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1 **Authigenic berthierine and incipient chloritization in shallow-buried sandstone reservoirs:**  
2 **key role of the source-to-sink context**

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13 **ABSTRACT**

14 Chlorite is recognized worldwide as a key mineral inhibiting the development of quartz  
15 cement in deeply buried sandstone reservoirs. Iron-rich chlorite is mainly formed by the  
16 transformation of a precursor clay mineral, however, few studies have focused on the early  
17 stages before the crystallization of chlorite. This study analyzed shallow-buried (400–  
18 1000 m) coastal sandstones from within the Wealden Group of the Paris Basin. Berthierine, a  
19 7 Å trioctahedral clay mineral belonging to the serpentine group, approximatively with same  
20 chemistry as chlorite but a different crystal structure, has been identified in a 900 m deep  
21 well, but not in a 400–600 m deep well. Berthierine has mainly been observed as clay  
22 coatings around detrital grains, with a typical honeycomb texture. Nanopetrographic  
23 observations suggest that the honeycomb textural organization of the clay particles found in  
24 deeper buried sandstone reservoirs (>1500 m) is acquired from a berthierine precursor at

25 shallow depths. Although, small amounts of quartz overgrowths are observed on the surface  
26 of detrital grains at shallow depths and low temperature (below 40 °C), it is believed that  
27 precursor berthierine coatings are primarily responsible for the inhibition of quartz  
28 overgrowths before the formation of Fe-rich chlorite. This suggests that the key mineral  
29 primarily controlling the reservoir quality of deeply buried sandstone reservoirs is  
30 berthierine rather than iron-rich chlorite, challenging the commonly accepted assertion that  
31 chlorite coating is the main process that inhibits quartz overgrowths. The source-to-sink  
32 context of the Paris Basin during the Early Cretaceous was decisive with respect to the  
33 supply of sands and berthierine clay precursors (in particular kaolinite and iron-rich hydroxy-  
34 interlayered clay minerals) to the center of the Basin.

## 35 **INTRODUCTION**

36 Reservoirs located in estuarine formations include abundant chlorite coatings that  
37 contribute to the formation of complex heterogeneous reservoirs with moderate-to-  
38 excellent reservoir quality at burial depths of more than 2 km (Ehrenberg, 1993; Bloch et al.,  
39 2002; Worden and Morad, 2003; Dowey et al., 2012; Saiag et al., 2016; Worden et al., 2020).  
40 It has been demonstrated that authigenic chlorite enhances the reservoir quality in deeply  
41 buried sandstone reservoirs by inhibiting the development of quartz overgrowths (Pittman  
42 and Lumsden, 1968; Larese, et al., 1984; Dixon et al., 1989; Billault et al., 2003; Morad et al.,  
43 2010; Bahlis and De Ros, 2013; Bottig et al., 2017; Worden et al., 2020). Therefore Fe-  
44 chlorite crystals that occur as coats around detrital sand grains play a decisive part in the  
45 preservation of unusually high primary intergranular porosity in these reservoirs (Ehrenberg,  
46 1993; Anjos et al., 2003; Worden et al., 2020). Laboratory experiments reproducing mineral  
47 nucleation show that Fe-rich chlorite can form from the transformation of precursor clay  
48 minerals, such as berthierine (an iron and aluminum-rich 7 Å trioctahedral clay mineral

49 belonging to the serpentine group), or odinite, or phyllite-V (Odin, 1988; Ehrenberg, 1993;  
50 Hornibrook and Longstaffe, 1996; Ryan and Reynolds, 1996; Aagaard et al., 2000; Ryan and  
51 Hillier, 2002; Morad et al., 2010; Beaufort et al., 2015; Haile et al., 2015). Chlorite grain coats  
52 have been reported from a wide range of depositional environments, but Fe-chlorite is most  
53 commonly found in coastal estuarine and deltaic environments (Dowey et al., 2012;  
54 Wooldridge et al., 2017; Griffiths et al., 2018a; Worden et al., 2020). Recent studies confirm  
55 that early clay coats form in modern estuarine environments are mainly composed of  
56 aggregates of detrital clays (illite, chlorite, kaolinite and sometimes dioctahedral smectite).  
57 So far, berthierine and odinite have not been observed, suggesting that they are not part of  
58 the initial sedimentary supply (Wooldridge et al., 2018; Griffiths et al., 2018a, 2018b, 2019;  
59 Virolle et al., 2019a).

60 Even if the chemical elements required for diagenetic Fe-chlorite crystallization did originate  
61 from the dissolution of the most reactive detrital minerals, it has been proposed that Fe-rich  
62 chlorite does not form directly from solutions by precipitation during eogenesis (Beaufort et  
63 al., 2015, and references therein). Instead, diagenetic chlorite is usually formed through  
64 complex chloritization processes that involve the formation of a precursor clay minerals  
65 (Odin and Matter, 1981; Ehrenberg, 1993; Morad et al., 2010; Worden et al., 2020).  
66 Aluminous silicates and iron-rich minerals of the serpentine group such as odinite and  
67 berthierine seem to be the primary precursor candidates (Odin, 1988; Ehrenberg, 1993;  
68 Hornibrook and Longstaffe, 1996; Ryan and Reynolds, 1996; Aagaard et al., 2000; Ryan and  
69 Hillier, 2002; Worden et al., 2020). It is believed that berthierine is either the product of  
70 direct neoformation or replacement during early diagenesis (Van Houten and Purucker,  
71 1984) or that the green clay odinite evolves into berthierine during early diagenesis,  
72 producing the well-organized 7 Å structure (Odin, 1988; Hornibrook and Longstaffe, 1996).

73 With increasing burial depth, these precursors are believed to then be transformed into  
74 chlorite via a mixed-layer mineral series under anoxic conditions (Hornibrook and Longstaffe,  
75 1996; Beaufort et al., 2015; Worden et al., 2020).

76 Several authors suggested that the formation of Fe-chlorite occurrence in sandstones  
77 requires sedimentary material that is essential for the formation of clay precursors such as  
78 reactive aluminous silicates and iron-rich minerals (Morad et al., 2010; Gould et al., 2010;  
79 Beaufort et al., 2015; Aja, 2019; Worden et al., 2020). Although green Fe-rich marine sands  
80 composed of glauconitic minerals (Fe-bearing dioctahedral smectite, glauconitic smectite,  
81 glauconitic mica), odinite and chamosite, an iron-rich 14 Å trioctahedral chlorite, are  
82 relatively well-known (Porrenga, 1967; Van Houten and Purucker, 1984; Odin, 1988;  
83 Hornibrook and Longstaffe, 1996) in both modern sediments and ancient sedimentary rocks,  
84 there is a shortage of studies documenting both the conditions (depth, temperature) and  
85 the timing of their formation throughout the shallow-burial history of the clastic sediments.  
86 In addition, few of the studies document both the petrography and mineralogy of siliciclastic  
87 sediments having undergone incipient chloritization at burial depths of 1000 m or more  
88 (Hornibrook and Longstaffe, 1996; Tinseau, 2002). In particular, little is known of the origin  
89 of berthierine in modern sediments.

90 Although the clays trapped in modern estuarine sands have been extensively studied in  
91 recent years (Wooldridge et al., 2018; Griffiths et al., 2018b; Virolle et al., 2020; Worden et  
92 al., 2020), there is a gap in the documentation of the suites of reactions that lead to the  
93 transformation of detrital clays into chlorite precursors such as berthierine. Therefore, a  
94 case study of shallow-buried clastic sediments in which berthierine has not started its  
95 transformation into Fe-chlorite is critically needed to better understanding of the conditions  
96 in which this clay mineral precursor forms and initiates chloritization (Hornibrook and

97 Longstaffe, 1996). Pisoids and pseudo-ooids composed of berthierine have been identified in  
98 outcrops of the Wealden Group sediments in South-East England (Taylor, 1990). In the Paris  
99 Basin (France) green clay minerals were reported in Wealden Group sandstones from core  
100 samples (Buissart et al., 1988). In the Paris Basin and in the Weald and Wessex Basins (UK),  
101 Lower Cretaceous Wealden Group sediments were mainly deposited in coastal settings,  
102 including fluvial, estuarine, deltaic and shoreface depositional environments (Allen, 1959;  
103 Buissart et al., 1988; Allen and Wimbledon, 1991; Thiry et al., 2006; Akinlotan, 2016, 2017).  
104 The Wealden Group sandstones of the Early Cretaceous period within the Paris Basin have  
105 not been well characterized in terms of sedimentology and mineralogy (Buissart et al.,  
106 1988).

107 The main goal of this paper is to provide petrographic and mineralogical analyses of green  
108 clay minerals in poorly consolidated Early Cretaceous sands having undergone shallow burial  
109 (depths less than 1000 m) during the geological evolution of the Paris Basin. These  
110 characterizations will be compared to the results of recent studies that reported detrital clay  
111 coats around sands in modern coastal environments (Wooldridge et al., 2018; Griffiths et al.,  
112 2018a; Virolle et al., 2019b; Worden et al., 2020; Duteil et al., 2020). The Wealden sediments  
113 will be used as an analogue for the eogenetic processes that modern sands undergo. Five  
114 wells from the Wealden Group sandstones of the Paris Basin with burial depths ranging from  
115 400 to 1000 m, have been selected to address the following specific questions relating to  
116 sedimentology of the Wealden Group sandstones and to early clay diagenesis in sandstones:

- 117 1. Do Wealden Group sandstones allow better characterisation of the intermediate  
118 diagenetic stage between the formation of detrital clay coats and the crystallization  
119 of true Fe-rich chlorite in sandstone reservoirs?

- 120 2. What are the facies and depositional environments of the Wealden Group  
121 sandstones of the Paris Basin?
- 122 3. What are the clay mineral assemblages of the Wealden Group sandstones of the  
123 Paris Basin?
- 124 4. Are incipient quartz overgrowths present within this reservoir?
- 125 5. Does incipient pre-chloritization processes already limit the development of early  
126 quartz overgrowths?
- 127 6. What are the detrital clay minerals that are precursors to chloritization?
- 128 7. What is the source to sink context suitable for chloritization?

129 **GEOLOGICAL SETTING**

130 The Paris Basin is located in northern France and forms an intracratonic basin about 600 km  
131 in diameter. The maximum burial depth reaches about 3200 m in the central basin (Fig. 1A-  
132 B, Guillocheau et al., 2000; Gély and Hanot, 2014). The basement of the Paris Basin is  
133 composed of Hercynian and Cadomian crystalline rocks covered by a series of sedimentary  
134 deposits laid down from the Triassic to the Miocene (Guillocheau et al., 2000; Fig. 1A-B, Gély  
135 and Hanot, 2014). This basin is surrounded by four Palaeozoic Massifs: the Armorican Massif  
136 to the west, the Central Massif to the south, the Vosges to the east and the Ardennes to the  
137 north. In its north-western part, the basin extends from the English Channel to the Wessex  
138 and Weald Basins in England. Basin structures and sedimentary formations are very similar  
139 on both sides of the English Channel.

140 Tectonic activity in the Paris Basin ceased at the beginning of the Miocene (Bergerat et al.,  
141 2007). From the Early Jurassic to the Oligocene, sediments were deposited in a marine  
142 environment, periodically coastal or lacustrine, in a series of transgressive and regressive  
143 episodes. Since the Triassic period, the depositional environments have produced a multi-

144 layered aquifer system made up of alternating permeable layers, dominated by either  
145 lithified or poorly consolidated limestones and sandstones, and less permeable layers  
146 consisting mainly of marls and clays (Fig. 1A, Mégnien and Mégnien, 1980). During the Early  
147 Cretaceous, geological structures of the Paris Basin were controlled by the progressive  
148 opening of the North Atlantic Ocean and by the earliest effects of the convergence between  
149 the Eurasian and African plates (Guillocheau et al., 2000). During the Early Cretaceous,  
150 sedimentation was marked in the Weald, Wessex and Paris basins by coastal, estuarine to  
151 fluvial deposits (Fig. 1C, Dercourt et al., 2000). Palaeogeographic reconstructions show that  
152 the north-eastern Paris Basin was located at tropical to subtropical latitudes during the Late  
153 Jurassic–Early Cretaceous (28–35°N, Dercourt et al., 2000). In England, Wealden Group  
154 sediments can reach a thickness of about 800–900 m as on the Isle of Wight (Allen, 1959).  
155 The thickness of the Wealden Group sandstones appears to be considerably reduced in the  
156 central part of the Paris Basin where it never exceeds 200 m (Buissart et al., 1988).  
157 Corresponding deposits on the north-eastern edges of the Paris Basin are absent (Thiry et  
158 al., 2006). The deposition area during the Early Cretaceous was reduced to a NW–SE oriented  
159 trough connected to the Tethys sea (Fig. 1C, Buissart et al., 1988; Thiry et al., 2006). During  
160 the Early Cretaceous, the Wealden trough extended from the Land of Bray, west of Beauvais,  
161 to Burgundy, region around Dijon (Thiry et al., 2006). Jurassic formations cropped out on  
162 both sides of the gutter and were submitted to weathering based on the presence of lateritic  
163 soils (Thiry et al., 2006). Alternating transgressive/regressive periods influenced the Wealden  
164 Group sands that are either (1) continental or (2) marine shallow-marine to coastal (Mégnien  
165 and Mégnien, 1980; Rusciadelli, 1996). Wealden Group sandstones represent several  
166 second-order transgressive/regressive sequences (Rusciadelli, 1996). Up to six second-order  
167 transgressive/regressive facies cycles have been identified within the overall first-order Early



168 Cretaceous transgressive phase (Jacquin et al., 1998). The top of Wealden Group sandstones  
169 is capped by a low permeability layer known as the Aptian shale (Jacquin et al., 1998). The  
170 Lower Cretaceous Wealden Group sandstones of the Paris Basin forms a strategic reservoir  
171 unit, supplying drinking water for Paris. At depths greater than 500–600 m, this formation is  
172 also a potential target for the future development of deep geothermal energy around Paris  
173 (Bel et al., 2012). Away from Paris, the Wealden Group sandstones are used for gas storage  
174 (Mégnyien and Mégnyien, 1980; Buissart et al., 1988; Vernoux et al., 1997; Bel et al., 2012;  
175 Seguin et al., 2015). This interval is generally referred to as the Neocomian reservoir in  
176 geochemical or hydrological studies of the Paris Basin (Castro et al., 1998). The reservoir  
177 units range from Berriasian to Barremian in age, or to the first Aptian–Albian marine layers  
178 in the Paris Basin (145 Ma to 195 Ma; Mégnyien and Mégnyien, 1980). Neocomian reservoirs  
179 are valuable aquifers for geothermal use in the Paris Basin. Previous studies have indicated  
180 current water temperatures of 32 °C at 744 m at Ivry-sur-Seine, in the South-Eastern suburbs  
181 of Paris (thermal gradient of 2.6 °C/100 m, Seguin et al., 2015) and 34 °C at 740 m at  
182 Bruyère-le-Chatel, located 30 km South-Western of Paris (thermal gradient of 3.9°C/100m,  
183 Le Nir et al., 2009).

## 184 **MATERIAL AND METHODS**

185 The Wealden Group core samples studied in this report consist of sandstones from three  
186 geographical sites in the Paris Basin: (1) Fouilleuse, (2) Beynes and (3) Crouy-sur-Ourcq (Fig.  
187 1A). Fouilleuse is located 10 km west of the Gournay-sur-Aronde underground gas storage  
188 site and about 60 km NNE of Paris in Wealden Group sandstones. Two wells (FO-01 and FO-  
189 06) from the Fouilleuse site were studied. Borehole FO-01 was drilled close to Avrechy  
190 (Oise), and borehole FO-06 was drilled in 1994 close to Saint-Rémy-en-l'eau (Oise), 1.5 km  
191 north-east of borehole FO-01. The studied sandstones are located at a depth of 445–510 m

192 in borehole FO-01 and 477–530 m in borehole FO-06. Two wells (A and B) were drilled in the  
193 Beynes gas storage site (Yvelines), 35 km west of Paris, which has been exploited since 1956.  
194 Sandstones were sampled at 390–430 m depth for well A and at 420–440 m depth for well B.  
195 Lastly, well CR12 was drilled near Crouy-sur-Ourcq on the Germigny-sur-Coulombs  
196 underground gas storage site, 60 km NE of Paris, at a depth of 900–970 m. The maximum  
197 burial depths of Wealden Group sandstones range from 440 m at Beynes to 1000 m at  
198 Crouy-sur-Ourcq. The present day temperature in well CR12 at a depth of 897 m is 36 °C  
199 yielding a thermal gradient of 2.6 °C/100 m. The presence of Upper Cretaceous and  
200 Palaeogene sediments suggests that the present-day temperature corresponds to the  
201 maximum burial temperature attained and maintained during the last 40 million years of the  
202 basin's history (Fig. 2, Torelli et al., 2020).

203 Some 250 m of cores from the five different wells were logged to determine the lithology,  
204 the vertical facies associations, and 60 rock fragment or plug samples were collected.  
205 Mineralogical analyses were made on all samples. Forty-seven thin sections were made for  
206 detailed petrographic observations.

207 Petrographic studies were carried out on thin sections and rock fragments using a polarizing  
208 optical microscope (Nikon Eclipse E600POL) and a scanning electron microscope (SEM) JEOL  
209 IT 500 equipped with an Bruker Energy Dispersive X-ray Spectrometer (EDS) using an XFlash  
210 4030 Silicon drift detector. SEM observations were performed in secondary electron imaging  
211 (SEI) mode for morphological documentation and backscattered electron (BSE) mode on  
212 carbon-coated thin sections for the imaging of chemical contrast and selection of local sites  
213 for sporadic chemical analysis. Analytical conditions were 15 kV, 1 nA, a counting time of  
214 50 sec, and at a working distance of 11 mm. The standards used for EDS consisted of albite  
215 (Na, Al, Si), almandine (Mg, Fe), diopside (Ca), orthoclase (K) and spessartite (Mn). Matrix

216 corrections were performed using the integrated programme (PhiRhoz correction). The  
217 reproducibility of the standard analyses was nearly 1.5% for all of the elements, except Na,  
218 which attained a reproducibility of 3%.

219 Focused Ion Beam ultra-thin sections were made at the CINaM centre (Université Aix  
220 Marseille, France). This nanofabrication station contains an FEI Helios 600 nanolab SEM  
221 coupled to a focused Ga<sup>+</sup> ion beam (FIB) column. The sections obtained were about 10 μm x  
222 8 μm x 50 nm in size.

223 The relative surface area (%) of the macropores and the solid components (coated and non-  
224 coated quartz, feldspars, lithics, micas, bioclasts, pyrite, iron-rich carbonates, diagenetic  
225 cements, clay matrix) were quantified from thin sections using the JmicroVision Image  
226 analysis software employing random grid point counting (Roduit, 2007). A minimum of 800  
227 counts was performed on 20 different images (2.5 mm x 2.5 mm) in each thin-section.

228 The chemical compositions of clay minerals derived from EDS analyses were expressed in  
229 oxide weight percentages, atomic percentages were used to calculate structural formulas on  
230 the basis of the stoichiometric number of oxygen. Atomic concentrations were plotted in  
231 ternary diagrams of  $MR^{3+} - 2R^{3+} - 3R^{2+}$  (Velde, 1985) to determine the compositional field of  
232 clay minerals and to highlight mixtures at the micrometre scale from the point count  
233 analysis.

234 X-Ray Diffraction (XRD) analyses of randomly oriented powders were acquired to determine  
235 the bulk mineralogy of each sample using a PANalytical X'Pert diffractometer. X-ray  
236 diffractograms of randomly oriented powders were acquired between 4° and 80° 2θ with a  
237 step size of 0.017° 2θ, a time/step of 3s using CuKα X-ray radiation at 45 kV, 40 mA with a  
238 0.0170 step size. A routine XRD analysis on the fraction less than 2 μm was acquired at the  
239 Géosciences Paris-Saclay laboratory (Université Paris-Saclay, France) using a PANalytical

240 X'Pert Prodiffractometer using CuK $\alpha$ 1 with a 0.0170 step size between 3° and 35° 2 $\theta$  at 45 kV  
241 and 40 mA. Semi-quantitative estimations of kaolinite, chlorite, illite/micas and smectite  
242 were realized with MacDiff software (Goethe Universität) based on the peak area of the  
243 ethylene–glycol diffractograms summed to 100%, the relative error for the peak area being  
244  $\pm$ 5%. A second set of detailed diffraction patterns of oriented and randomly oriented  
245 preparations of the clay size fraction (less than 2  $\mu$ m and less than 0.2  $\mu$ m) was acquired at  
246 the Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP) laboratory (Université de  
247 Poitiers, France) using a Bruker D8 XRD diffractometer (CuK $\alpha$  radiation) equipped with a  
248 linxeye detector. The XRD patterns of randomly oriented powders were recorded over the  
249 range of 2–65° 2 $\theta$  with 0.02° 2 $\theta$  steps and 5 seconds per step. XRD patterns of oriented  
250 preparations were recorded over the 2–30° 2 $\theta$  range with 0.02° 2 $\theta$  steps and 1 second per  
251 step.

252 Due to their poorly consolidated nature, sandstone samples were gently disaggregated in  
253 water and the clay fraction put in suspension by ultrasonic treatment without grinding. Clay  
254 size fractions <2  $\mu$ m and <0.2  $\mu$ m were extracted by sedimentation and centrifugation,  
255 respectively. No cation exchange was performed on the clay material. Particles less than  
256 0.2  $\mu$ m in size were extracted from the infra 2  $\mu$ m clay suspension by using a Beckman J2-21  
257 continuous centrifuge rotating at 5000 rotations per minute with a constant flux of the  
258 suspension passing through the rotor set at 150 ml per minute.

259 XRD patterns of mixed-layer minerals have been interpreted on the basis of comparison with  
260 one-dimensional diffraction profiles calculated using Newmod 2<sup>TM</sup> software.

261 Fourier Transform Infrared Spectroscopy (FTIR) was obtained from the less than 2  $\mu$ m  
262 fraction, only from samples in which X-ray diffraction indicated the presence of berthierine.

