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## First record of early Aptian Oceanic Anoxic Event 1a from the Paris Basin (France) - Climate signals on a terrigenous shelf

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1 **First record of early Aptian Oceanic Anoxic Event 1a from the Paris Basin (France) -**  
2 **climate signals on a terrigenous shelf**

3

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13

14 Abstract

15 In 2013, Andra (French National Radioactive Waste Management Agency) drilled boreholes  
16 to the south-east of the Paris Basin, to characterise Aptian and Albian clayey formations,  
17 including the ‘Argiles à Plicatules’ Formation dated as early Aptian. One of these boreholes  
18 intersected this formation with an excellent recovery allowing detailed biostratigraphy  
19 (ammonites), sedimentology, clay mineralogy, isotope geochemistry ( $\delta^{13}\text{C}_{\text{org}}$ ) and Rock-Eval  
20 analyses to be performed. The base of the formation corresponds to transgressive dark-grey  
21 silty clays with iron oolites and plant debris indicating a coastal environment evolving up-  
22 section to upper offshore environments. Higher in the succession, clays with less than 4%  
23  $\text{CaCO}_3$  and less than 0.8% of organic matter were deposited in lower offshore environments.  
24 The occurrence of ammonites can be used to draw a biostratigraphic scheme, and in  
25 particular, to recognise the *deshayesi* and *furcata* ammonite Zones.

26 The clay mineral assemblages are composed of illite and kaolinite associated with minor  
27 amounts of chlorite, vermiculite and smectite. The  $\delta^{13}\text{C}_{\text{org}}$  values range between -24 and -  
28 25‰ except in a particular interval characterised by a prominent negative excursion of about -  
29 3‰, that is recognised worldwide and precedes Oceanic Anoxic Event 1a (OAE1a). This  
30 interval is also characterised by an abundance of kaolinite and the absence of smectite  
31 suggesting an acceleration of the hydrological cycle and enhanced runoff and hydrolysing  
32 conditions over the emerged landmasses just before and during the onset of OAE1a. This  
33 climate change is consistent with isotope and palynological data indicating warm and humid  
34 climate conditions before and during the onset of OAE1a. Surprisingly, the interval  
35 corresponding to OAE1a is not significantly enriched in organic matter and its lithology is not  
36 different from the rest of the core suggesting that Tethyan anoxic water masses did not reach  
37 the relatively shallow epicontinental environments of the Paris Basin.

38

39 Keywords: Lower Cretaceous, Aptian, Oceanic Anoxic Event, Paris Basin, Clay minerals,  
40 Organic carbon isotopes

41

42

43 Introduction

44 Identified for the first time by Schlanger and Jenkyns (1976), Oceanic Anoxic Event  
45 (OAE) 1a (early Aptian) is characterised by the worldwide preservation of organic matter in  
46 black shales as a consequence of intensification in marine primary productivity under oceanic  
47 oxygen-depleted conditions (Coccioni et al., 1987; 1992; Erba, 1994, Erba, 2004; Erbacher et  
48 al., 1996; Leckie et al., 2002; Jenkyns, 2010; Föllmi, 2012; Erba et al., 2015). A global  
49 perturbation in the carbon cycle is associated with this event, recorded by a prominent  
50 negative excursion followed by a shift towards more positive values (Menegatti et al., 1998).

51 The negative excursion is generally explained by an intense volcanic episode at the origin of  
52 the formation of the Ontong-Java oceanic plateau (Tarduno et al., 1991; Larson and Erba,  
53 1999; Méhay et al., 2009; Tejada et al., 2009; Bottini et al., 2012; Erba et al., 2015;  
54 Charbonnier and Föllmi, 2017) while the following positive excursion is seen as a  
55 consequence of organic matter burial in oceanic sediments. The duration of the negative  
56 excursion, first underestimated between 27 and 44 kyr (Li et al., 2008), is likely longer with a  
57 duration estimated between 280 and 350 kyr (Lorenzen et al., 2013). The duration of OAE1a  
58 itself is estimated between 1 and 1.3 myr (Li et al., 2008). These environmental changes were  
59 associated with rising sea surface temperatures (Mutterlose et al., 2014; Bottini et al., 2015)  
60 and a calcification crisis in calcareous nannoplankton known as the ‘nannoconid crisis’ (Erba,  
61 1994). Despite its widespread extension and its recognition in numerous sedimentary basins  
62 (Bréhéret, 1997; Bellanca et al., 2002; Ando et al., 2008; Vincent et al., 2010; Giraud et al.,  
63 2018 among others) and shallow water carbonate platforms (Baudin et al., 1996; Luciani et  
64 al., 2006; Najjarro et al., 2011; Graziano, 2013; Godet et al., 2014; Pictet et al., 2015; Amodio  
65 and Weissert, 2017; Hueter et al., 2019), OAE1a has not yet been described in the Paris Basin  
66 mainly because lower Aptian clayey deposits are poorly outcropping. In 2013, several  
67 boreholes were drilled by Andra (the French National Radioactive Waste Management  
68 Agency) to the south-east of the Paris Basin in order to characterise Aptian and Albian clayey  
69 formations including Argiles à Plicatules, a so-called formation because of the occasional  
70 occurrence of *Plicatula placunea* Lamarck, 1819, a common warm water bivalve (Squires and  
71 Saul, 1997). One of these boreholes (AUB 121) intersected the Argiles à Plicatules Formation  
72 with excellent recovery allowing detailed sedimentological, mineralogical and geochemical  
73 studies to be performed; it also provided an opportunity to search for a record of OAE1a in  
74 the Paris Basin. As a result, facies descriptions as well as mineralogical, Rock-Eval and  
75  $\delta^{13}\text{C}_{\text{org}}$  analyses were performed to characterise the Aptian sediments deposited in the Paris

76 Basin. The main objectives were to precisely describe the whole succession of the Argiles à  
77 Plicatules Formation, to highlight the record of OAE1a in the terrigenous shelf environment  
78 of the Paris Basin and to specify climatic conditions, notably the fluctuations in the  
79 hydrological cycle that prevailed during the Aptian through a high resolution study of the clay  
80 minerals.

81

## 82 I - Geological context and biostratigraphy

83 The Paris Basin is a Meso-Cenozoic intracontinental basin that, today, is bordered by  
84 Palaeozoic massifs including the Armorican Massif to the west, the Massif Central to the  
85 south, the Vosges to the east and the Ardennes Massif to the north. During the Aptian, the  
86 Paris Basin was occupied by a narrow epicontinental sea (strait) between the London-Brabant  
87 Massif (LBM) and the Rhenish Massif (RM) to the north and a landmass comprising the  
88 Armorican Massif (AM) and the Massif Central (MC) to the south (Fig. 1). This narrow  
89 epicontinental sea, situated at a latitude comprised between 30 and 35°N, connected the  
90 Tethys Ocean located to the south-east to the boreal realm toward the north-west (Masse et  
91 al., 2000).

92 After a long period of continental evolution of the Paris Basin starting at the  
93 Jurassic/Cretaceous transition (Purbeckian facies), transgressive marine sediments were  
94 deposited above Early Cretaceous variegated continental and deltaic sediments, the so-called  
95 Wealden facies (Allen, 1998; Guillocheau et al., 2000; Radley and Allen, 2012). To the south-  
96 east of the Paris Basin, the Early Cretaceous continental sedimentation (Berriasian to  
97 Barremian) was occasionally interrupted by the deposition of shallow marine sediments  
98 including the early Hauterivian “Calcaires à Spatangues” Formation and the early Barremian  
99 “Argiles Ostréennes” Formation, as a consequence of transgressions originating from the  
100 south-east (Tethyan domain), whereas the late Barremian continental deposits consist of

101 variegated clays showing common root traces. From the Aptian, a continuous marine  
102 sedimentation took place until the end of the Cretaceous.

