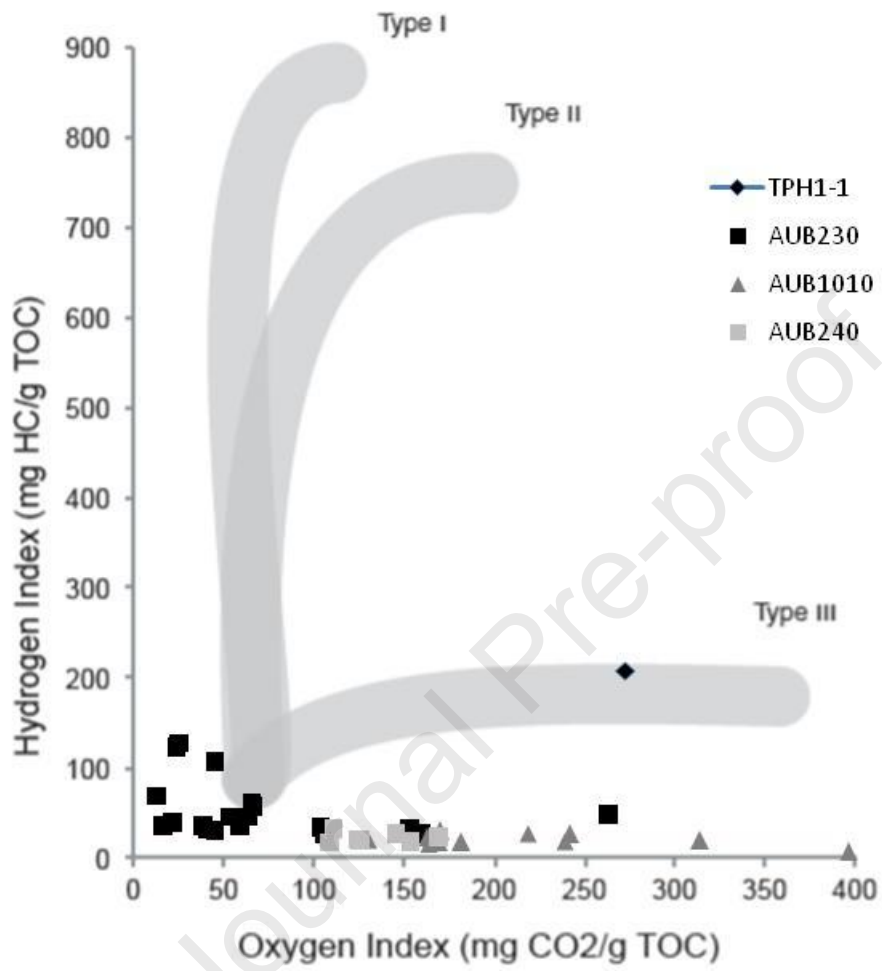
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50 Fig. 4 Pseudo van-Krevelen diagram type for the different samples.