263 The mid-infrared (MIR) spectra (400–4000 cm<sup>-1</sup>) were acquired on KBr pellets using a Nicolet

264 760 FTIR spectrometer equipped with a potassium bromide (KBr) beamsplitter and a DTGS-  
265 KBr detector. The resolution was set to  $4\text{ cm}^{-1}$  with a co-addition of 100 scans. KBr pellets  
266 were made with 1 mg of clay material dispersed in 150 mg of KBr powder and pressed under  
267 8 tons for 5 minutes in a hydraulic press before being dried for 12 hours at  $200\text{ }^{\circ}\text{C}$ . Heating to  
268  $200\text{ }^{\circ}\text{C}$  was used to remove the OH bending and stretching bands of adsorbed water (weakly  
269 bonded OH) which absorb IR radiation in the same range of frequencies as the OH stretching  
270 bands of berthierine (near  $3400\text{ cm}^{-1}$ ). Details of location, petrographical and clay mineral  
271 compositions by sample are provided in Supplemental Material<sup>1</sup> Table S1 (sample  
272 description).

273

## 274 **RESULTS**

### 275 **Sedimentary Facies**

276 From the core descriptions, we identified the depositional environments as ranging from the  
277 most distal (offshore) to the most proximal (alluvial plain) environments. We grouped the  
278 facies into five facies associations, typical of five depositional environments (Fig. 3, Table 1).  
279 Observations and descriptions are summarized in Table 1. Well CR12 shows the variability in  
280 the sedimentary environments identified within the Wealden Group sandstones of the Paris  
281 Basin (Fig. 3).

282 The first facies association (FA1) consists of fluvial deposits, such as trough cross-bedded  
283 sandstones (which can be locally conglomeratic) with numerous soft mud pebbles, current-  
284 rippled sandstones, nodular siltstones, laminated siltstones, dark rooted silty mudstones,  
285 and coal beds (Fig. 3, Fig. 4A-B). This facies association exhibits an overall fining-upward  
286 succession ranging from medium to upper fine-grained trough cross-beds to fine-grained  
287 ripple-laminated sandstones. Continental conditions are highlighted by the absence of

288 marine microfossils, the abundance of continental organic material (wood fragments, leaf  
289 debris), and the relative abundance of the fresh-water algae *Botryococcus spp.*, or  
290 continental spores *Densoisporites spp.* as reported by Rusciadelli (1996).

291 The second facies association (FA2) is estuarine (Fig. 4C-G) and is similar to the well-  
292 characterized vertical facies association described on cores from the modern Gironde  
293 estuary. FA2 appears to be a mixed environment, with some continental indicators, an  
294 assemblage of pollens and spores, such as *Classopolis spp.* or *Exesipollenites spp.*  
295 (Rusciadelli, 1996), and some marine indicators, *Muderongia crucis*, *Stiphrosphaeridium*  
296 *anthophorum* and dinoflagellate *Rhynchodiniopsis fimbriat*. This facies association is key to  
297 understanding the development of early clay grain coats. Three facies make up this facies  
298 association:

299 (1) The first facies (FA2a) consists of medium- to fine-grained sandstones with trough cross-  
300 stratifications, separated by thin clay layers. Foresets are highlighted by clay drapes and  
301 organic matter (Fig. 4C). Reactivation surfaces are also visible. Compositionally, FA2a  
302 consists of angular to sub-rounded, quartz grains, feldspar and mica, with rare glauconite  
303 ooids. Foresets with clay drapes, trough cross-stratifications, reactivation surfaces and a mix  
304 between continental and marine pollens and spores are consistent with small sandy tidal  
305 dunes, deposited in subtidal or intertidal zones, forming tidal bar deposits in an estuary.

306 (2) Facies FA2b is characterized by three types of fine bedding that are vertically stacked: (i)  
307 flaser bedding composed of medium-grained, current-rippled sands with muddy couplets  
308 (Fig. 4D-E); (ii) wavy bedding, with alternating millimetre-to-centimetre, fine-grained sandy  
309 ripples and amalgamated levels of tidal slack water clay drapes (Fig. 4F), and (iii) fine-  
310 grained, lenticular to wavy bedding sandy ripples, with alternating millimeter-scale silty  
311 linsens and high-tide slack water clay and clay drapes (Fig. 4G). Rare bioturbation fabrics are

312 observed, composed mainly of *planolites*. The variable bedding types and the mix between  
313 continental and marine pollens and spores suggests tidal flat deposits.

314 (3) The third facies (FA2c) is composed of amalgamated clay drapes, rich in organic matter,  
315 with localised reed roots and oxidized pedogenic horizons. The presence of roots, organic  
316 matter and oxidized pedogenic horizons suggests supratidal marsh facies covering the tidal  
317 flat of an estuarine alluvial plain.

318 The FA2 association, as a whole, may be interpreted as ranging from fining upward, tidal bar  
319 and tidal channel deposits to prograding estuarine alluvial plain deposits.

320 The deltaic facies association (FA3) consists of cross-bedded sandstones overlain by shales  
321 and limestones with fragments of marine bivalves, echinoderms and brachiopods. Vertical  
322 tubes of *Skolithos linearis*, *planolithes* or *teichichnus* are present (Fig. 4H) and marine  
323 microfossils, such as the dinoflagellate *Muderongia crasis* or *Oligosphaeridium asterigerum*  
324 (Rusciadelli, 1996) are also present.

325 FA4 is interpreted as a shoreface facies association. It is mainly composed by fine- to  
326 medium-grained, clean, well-sorted sandstones in 20 cm to 1 m thick beds, with hummocky,  
327 swaley, low-angle to horizontal planar cross-stratifications which are locally scrambled and  
328 heavily bioturbated (Fig. 4I). Locally, vertical burrows (*skolithos*) are present, as well as  
329 variably abundant *ophiomorpha* burrows in the coarser sands. Dispersed marine shell  
330 fragments and local accumulations of shells are also present in the upper section (Fig. 3).

331 FA5 consists of shale, with thin horizontal laminae of siltstone, which commonly contains a  
332 mixture of bivalves, coccoliths, foraminifera and scattered shell fragments. This is  
333 interpreted as an offshore facies association.

334 The vertical stacking pattern is complex, with the presence of numerous  
335 erosion/reactivation surfaces suggesting relatively limited accommodation space.

336

337 **Mineralogy of Pre-Burial Sediments (Early Cretaceous, Surface Sediments)**

338 ***Grain Composition and Grain Coating***

339 Sandstones of the Wealden Group sandstones of the Paris Basin are mainly composed of  
340 quartz (34% on average) and feldspars (5% on average) associated with lithics such as Fe  
341 ooids or mud clasts (9% on average), (Fig. 6E, 6G-H), and micas (Fig. 5, Table 2). Iron-ooids  
342 are present in some samples (Fig. 6E, G-H). XRD and SEM/EDS analyses indicate that these  
343 ooids are composed of goethite, an iron hydroxide mineral, which crystallized around a  
344 quartz sand nucleus (Fig. 6H). Locally, these iron-coated grains can be abundant, forming  
345 green sands (Fig. 6E). Grain size varies from well to well, but mostly consists of fine to  
346 medium grained sub-rounded to sub-angular, moderately well sorted sandstones which are  
347 mostly classified as feldspathic litharenite (Folk Classification, Folk, 1974). Minor amounts of  
348 lithic arkose, litharenite or sublitharenite were also identified (Fig. 5, Table 2).

349 Many of the sand grains are coated by fine grained material (Fig. 6A-D) composed of clay,  
350 silt, and very fine grained non-clay silicates, such as coccoliths (Fig. 6B-F). The clay coats form  
351 bridges (Fig. 6A), aggregates (Fig. 6C), ridges (Fig. 6D), or clay drapes around and between  
352 quartz grains that are very similar to textures observed in modern estuaries (Wooldridge et  
353 al., 2017; Virolle et al., 2019a) (Fig. 6).

354 All facies association are coated with variable amounts of detrital clay (Fig. 7), Fluvial facies  
355 association = 37%; Estuarine facies association = 39%; Deltaic facies association = 5%;  
356 Shoreface facies association = 12%; and in the Offshore facies association = 2% (Fig. 7, Table  
357 2). In addition, detrital grain coats are present in all wells (Supplemental Material<sup>1</sup> Table S1).  
358 In fluvial and estuarine facies associations, detrital coats cover 15–30% of the surface of  
359 sand grains (Fig. 7, Table 2). However, all facies combined, well CR12 also has a lowest clay



360 fraction (6 wt% on average) compared to 10 and 23 wt% in the Fouilleuse and Beynes wells  
361 respectively (Supplemental Material<sup>1</sup> Table S1).

362

### 363 ***Clay Minerals***

364 XRD analyses of the less than 2  $\mu\text{m}$  clay fraction reveals a clay mineral assemblage that is  
365 composed mainly of kaolinite (42% on average, based on peak areas), chlorite (22% on  
366 average), illite/micas (26% on average) and smectite (11% on average); (Fig. 3 and Table 2).

367 This detrital clay mineral assemblage was observed in all wells (Fig. 3 and Supplemental  
368 Material<sup>1</sup> Table S1).

369 XRD patterns obtained from oriented preparations of less than 2  $\mu\text{m}$  particles of the clay  
370 coats are reported in Figure 8. They highlight a much more complex mineralogical  
371 composition than obtained from the preliminary routine XRD analysis which considered only  
372 mixtures of discrete kaolinite, illite/mica (named illite hereafter for simplicity), chlorite and  
373 smectite (Fig. 3).

374 Discrete illite and kaolinite are identified by the presence of rational  $00\ell$  reflections at  
375 9.99 Å, 4.98 Å and 3.33 Å and at 7.14 Å and 3.57 Å respectively, after air drying and ethylene  
376 glycol treatments. In all investigated samples, the diffraction maximum at 14.3 Å observed in  
377 air drying state, does not fit with the  $d_{001}$  reflection of chlorite due to the lack of rational  
378 subordinate reflections and by a partial but limited shift towards lower angle positions (up to  
379 16.3 Å, Fig. 8A) in the ethylene glycol state, which is inconsistent with that of smectite in  
380 most samples. Such behaviour is typical of iron-rich hydroxy-interlayered clay minerals (HIM)  
381 that commonly occur in acidic soil environments and contain Al and Fe cations (Barnhisel  
382 and Bertsch, 1989; Meunier et al., 2007; Lanson et al., 2015). In those studies, XRD profiling  
383 suggests that hydroxy-interlayered clay minerals (HIM) consist of no less than 10

384 mineralogical clay phases (Viennet et al., 2015, 2016). Barnhisel and Bertsch (1989) reported  
385 that hydroxy-interlayered smectite (HIS) and hydroxy-interlayered vermiculite (HIV) are  
386 intermediate mineral phases of the solid-solution series between fully expandable  
387 dioctahedral 2:1 phyllosilicates (smectite) and pure Al-chlorite (dombassite). These clays are  
388 believed to form during the weathering process in acidic soils which results in the interlayer  
389 Al-hydroxylation and Fe-hydroxylation of 2:1 phyllosilicates (Carstea, 1968).

390 The XRD patterns of the clay material which partially coats the sand grains are analogous to  
391 those reported by Viennet et al., (2015) for the temperate acidic soils in a forest. On the low  
392 angle side (i.e. between 10 and 17 Å) the XRD patterns obtained after air drying and  
393 ethylene glycol treatment are complex:

394 (1) In a few samples, the peak shifting toward lower angles after ethylene glycol treatment  
395 does not reach the 17 Å d-spacing value of the  $d_{001}$  of smectite (Fig. 8A). This observed d-  
396 value near 16 Å (Fig. 8E) is attributed to the presence of a HIS clay phase (Barnhisel and  
397 Bertsch, 1989; Meunier et al., 2007); (2) There is a very limited shift of the 14.3 Å peak after  
398 EG treatment (Fig. 8B, C, D,) which is attributed to the presence of the HIV phase (Barnhisel  
399 and Bertsch, 1989; Meunier et al., 2007). This could correspond to the presence of a di-  
400 dioctahedral chlorite-like clay phase which represents the final stage of complete Al-  
401 hydroxylation of the interlayer sheet of HIMs and/or to the presence of a very small amount  
402 of detrital chlorite (Chlorite has been identified from SEM observations in a few samples);  
403 and (3) a very broad diffraction peak (or shoulder) with maxima near 12 Å in the XRD pattern  
404 of the air dried assay (Fig. 8B, C, D) and with a limited shift toward lower angles after  
405 ethylene glycol treatment. Such positions have been interpreted as due to the presence of  
406 mixed layer minerals (MLM) composed of illite and hydroxyl-interlayered layers, with most  
407 likely minor amounts of smectite (Viennet et al., 2015, and references therein).

408 On the high angle side, the broad peaks observed near 7.7 Å, 4.80 Å and 3.50 Å are  
409 consistent with the presence of MLM composed of expandable HIMs, especially HIS and  
410 non-expandable HIMs with a di-dioctahedral chlorite structure (i.e. dombassite-like clay  
411 phase).

412 Moreover, comparison between the XRD patterns of clay particles from different grain sizes  
413 populations (Fig. 8C-8D) shows that the amount of discrete illite and kaolinite falls markedly  
414 (in FO6-12 sample, fraction lower than 0.2 µm), having been replaced by HIMs and complex  
415 mixed-layer minerals (MLMs) in the smaller clay fraction (less than 0.2 µm, Fig. 8D).

416 The chemical compositions representative of clay particles from pre-burial clay-coats (before  
417 burial, at the surface) are presented in Table 3 (analyses 1 to 4). Chemically, the pre-burial  
418 clay coats are characterized by a large range of high Al<sub>2</sub>O<sub>3</sub> content (from 21 to 37%) and  
419 moderate to high iron content expressed as Fe<sub>2</sub>O<sub>3</sub> content depending on their weathering  
420 origin (3–15%). When plotted in the MR<sup>3+</sup>- 2R<sup>3+</sup>-3R<sup>2+</sup> ternary diagram (Velde, 1985), the  
421 point chemical analyses of detrital clay coats fit within an overall compositional field of  
422 dioctahedral phyllosilicates which extends over the fields for illite, dioctahedral smectites,  
423 and kaolinite/dombassite (Fig. 9A). Such a compositional field is consistent with the  
424 aforementioned XRD identification of pre-burial clay minerals. When plotted in an Fe-Al-Mg  
425 ternary diagram (Fig. 9B), the compositional field of pre-burial clays spreads over a large  
426 range of Fe content which varies with the relative amounts of soil kaolinite (3–4% Fe<sub>2</sub>O<sub>3</sub>) and  
427 HIMs (up to 15% Fe<sub>2</sub>O<sub>3</sub>) in the analysed particles.

428 SEM/EDS analyses indicate that green clay minerals forming sand grains are composed of Fe-  
429 rich chlorite detrital grains observed in a few samples only (such as FO6-17). Although clay  
430 minerals of pedogenic origin have been identified in each well, their relative proportion  
431 seems to vary with their sedimentology. Discrete kaolinite is dominant in the sandy facies of

432 the estuarine environment while HIMs and associated MLMs are dominant in sandy/muddy  
433 facies of the estuarine environment.

434

#### 435 **Authigenic Minerals**

436 Based on petrographic observations, we recognize two primary diagenetic stages which  
437 were characterized by cementation, dissolution and recrystallization.

438 **The first stage** consists in the crystallization of authigenic pyrite, siderite, ankerite and  
439 vermicular kaolinite. We identify kaolinite in all the wells studied, regardless of sample burial  
440 depth.

441 Pyrite is commonly observed within the detrital clay coats and exhibits a typical framboidal  
442 texture. It is composed of spherical aggregates of pyrite octahedrons (0.5–2  $\mu\text{m}$  in diameter)  
443 which are frequently embedded in the clay material (Fig. 10A, 10F and 10J). Framboidal  
444 pyrite is very common in reducing marine sediments and has been interpreted to be the  
445 result of pyritization associated with the decay of organic matter mediated by bacteria  
446 during the first stage of diagenesis (McKay and Longstaffe, 2003). Blocky crystals of pyrite  
447 are relatively rare in these sediments (Fig. 10B).

448 Fe-rich carbonates occur as euhedral crystals, forming a discontinuous coating on the  
449 surface of the framework silicates (Fig. 10C-I). They are believed to have formed as a primary  
450 cementation stage during the early diagenesis of the sandstones.

451 Siderite (Fig. 10C-F) and ankerite (Fig. 10G-I) occur as equant or elongate rhombic crystals  
452 with a mean size ranging from 10 to 100  $\mu\text{m}$  (Fig. 10C-F) and show evidence of chemical  
453 zoning (Fig. 10E-F). Siderite is typically associated with the pyrite crystals (Fig. 10F).

454 SEM observations revealed that the initial clay formation consisted of the precipitation of  
455 stacks of relatively coarse-grained pseudo-hexagonal (about 10  $\mu\text{m}$  in diameter) of

456 vermicular kaolinite on detrital clay coats in the open pore space (Fig. 11A-B). FTIR spectra of  
457 the clay material in the hydroxyl-stretching band region of phyllosilicates reveals the four  
458 diagnostic bands of kaolinite (i.e., 3695, 3668, 3652 and 3620  $\text{cm}^{-1}$ ) in all studied wells and  
459 indicates the presence of two types of kaolinite with specific crystal-chemical properties (Fig.  
460 11C). In the shallower samples, poorly crystallized kaolinite of detrital origin (characterized  
461 by a weak and broad band reflection at 3668  $\text{cm}^{-1}$  and a band at 3598  $\text{cm}^{-1}$  which is  
462 indicative of vibration of the  $\text{AlFe}^{3+}\text{-OH}$  bond (Delineau, 1994)), is particularly abundant. In  
463 contrast, deeper samples (CR-12, Fig. 11C) are characterized by well-crystallized kaolinite  
464 with sharp diagnostic bands and the absence of the  $\text{AlFe}^{3+}\text{-OH}$  bands. This suggests that  
465 during the shallow burial history of these sandstones, iron-rich and poorly crystallized  
466 kaolinites in the detrital clay matrix, underwent recrystallization resulting in the formation of  
467 well-crystallized vermicular kaolinite, similar to what has been described by Beaufort et al.,  
468 (1998).

469 **The second stage** consists of the crystallization of a thin clay coat composed of tiny flakes of  
470 Fe-rich clay minerals which covers both detrital and authigenic minerals during the first  
471 stage of diagenesis. These diagenetic clay coats are continuous at the scale of SEM  
472 observations and have only been observed in sandstones buried at depths exceeding 900 m  
473 (well CR12). SEM observations document the presence of honeycomb, Fe-rich clay coats  
474 covering the entire surface of the pre-existing minerals (Fig. 12A, 12B). Detailed SEM  
475 observations of ultra-thin FIB sections cut perpendicularly to the contact between detrital  
476 quartz and authigenic Fe-rich clay coats (Fig. 12C) reveal small (less than 100 nm) quartz  
477 overgrowths on the detrital quartz grains. These incipient quartz overgrowths are limited to  
478 the interstices between the Fe-rich clay crystallites and the detrital quartz grain surface. This  
479 nanopetrographic observation is very similar to that documented from TEM investigations at

480 the interface between detrital quartz and Fe-chlorite coats in several sandstone reservoirs  
481 (Billault et al., 2003). Moreover, the vermicular kaolinites which formed during the first  
482 diagenetic stage, show irregular, rounded shapes with eroded edges, suggesting partial  
483 dissolution, when the kaolinite was in contact with the iron-rich clay particles (Fig. 12B).

484 The Fe-rich clay minerals, which comprise the diagenetic Fe-rich clay coats, have been  
485 identified as berthierine on the basis of XRD, TEM and FTIR results. Berthierine is difficult to  
486 identify from XRD patterns of oriented preparation of the clay fraction because of its intense  
487 00 $\ell$  reflections which is similar to kaolinite (Fig. 13). The Fe-rich clay coating identified by  
488 SEM/EDS and from the XRD patterns of randomly oriented powder preparations (Fig. 14A) as  
489 berthierine, has only been identified in samples buried at depth exceeding 900 m (Figs. 9  
490 and 12). These XRD patterns differ from those of shallow buried samples (depth less than  
491 500m, Fig. 14) in that they contain all of the peaks corresponding to the diagnostic hk  
492 reflections of berthierine, as referenced in literature (Brindley and Brown, 1980). More  
493 particularly, berthierine is unambiguously indicated from a series of peaks, marked by an  
494 asterisk in Figure 14A (d-spacing = 4.67 Å, 2.68 Å, 1.56 Å and 1.52 Å respectively). These  
495 peaks are not overlapped by the peaks of kaolinite or any other 2:1 dioctahedral  
496 phyllosilicates, such as HIMs or illite (Fig. 14A). In addition, the 060 reflection close to 1.56 Å  
497 (Fig. 14B) is indicative of a *b* parameter ( $b=9.36$  Å) which is similar to that given in literature  
498 for berthierine (Brindley and Brown 1980). From the XRD results, it appears that the  
499 increasing amount of berthierine, in the clay fraction of samples buried at depth exceeding  
500 900 m, is coupled with a marked decrease in the amount of detrital kaolinite and HIMs (Fig  
501 14B). No diffraction peaks of chlorite can be identified in the XRD patterns of samples  
502 containing berthierine. The broad bands near 3550 and 3400 cm<sup>-1</sup> observed in the FTIR  
503 spectra on dehydrated samples of sandstones in which diagenetic clay coats were observed

504 (Fig. 15) are also key diagnostic features for the identification of natural or synthetic  
505 berthierine minerals (Mackenzie and Berezowski, 1984; Rivard et al., 2013 and references  
506 herein).