103

#### 104 I-1. Lithology of the AUB 121 borehole

105 The AUB 121 borehole is situated to the south-east of the Paris Basin, at Juzanvigny,  
106 near Brienne le Château (Fig. 2). The lithological succession has been described in detail by  
107 Amédéo et al. (2017). The 31 m-thick Argiles à Plicatules Formation is underlain by upper  
108 Barremian continental deposits (Wealden facies) corresponding to weathering profiles  
109 (laterite) and overlain by upper Aptian glauconitic sands corresponding to the “Sables Verts  
110 de l’Aube” Formation (Fig. 3). Three distinct intervals (1 to 3) were defined within the  
111 Argiles à Plicatules Formation:

- 112 - Unit 1, from 116.76 m to 111.90 m, includes black to grey clays with traces of  
113 palaeosoils at the base. Woody debris and coalified compressions of pteridophytes  
114 are common in this part of the formation (Fig. 4A). Some iron oolites-rich layers  
115 (Fig. 4B) occasionally filling burrows occur at the base of this unit, while the top is  
116 marked by the presence of prominent shelly beds (between 112.40 m and 111.90  
117 m) (Fig. 4C).
- 118 - Unit 2, from 111.90 m to 106.30 m, consists of a grey-brown bioturbated  
119 (*Chondrites*) clay, which appears to be homogeneous (no cycles can be  
120 distinguished). Some *Plicatula* occur occasionally and ammonites are common in  
121 the upper part of this unit.
- 122 - Unit 3, from 106.30 m to 86.10 m, corresponds to bioturbated khaki clays  
123 (*Chondrites*) in which the cycles are clearly individualised and limited at the base  
124 by bioturbated surfaces likely corresponding to firmgrounds. This poorly  
125 fossiliferous unit shows scattered *Plicatula*, some oysters and ammonites which

126 allow a biostratigraphic division to be established. Coarser quartz grains and  
127 glauconite occur at the topmost part of the formation announcing the overlying  
128 sandy glauconitic sedimentation (Sables Verts de l'Aube Formation).

129

## 130 I-2. Biostratigraphy

131 Ammonites have been systematically collected along the core (Fig. 3). Although they  
132 are not abundant, their study provides valuable information. A total of 19 ammonites were  
133 found in the 30.66 m of the Argiles à Plicatules Formation recovered in borehole AUB 121, of  
134 which 15 could be determined, at least at the generic level. They occur mostly as imprints in  
135 clays, and in a few cases as internal moulds preserved either in the form of pyritic nuclei or  
136 calcium phosphate nodules (Amédéo et al., 2017). All recognised taxa are cosmopolitan, with  
137 a geographic distribution that includes the boreal, Tethyan and sometimes even southern  
138 realms. This wide geographic distribution is explained by the fact that the summit of the early  
139 Aptian corresponds to a high sea level (transgression of a second order eustatic cycle, see  
140 Jacquin et al., 1998). The vertical distribution of the ammonites permits to establish a  
141 biostratigraphic scheme.

142 The lower three meters of the Argiles à Plicatules Formation did not provide determinable  
143 ammonites in the Juzanvigny boreholes and therefore the stratigraphic attribution of the  
144 lowermost part of this formation remains uncertain. The occurrence of several *Roloboceras*  
145 *transiens* Casey, 1961 in the neighbouring department of Yonne and *Megatyloceras* at the  
146 base of the Argiles à Plicatules Formation (unpublished data) suggests that the interval could  
147 be attributed to the *Deshayesites forbesi* Zone, as these ammonites are characteristic of this  
148 biozone. The *Deshayesites deshayesi* Zone is undoubtedly recognised from 113.70 m to  
149 105.15 m by the presence of an association including *Aconoceras (Aconoceras) nisoides*  
150 Sarasin, 1893, *Pseudosaynella bicurvata* Michelin, 1838, *Deshayesites deshayesi* d'Orbigny,

151 1841 and *Lithancylus grandis* J. de C. Sowerby, 1828. The *Dufrenoyia furcata* Zone sensu  
152 Reboulet compiler (2018) [= the *Tropaeum bowerbanki* Zone described by Casey (1961)] is  
153 clearly identified from 102.50 m to 90.60 m by the occurrence of *Dufrenoyia cf. formosa*  
154 Casey, 1964 and *Dufrenoyia cf. furcata* J. de C. Sowerby, 1836.

155

## 156 II – Analytical methods

### 157 II–1. Carbon stable isotopes, Total Organic Carbon and calcimetry

158 Organic carbon isotope compositions ( $\delta^{13}\text{C}_{\text{org}}$ ) and Total Organic Carbon (TOC) were  
159 measured on carbonate-free residues of 80 samples at the Biogéosciences Laboratory,  
160 Université Bourgogne/Franche-Comté in Dijon. Sample powders were reacted with HCl (2N)  
161 at room temperature for 24 h to remove the carbonate phases. Residues were rinsed with  
162 deionised distilled water until neutral, centrifuged (4500 rpm for 15 min), and then dried at  
163 50°C overnight. Aliquots of dried decarbonated samples (~7–50 mg) were then weighed in tin  
164 capsules. TOC content and  $\delta^{13}\text{C}_{\text{org}}$  measurements were performed at the Biogéosciences  
165 Laboratory of the University of Bourgogne/Franche-Comté (Dijon, France) on a Vario  
166 MICRO cube elemental analyzer (Elementar, Hanau, Germany) coupled in continuous flow  
167 mode to an IsoPrime stable isotope ratio mass spectrometer (Isoprime, Manchester, UK).  
168 USGS40 L-Glutamic acid (C = 40.8 wt%;  $\delta^{13}\text{C}_{\text{VPDB}} = -26.39 \pm 0.04\text{‰}$ ) and IAEA-600  
169 Caffeine ( $\delta^{13}\text{C}_{\text{VPDB}} = -27.77 \pm 0.04\text{‰}$ ) certified reference materials were used for calibration.  
170 The carbon isotopic composition is expressed in delta notation and reported in per mil (‰)  
171 relative to the Vienna Pee Dee Belemnite (V-PDB) standard; the external reproducibility  
172 based on duplicate analyses of the samples is better than  $\pm 0.2\text{‰}$  ( $1\sigma$ ).

173 The proportion of  $\text{CaCO}_3$  is deduced by the difference in weight before and after  
174 decarbonation.

175



176 II-2. Organic matter characterisation

177 A Rock-Eval 6 Turbo apparatus (Vinci Technologies) was used for the quantitative  
178 and qualitative study of organic matter from 34 selected samples distributed over the entire  
179 section. The method, described in detail by Lafargue et al. (1998) and Behar et al. (2001),  
180 consists of a two-step analysis with programmed temperature: pyrolysis, under inert  
181 atmosphere (N<sub>2</sub>), followed by oxidation. Samples were analysed at the Institut des Sciences de  
182 la Terre de Paris (UMR7193/Sorbonne Université). Crushed samples are first subjected to a 3  
183 min isotherm at 300°C at which free hydrocarbons are volatilised (peak S1). Then, a heating  
184 step with a ramp rate of 25°C/min leads to the vaporisation of products via the thermal  
185 cracking of organic matter up to 650°C (peak S2). Pyrolysis effluents are continuously  
186 detected by a flame ionisation detector (FID) and expressed in mg per g of sample. Organic  
187 CO and CO<sub>2</sub> are measured online as well by an infrared cell (peak S3). At the end of the  
188 pyrolysis step, samples are automatically transferred into an oxidation oven where they are  
189 subjected to a 1 min isotherm at 300°C then a ramp rate of 20°C/min up to 850°C. The total  
190 signals of both organic and mineral CO and CO<sub>2</sub> are expressed in mg per g of samples. All  
191 these parameters can be used to calculate the TOC content. The hydrogen index (HI),  
192 corresponding to the quantity of hydrocarbon compounds released during pyrolysis relative to  
193 the TOC (S2/TOC) in mg of HC per g of TOC as well as the oxygen index (OI)  
194 corresponding to the organic CO<sub>2</sub> released during pyrolysis relative to the TOC (S3/TOC) in  
195 mg of CO<sub>2</sub> per g of TOC are also calculated. HI and OI are correlated to the H/C and O/C  
196 atomic ratios respectively, which can be used to determine the origin of the organic matter.  
197 T<sub>max</sub> is defined as the pyrolysis temperature at which the maximum amount of hydrocarbon is  
198 yielded by kerogen (Espitalié et al., 1977). T<sub>max</sub> increases linearly with the maturation degree  
199 of the organic matter, thus giving a rapid estimate of the thermal maturity of sedimentary  
200 basins (Espitalié, 1986).