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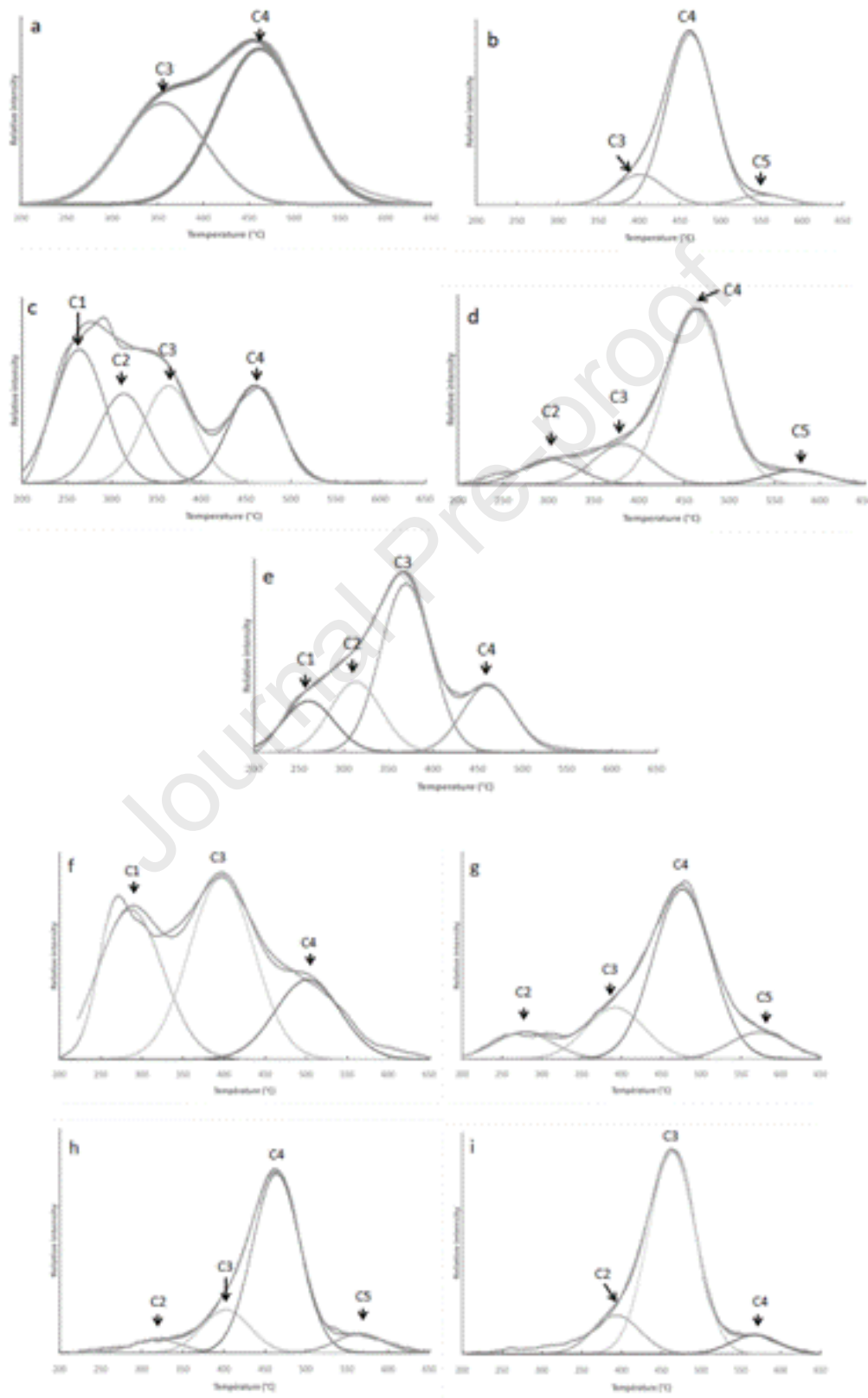
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64 Fig. 5 Deconvolution of multilobed S2 signals from RE pyrolysis for *a* TPH1-1 030 ( $r^2 = 0.996$ ), *b* AUB240 39 ( $r^2 = 0.999$ ), *c*  
 65 AUB230 6.10 ( $r^2 = 0.994$ ), *d* AUB230 25.32 ( $r^2 = 0.997$ ), *e* AUB230 67.45 ( $r^2 = 0.998$ ), *f* AUB1010 1.88 ( $r^2 = 0.974$ ), *g* AUB1010  
 66 3.31 ( $r^2 = 0.996$ ), *h* AUB1010 14.47 ( $r^2 = 0.998$ ), *i* AUB1010 20.95 ( $r^2 = 0.995$ ). Black-grey curves are the rebuilt S2 signal from  
 67 deconvolution.  
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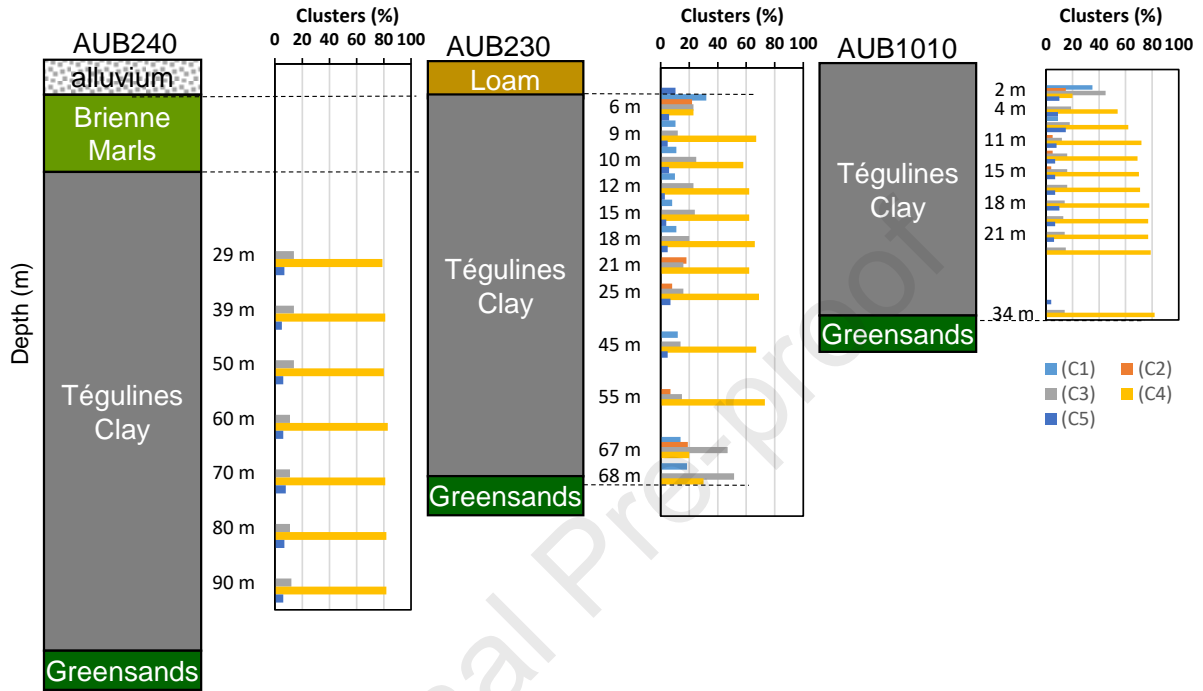