507 When plotted in the  $MR^{3+}-2R^{3+}-3R^{2+}$  and Al-Fe-Mg ternary diagram, the EDS analyses of the  
508 diagenetic clay coats spread over compositional fields (Fig. 10A and 10B) which extend  
509 between that determined in the pre-burial clays and that of berthierine as determined from  
510 data in the literature (Bhattacharyya, 1983 and references herein). More particularly, the  
511 chemical composition of the iron-rich particles is very similar to that of berthierine as  
512 determined in the Wealden Group sediments in South-East England (Taylor, 1990). Such an  
513 overall compositional field suggests that, in many cases, admixture with, or juxtaposition to,  
514 berthierine of very fine particles of pre-burial clay minerals (illite, smectite, kaolinite, HIMs,  
515 etc.) still persists in the diagenetic clay coat. Locally, the last diagenetic phase is marked by  
516 blocky calcite cement filling the residual intergranular space.

517

## 518 **DISCUSSION**

### 519 **Paragenetic Sequence Of The Wealden Group Sandstones**

520 From the petrographic observations, we specify the timing of the diagenetic events (Fig. 16).  
521 This paragenetic sequence was established by cross-referencing and superimposing textural  
522 features observed using the optical microscope and SEM (Figs. 10, 12 and 16).

523 First, detrital clay coats form around sand grains at the time of sedimentation. The  
524 mineralogy of these detrital clay coats consists of variable quantities of kaolinite, illite,  
525 smectite and HIMs, the relative proportions of which vary depending on the original  
526 depositional setting (Table 1). Detrital clay coats consist of various textures, such as bridged

527 or ridged clay coats. The percentage of grains with detrital clay coats ranged from 37% in  
528 fluvial facies (Table 1) and 39% in estuarine facies (Table 1) which is far higher than the 20%  
529 reported from the modern tidal bars of the Gironde estuary, but similar to values reported in  
530 the estuarine point bars of the Garonne (Virolle et al., 2019a, 2020). Coat coverage is also  
531 similar to the alluvial part of the Ravenglass estuary (U.K.), where the majority of the sand  
532 grains are covered by approximately 30% clay coats (Griffiths et al., 2018a, 2019). Fe-ooids  
533 are found in wells FO-01 and FO-06 in the deltaic facies (FA3), but also in well, CR12. XRD,  
534 SEM/EDS and IR indicates that Fe-ooids consist of goethite (Fig. 6H, Fig. 13, Fig. 14 and Fig.  
535 15), similar to what has been reported in the Wealden Group sandstones of the Eastern Paris  
536 Basin (Brigaud et al., 2018). Considering all facies, the coated grain content is on average  
537 higher in the deeper well (CR12, 41%) than in the shallow boreholes (Beynes and Fouilleuse  
538 with: 23% and 28% respectively).

539 During the first stage of diagenesis (eodiagenesis), framboidal pyrite (<20  $\mu\text{m}$ ) form in the  
540 detrital clay coats, probably in response to the reducing conditions imposed on the marine  
541 sediments during the decay of organic matter (McKay and Longstaffe, 2003).

542 The next event, early in the burial history (at a depth of about 500 m), includes kaolinite  
543 recrystallization through a dissolution-crystallization mechanism which gradually  
544 improvement its crystallinity (Fig. 11). At much the same time, siderite and ankerite formed  
545 as they are also observed coating grains, including around Fe-ooids that later partly  
546 dissolved (Fig. 10C-I). At greater depth, only within the deepest well CR12, some minerals  
547 were partially dissolved, including the iron ooids (goethite), kaolinite, and detrital micas (Fig.  
548 10B-C). Authigenic berthierine crystallized forming a thin and continuous clay coat on both  
549 detrital and earlier eogenetic minerals (Fig. 12). The coat morphology also changed with



550 burial depth, from partial coats (ridges, bridges) to more complete berthierine coats around  
551 the sand grains (Fig. 12). Berthierine coats completely cover grain surfaces, including  
552 eogenetic pyrite and some incipient low temperature quartz overgrowth (Fig. 12). The  
553 growth of quartz was stopped by the formation of the berthierine grain coats (Fig. 12C).  
554 Ankerite coatings coexisted with the berthierine, suggesting that iron played a key role in the  
555 paragenesis. At even greater depths, within the deepest well (CR12), blocky calcite cement  
556 formed partially filling available intergranular pore space.

557 It is believed that the precipitation of berthierine is the first step before the chloritization  
558 and that early berthierine clay coats are the precursor mineral for the iron-rich chlorite,  
559 frequently observed in deeper buried sandstone reservoirs around the world (Morad et al.,  
560 2010; Worden et al., 2020). In our study, it is believed that the berthierine observed at a  
561 burial depth of about 900 m, marks the initiation of chloritization.

562 Quartz overgrowths and authigenic berthierine clay coats formed on the surface of detrital  
563 grains of poorly consolidated sandstones buried at depths of less than 1 km. These two  
564 minerals are cogenetic but growth of secondary quartz in the pore space appears to have  
565 been prevented by the formation of berthierine crystallites at the base of the diagenetic clay  
566 coat. This means that, in the Wealden Group sandstones case study, the inhibition of quartz  
567 cementation in pore spaces of sandstones, which is of major importance for the  
568 preservation of good reservoir quality, was initiated before and not after the conversion of  
569 berthierine to Fe-chlorite, as usually considered in the literature (Pittman and Lumsden,  
570 1968; Larese, et al., 1984; Ehrenberg, 1993; Bloch et al., 2002; Beaufort et al., 2015; Saiäg et  
571 al., 2016; Worden et al., 2020). In the 1990's, works on temperature and kinetics of quartz  
572 growth suggested that most quartz cement precipitates at temperature higher than 80 °C

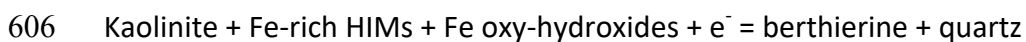
573 (Walderhaug, 1994b, 1994a, 1996; Lander and Walderhaug, 1999; Walderhaug et al., 2000;  
574 Lander et al., 2008) This minimum temperature of 80 °C was partly suggested because  
575 quartz cements were infrequently observed in sandstones that have never been buried at  
576 temperatures greater than 70-80 °C, and also because fluid inclusions in quartz overgrowths  
577 rarely reveal homogenization temperatures below 70-80 °C (Walderhaug, 1994b, 1994a). In  
578 this study, we have shown that small quantities of quartz overgrowths, formed on the  
579 surface of detrital quartz grains at depths of less than 1 km and temperature below 40 °C.  
580 These secondary quartz overgrowths are cogenetic with berthierine minerals, but growth of  
581 quartz was inhibited by the formation of early berthierine clay coats. Thus, this diagenetic  
582 study of the Wealden Group sandstones provides proof that minor amounts of quartz  
583 cement does precipitate at low temperature (<40°C) and shallow burial, giving a clear  
584 exception to the idea that quartz overgrowth in sandstone reservoirs only precipitates at  
585 temperature higher than 80 °C.

#### 586 **Berthierine Crystallization and Reaction Pathway**

587 Berthierine crystallization in sandstone has been interpreted as an early diagenetic process  
588 of iron oxy-hydroxide and kaolinite under anoxic conditions (Taylor, 1990; Hornibrook and  
589 Longstaffe, 1996). The crystallization of berthierine has been reproduced in experiments by  
590 Harder (1989) from iron hydroxide particles in solution under reducing conditions. In  
591 addition, pre-burial berthierine-rich clays have been previously reported in Wealden Group  
592 sediments on the Isle of Wight, UK (Huggett et al., 2018) and in the Weald basin, UK (Taylor,  
593 1990). In these cases, berthierine crystallization was interpreted as replacing faecal pellets  
594 (Huggett et al., 2018) or from iron oxy-hydroxide ooids and kaolinite formed in soils and  
595 transported into the basin. In the present study, we believe the berthierine is  
596 unambiguously of diagenetic origin. It crystallized (1) as authigenic clay coats around detrital

597 grains and early eogenetic minerals (Fig. 12); and (2) by replacement of ooid grains (Fig. 9C).  
598 To form berthierine, specific chemical elements are required such as Fe and Al in a reducing  
599 environment (Hornibrook and Longstaffe, 1996). In our case, berthierine appears to have  
600 formed from a source material consisting of aluminous and ferric detrital clays (mainly  
601 kaolinite, HIMS) and ferruginous-aluminous ooids (Taylor, 1990; Hornibrook and Longstaffe,  
602 1996; Worden and Morad, 2003; Worden and Burley, 2003; Beaufort et al., 2015; Huggett et  
603 al., 2018; Worden et al., 2020).

604 From the mineralogical characteristics of the Wealden Group sandstones of the Paris Basin,  
605 we propose that berthierine is a product of the following reaction:



607 Furthermore, in the absence of silica released from significant compaction of the sediments,  
608 the silica required for the crystallization of the tiny quartz overgrowths formed at the  
609 interface between detrital quartz and berthierine clay coats may also be provided by the  
610 same mineralogical reaction.

611 A basic pH ( $\text{pH} > 7$ ) and low  $\text{pCO}_2$  compatible with a connate seawater are required for the  
612 formation of berthierine (Maynard, 1986). The predominance of  $\text{Fe}^{2+}$  within berthierine  
613 suggests that reducing conditions are necessary (relatively low dissolved oxygen content in  
614 pore waters), such as in sub-oxic iron reducing conditions (Worden and Morad, 2003;  
615 Worden et al., 2020). We also observe berthierine as ooid grains replacing iron oxy-  
616 hydroxide and kaolinite (Fig. 10B-C). Since these sandstones are relatively rich in organic  
617 debris and decaying of organic matter that would explain changes of Eh towards reducing  
618 conditions. The reduction of iron in ferric and aluminous clays and ooids are prerequisites of  
619 prime importance for the crystallization of berthierine. The reduction of ferric iron in  
620 octahedral sheets allows the breakdown of the crystal structure of the ferric detrital clays

621 and the release of  $\text{Fe}^{2+}$ ,  $\text{Si}^{2+}$  and  $\text{Mg}^{2+}$  in solution, while maintaining residual aluminous  
622 sheets, due to the the very low solubility of Al in diagenetic waters. These residual  
623 aluminous sheets form the building blocks for the nucleation and growth of berthierine  
624 crystals when the conditions of stability for this mineral are reached.

625 Within the cores studied, the actual maximum burial depth of Wealden Group sandstones  
626 ranges from 450 m (Beynes wells A and B) to 1000 m (CR12). Comparisons between the  
627 shallower wells and the deeper well confirmed that berthierine only occurred in well CR12 at  
628 910-922m, not in the shallower wells. The present-day temperature of the CR12 well is 36 °C  
629 at a depth of about 900 m. Some studies have shown that the aquifer, located at 900 m  
630 depth, has a present-day temperature of about 38–40 °C (Le Nir et al., 2009; Seguin et al.,  
631 2015). The burial reconstruction for the CR12 well suggests that the Wealden Group  
632 sandstone reservoir is presently at its maximum burial depth, and has probably been at the  
633 same depth for 40 m.y. (Fig. 2). Well CR12 has been buried at more than 800 m since 60 Ma,  
634 and the studied samples may have only been at a temperature of more than 30–33 °C for 60  
635 m.y. (Fig. 2). Therefore, berthierine and the early quartz overgrowths formed at  
636 temperatures ranging from 30 to 36 °C and depths ranging from 850 to 920 m. This zone  
637 would mark the transition from unconsolidated sands to lightly consolidated or brittle  
638 sandstones.

### 639 **The Source-To-Sink Control For Berthierine Crystallization**

640 Iron-rich ooids were well-developed in the upper part of the Wealden Group sandstones in  
641 the deltaic facies association in all the studied wells. These iron-ooids and ironstones are  
642 also reported in the Wealden Group sandstones of the Weald basin, 250 km north-west of  
643 the study area (Taylor, 1990; Akinlotan, 2018, 2019), and in the eastern Paris Basin, 150 km  
644 east of the study area (Meyer, 1976).

645 Some studies show that thick lateritic weathering soils developed during the Early  
646 Cretaceous after successive tectonic events and several sea level falls which resulted in the  
647 emersion and erosion of local domains in western Europe (Meyer, 1976; Thiry et al., 2006;  
648 Barbarand et al., 2018). Laterite refers to iron oxides and aluminium rich soils whereas  
649 ferricrete refers to iron-rich duricrusts in soils, which here are referred to as paleosoils. For  
650 example, on the Hercynian basements, thick kaolinitic weathering profiles and ferricrete  
651 formed during the Early Cretaceous according to palaeomagnetic dating (Fig. 16, Thiry et al.,  
652 2006). Meyer (1976) described the development of soils during the emersion of Wealden  
653 Group sediments in the eastern part of the Paris Basin. In addition, very early sideritic  
654 ironstones (ferricrete) have been reported from the Wadhurst Clay Formation (Valanginian)  
655 within the Weald Basin, SE England (Akinlotan, 2019). These studies suggest that during the  
656 Early Cretaceous, periods of emersion in the basin induced continental conditions, which  
657 resulted in lateritic weathering, followed by erosion on the basin edges (i.e. Ardennes,  
658 Brabant, Central and Armorican Massifs). As several tributaries would have flowed into the  
659 Wealden gutter (Thiry et al., 2006), erosion and weathering by-products such as aluminium  
660 and iron, may have been deposited into the NW–SE Wealden gutter during deposition of the  
661 Wealden Group sandstones (Thiry et al., 2006 and references therein; Fig. 17). Taylor (1990)  
662 suggested that iron-oids or kaolinite ooids resulted from pedogenic processes in laterite  
663 soils which were eroded and then transported to the basin. Such pedogenic processes are  
664 also very good candidates for the supply of HIMs.

665 The Al may also have originated from the dissolution of Al minerals identified within the  
666 Wealden Group sandstone such as kaolinite, smectite, illite or mica (Rivard et al., 2013).  
667 Within the samples studied, partly dissolved kaolinite and detrital mica is observed in  
668 samples containing diagenetic berthierine (Fig. 12). Concerning Fe availability, detrital HIMs

669 may have also played a role. These minerals are important because their high iron ( $\text{Fe}^{3+}$ )  
670 content may have significantly contributed to the source of iron required to form the deeper  
671 berthierine (in the  $\text{Fe}^{2+}$  state). HIMs formation involved in weathering processes are known  
672 to have formed thick kaolinitic weathering profiles and ferricrete levels around the Paris  
673 Basin during the Early Cretaceous (Meyer, 1976; Thiry et al., 2006). The source-to-sink  
674 system in the basin during the Early Cretaceous was conducive to sand sedimentation with a  
675 massive supply of iron ooids and kaolinite in the clay assemblage ( $\approx 40\%$  of kaolinite on  
676 average in the clay assemblage of the Wealden Group sandstones in the Paris Basin). The  
677 origin of these Fe-ooids is not easy to characterize and is a continuing problem in  
678 sedimentary geology (Sturesson et al., 2000; Di Bella et al., 2019). Iron ooids have been  
679 associated with lateritic soil formation in many low latitude areas (Young and Taylor, 1989).  
680 Iron ooids in the Wealden Group sandstones of the Paris Basin around Germigny-sur-  
681 Coulombs have been documented by Taylor (1996). These ooids were characterized by  
682 concentric laminations of goethite around quartz or iron oxide nuclei (Taylor, 1996). Taylor  
683 (1996) proposed a marine environment origin for the goethite ooids in the Wealden Group  
684 sandstones, suggesting that precipitation occurred on the sea-floor or just below the  
685 sediment/marine water interface. A similar process has been suggested by Collin et al.  
686 (2005) for the origin of goethite ooids in Jurassic marine environments of the Eastern Paris  
687 Basin. In the Wealden Group sandstones, the presence of quartz or ironstone nuclei suggests  
688 that the detrital grains (iron fragments and quartz) were most likely derived from the  
689 lateritic and ferricrete paleosoils located in the Eastern Paris Basin (Taylor, 1996). Although  
690 weathering during a warm climate during the Early Cretaceous is undeniable (Thiry et al.,  
691 2006), we believe an eodiagenesis process in estuarine environments, at the sediment  
692 surface and accretion of Fe-oxy-hydroxide around nuclei, is a more reasonable explanation

693 for the origin of goethite ooids (Schiavon, 1988; Taylor, 1996). Iron-oxidizing bacteria and/or  
694 fungi could have promoted this eodiagenetic process (Préat et al., 2008). Weathering  
695 processes also release kaolinite and HIMs within oxidizing waters, which promotes the  
696 particulate transport of Al and Fe into the clastic sedimentary formations (Morad et al.,  
697 2000). After shallow burial (here, greater than 800 m), dissolution of the Fe-bearing minerals  
698 under reducing condition would release  $\text{Fe}^{2+}$  in solution to form berthierine by the  
699 interaction between dissolved iron in waters and kaolinite during shallow burial (Rivard et  
700 al., 2013). Therefore, the contribution of minerals from Al and iron-rich soils (such as HIMs)  
701 to the source material appears to play a key role in the formation of berthierine  
702 crystallization and thus the subsequent chloritization of the sandstones that will occur at  
703 greater burial depths.

#### 704 **Implications for the early Determinism of the Reservoir Qualities of Chloritized Sandstones**

705 Berthierine in the Lower Cretaceous Wealden sediments of the Paris Basin can be  
706 considered as a precursor of Fe-rich chlorite coatings (e.g. Worden et al., 2020). With  
707 increasing burial depth, berthierine would be converted into Fe-rich chlorite through a  
708 chlorite-berthierine mixed as observed in the Springhill sandstones (Early Cretaceous,  
709 Argentina, Austral Basin) which were buried to about 2400 m and at a temperature of more  
710 than 80 °C (Tinseau, 2002). This berthierine to Fe-Chlorite transformation in sandstones has  
711 been reproduced experimentally by Aagaard et al. (2000) and chlorite-berthierine mixed-  
712 layers have been reported from XRD investigations in many chloritized sandstone reservoirs  
713 around the world (Reynolds, 1988, 1992; Hillier and Velde, 1992; Ryan and Reynolds, 1996;  
714 Ryan and Hillier, 2002). Finally, on the basis of high resolution TEM investigations,  
715 microstructural models have been proposed to explain the volume-conserving aspect of the

716 berthierine-to-chlorite reaction and the related formation of chlorite-berthierine mixed  
717 layers (Banfield and Bailey, 1996; Xu and Veblen, 1996). Although still debated, it is broadly  
718 agreed that the temperature at which Fe-rich chlorite replaces berthierine in natural  
719 systems through mixed-layer minerals ranges from 40 to 120 °C (Jahren and Aagaard, 1989;  
720 Hillier and Velde, 1992; Ehrenberg, 1993; Aagaard et al., 2000; Worden and Morad, 2003;  
721 Beaufort et al., 2015; Šegvić et al., 2020; Worden et al., 2020). Sandstones of the Wealden  
722 Group of the Paris Basin whose maximum burial depth and temperature never exceeded  
723 1 km and 40 °C respectively, appear to allow a perfect case study for examining the  
724 petrographic and mineralogical characteristics of sandstones which underwent only incipient  
725 pre-chloritization processes (i.e. in which replacement of the berthierine precursor by Fe-  
726 bearing chlorite has not occurred).

727 A major finding of this study is that authigenic berthierine coats form at shallow depths and  
728 at lower temperatures than that at which the berthierine-to-chlorite conversion is effective  
729 and that berthierine grain coats inhibit incipient, low-temperature quartz cementation on  
730 detrital quartz grains (Fig. 12C). This means that the key mineral primarily controlling  
731 reservoir quality of the deeply buried sandstone reservoirs by inhibiting excessive quartz  
732 growth is berthierine, rather than iron-rich chlorite.

### 733 **CONCLUSIONS**

734 1. Based on detailed petrographic and diagenetic study of the Wealden Group  
735 sandstones of the Paris Basin we document formation of berthierine minerals at  
736 shallow depths and low temperatures (0.8–1 km and 35–40 °C) prior to the formation  
737 of chlorite.



- 738 2. The sandstones are mainly feldspathic litharenites deposited in a transgressive  
739 sequence of coastal environments ranging from fluvial, estuarine and deltaic  
740 environments to shoreface environments.
- 741 3. In core samples from 400 m to 600 m depth, sandstones include iron-ooids  
742 (goethite), kaolinite and hydroxy-interlayered clay minerals (HIMs). In a different well  
743 (CR12) sampled at a depth of 900–970 m, clay minerals are quite different, and  
744 include berthierine, which occurs as authigenic clay coats around detrital grains with  
745 a typical honeycomb texture. The main controlling factor in the formation of  
746 berthierine is burial depth.
- 747 4. Small incipient quartz overgrowths were documented on the surface of detrital  
748 quartz grains that were buried less than 1 km of burial depth and at temperatures  
749 below 40 °C.
- 750 5. The arrangement of berthierine crystals at the base of an early clay grain coat  
751 appears to have inhibited the development of early quartz overgrowths. Our study  
752 reveals that the key mineral controlling reservoir quality of deeply-buried sandstone  
753 reservoirs is berthierine, challenging the common assumption that iron-rich chlorite  
754 is the most important mineral inhibiting the development of quartz cement. Iron-rich  
755 chlorite is known to replace berthierine at depth and high temperatures (>70-80°C)  
756 but this study suggests that berthierine is already a decisive factor in inhibiting quartz  
757 overgrowth at shallower burial depths.
- 758 6. During a period conducive for the development of thick kaolinite-rich weathering  
759 profiles or ferricrete, iron-ooids, kaolinite or hydroxy-interlayered clay minerals  
760 (HIMs) produced from the lateritic soils were eroded and then transported into the  
761 basin. Kaolinite or hydroxy-interlayered clay minerals (HIMs) are key candidates to be

762 the precursor and source of berthierine. During burial, the crystallization of  
763 authigenic berthierine and early quartz overgrowth are associated with the  
764 dissolution of kaolinite and Fe-rich HIMs and replacement of iron-oids under  
765 reducing conditions. The reduction of ferric iron ( $\text{Fe}^{3+}$ ) in ferric clays and ooids  
766 releases  $\text{Fe}^{2+}$  which is conducive to the nucleation and growth of berthierine.

767 7. The source-to-sink context of the Paris Basin during the Early Cretaceous controlled  
768 the supply of sands, clays, in particular kaolinite and HIMs, and iron-oids in the  
769 Wealden gutter in the centre of the Paris Basin.