201

## 202 II-3. Clay mineralogy

203 A total of 80 samples were analysed using X-Ray Diffraction (XRD). After moderate  
204 grinding in a mortar, powdered samples were decarbonated with a 0.2N HCl solution. The  
205 < 2  $\mu\text{m}$  fraction (clay-sized particles) was extracted with a syringe after deflocculation and  
206 decantation of the suspension for 95 minutes following Stokes' law; this fraction was then  
207 centrifuged. Clay residue was then smeared on oriented glass slides and run in a Bruker D8  
208 diffractometer with  $\text{CuK}\alpha$  radiations, a LynxEye detector and a Ni filter with a voltage of 40  
209 kV and an intensity of 25 mA (Biogéosciences laboratory, Université Bourgogne/Franche-  
210 Comté in Dijon, France). Goniometer scanning ranged from  $2.5^\circ$  to  $28^\circ$  for each analysis.  
211 Three runs were performed for each sample to discriminate the clay phases: 1) air-drying; 2)  
212 ethylene-glycol solvation at room temperature during 24 hours; and 3) heating at  $490^\circ\text{C}$   
213 during 2 hours, as recommended by Moore and Reynolds (1997). Clay minerals were  
214 identified using their main diffraction ( $d_{001}$ ) peaks and by comparing the three diffractograms  
215 obtained. The relative proportions of the clay minerals are estimated using peak intensity  
216 ratios. The error margin of the method is approximately  $\pm 5\%$ .

217

## 218 III – Results

### 219 III-1. $\text{CaCO}_3$ , Organic matter characterisation and $\delta^{13}\text{C}_{\text{org}}$

220 In the Argiles à Plicatules Formation, the proportion of  $\text{CaCO}_3$  is very low (around  
221 3%) in all of the samples studied (Fig. 5). The total organic carbon (TOC) content measured  
222 on the 34 selected samples using Rock-Eval pyrolysis is also very low, comprised between  
223 0.1 and 0.52% (Table 1). As the quantity of organic matter (OM) is low, the Rock-Eval  
224 parameters are only partly reliable. However, some reliable  $T_{\text{max}}$  values lower than  $420^\circ\text{C}$   
225 indicate that OM is immature (below the oil window). Organic matter is more abundant in

226 lithological unit 1 at the base of the section; this was expected since macroscopic woody  
227 debris and fern pinnules preserved as coalified compressions were observed (Fig. 4B).

228 The  $\%C_{org}$  obtained after isotopic analyses is between 0.15 and 0.82 (Fig. 4),  
229 systematically showing slightly higher values than those obtained using Rock-Eval pyrolysis,  
230 but with the same trends. Higher values are recorded at the base of the core in lithological unit  
231 1 which is enriched in continental organic matter. By comparison with unit 3, a slight increase  
232 is recorded in the interval corresponding approximately to lithological unit 2 (Fig. 5);  
233 however, significant enrichment in marine organic matter, which would have indicated it was  
234 preserved in a significantly oxygen-depleted environment, is not recorded.

235 The  $\delta^{13}C_{org}$  values fluctuate between  $-24.19\text{‰}$  and  $-27.91\text{‰}$  (Fig. 4). A prominent  
236 negative excursion is recorded between 112 and 110 m at the base of lithological unit 2,  
237 followed by a shift to higher (close to  $-25\text{‰}$ ) and relatively constant values up-section.

238

### 239 III-2. Clay mineralogy

240 The following main clay minerals were identified: a R0 type illite-smectite mixed-  
241 layer (17 Å based on a glycolated run condition) referred to as smectite for the following  
242 sections; chlorite (14.2 Å, 7.1 Å, 4.7 Å and 3.54 Å peaks); illite (10 Å, 5 Å, 3.33 Å peaks);  
243 kaolinite (7.18 Å and 3.58 Å peaks) and vermiculite (14 Å in air-drying conditions, 14.5-15 Å  
244 after ethylene-glycol solvation and 10 Å peaks after heating). In addition, traces of  
245 pyrophyllite are occasionally suspected by the occurrence of a small peak at 9.3 Å. The clay  
246 mineral assemblages are predominantly composed of illite generally between 40 and 50% and  
247 kaolinite with proportions comprised between 20 and 45%. Minor amounts of chlorite (less  
248 than 10%), vermiculite (around 10%) and smectite (generally less than 10%, except at the top  
249 of the formation where the proportions of this mineral may reach 50%) are associated with  
250 these two clay species (Fig. 6). Traces of pyrophyllite are only identified at the base of the

251 core. Four stratigraphic intervals can be distinguished according to the clay mineralogy.  
252 Interval 1 corresponds to the lowermost part of the formation below the bioclastic  
253 accumulation and coincides with lithological unit 1. In this interval, the proportion of  
254 vermiculite is relatively high and decreases up-section while the proportion of illite increases.  
255 The second interval, from 112 to 104.5 m is characterised by the relative abundance of  
256 kaolinite (30 to 45%) notably at the base of this interval where the proportions of this mineral  
257 show a maximum (45%), and by the absence of smectite. The third interval from 104.5 m to  
258 87.5 m shows a monotonous clay assemblage without any significant change and is composed  
259 of approximately 5% of chlorite, 45% of illite, 10% of vermiculite, 10% of smectite and 30%  
260 of kaolinite. The uppermost part of the formation (interval 4) shows a sharp increase in the  
261 proportions of smectite balanced by significant decreasing proportions of illite and kaolinite.

262

#### 263 IV - Discussion

##### 264 IV-1. Depositional environments of the Argiles à Plicatules Formation

265 The lowermost part of the formation overlying the continental Wealden facies and  
266 consisting of dark grey clays with abundant iron oolites (Fig. 4A) and common terrestrial  
267 plant remains (woods and foliar remains, Fig. 4B) likely corresponds to transgressive  
268 sediments deposited in coastal environments. Similar facies were described in boreholes  
269 drilled close to Soulaines to the east of Juzanvigny (Fig. 2) where transgressive facies are  
270 clearly separated by emersion features suggesting, several transgressive events at the  
271 beginning of the Aptian transgression (Ferry, 2000). Foliar meso- and macro-remains  
272 exclusively consist of fragments of pinnae and isolated fern pinnules preserved as coalified  
273 compressions (Fig. 4B). The largest pinna fragment is 22 mm long. The pinnae bear up to 8  
274 mm long and 3 mm wide alternate to subopposite, oblong, thick and leathery pinnules. They  
275 are attached by a broad base to the rachis and display a rounded apex and an entire margin.

276 Sometimes the pinnules are slightly inclined forward. The midrib is straight and ends before  
277 the apex of the pinnule. These features as well as the reticulate veins allow to ascribe these  
278 specimens to *Weichselia reticulata* (Stokes and Webb) Fontaine which is a common fern in  
279 the Early Cretaceous flora from Europe (Blanco-Moreno et al., 2018). In France, *W. reticulata*  
280 was previously reported from the Wealden facies of the Nord department (Carpentier, 1927)  
281 and the Oise department (Carpentier, 1929). The abundance of plant remains in oolitic facies  
282 shows that the depositional environment was influenced by strong terrestrial inputs. Although  
283 *Weichselia* mostly occurred in a continental environment in Europe (Blanco-Moreno et al.,  
284 2018), this report shows that *W. reticulata* was one of the components of littoral flora during  
285 the earliest Aptian.

286 As they occur immediately above the upper Barremian lateritic palaeo-alteration, iron  
287 oolites may be reworked from the lateritic soils (Bhattacharyya, 1983). However, iron oolites  
288 may also have formed as a replacement of a pre-existing ooid structure or via the precipitation  
289 of an iron aluminosilicate (chamosite/berthierine) grain in shallow marine environments  
290 (Velde, 1989). Iron may be provided in the sedimentary environment by the weathering of the  
291 proximal continental areas. In most cases iron oolites are associated with transgressive  
292 deposits, which is the case in the lowermost part of the Argiles à Plicatules Formation, and are  
293 indicators of condensed sections (Collin et al., 2005; Clement et al., 2020).

294 Up-section, the deposits increasingly less silty show common bivalves. The first  
295 ammonite occurs at 113.70 m indicating open-marine environments. The prominent shell  
296 horizon intercalated in the clayey succession at the top of lithological unit 1 between 112.40  
297 m and 111.90 m (Fig. 4C) can be divided into two parts. The first corresponds to a bed  
298 comprising pluri-centimetric bivalve shells forming the base of a 30 cm-thick fining up  
299 sequence. The top of this bed, which is 112.05 m (Fig. 4C), is bioturbated. Above, a second  
300 accumulation of bivalves is associated with centimetric clasts. The succession may

301 correspond to two successive storm deposits separated by a bioturbated surface. This suggests  
302 a deposition above storm wave base in upper offshore environments and a deepening trend of  
303 the basin as a consequence of the Aptian transgression. This trend continues up-section from  
304 111.90 m to 106.30 m, as the homogenous faintly bioturbated clays without any sedimentary  
305 structure suggest a deposition in a quiet environment, below the storm wave base (lower  
306 offshore). Rare calcareous nannofossils observed in smear slides occur in most of the samples  
307 and are likely responsible for the carbonate content (close to 3%) of the sediment. From  
308 106.30 m to the top of the formation, the clays contain more silt. Bioturbated surfaces indicate  
309 sedimentation breaks that are consistent with the common occurrence of phosphate  
310 (carbonate-apatite) nodules.