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Fig. 6 Contribution of the different clusters (C1-C5, %) AUB240, AUB230 and AUB1010 samples

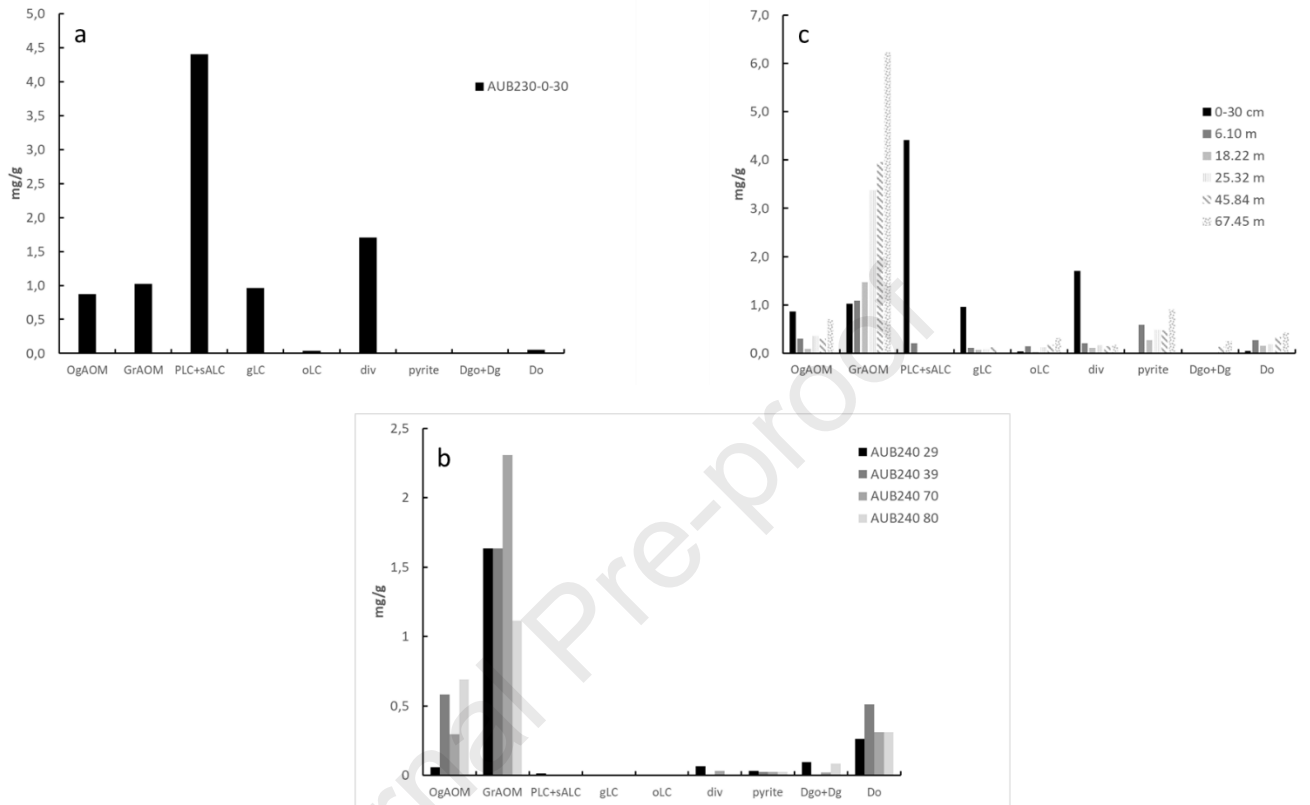


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90 Fig. 7 Distribution of the different particles in: (a) TPH1-1 0-30 sample; (b) AUB240 borehole (29,39,70 and 80  