770 8. Estuarine and deltaic sedimentary environments were ideal for berthierine  
771 crystallization, favouring mixing between sands, kaolinite and ferric and aluminium-  
772 rich clay assemblages and iron-oids (and organic matter entrapment, reducing  
773 conditions). This study enhances our knowledge both of the mineral reactions  
774 involved and mode of formation. This study also shows how understanding mineral  
775 reactions in low temperature, shallow burial settings can provide important insights  
776 into the key factors that controlling deep reservoir quality.

777

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1127

## 1128 **FIGURE CAPTIONS**

1129 **Figure 1:** A- Geological map and generalized column for the Paris Basin (scale 1:1,000,000),  
1130 showing the location (black stars) of the five Wealden Group sandstone wells examined in  
1131 this study. FO= Fouilleuse wells (FO-01 and FO-06), Beynes wells (A & B), and CR= Crouy-sur-  
1132 Ourcq well (CR12). B- West-East geological cross section of the Paris Basin, modified after  
1133 Gély and Hanot (2014). Well CR12 is projected onto the cross-section. C- Palaeogeographical  
1134 map of the Paris basin during the Hauterivian stage, (modified from Dercourt et al., 2000).

1135

1136 **Figure 2:** Burial history curve for the CR12 well at Crouy-sur-Ourcq, Paris Basin  
1137 (decompaction not computed). The geothermal gradient at 2.6 °C/100 m is based on the a  
1138 present-day temperature of 35.5 °C in the well at a depth of 900 m.

1139

1140 **Figure 3:** Composite log from well CR12 (Crouy-sur-Ourcq) showing location of samples,  
1141 average grain size, sedimentary structures, faunal assemblages, corresponding palaeo-

1142 environment interpretation; well log gamma-ray; interpreted transgressive/regressive cycles  
1143 (derived from Rusciadelli, 1996); dominant clay types (XRD<2 µm fraction); and estimated  
1144 grain coat coverage for selected samples.

1145

1146 **Figure 4** : Core photographs showing primary facies in : A- Facies association FA1 (Fluvial)  
1147 (Well CR12 #CR-03 – 967.70 m) Medium grained, through-cross bedded sandstones, with  
1148 granules and organic debris. B- FA1 (Fluvial) (Well CR12 #CR-02 – 971.90 m) Muddy  
1149 siltstones, with coal debris and deformed and compacted root trace. C Facies association  
1150 FA2 (Estuarine) (Well CR12 #CR-19 – 904.45 m) Medium-grained sandstones with foresets  
1151 underlined by organic debris (black arrows) interpreted as small tidal dunes. Trace fossils  
1152 include *Teichichnus* (Te), *Psilonichnus* (Psi) and *Palaeophycus* (Pa). The top of dunes appears  
1153 eroded and largely bioturbated. D- FA2 (Estuarine) (Well FO-01 – 454.30 m) Fine to medium  
1154 grained; current-rippled sandstones with tidal mud couplets (arrows). E- FA2 (Estuarine)  
1155 (Well A – 417.80 m) Fine grained sandstones with visible current ripples (CR) and silty-clay  
1156 drapes (arrows). F- FA2 (Estuarine) (Well CR12 – 940.60 m) Heterolithic fine grained, wavy  
1157 bedded (WB) sandstones with clay drapes. Low biodiversity bioturbations (*Planolithes*: PI).  
1158 G- FA2 (Estuarine) (Well CR12– 914.5 m) Very fine to fine grained sandstones, with clay  
1159 drapes, lenticular bedding (LB), wavy bedding (WB) and flaser bedding (FB). H- Facies  
1160 association FA3 (Deltaic) (Well CR12- 978.50 m) Alternating claystone and silty to very fine-  
1161 grained, current-rippled sandstone, with syneresis cracks (SC) and *Planolithes* (PI). I- Facies  
1162 association FA4 (Shoreface) (Well CR12 – 897-899 m) Well sorted, medium to coarse-grained  
1163 sandstones with low angle cross stratification and visible *Skolithos* burrows (arrow).

1164

1165 **Figure 5:** Quartz, Feldspar, Lithic (QFL) ternary diagrams with samples from the five studied  
1166 wells after the Classification of Folk (1974). Key to Facies Nomenclature: FA1-Fluvial, FA2-  
1167 Estuarine; FA-3-Deltaic; FA5-Offshore

1168

1169 **Figure 6:** Thin section and Scanning Electron Microscopy (SEM) photomicrographs from  
1170 fluvial and estuarine samples. A- Thin section image showing clay-coated sand grains (quartz,  
1171 feldspars and lithics) with visible bridges or aggregates (Well CR12, sample CR12-04, 956 m).  
1172 B- SEM photomicrograph showing clay-coated quartz grain, with visible ridges and/or  
1173 aggregated clay coats (Well CR12, sample CR12-04, 957 m). C- SEM photomicrograph  
1174 showing aggregated clay coat on detrital quartz grain (Well CR12, sample CR12-12, 931 m).  
1175 D- Closeup view of C showing that coatings are mainly composed of clay minerals. E- Thin  
1176 Section image of greensand containing abundant compacted green peloids (Well FO-06,  
1177 sample FO-06-17, 487.7 m). F- Backscatter SEM image of polished thin section showing clay  
1178 grain coats and bridges (Well FO-06, sample FO-06-12, 498.2 m). G- Thin section image of  
1179 iron-oid facies showing ooids of goethite (G), (Well FO-01, sample FO-01-10, 448 m). H-  
1180 SEM photomicrograph showing detrital quartz (Qz) grain coated by successive laminae of  
1181 goethite (well FO-06, sample FO-06-15, 490 m). Key: Qz.= Quartz; Fd= Feldspars; G =  
1182 Goethite; Gp = Green peloids.

1183

1184 **Figure 7:** Chart showing average clay coat coverage by facies. The total coat coverage classes  
1185 are shown above the histograms for each facies. Visual coat coverage estimates are  
1186 summarized in Legend.

1187

1188 **Figure 8:** X-Ray diffractograms of the pre-burial clays extracted from Wealden Group  
1189 sandstones. A.D. = Air Dried; E.G. = Ethylene-Glycol.

1190

1191 **Figure 9:** Ternary diagrams of the point chemical analyses for the different types of clay  
1192 particles identified in pre-burial and diagenetic clay coats of the Wealden Group sandstones.  
1193 A-  $MR^{3+}$ -  $2R^{3+}$ - $3R^{2+}$  diagram (Velde 1985). B- Al-Fe-Mg diagram. Iron has been arbitrarily  
1194 considered as  $Fe^{3+}$  in pre-burial clay particles and  $Fe^{2+}$  in diagenetic clay particles.

1195

1196 **Figure 10:** Thin section and SEM photomicrographs from estuarine samples showing: A- SEM  
1197 view of framboidal pyrite (Py) embedded within clay coat with ridged texture (Well CR12,  
1198 sample CR12-12, 931.1 m). B- Backscatter SEM view of pyrite (Py) embedded within clay  
1199 coating, a partially dissolved iron-rich ooid, and pore-bridging clay (white arrow), (Well CR12,  
1200 sample CR12-11, 934 m). C- Thin section image showing small diagenetic siderite rhombs  
1201 (white arrow) intermixed with clay grain coat on a detrital quartz grain (Well CR12, sample  
1202 CR12-18, 909 m). D-F- SEM views showing morphology of rhombic siderite on quartz (Well  
1203 CR12, sample CR12-18, 909 m). G- Thin section image showing patchy ankerite grain coat  
1204 (Well FO1, sample FO1-09, 453.9 m). H-I -SEM views showing the morphology of patchy  
1205 ankerite on detrital grain (Well FO1, sample FO1-09, 453.9 m). J- SEM view showing  
1206 framboidal pyrite intermixed with clay coat. Framboidal or cubic pyrite was observed  
1207 associated with both types of Fe-carbonates. Well FO1, sample FO1-09, 453.9 m). Key: Qz.=  
1208 Quartz Py. = Pyrite; Fd = Feldspar

1209

1210 **Figure 11:** A-B- SEM images showing vermicular kaolinite (arrow) intermixed with detrital  
1211 clay coats partially filling a pore in fluvial facies (FA1), (Well FO-01, sample FO-01-03, 505 m).

1212 C- Composite FTIR spectra of samples from well FO-01 in the OH-stretching bands region  
1213 showing decreasing structural ferric iron content and increasing crystallinity of kaolinite with  
1214 increasing depth.

1215

1216 **Figure 12:** SEM images of authigenic clay coats in sample CR12-14 from the estuarine facies.  
1217 A- Low magnification view of clay-coated grains. B- Closeup showing honeycomb  
1218 morphology of iron-rich berthierine coating intermixed with framboidal pyrite and  
1219 vermicular kaolinite. C- SEM image of an ultra-thin FIB section showing the contact between  
1220 iron-rich clay minerals (berthierine) and the detrital quartz grain small incipient quartz  
1221 overgrowths that appear to be inhibited by the crystallization of the early berthierine clay  
1222 coat.

1223

1224 **Figure 13:** Comparison of air-dried (A.D.) and ethylene glycol (E.G.) saturated, oriented XRD  
1225 pattern of berthierine-bearing clay material (<2  $\mu\text{m}$ ) from an estuarine sandstones buried at  
1226 a depth exceeding 900m (Well CR12, sample CR12-18, 909.8m). Key: HIMs = hydroxy-  
1227 interlayered clay minerals; solid bar = theoretical  $00\ell$  reflection of berthierine; dotted bars =  
1228 theoretical  $00\ell$  reflections of berthierine.

1229 **Figure 14:** Comparison showing XRD patterns of randomly oriented clays from sandstones  
1230 buried in shallow wells (Well B, sample B-06 at 423.7 m and Well FO-06, sample FO-06-12 at  
1231 426.2 m) compared to deeper well CR12 (Well CR12, samples CR12-18 at 909.8 m and CR12-  
1232 14 at 922.3 m). A- Diffractograms show difference between kaolinite reflections (dotted  
1233 lines) and berthierine reflections (solid lines). The solid lines marked with an asterisk  
1234 correspond to the XRD reflections of berthierine which do not overlap with reflections of  
1235 kaolinite or any other types of 2:1 dioctahedral phyllosilicates (such as HIMs or illite). B-

1236 Closeup of the XRD peaks in the angular region of 060 reflection for phyllosilicates (58-64°  
1237 2θ, Cu Kα). Miller indices are indicated for each hk reflection.

1238

1239 **Figure 15:** FTIR spectra comparing the clay fraction for different estuarine samples in Well  
1240 CR12. Berthierine has been identified by SEM observations and X-ray diffraction in each of  
1241 these samples (CR12-14, CR12-18 and CR12-19).

1242

1243 **Figure 16:** Paragenetic sequence for the Wealden Group sandstones in the Paris Basin. A list of  
1244 potential pre-burial aluminium/iron-rich minerals includes: Fe-Al ooids; Fe-bearing kaolinite;  
1245 and Hydroxy-interlayered clay minerals (HIMs).

1246

1247 **Figure 17:** A- Palaeogeographic map of France and Belgium during the Early Cretaceous  
1248 period showing palaeo-weathering zones (from Thiry et al., 2006). B- NW–SE transect (A-A'  
1249 on map A) showing structure of the Wealden gutter and its edges during the Barremian  
1250 (from Thiry et al., 2006).

1251

1252 **Table 1:** Summary of facies and facies association identified in the Wealden Group  
1253 sandstones of the Paris Basin.

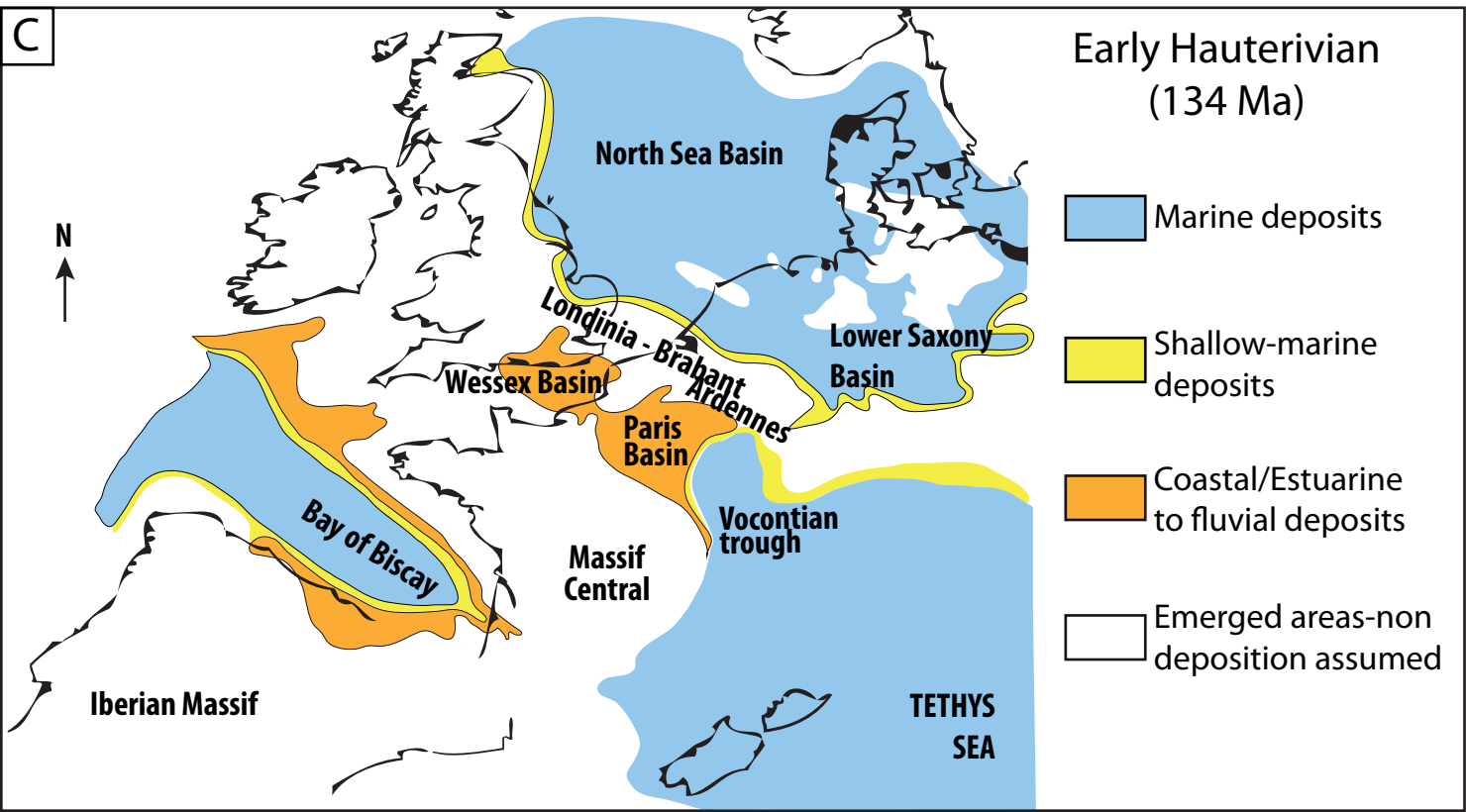
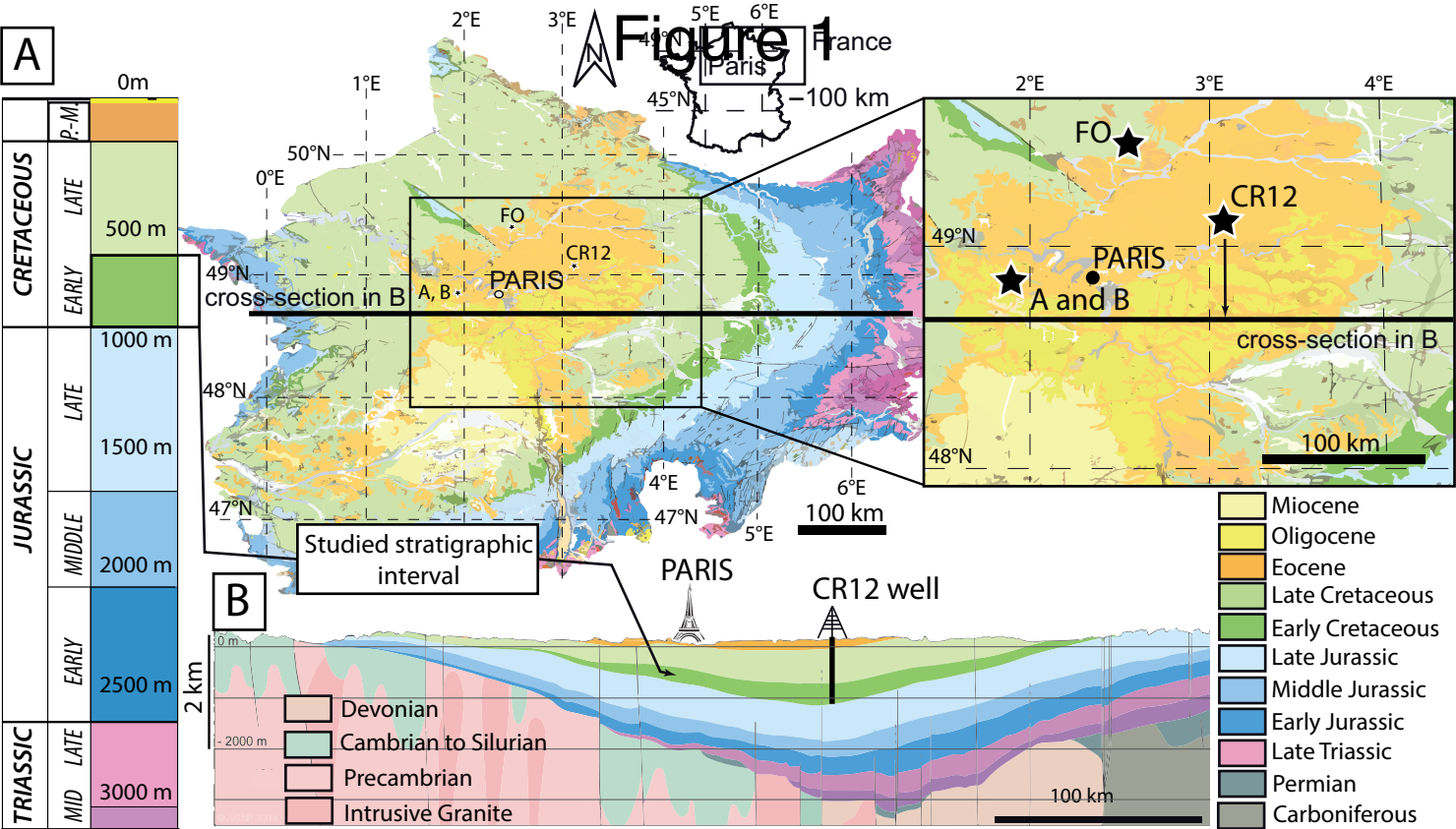
1254 **Table 2:** Average grain composition by automated point count analysis, estimated clay coat  
1255 coverage, and clay fraction composition (XRD) by facies association.

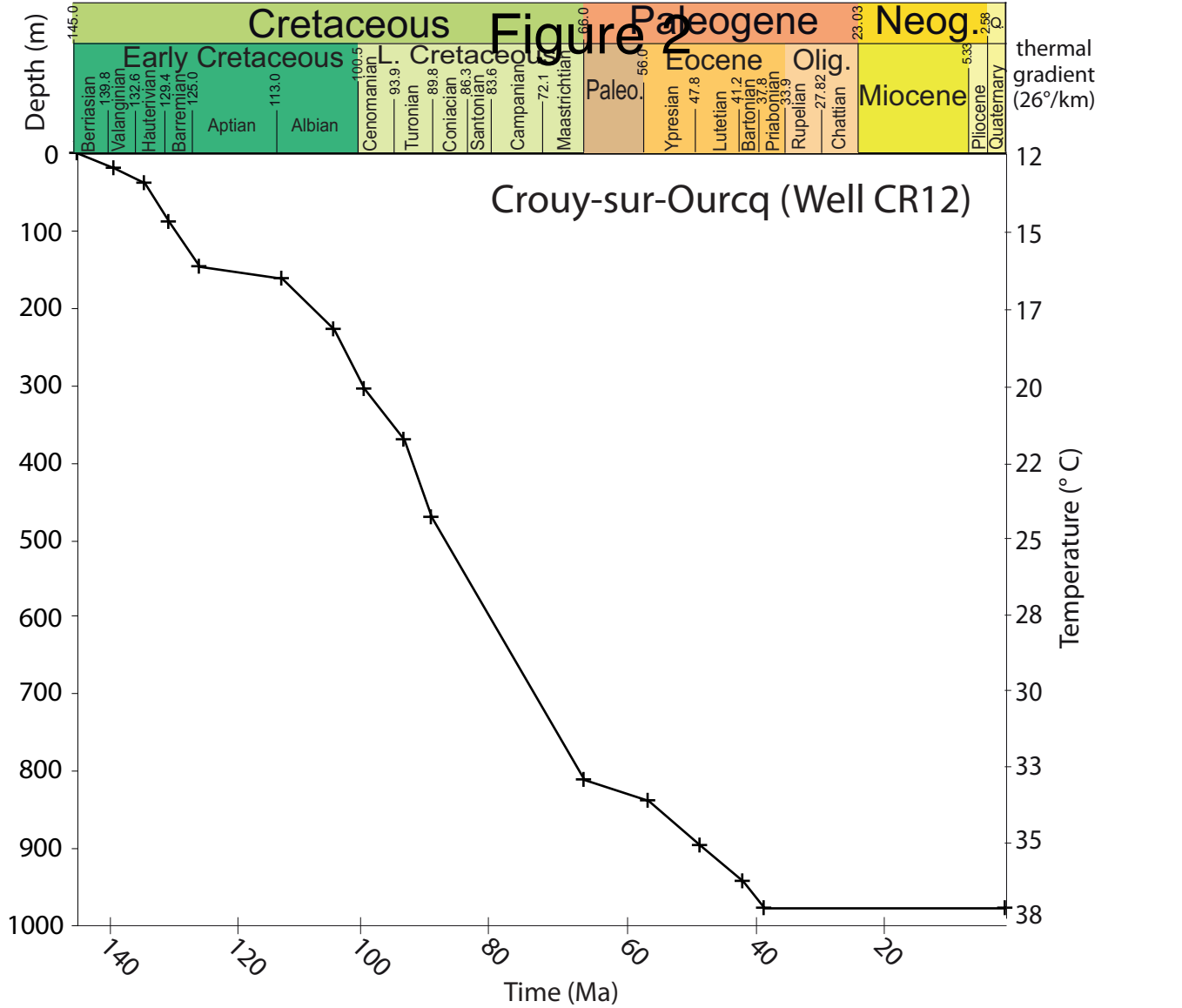
1256 **Table 3:** Chemical compositions of clay particles from clay coats within Wealden Group  
1257 sandstones.