311 The Argiles à Plicatules Formation encompasses a transgressive interval from the base  
312 to a maximum flooding surface located in the interval between 111.90 m and 106.30 m. The  
313 uppermost 20 m of the formation corresponds to a highstand system tract terminated by a  
314 prominent bioturbated surface between the Argiles à Plicatules and the Sables Verts de l'Aube  
315 formations deposited at a shallower water depth in shoreface environments.

316

#### 317 IV-2. Evolution of the $\delta^{13}\text{C}_{\text{org}}$ and organic matter contents

318 Several of the isotopic segments initially distinguished by Menegatti et al. (1998)  
319 across the "Livello Selli", which includes OAE1a, or its equivalent in the Tethys Ocean, and  
320 which were subsequently recognised worldwide and used as a reliable tool for  
321 chemostratigraphic correlations, are clearly identified in the studied borehole: C2 at the base  
322 of the section, C3 corresponding to the negative excursion showing the lowest values of  
323  $\delta^{13}\text{C}_{\text{org}}$  between 111.80 and 110 m, C4, C5 and C6 characterised by a shift to higher values  
324 and finally C7 (Fig. 5).

325           The ‰ negative excursion that occurs immediately before OAE1a and corresponding  
326 to the C3 segment is clearly identified. It occurs probably in the *deshayesi* Zone just above the  
327 bioclastic accumulations interpreted as storm deposits, with an amplitude comparable to that  
328 observed in many sedimentary basins (Menegatti et al., 1998; Ando et al., 2008). The C3  
329 segment is relatively thick (1.80 m) indicating a relatively high sedimentation rate and shows  
330 two distinct negative excursions separated by a positive excursion with a small amplitude,  
331 which can also be observed in the  $\delta^{13}\text{C}_{\text{carb}}$  curves from sections from south-east France (Kuhnt  
332 et al., 1998; 2011). This may suggest the existence of, at least, two successive volcanic CO<sub>2</sub>  
333 pulses at the origin of the emplacement of the Ontong Java-Manihiki-Hikurangi Plateau  
334 (Lorenzen et al., 2013; Naafs et al., 2016).

335           Surprisingly, the interval corresponding to the  $\delta^{13}\text{C}_{\text{org}}$  positive excursion is not  
336 significantly enriched in organic matter and the facies of the Argiles à Plicatules Formation  
337 are extremely homogeneous, unchanged in colour and without any laminations. The absence  
338 of significant organic matter enrichment is surprising since the deep, quiet lower offshore  
339 depositional environment was favourable to the preservation of marine organic matter. Some  
340 authors report an absence of significant marine organic matter enrichment in several  
341 sedimentary basins of northern Spain including the Basco-Cantabric Basin (Garcia-Mondejar  
342 et al., 2015) and the Organyà Basin (Sanchez-Hernandez and Maurasse, 2016) although they  
343 correspond to oxygen-depleted environments but without prolonged anoxia.

344           In the Paris Basin, the absence of OM enrichment can be explained in several ways.

345           1) The primary productivity was probably low as suggested by the very low carbonate  
346 content of the succession. The carbonate fraction of the Argiles à Plicatules Formation, which  
347 does not exceed 4%, is composed of rare nannofossils including the genus *Watznaueria*,  
348 *Zeugrhabdotus*, *Rhagodiscus*, *Biscutum*, *Discorhabdus* and *Cyclagelosphaera* (F. Giraud, *in*

349 Ferry, 2000). The scarcity of fauna and flora suggests that the environment must have been  
350 oligotrophic.

351 2) The absence of anoxia in the Aptian sea-way between the LBM/RM and the  
352 AM/MC (Fig. 1) may be also explained by the presence of marine currents flowing through  
353 the strait thus favouring relatively well-oxygenated environments. However, except the  
354 occasional occurrence of phosphate nodules that may indicate low sedimentation rate due to  
355 the winnowing of fine particles, there is no evidence of hydrodynamic influences expressed in  
356 the sedimentary facies.

357 3) The oxygen-minimum zone that was clearly expressed in the Tethys Ocean was  
358 deeper and did not reach the relatively shallow environments of the Paris Basin. This is  
359 plausible, given that Coccioni et al. (1987) and Westermann et al. (2013) show that anoxic to  
360 euxinic conditions developed in the deeper part of the Tethys Ocean during OAE 1a, while  
361 conditions were not as reducing in shallower environments.

362 By comparison with several sections from the Tethys ocean, the  $\delta^{13}\text{C}_{\text{org}}$  positive  
363 excursion is less pronounced than expected, what could be the result of several gaps coeval  
364 with the positive excursion like those observed in carbonate platform environments (Wissler  
365 et al., 2005). However, except the occurrence of bioturbated surfaces and some scattered  
366 phosphate nodules, there is no clear evidence of significant sedimentation breaks.

367

#### 368 IV-3. Significance of clay mineral assemblages

##### 369 IV-3-1. Diagenetic influences

370 Before examining the significance of clay mineral assemblages in terms of the  
371 palaeoclimate and palaeoenvironment, it is essential to ensure that they are predominantly  
372 detrital in origin without any significant influence of burial diagenesis, thermal influences or  
373 authigenic growth during early or late diagenesis. The post-Aptian sedimentary successions



374 probably never exceeded 1100 m (Robaszynski et al., 2005), which is consistent with a weak  
375 thermal impact (Torelli et al., 2020) compatible with the occurrence of smectite and immature  
376 organic matter. Consequently, it is unlikely that clay minerals may have been transformed  
377 during burial diagenesis. This conclusion is consistent with many studies performed to the  
378 east of the Paris Basin on upper Jurassic deposits showing that the thermal influences remain  
379 very weak even when these deposits are more deeply buried (Pellenard et al., 1999; Pellenard  
380 and Deconinck, 2006; Blaise et al., 2014; Mangenot et al., 2018).

381         Small quantities of glauconite commonly occur in the uppermost part of the Argiles à  
382 Plicatules Formation at the transition with the overlying Sables verts de l'Aube Formation.  
383 Glauconite is an iron-rich illite and the granules are coarser than the clay fraction and  
384 normally not included in the clay fraction. However, as the samples are ground in preparation  
385 for XRD analyses, it is possible that glauconite was partly introduced in the clay fraction and  
386 slightly increases the total proportion of illite at the top of the formation.

387

388         Therefore, we assume that most clay minerals are detrital in origin and may be useful  
389 to precise environmental conditions that prevailed during the early Aptian around the Paris  
390 Basin.

391

#### 392                 IV-3-2. Environmental control of the clay sedimentation

393         Primary minerals, including illite, chlorite and pyrophyllite constitute more than half  
394 of the clay fraction. The abundance of these minerals suggests a relatively intense erosion on  
395 the continental areas bordering the Paris Basin. Although clay minerals may be transported  
396 over long distances, they likely originated from the Palaeozoic massifs surrounding the Paris  
397 Basin. Illite, chlorite and pyrophyllite originated from the erosion of igneous and  
398 metamorphic rocks from the AM/MC and from the low grade metamorphic rocks from the

399 LBM. Vermiculite is also common, notably at the base of the formation. This mineral also  
400 occurs in lower to middle Albian clayey strata of the Paris Basin and likely originated from  
401 the north, i.e. from the LBM (Gale et al., 1996; Corentin et al., 2020). Vermiculitic clays  
402 corresponding to illite/vermiculite mixed-layers were also identified together with illite and  
403 kaolinite in the Aptian deposits of the Lower Saxony Basin of Germany (Benesch et al., 1998)  
404 and likely originate from the moderate weathering of chlorite.