 91 deep); (c) AUB230 borehole (6.10, 18.22, 25.32, 45.84, 67.45 m and comparison with the TPH1-1 0-30)

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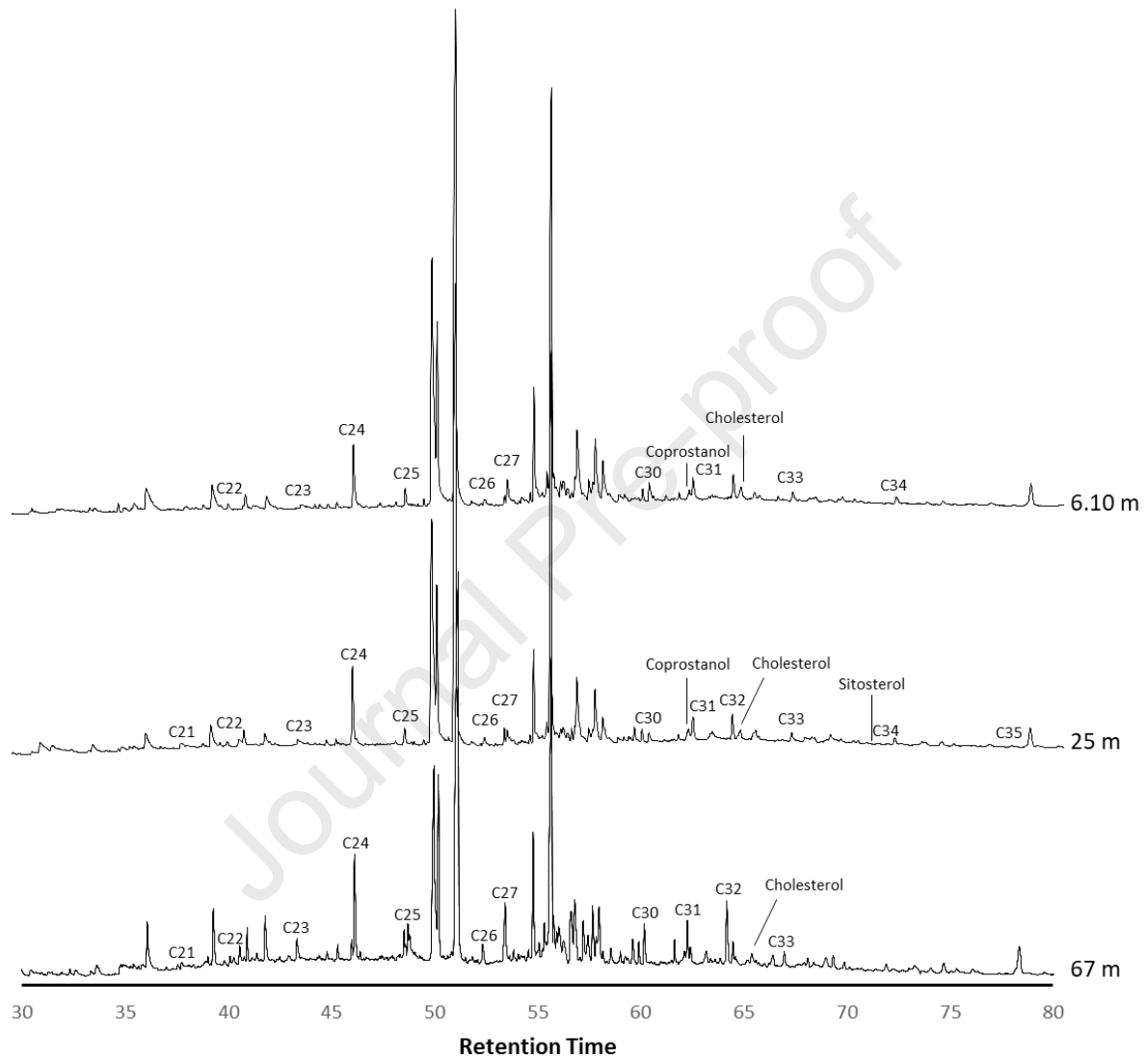
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110 Fig. 8 Chromatograms of the Tégulines Clay formation at 67 m; 25 m and 6.10 m