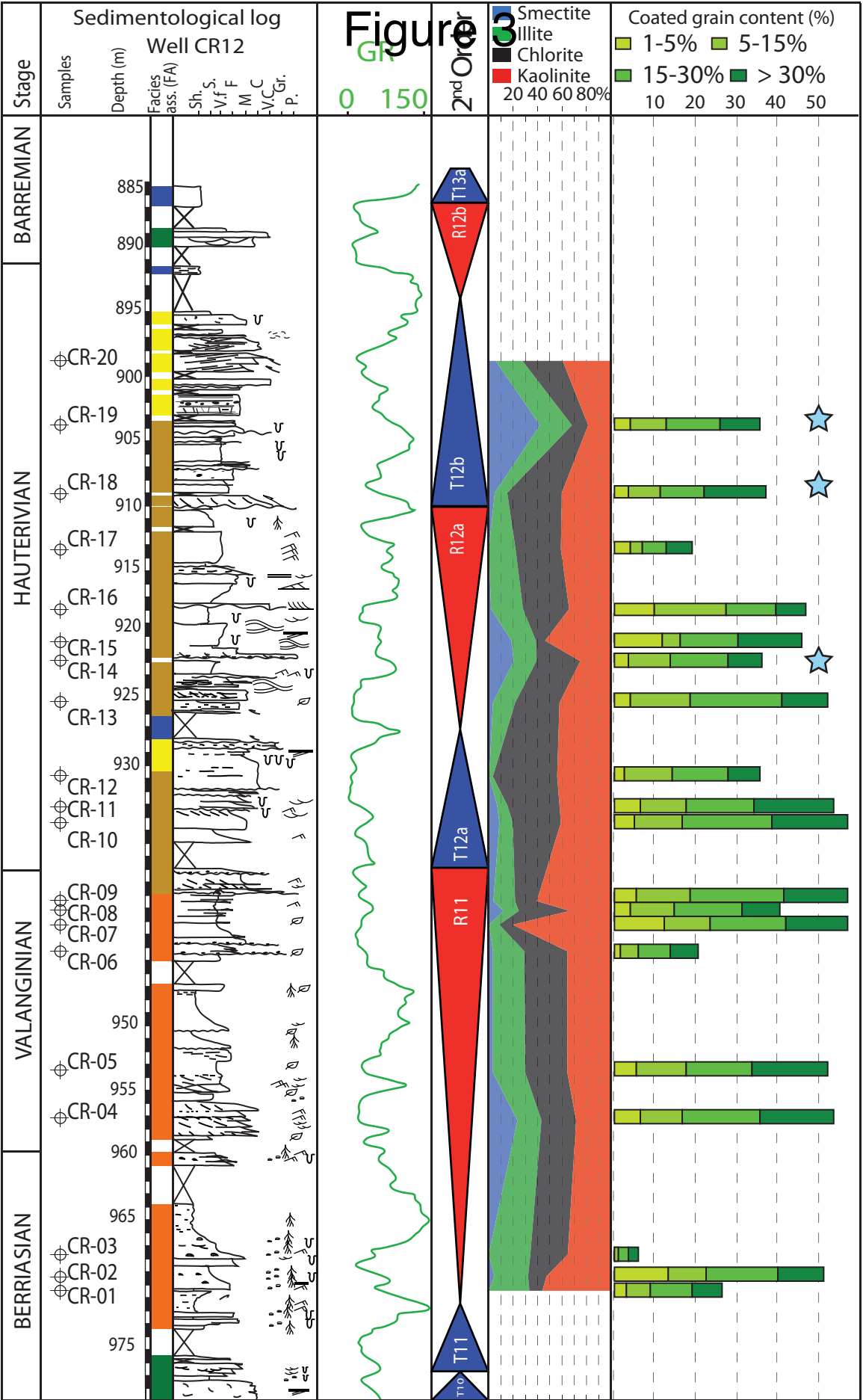
1258

1259 <sup>1</sup>GSA Data Repository item 20XXxxx, Supplemental Material Table S1 displaying sample  
1260 description and petrographical/mineralogical composition (sample list, well location  
1261 projection WGS84, sample depth, petrographical and clay mineral quantifications), is  
1262 available online at [www.geosociety.org/pubs/ft20XX.htm](http://www.geosociety.org/pubs/ft20XX.htm), or on request from  
1263 [editing@geosociety.org](mailto:editing@geosociety.org).









Facies associations

FA1: Fluvial    FA2: Estuarine    FA3: Delta    FA4: Shoreface    FA5: Offshore

\ / Ripple    \ / Hummocky cross-stratification    \ / Roots    \ / Bivalves  
 \ / Climbing ripple    \ / Lenticular bedding    \ / Leaves debris    \ / Berthierine  
 \ / Trough-cross bedding    \ / Low angle stratification    \ / Bioturbation

# Figure 4

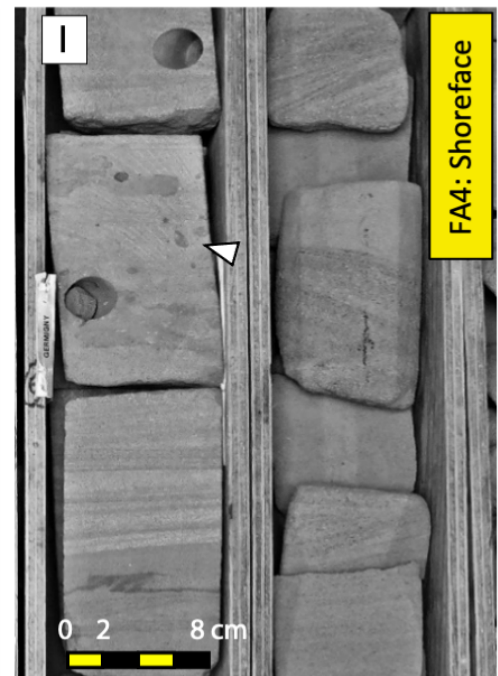
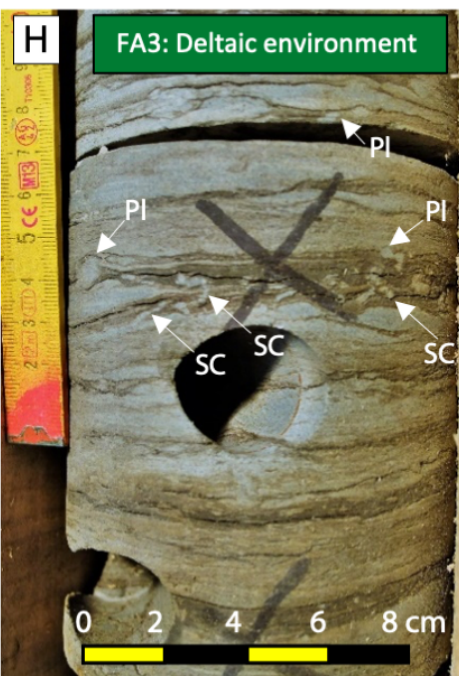
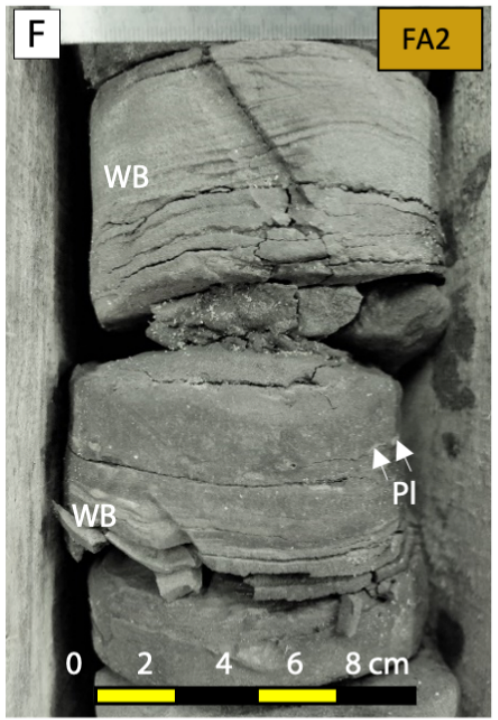
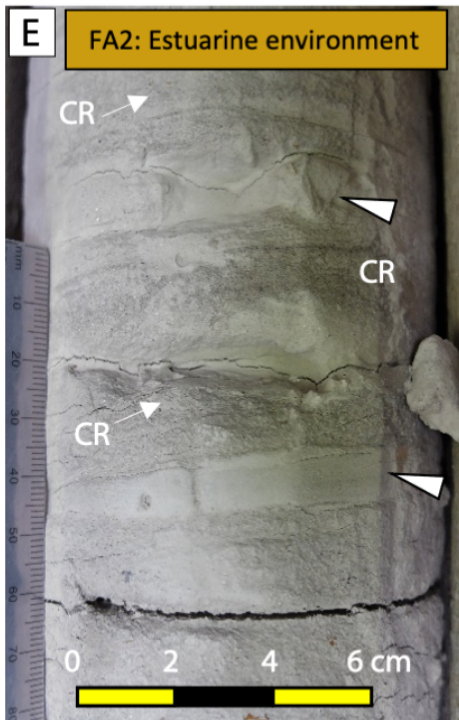
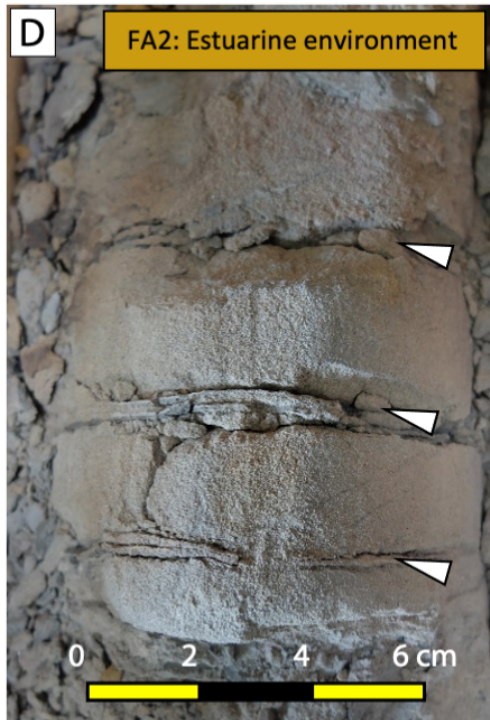
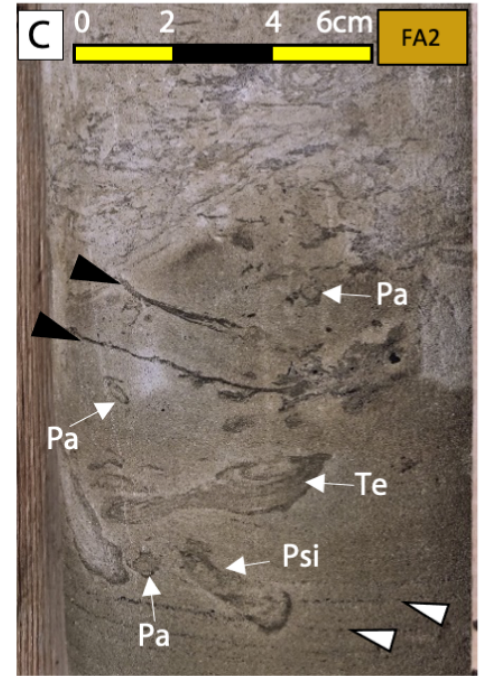


Figure 5

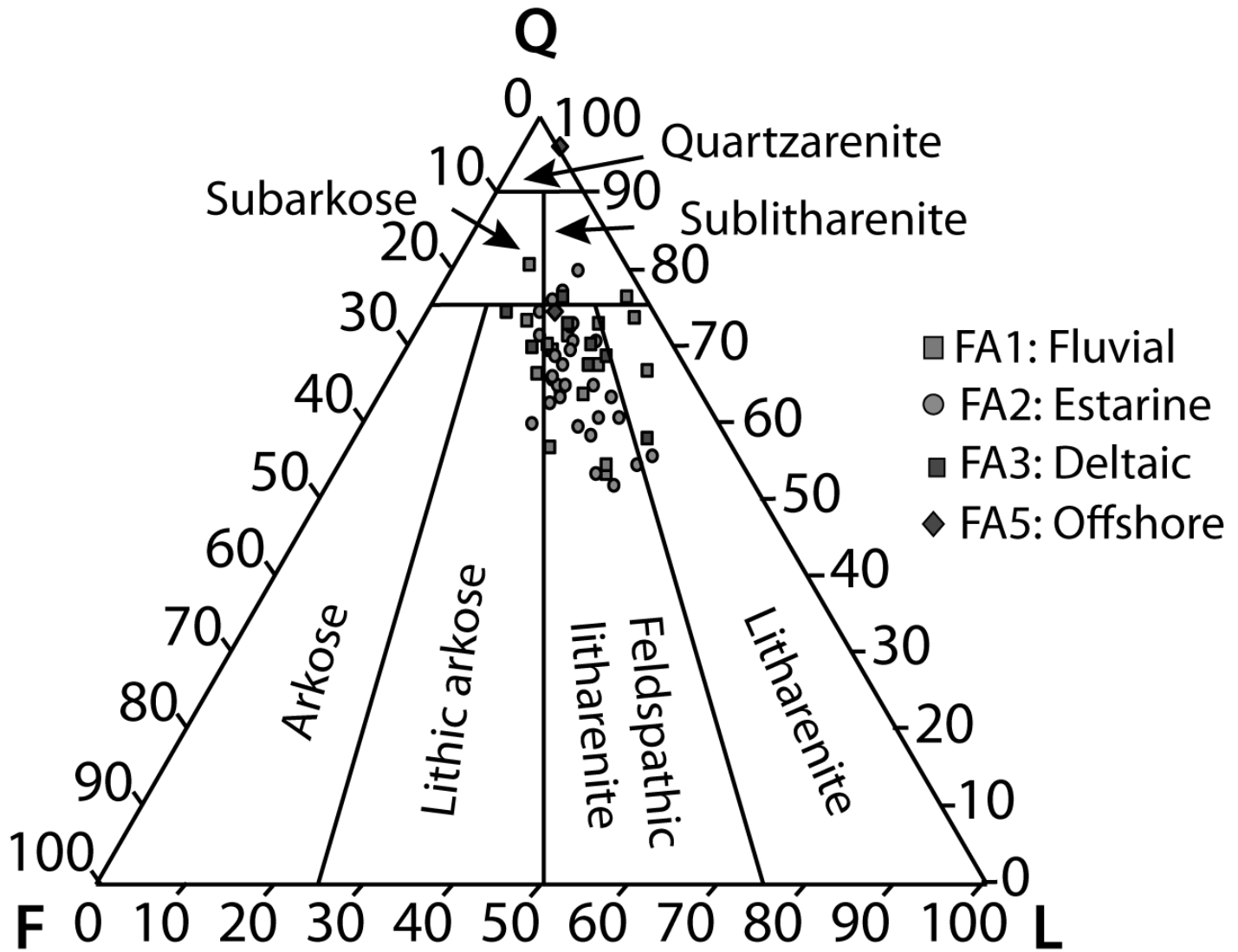
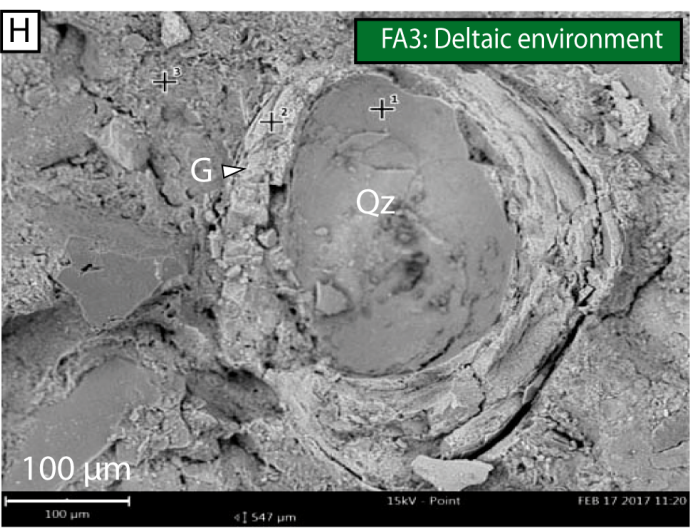
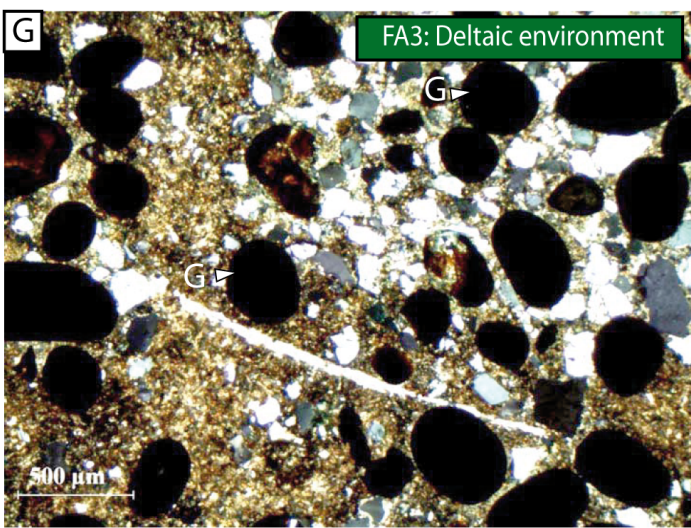
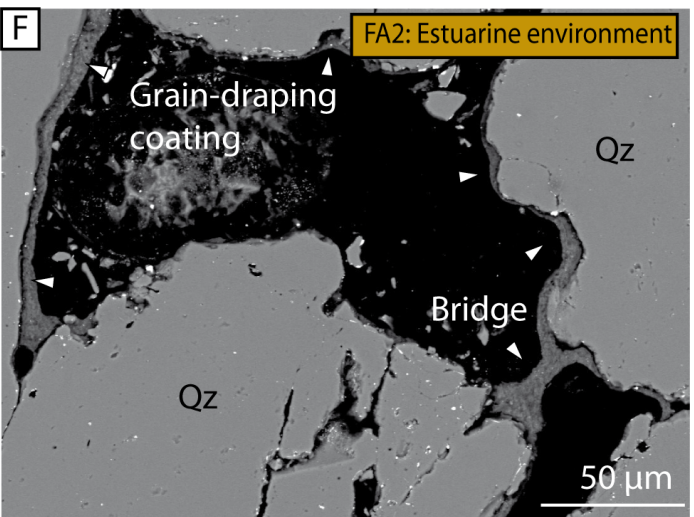
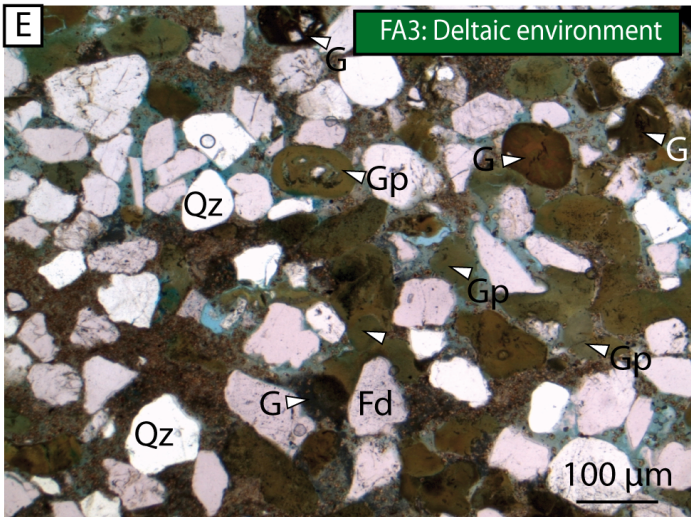
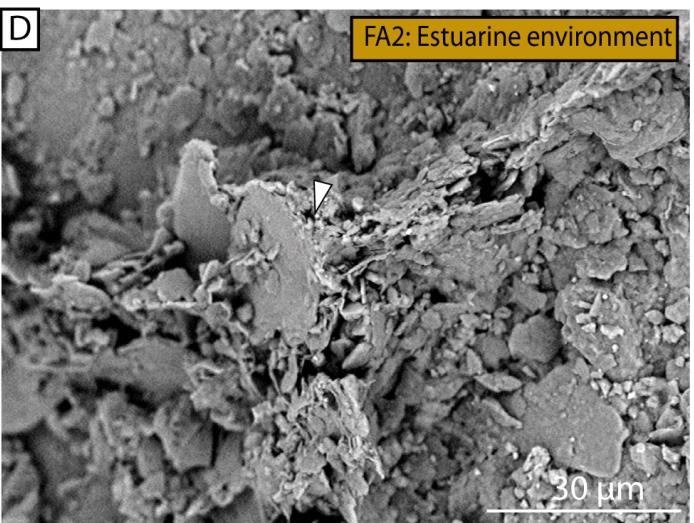
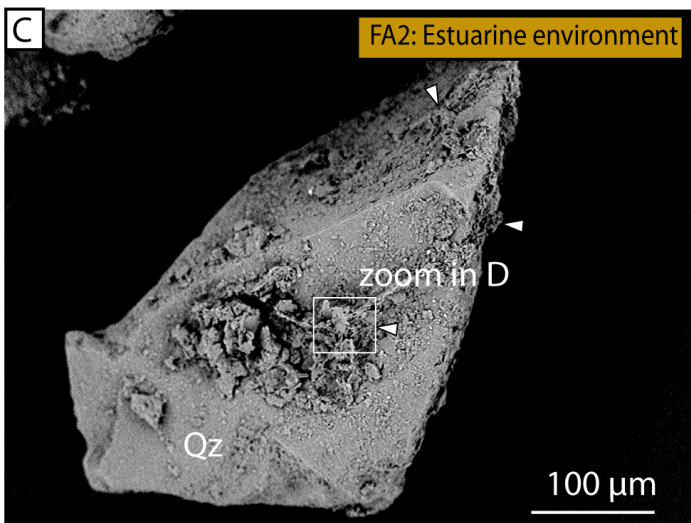
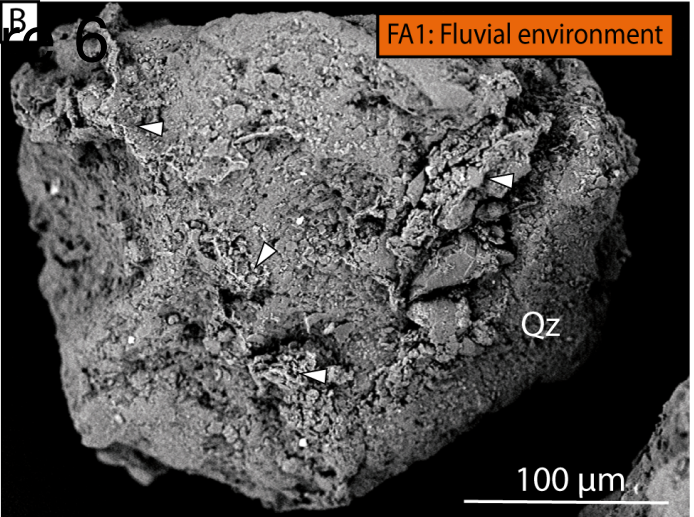
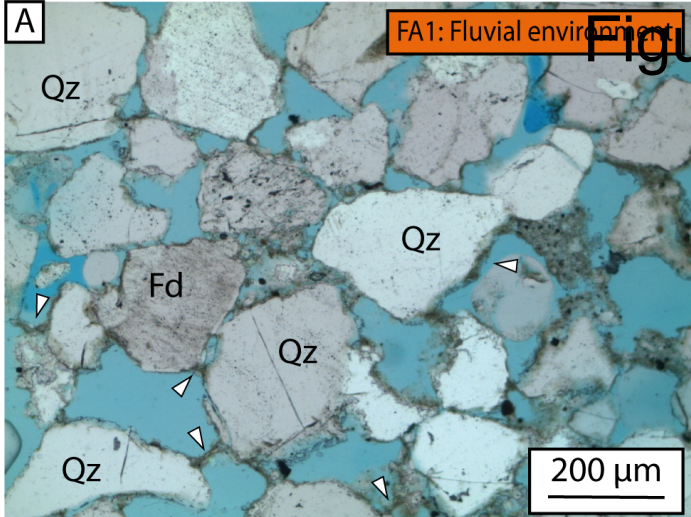
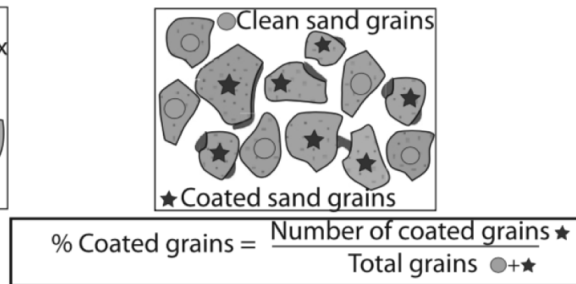
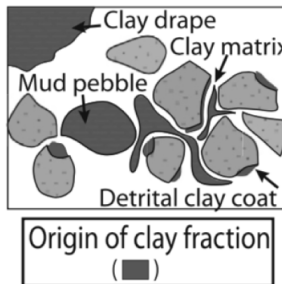
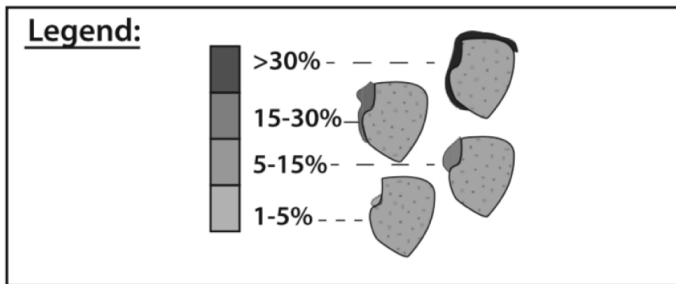
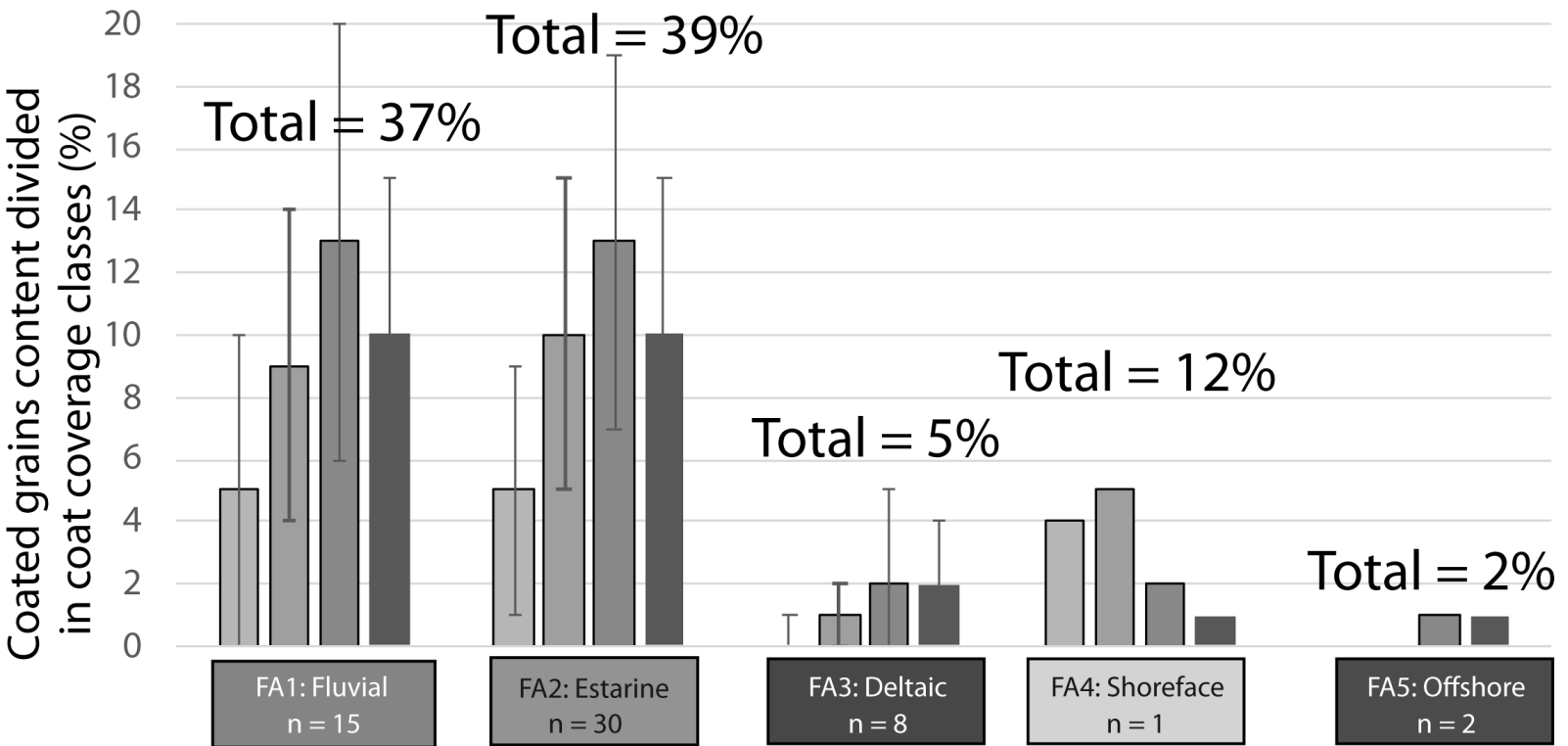