405         Kaolinite is also abundant with maximum values in interval 2 characterised by the  
406 homogeneous clay deposited in the deepest environments. Therefore, in the present case, the  
407 abundance of kaolinite cannot be a consequence of its preferential deposition in nearshore  
408 environments as suggested by Godet et al., (2008). The stratigraphic interval coinciding with  
409 the  $\delta^{13}\text{C}_{\text{org}}$  negative excursion is strongly depleted in smectite suggesting that a particularly  
410 hydrolysing (warm and humid) climate was established at that time (Chamley, 1989; Ruffell  
411 et al., 2002). By contrast, in the topmost part of the Argiles à Plicatules Formation, the  
412 decreasing proportions of kaolinite balanced by increasing proportions of smectites suggest  
413 increasingly arid climate conditions confirming a certain variability in the Aptian climate  
414 (Dumitrescu et al., 2006; Bottini et al., 2015; Naafs and Pancost, 2016). These arid climatic  
415 conditions also seem to have prevailed during the Aptian-Albian in the Algarve Basin  
416 (Southern Portugal) where sedimentary rocks are depleted in kaolinite and show a high  
417 amount of the xerophytic pollen *Classopollis* (Heimhofer et al., 2008). Aridity may be a  
418 consequence of colder climate (cold snaps) recorded at the Aptian/Albian transition  
419 (Mutterlose et al., 2009; Maurer et al., 2012; Millán et al., 2014).

420

#### 421         IV.4. Climate evolution during the deposition of the Argiles à Plicatules Formation

422         A comparison of  $\delta^{13}\text{C}_{\text{org}}$  and the mineralogical data shows that the C3 segment  
423 corresponding to the negative excursion recorded prior to the OAE1a is characterised by an

424 increase in the proportions of kaolinite (Fig. 7) at the same time as a decrease in the  
425 proportions of smectites. This suggests the installation of a more humid climate as a  
426 consequence of an acceleration of the hydrological cycle induced by the warming triggered by  
427 the increase in pCO<sub>2</sub> (Keller et al., 2011; Bodin et al., 2015; Naafs and Pancost, 2016). There  
428 are several lines of evidence for such a climatic change. Wortmann et al. (2004) suggested  
429 that the widespread occurrence of sandstones in the Tethys-Atlantic seaway was a  
430 consequence of increasing erosion rates due to the acceleration of the hydrological cycle in  
431 the wake of the early Aptian carbon cycle perturbation. Increasing global weathering intensity  
432 coeval with OAE1a is also suggested by calcium isotopes (Blättler et al., 2011) measured in  
433 carbonate deposits from several areas including southern England, Italy and Resolution Guyot  
434 from the mid-pacific mountains. Hochuli et al. (1999) also describe global warming resulting  
435 in increasing riverine fluxes. The warming is evidenced by a drop in δ<sup>18</sup>O, TEX<sub>86</sub> data and by  
436 pollen records. The δ<sup>18</sup>O data from many sedimentary basins including the South Pacific  
437 shows, that the ocean waters warmed strongly during the negative excursion and that  
438 temperatures then decreased probably due to the storage of organic matter in the sediments  
439 (Ando et al., 2008; Stein et al., 2011; Zakharov et al., 2013). These observations are in  
440 agreement with the maximum proportions of kaolinite and the decrease in the proportion of  
441 *Classopollis*, (xerophytic pollen) in the Maestrat Basin (eastern Spain) during OAE1a (Cors et  
442 al. 2015). Tex<sub>86</sub> data obtained in the Selli level (or other equivalents of the OAE1a) also  
443 indicate particularly warm sea-surface temperatures (Schouten et al., 2003; Dumitrescu and  
444 Brassel, 2006; Mutterlose et al., 2010, 2014).

445         The global warming that occurred prior to OAE1a is therefore likely responsible for an  
446 acceleration of the hydrological cycle and for the increase of kaolinite because of increasing  
447 runoff and hydrolyses on the continental areas bordering the Paris Basin. The high  
448 proportions of kaolinite in Aptian deposits of the Paris Basin could be explained by the

449 formation of kaolinite in soils, but the duration of the climatic perturbation is relatively short,  
450 between 280 and 350 kyr (Lorenzen et al., 2013), while the formation of kaolinite in soils  
451 required a longer time estimated at least to 1 myr (Thiry, 2000). It is more likely that kaolinite  
452 was principally reworked from kaolinite-rich weathering profiles developed over the  
453 Palaeozoic massifs during the Early Cretaceous (Jurassic-Cretaceous transition to Barremian)  
454 (Meyer, 1976; Gilg, 2000; Quesnel, 2003; Yans, 2003; Thiry et al., 2005, 2006; Corentin et  
455 al., 2020). As detrital clays including kaolinite may be reworked from older rocks or from  
456 palaeo-alterations, their climatic significance may be questioned (Jeans et al., 2001), but  
457 overall, illite and kaolinite dominated clay assemblages of the Aptian in the Paris Basin point  
458 to a significant runoff and consequently to humid climate conditions. It is probable, that  
459 fluctuations in the hydrological cycle controlling fluvial inputs occurred before and during  
460 OAE1a as evidenced by changing environmental conditions in terms of anoxia/dysoxia  
461 (Socorro and Maurasse, 2018; 2020).

462         Although the reliability of  $\delta^{18}\text{O}$  data has recently been confirmed (O'Brien et al.,  
463 2017), the acceleration of the hydrological cycle following the very hot episode preceding  
464 OAE1a can be used to address the question of the significance of the low  $\delta^{18}\text{O}$  values  
465 recorded prior to OAE1a.  $\delta^{18}\text{O}$ -values may also be a result of a slight decrease in ocean  
466 salinity. This question, already addressed for other periods, shows that it is essential to take  
467 better account of the fluctuations in the hydrological cycle in the context of climatic  
468 reconstructions. In addition, higher runoff may increase thermohaline stratification that may  
469 be involved in the development of an OAE (e.g. Erbacher et al., 2001; Van Helmond et al.,  
470 2015).

471

472         Conclusions

473 For the first time, OAE1a is clearly identified in argillaceous deposits, the so-called  
474 Argiles à Plicatules Formation, deposited in the Paris Basin. Most of the C-isotope segments  
475 defining the OAE 1a interval are identified in the stratigraphic succession. However, the  
476 section is devoid of any significant marine organic matter enrichment likely because the  
477 Tethyan oxygen-depleted deep-water masses did not reach the epicontinental areas of the  
478 Paris Basin. The global warming preceding OAE1a is likely responsible for an acceleration of  
479 the hydrological cycle, an increase in runoff and the reworking of kaolinite from  
480 palaeoweathering profiles cropping out on the Palaeozoic massifs bordering the Paris Basin.  
481 As indicators for an acceleration of the hydrological cycle are also recorded in other areas, a  
482 slight decrease in ocean salinity prior to OAE1a may be responsible in part for its  
483 development and questions the reliability of the sea surface temperature deduced from the  
484  $\delta^{18}\text{O}$  values. The hydrolysing conditions were so intense prior to and during OAE1a that  
485 smectite totally disappeared from the clay fraction. However, smectite increases in the upper  
486 part of the succession suggesting, that more arid conditions prevailed at that time possibly in  
487 relation with a colder climate during the Aptian/Albian transition. The changing clay mineral  
488 assemblages suggest, that the Aptian stage was characterised by a climate instability marked  
489 not only by changes in temperature but also in the hydrological cycle.

490

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495

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822

823 Figure captions

824

825 Fig. 1. Palaeogeographic map modified from R. Blakey: <https://www2.nau.edu/rcb7/>.

826 AM = Armorican Massif, MC = Massif Central, LBM = London Brabant Massif, RM =  
827 Rhenish Massif, BM = Bohemian Massif, CSM = Corso-Sardinia Massif, AB =  
828 Algarve Basin, PB = Paris Basin, LSB = Lower Saxony Basin.

829

830 Fig. 2. Simplified geological map of the area to the east of the Paris Basin and location of the  
831 AUB 121 borehole near Juzanvigny.

832

833 Fig. 3. Lithology of the AUB 121 borehole from the lower Barremian “Argiles ostréennes”  
834 Formation to the lowermost part of the “Argiles tégulines de Courcelles” Formation  
835 (lower Albian) (modified after Amédéo et al., 2017). The lower Aptian Argiles à  
836 Plicatules Formation comprises three distinct lithological units and are dated by  
837 ammonites. The *deshayesi* and *furcata* ammonite Zones are clearly identified while the

838 lowermost part of the formation may belong to the *forbesi* Zone (see text). (A.P. =  
839 Argiles à Plicatules).

840

841 Fig. 4. Base of the “Argiles à Plicatules” Formation. A. Thin section showing an iron oolite in  
842 a clayey matrix with quartz grains (Q) (sample AUB 121 116.70 m). B. sample AUB  
843 121, at an altitude of 116.60 m, shows abundant plant debris and notably *Weichselia*  
844 *reticulata*. C. Picture of the core showing the top of Unit 1 (grey clays) with the  
845 prominent shelly beds, and the base of Unit 2 (grey-brown clays).