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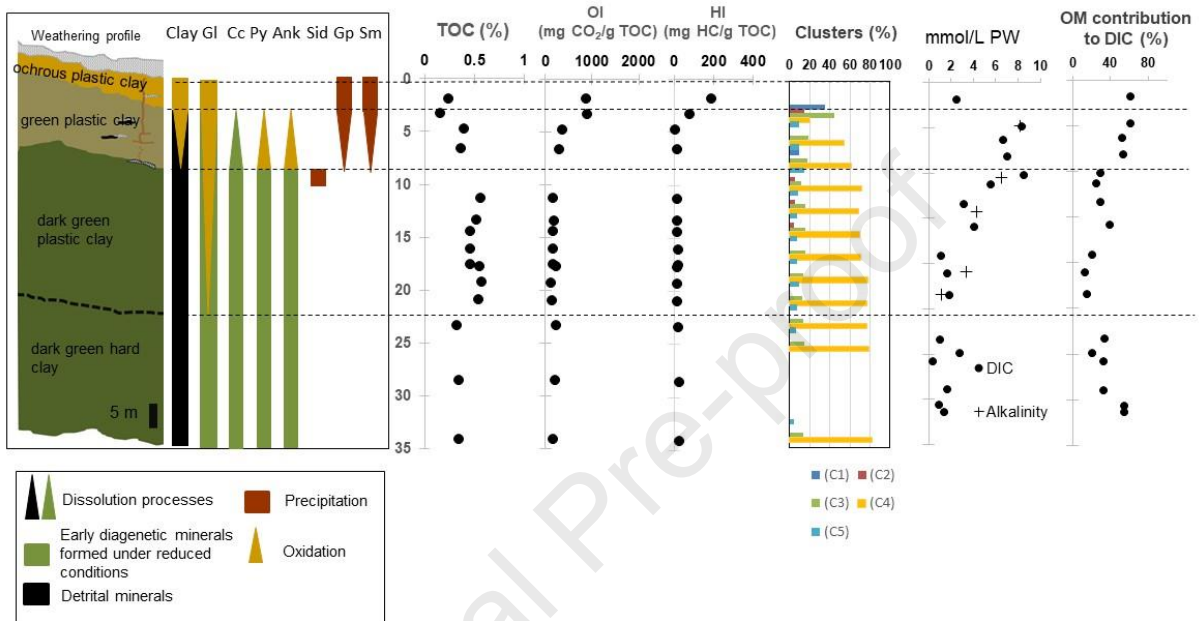
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Fig. 9 Main characteristics of the organic matter through the weathering profile developed in Tégulines clay, compared with mineral changes (Lerouge et al., 2018), dissolved inorganic carbon concentration (DIC) in pore waters (PW) and contribution of degradation of organic matter (OM) to the DIC (Lerouge et al., 2020).



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- OM characterization of the Tégulines Clay formation using bulk and molecular data
- Vertical variation of the oxidation profile as a result to the vicinity to the surface
- First upper 10 m of the clays subjected to oxidative events, below 10 m OM preserved
- Spatial variations of the oxidation state due to different topography of the boreholes
- OM bulk and molecular techniques are a good association for critical zone studies

Journal Pre-proof

## **Conflict of Interest**

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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