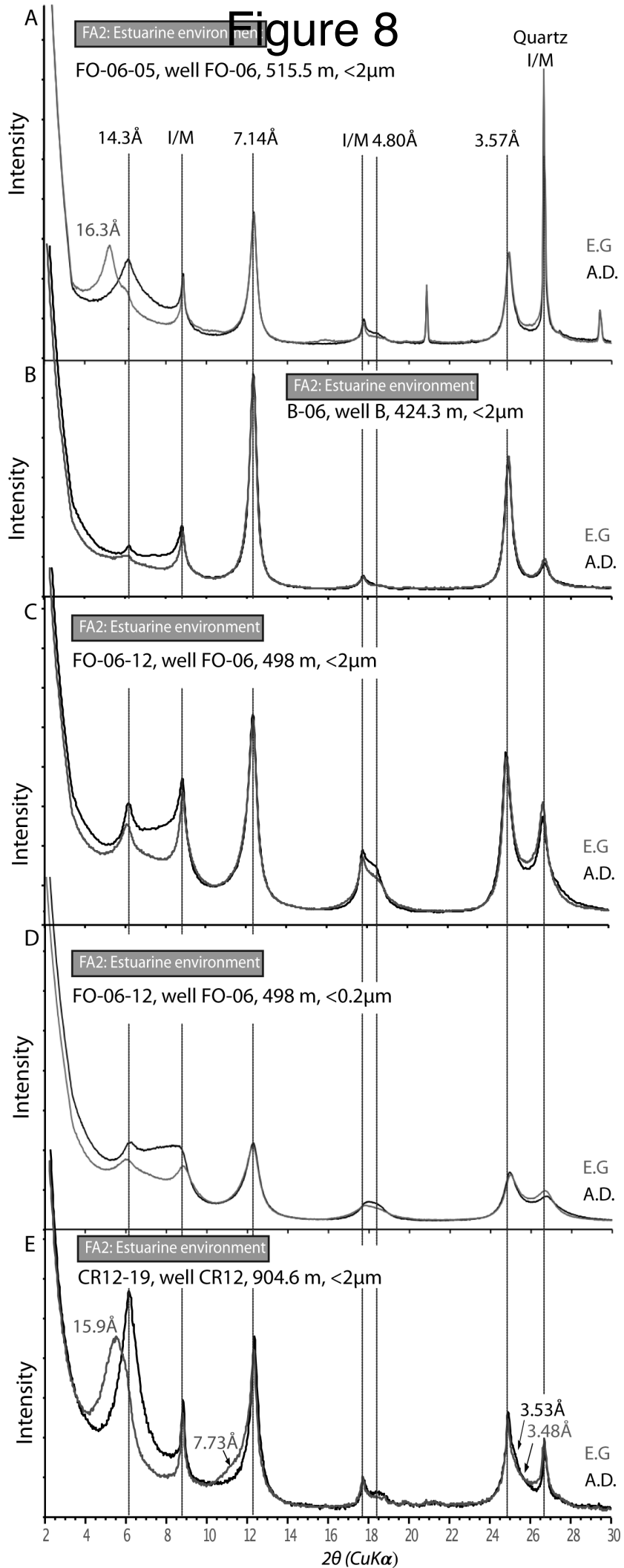
Figure 6



# Figure 7

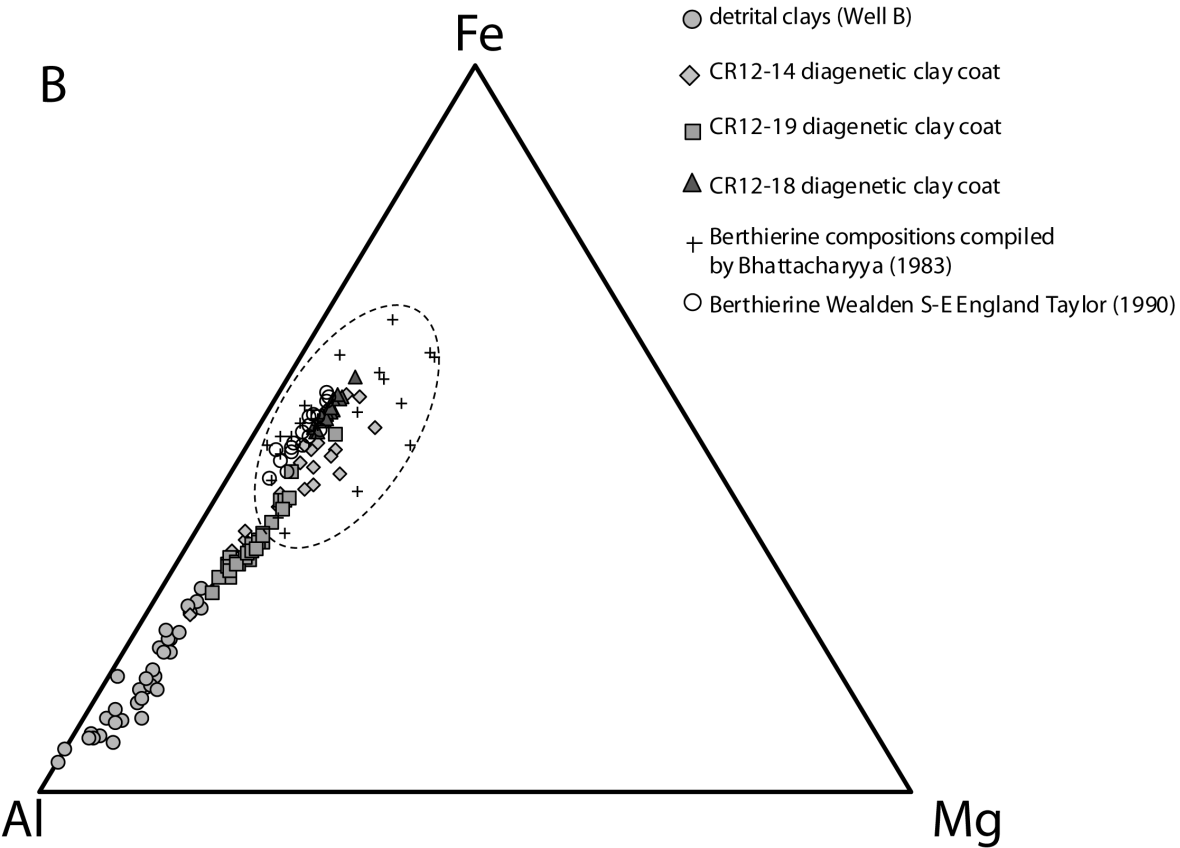
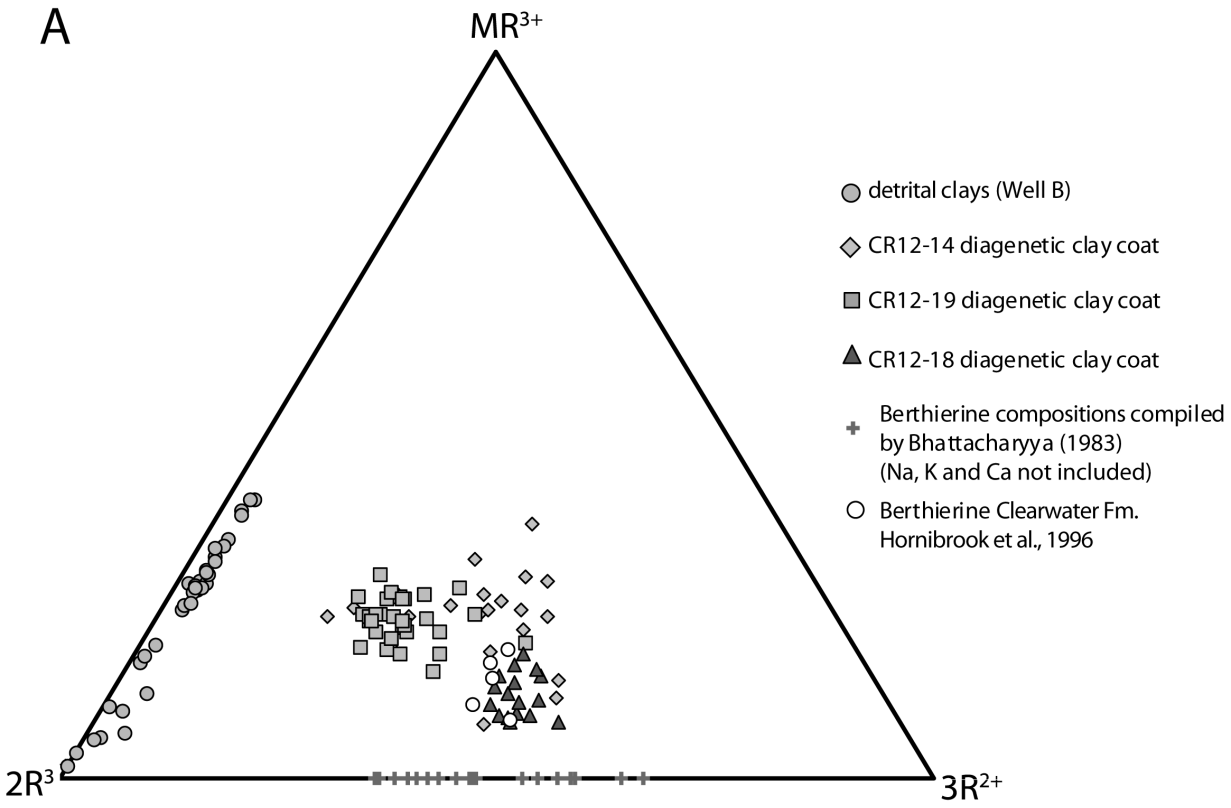