846

847 Fig. 5. CaCO<sub>3</sub> content, %C<sub>org</sub> and δ<sup>13</sup>C<sub>org</sub> stratigraphic trends along the “Argiles à Plicatules”  
848 Formation. The prominent δ<sup>13</sup>C<sub>org</sub> negative excursion occurring prior to the OAE1a is  
849 compared with the δ<sup>13</sup>C<sub>org</sub> of the Roter Sattel reference section. Most of the segments  
850 (C2 to C7) defined by Menegatti et al. (1998) are recognised in the Argiles à Plicatules  
851 Formation.

852 W.F. = Wealden facies, *D. forb* = *Deshayesites forbesi*, Barr. = Barremian, Alb. = Albian.

853 MFS = Maximum Flooding Surface, TST = Transgressive System tract, HST = Highstand  
854 system tract.

855

856 Fig. 6. Clay mineralogy of the Argiles à Plicatules Formation (the proportions of chlorite,  
857 approximately 5% throughout the formation, are not plotted). *D. forb* = *Deshayesites*  
858 *forbesi*, W.F. = Wealden facies.

859 MFS = Maximum Flooding Surface, TST = Transgressive System tract, HST = Highstand  
860 system tract.

861

862 Fig. 7. Early Aptian climate trends deduced from  $\delta^{13}\text{C}_{\text{org}}$  and kaolinite content through the  
863 Argiles à Plicatules Formation.

864 MFS = Maximum Flooding Surface, TST = Transgressive System tract, HST = Highstand  
865 system tract.

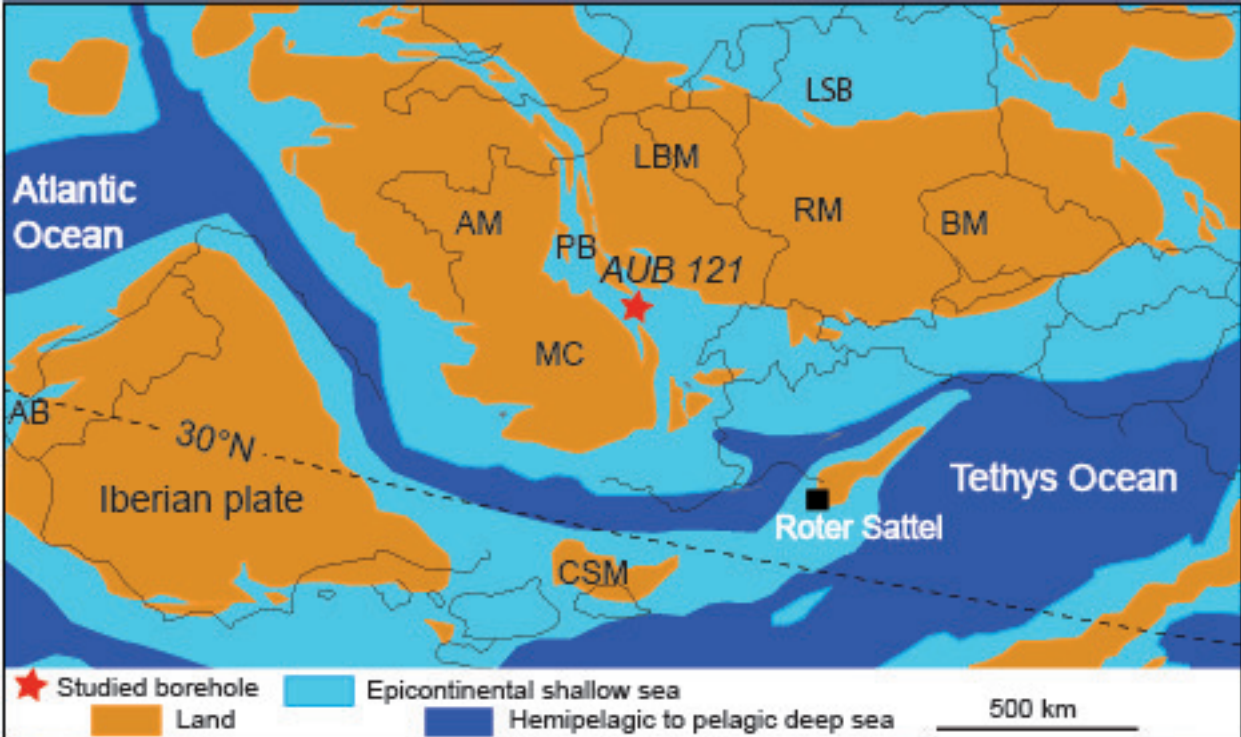
866

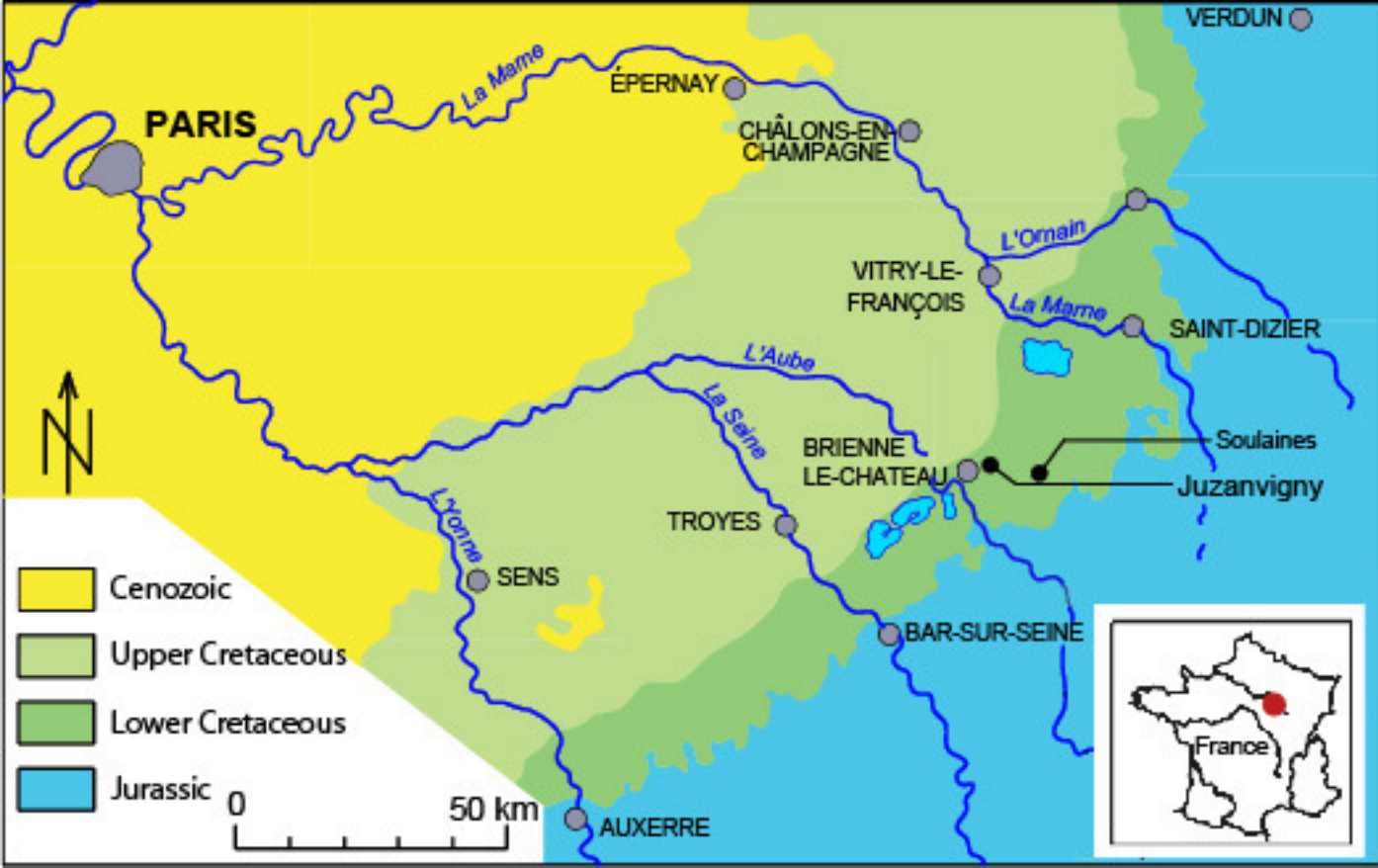
867

868 Table 1. Rock-Eval data of the studied samples (TOC = Total Organic Carbon, OI = Oxygen  
869 index, HI, Hydrogen index).