# Figure 8





# Figure 9



# Figure 10

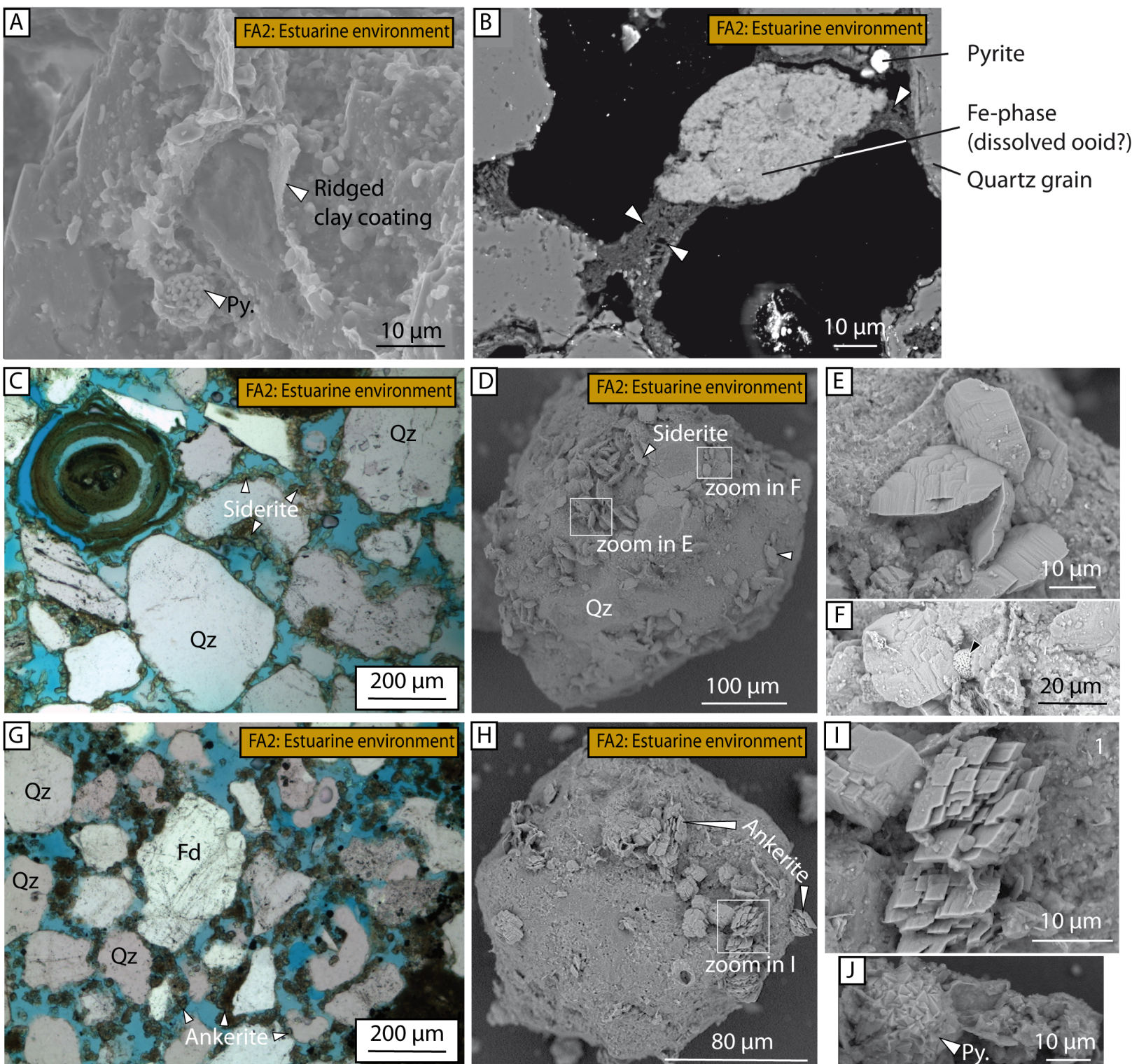


Figure 11

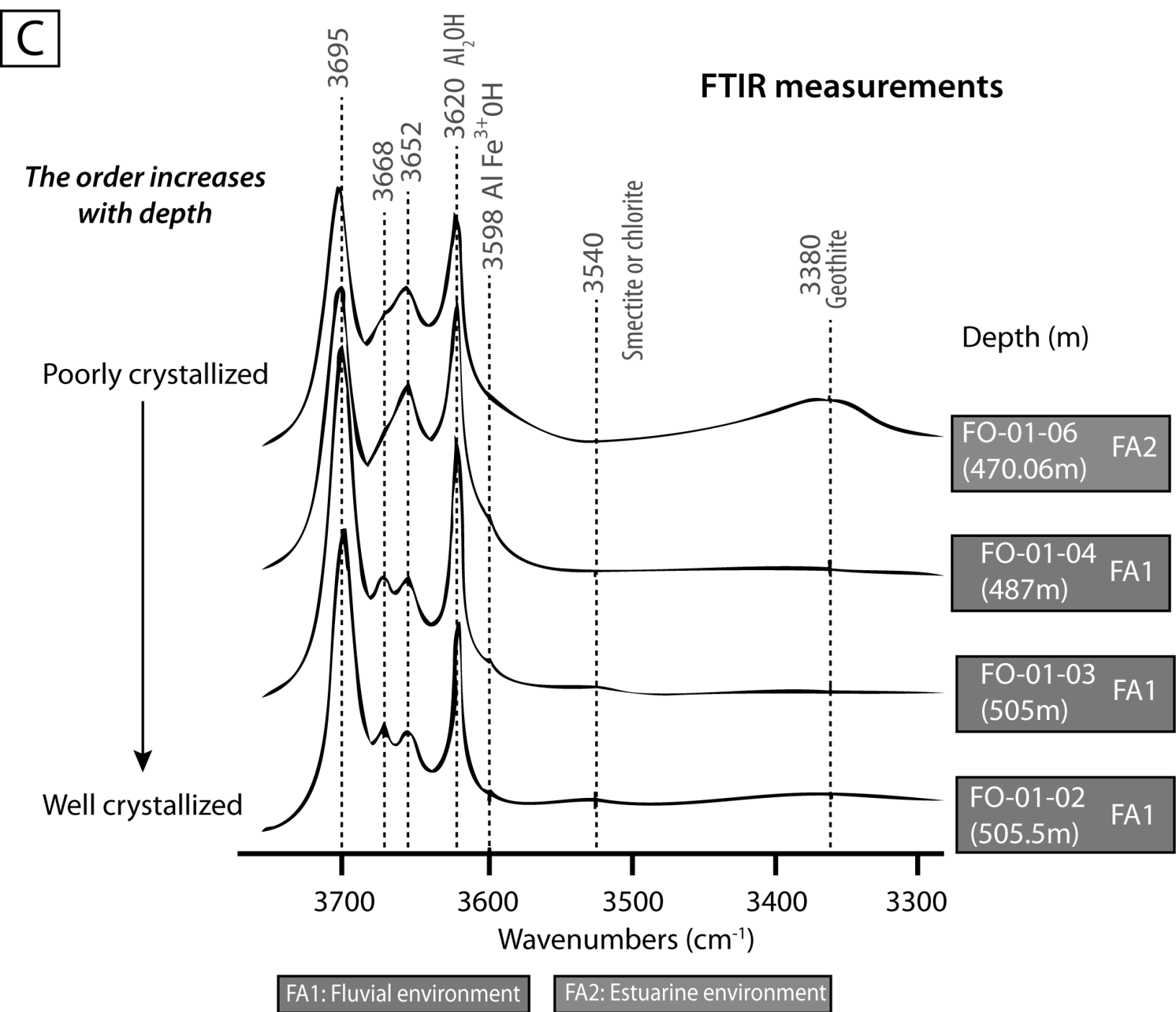
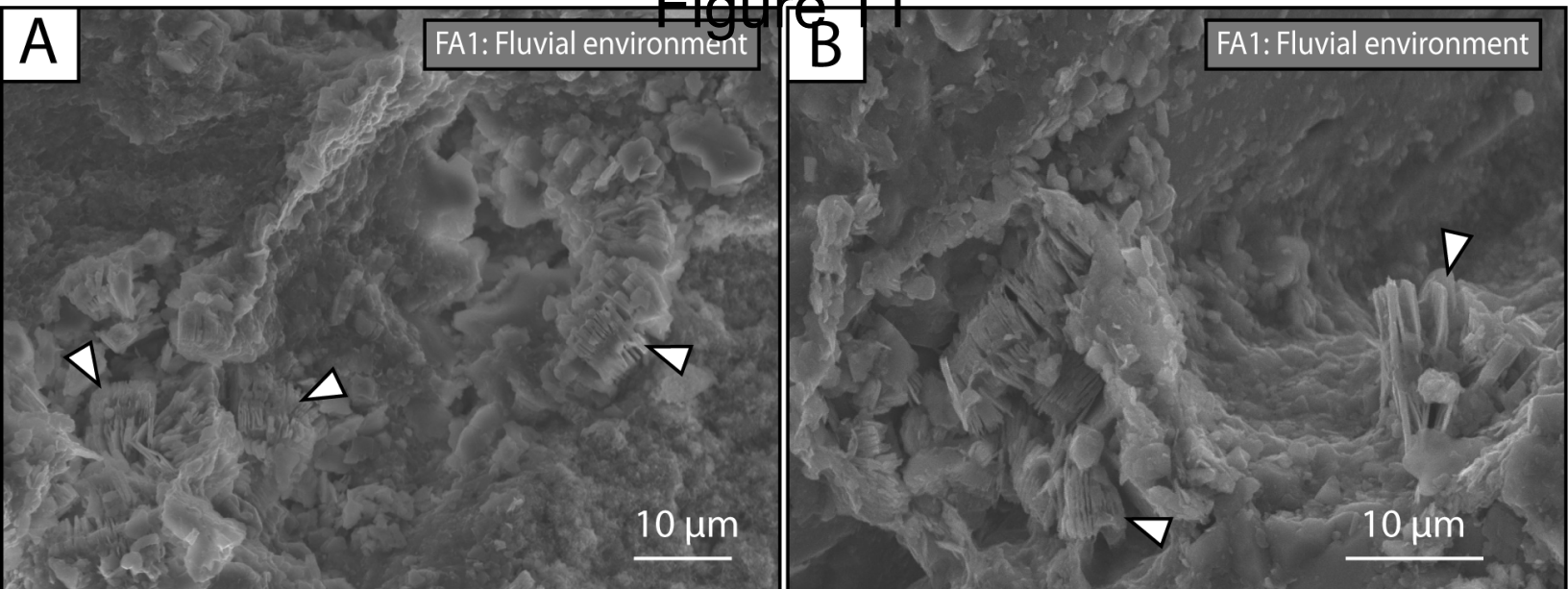
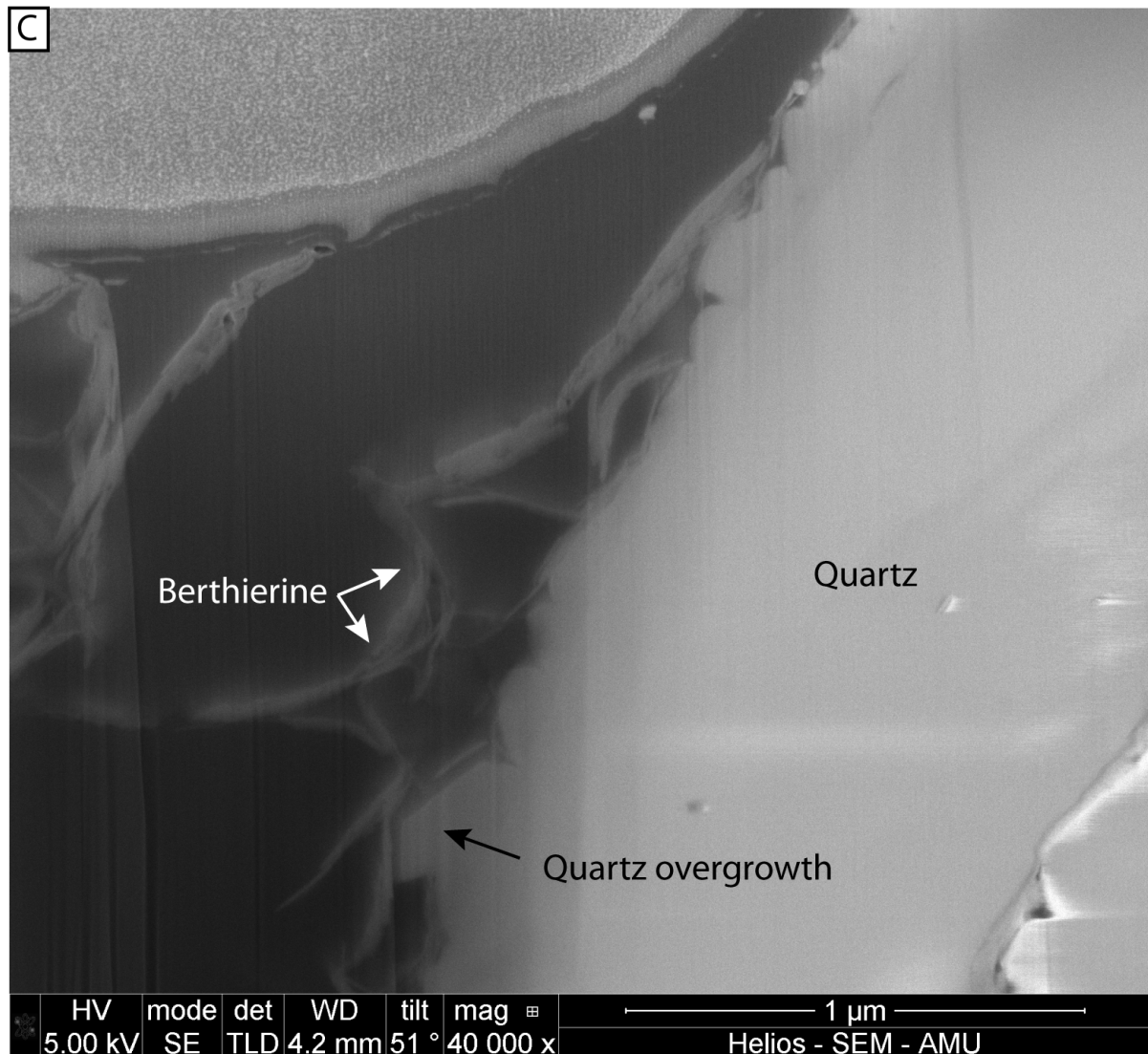
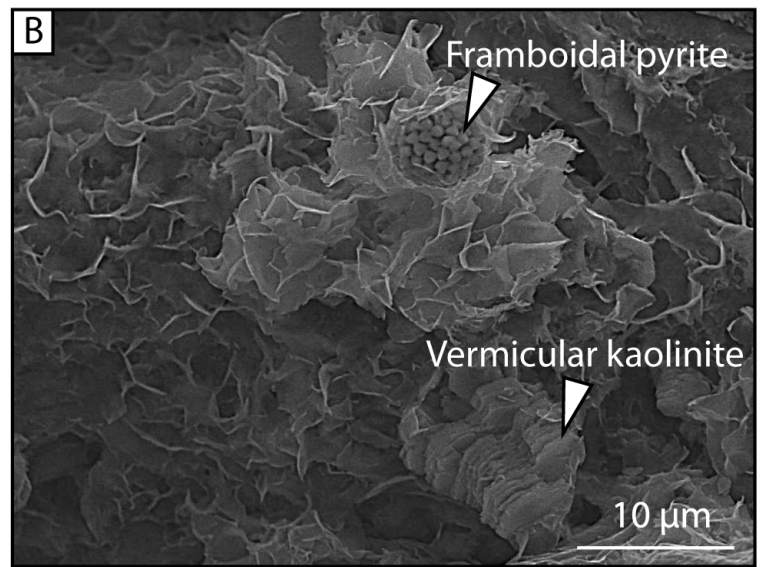
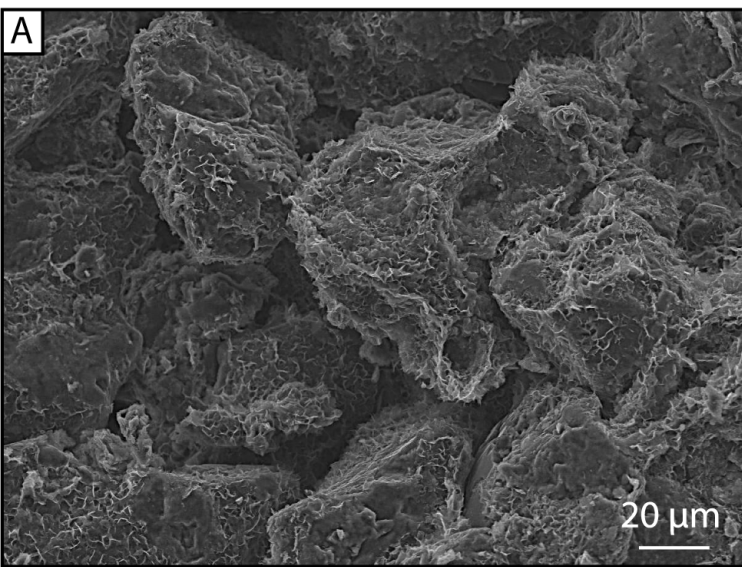


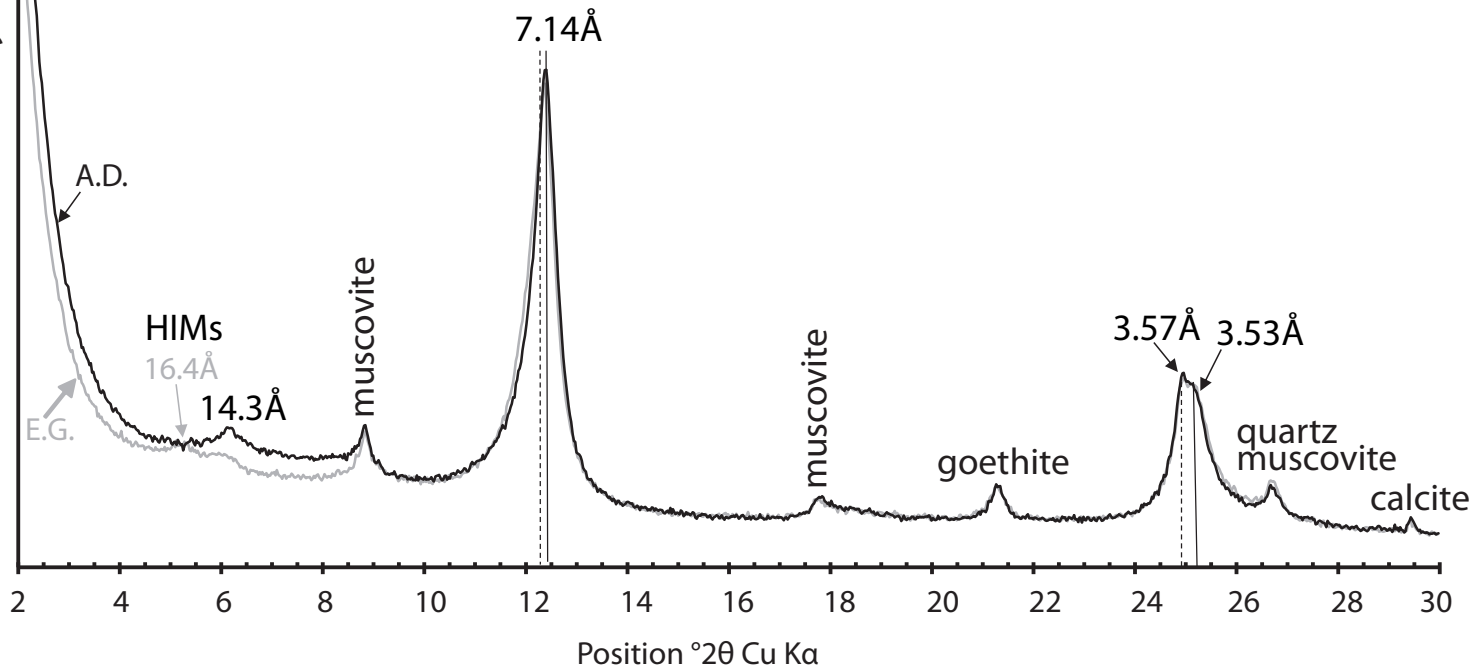
Figure 12



# Figure 13

CR12-18 (909.8m)  
air dried (A.D.)  
ethylene glycol (E.G.)

Intensity



# Figure 14

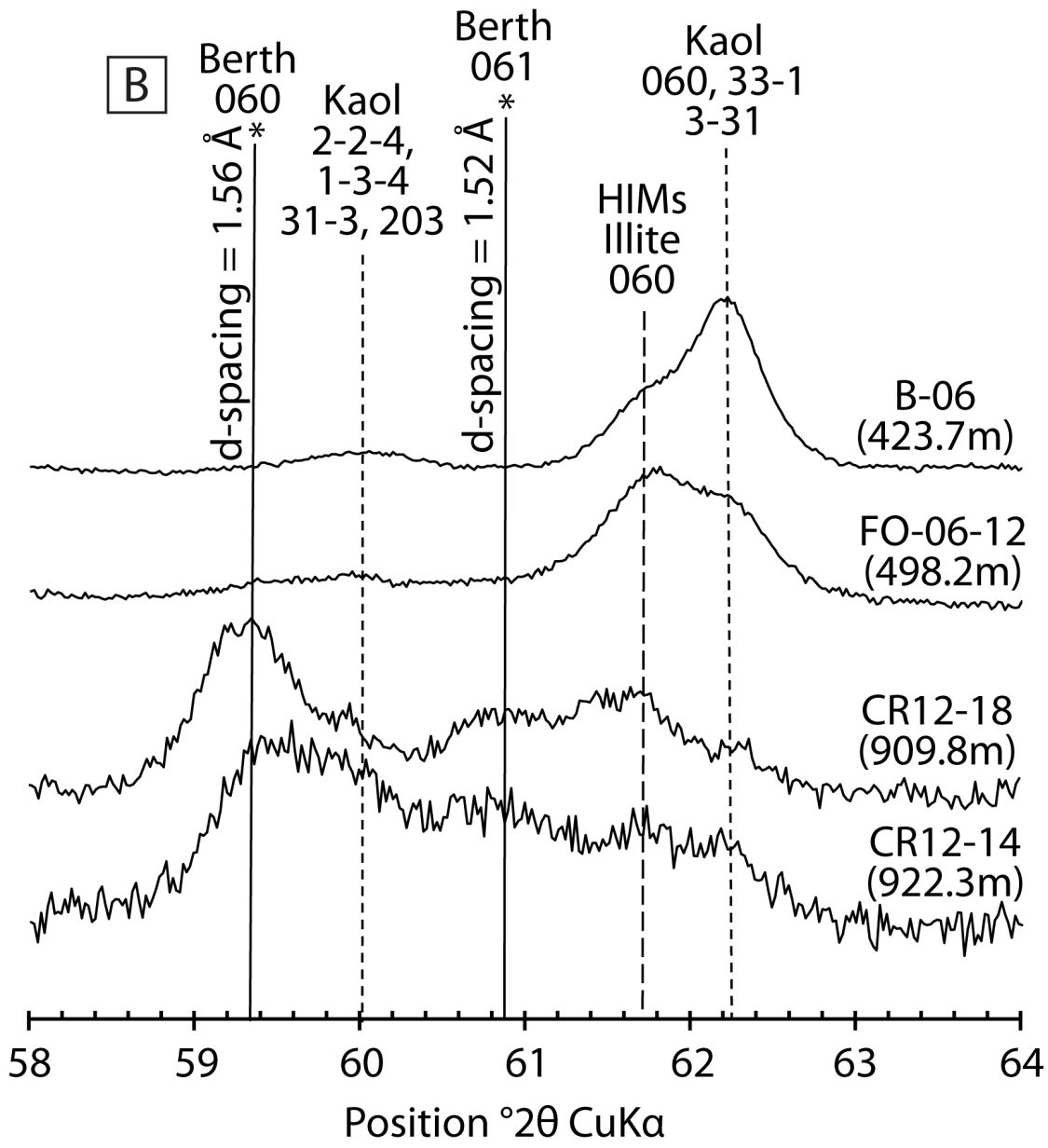
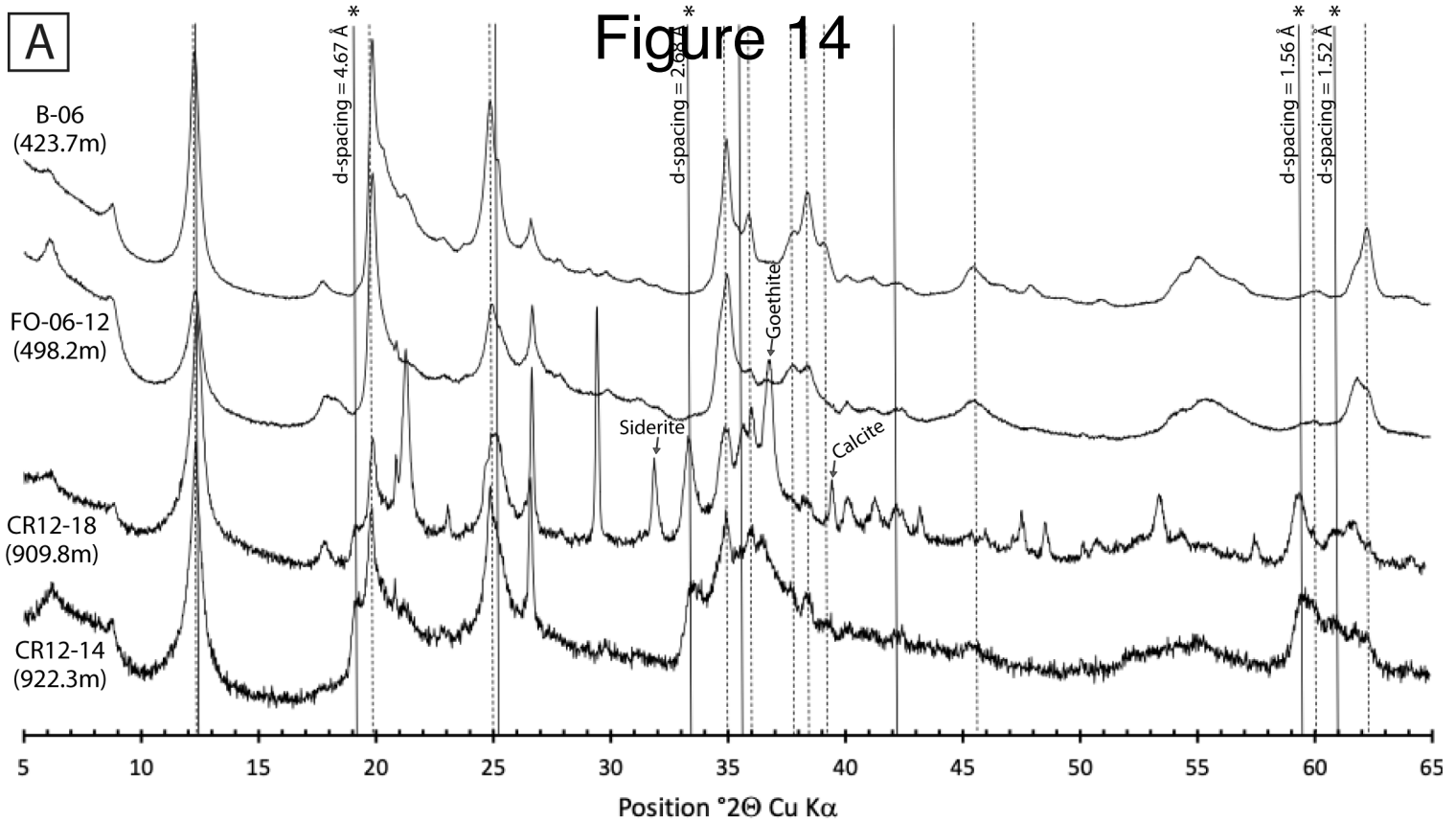
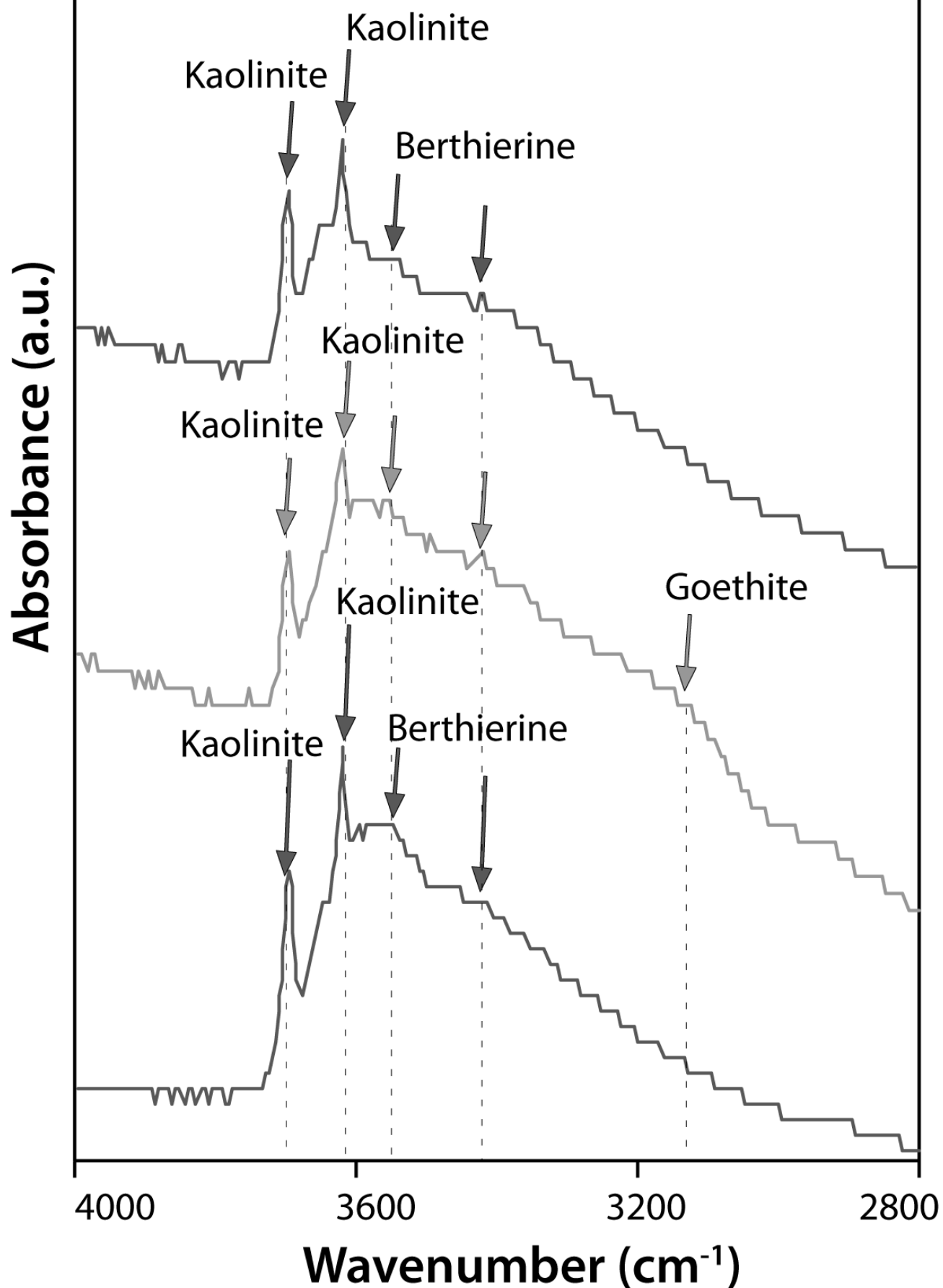


Figure 15

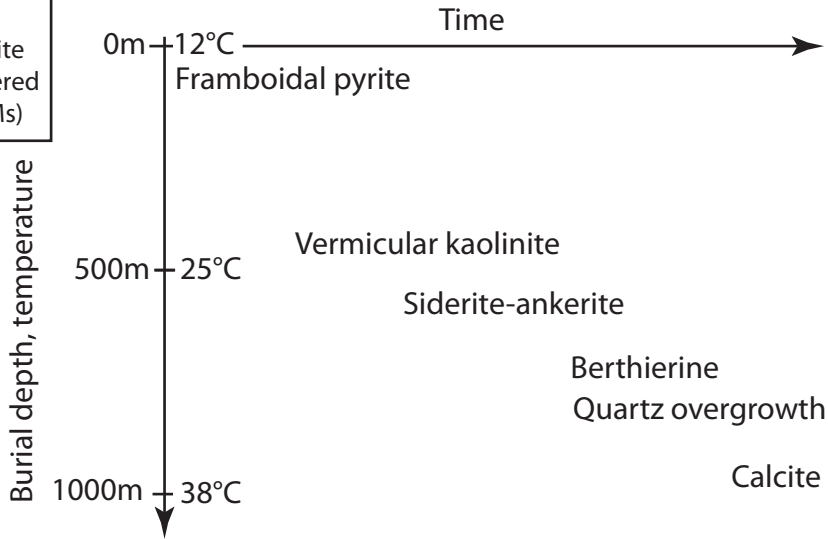
- CR12-19 (904.6m)
- CR12-18 (909.8m)
- CR12-14 (922.3m)



# Figure 16

Pre-burial minerals  
(Al, Fe<sup>3+</sup>)-rich minerals

- Fe-Al ooids
- Fe bearing kaolinite
- Hydroxy-interlayered clay minerals (HIMs)





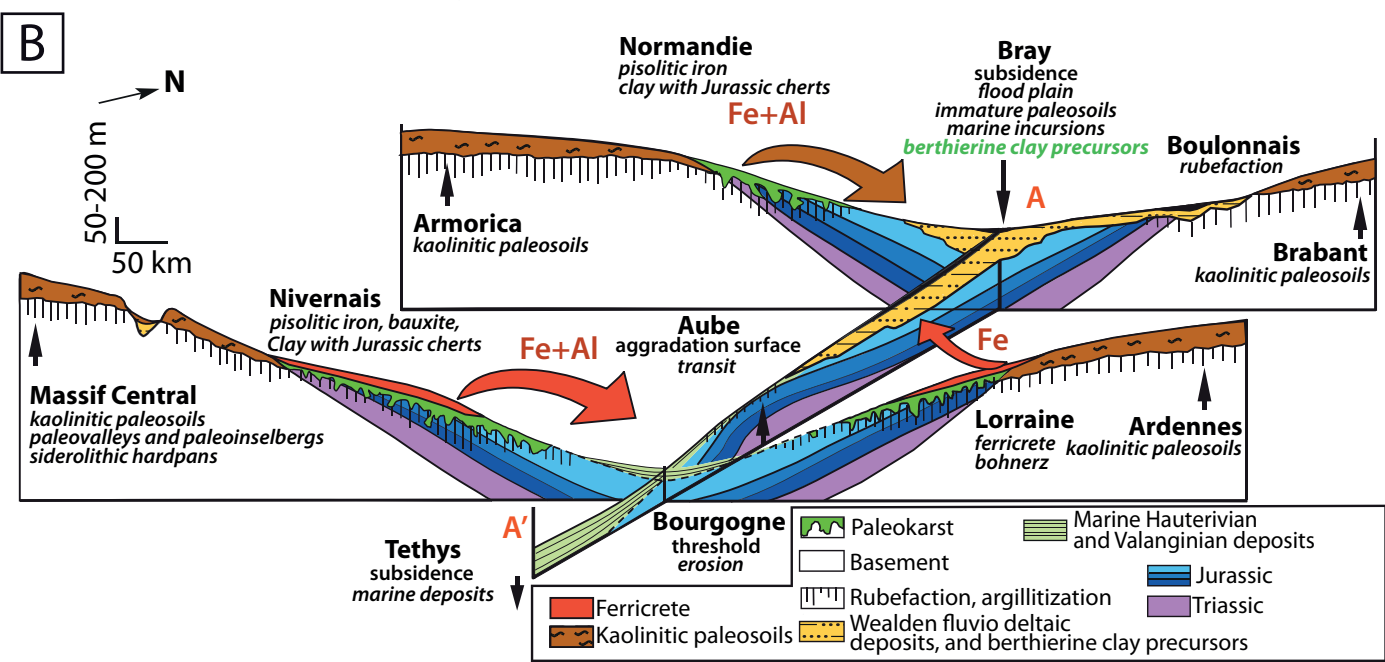
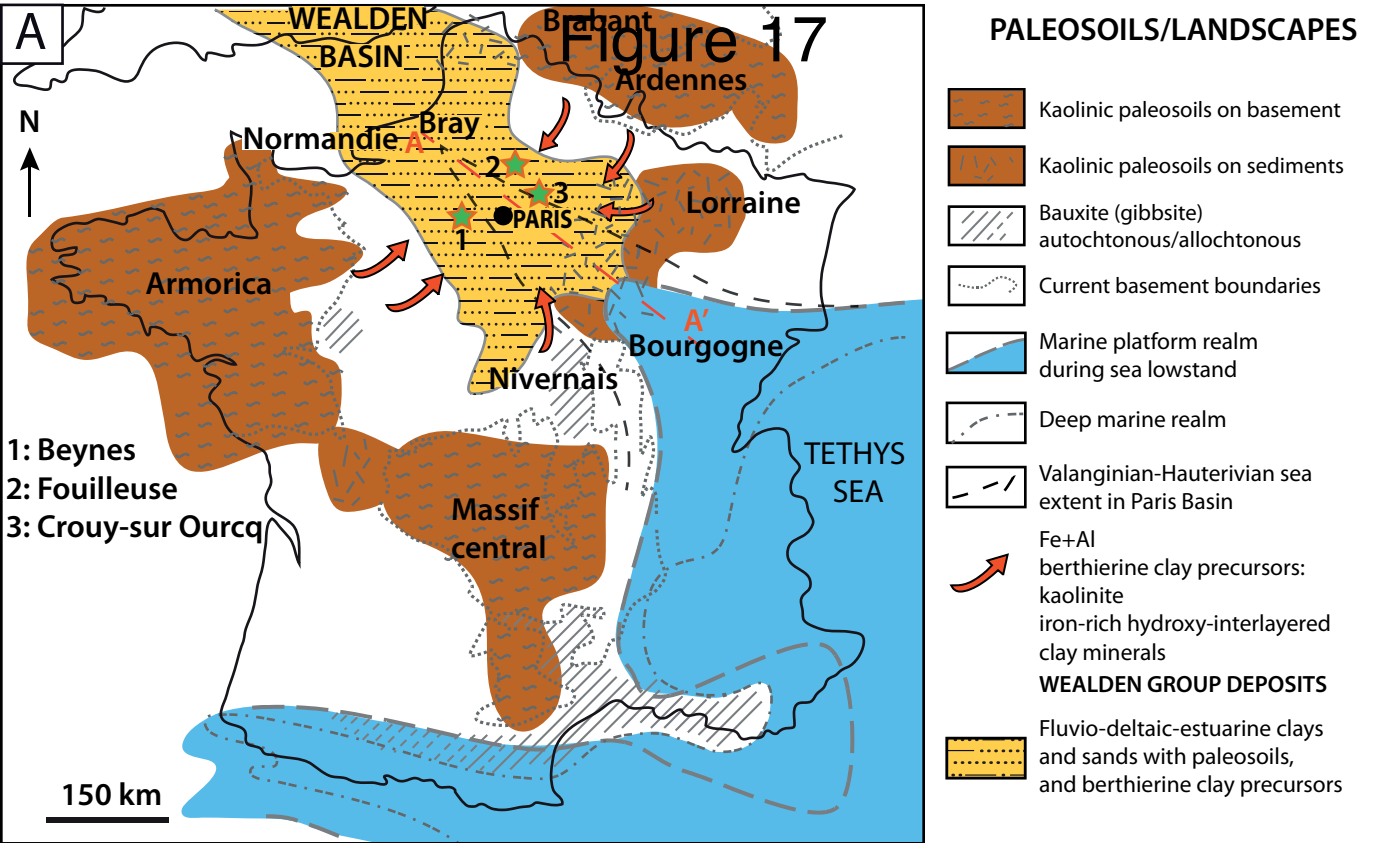


TABLE 1. SUMMARY OF F

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<b>Facies</b>	<b>Facies</b>
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**Association and environment**

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FA1  
FLUVIAL

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FA2  
ESTUARINE

FA2a

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FA2b

---

FA2c

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FA3  
DELTAIC

---

FA4  
SHOREFACE

---

FA5  
OFFSHORE

---

## FACIES AND FACIES ASSOCIATION IDENTIFIED IN THE WEALDEN GROUP SAND

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### Description

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1) Trough cross-bedded, medium to upper fine grained sandstones, locally conglomeratic. Numerous soft mud pebbles

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2) Current-rippled upper fine to very fine grained sandstone with leaves and wood debris

---

3) Nodular siltstone & laminated siltstone, organic matter rich, and rooted silty mudstones and coal beds

---

Medium- to fine-grained sandstones, trough cross-bedding intercalated with thin clay layers. Foresets with clay drapes and organic matter debris. Reactivation surfaces. quartz, feldspars, mica and surrounded grains. Rare glauconite ooids.

---

- 1) Flaser bedding composed of medium-grained, current-rippled sands with muddy flasers; (ii)
  - 2) Fine grained, wavy bedding, with mm-to-cm fine-grained sandy rippled sands, draped by tidal slack water clay drapes,
  - 3) Lenticular bedding with fine-grained sand ripples, mm of silty lenses and high-tide slack water clay drape.
- 

Amalgamated clay drapes, organic matter rich with reed roots, with oxidized pedogenetic horizons. Stratification not always observed due to pedogenetic processes or due to reed roots.

---

1) Shales, silt and 10-50 mm current rippled very fine grained sandstones, with organic matter debris, synaeresis cracks, bioturbated.

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2) Current-rippled fine grained sandstones (quartz and goethite ooids) to trough cross bedded fine to medium sandstones. Foresets highlighted by organic matter debris.

---

3) Silty-claytones to silty sands, with no obvious sedimentary features, locally heavily bioturbated, with cm to pluri-cm intercalation of coal beds and locally rooted.

---

3) Silty-claytones to silty sands, with no obvious sedimentary features, locally heavily bioturbated, with cm to pluri-cm intercalation of coal beds and locally rooted.

---

Clean, well sorted, fine to medium / coarse grained sandstones. Low-angle, hummocky and swaley cross-bedding, locally well laminated or scrambled and heavily bioturbated. Occasional dispersed shell fragments. Marine shell lags.

---

Bioturbated shale with thin horizontal laminae of siltstone. Common bivalves and scattered shell fragments. Rich in organic carbon.

---

OSTONES OF THE PARIS BASIN.

Geometry	Bioturbations Fossils / microfossils
Finning-upward, 20-50 cm bedsets	Roots / Fresh water algae ( <i>Botryococcus spp.</i> ) continental spores <i>Densioisporites spp</i> wood & leaf debris
Infra-cm to pluri-cm beds, up to 70 cm bedsets	
Frequently deformed, roots, up to 2-3 meters	Roots, wood and leaf debris, coal intervals
10-25 small tidal dunes, reactivation surfaces.	See below
mm to several mm thick beds. Amalgamated in besets up to 15 to 50 cm thick.	Rare bioturbations, mainly <i>planolites</i> Firm grounds / <i>Glossifungites</i> (917-914m) - Iron-oxydes Continental input: pollens and spores <i>Classopolis spp.</i> or <i>Exesipollenites spp.</i> Marine input: <i>Muderongia crucis</i> or <i>Stiphrosphaeridium anthophorum</i> or dinoflagellate <i>Rhynchodiniopsis fimbriat</i> (Rusciadelli, 1996)
mm-thick laminae. Stratification	Reed roots
Planar bedding	Rare bioturbation, <i>planolites</i> Marine microfossils such as dinoflagellate <i>Muderongia crucis</i> or <i>Oligosphaeridium asterigerum</i>
15-50 cm bedsets, dipping angle 5-10° Coarsening-up trend, 20-80 cm bedsets	
20-250 cm bedsets coal intercalation	<i>Planolites</i> , <i>skolithos linearis</i> , <i>teichichnus</i> roots
Finning-up bed sets, with erosive base	None. Roots ?
Frequent reactivation surfaces, 35 cm to 200 cm bedsets	<i>Skolithos</i> , frequent <i>ophiomorpha</i> ichnofacies
Massive claystones intervals (1 to 2m thick) - Low core recovery	Bivalves, oncoids Coccoliths, foraminifera

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## Interpretation

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Fluvial channels, with  
levees - flood plain

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Tidal bars

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Tidal flats

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Supra-tidal marsh

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Prodelta

---

Prograding Lower delta

---

Delta plain

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Distributary channel

---

Wave action  
Storm deposits  
Lower to Upper  
Shoreface

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Offshore, open marine

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TABLE 2. COMPOSITION OF QUARTZ, FELDSPAR, LITHIC AND CLAY COATS IN SAMPLES ACCORDING TO FACIES.

Facies Associations	Grain composition					Coated grain content and coat coverage classes (percentage of the outer surface coated)					Clay fraction content and clay assemblage within clay fraction			
	Quartz (%)	Feldspars (%)	Lithic grains (%)	Clays (%)	Others	1–5%	5–15%	15–30%	>30%	Total coated grains (%)	% Smectite	% Illite	% Chlorite	% Kaolinite
FA1	41	7	12	12	29	5	9	13	10	37	7	23	25	45
FA2	39	8	12	9	32	5	10	13	10	39	10	19	26	45
FA3	33	5	9	9	43	0	1	2	2	5	9	33	26	32
FA4	30	5	8	18	39	4	5	2	1	12	3	20	29	48
FA5	27	2	3	23	46	0	0	1	1	2	0	33	22	44
Total/Mean	34	5	9	14	38	3	5	6	5	19	6	26	26	43

TABLE 3. CHEMICAL COMPOSITIONS OF CLAY PARTICLES FROM CLAY COATS WITHIN WEALDEN GROUP SANDSTONES.

	1	2	3	4	5	6	7	8
SiO <sub>2</sub>	45.59	52.90	42.51	46.53	26.37	28.60	27.36	30.10
Al <sub>2</sub> O <sub>3</sub>	36.47	24.44	26.47	21.84	16.79	19.12	18.12	16.25
FeO	0.00	0.00	0.00	0.00	38.38	34.34	36.47	34.45
Fe <sub>2</sub> O <sub>3</sub>	3.41	4.36	10.64	12.30	0.00	0.00	0.00	0.00
MgO	0.14	0.67	1.16	1.15	2.94	2.62	2.63	3.39
TiO <sub>2</sub>	0.10	0.53	0.72	0.59	0.00	0.00	0.04	0.04
MnO	0.05	0.07	0.06	0.00	0.38	0.12	0.12	0.26
Na <sub>2</sub> O	0.05	0.31	0.34	0.18	0.14	0.14	0.05	0.62
K <sub>2</sub> O	0.16	1.55	3.72	3.17	0.66	0.69	0.82	0.76
CaO	0.03	1.17	0.38	0.24	0.34	0.37	0.39	0.13

*Note:* Analyses 1 to 4 are representative of pre-burial clay coats (1: detrital kaolinite, sample B-6, well B; 2: smectite-rich detrital clay material, sample B-5, well B; 3–4: hydroxy-interlayered-rich detrital clay material, sample B-12, well B). Analyses 5 to 8 are representative of diagenetic clay coats (authigenic berthierine); analyses 5 to 7: sample CR12-18, well CR1, analyses 8: sample CR12-14, well CR12. Compositions were calculated from Energy Dispersive X-ray analyses (EDS) in the SEM and expressed in oxide weight percent. For easier comparison, they were normalized to a sum of 86% (which is the theoretical sum of oxide weight percent for dehydrated kaolinite and berthierine) for easier comparison. Total iron has been arbitrarily considered as ferric in detrital clays and as ferrous in authigenic berthierine.