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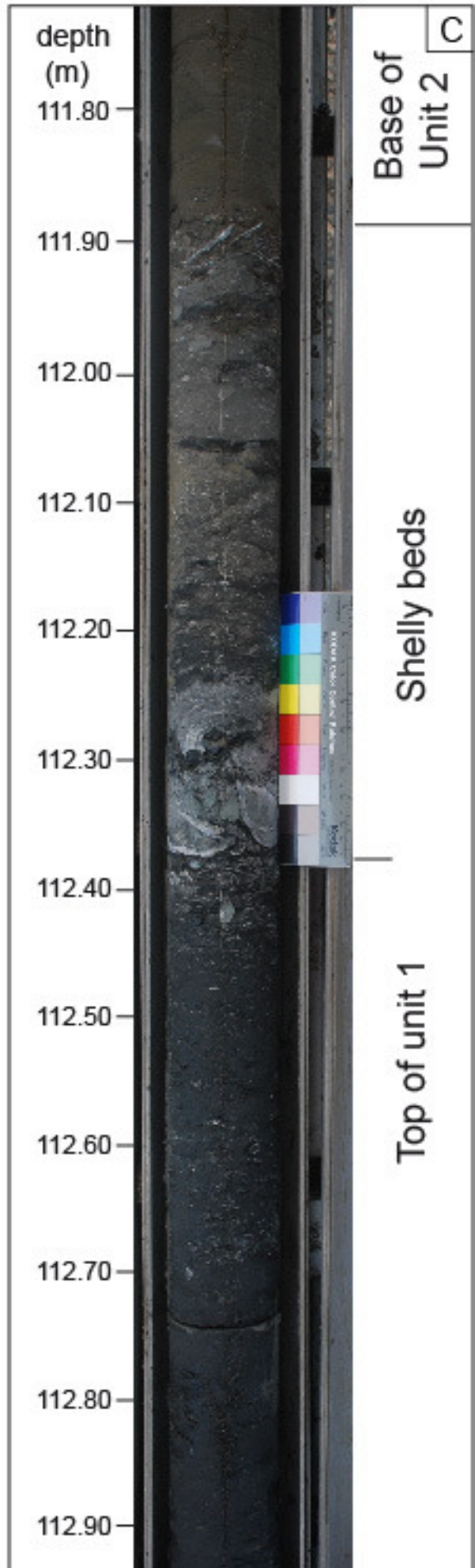
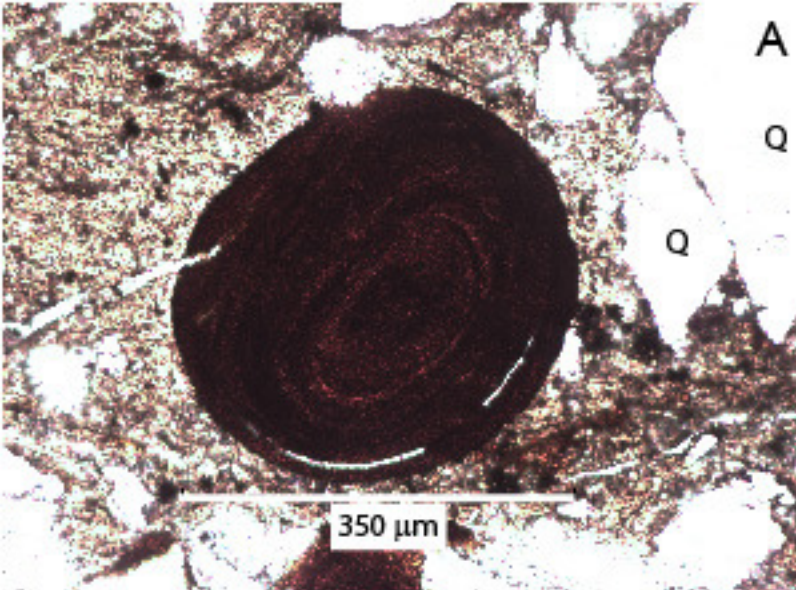
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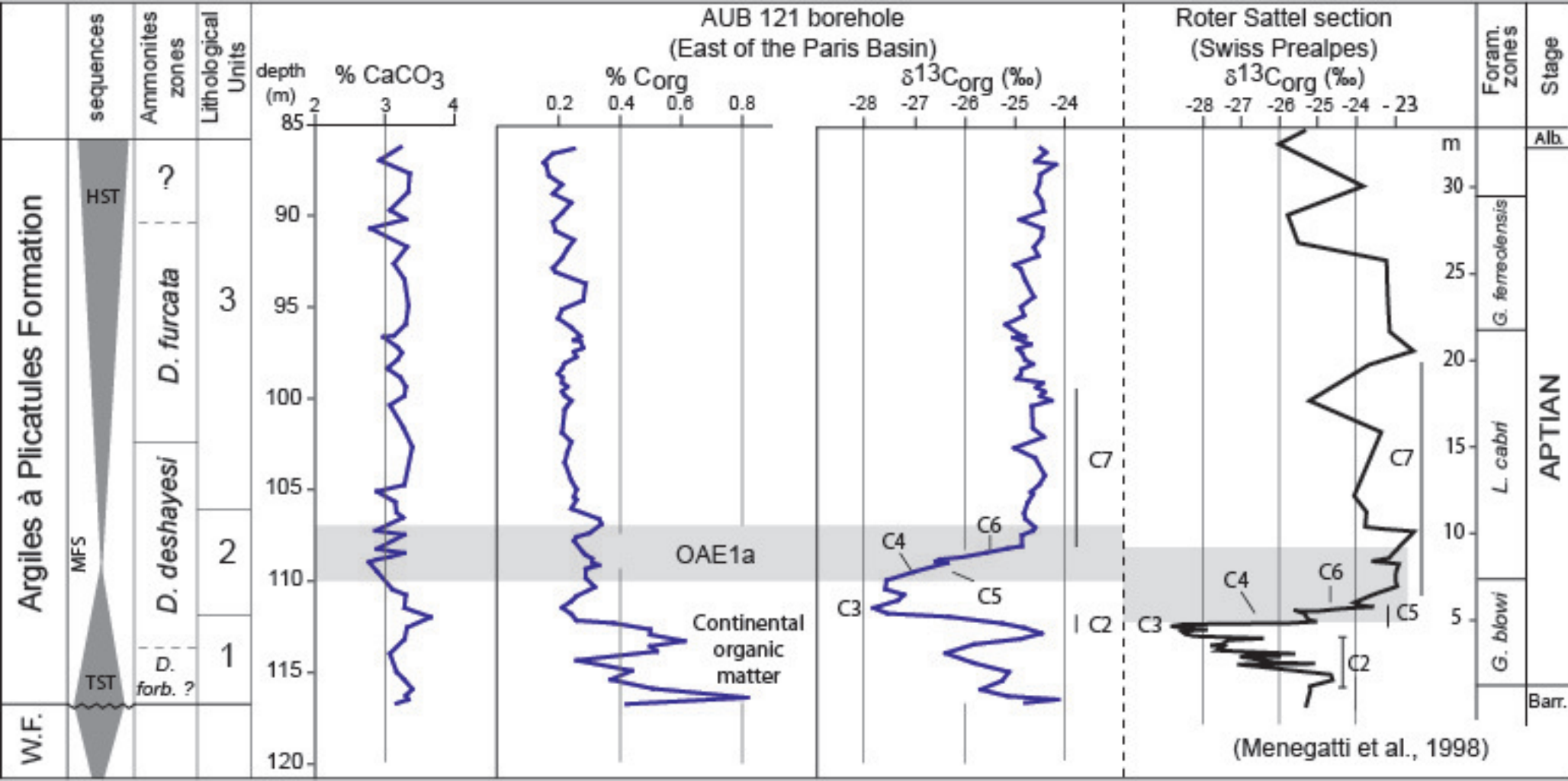


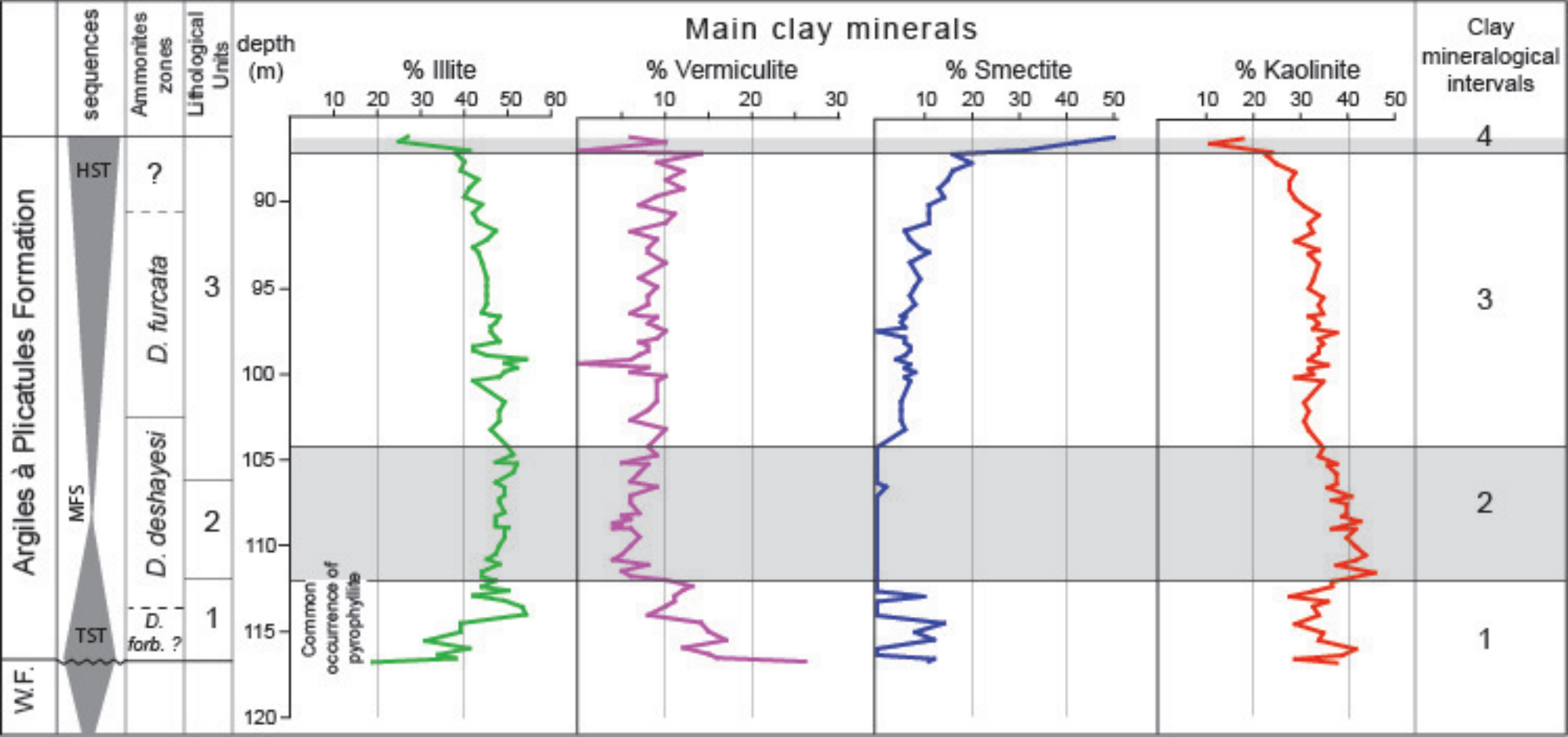


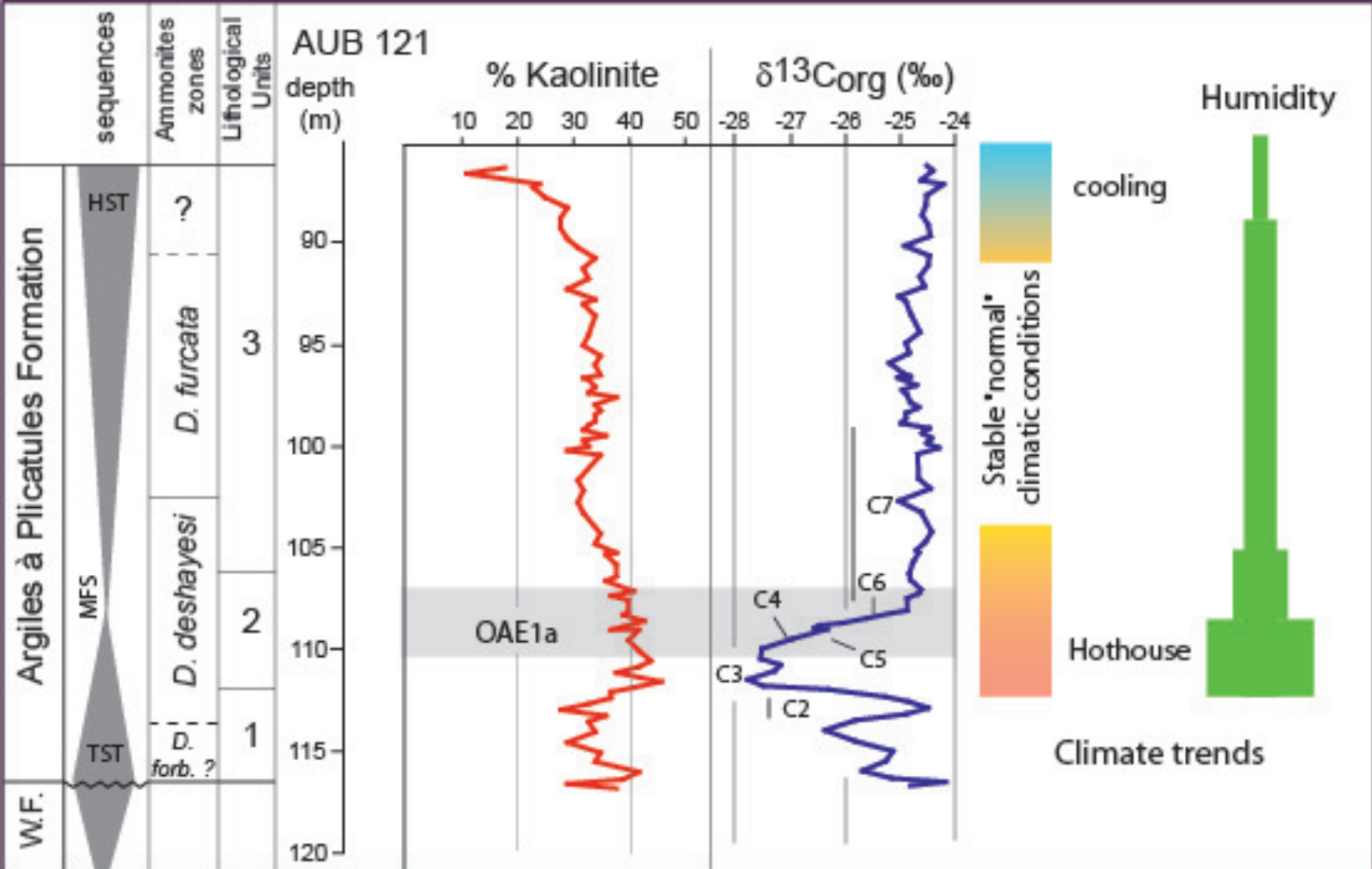












Sample (depth m)	reliable Tmax (°C)	TOC(%)	HI (mgHC/g TOC)	OI (mgCO2/gTOC)
86.45		0.13	54	208
87.12		0.1	70	250
88.15		0.18	67	233
89.15		0.18	33	139
90.15		0.13	54	269
91.15		0.18	39	144
92.15		0.15	33	233
92.90		0.12	52	300
94.42		0.23	43	135
96.42		0.22	45	132
97.00		0.22	45	132
97.50		0.21	33	133
98.13		0.17	53	194
98.63		0.17	53	218
99.13		0.18	44	172
99.63		0.18	36	180
100.13		0.18	44	128
101.10		0.17	41	135
102.10	398	0.21	100	152
103.23		0.17	47	141
104.23		0.2	50	150
105.23		0.19	63	221
107.07		0.21	48	190
108.00		0.16	59	256
110.00	418	0.23	83	148
111.00		0.17	53	229
111.80		0.13	77	277
112.35		0.26	38	92
112.92	384	0.52	56	92
113.52	419	0.44	34	139
114.52b	365	0.38	53	216
114.52a	394	0.4	55	258
115.50		0.42	26	129