

## Small-scaled lateral variations of an organic-rich formation in a ramp-type depositional environment (the Late Jurassic of the Boulonnais, France): impact of the clastic supply

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**Abstract** – We studied a potential petroleum source rock deposited in a clastic-dominated ramp environment: the Argiles de Châtillon Formation (Kimmeridgian-Tithonian, Boulonnais area, northern France). The formation was deposited along a proximal-distal gradient on this ramp affected by synsedimentary fault movements. A sedimentological, mineralogical and geochemical study was conducted to decipher the distribution patterns of sedimentary parameters along such a depth increase over the ramp. It comes out that smectite distribution unexpectedly mimics the lateral depth evolution despite the good floatability of the mineral. It is also observed that the Argiles de Châtillon could accumulate noticeable amounts of organic matter in spite of paleoenvironmental conditions that were not specifically prone to organic matter preservation and burial (sedimentation rate, mineral particle grain size, productivity, oxygenation level...). Conversely, reactive iron, when being present in limited abundance, must have allowed sulfide ions to react with organic molecules instead of forming iron sulfides, which fostered organic matter preservation and accumulation. This protecting role of organic sulfide incorporation (additional to other favorable factors) cannot exist if reactive iron is relatively abundant. Lastly, our results (still fragmentary) suggest that smectite minerals could carry reactive iron, which would have occasionally hampered organic-matter preservation.

**Keywords:** Kimmeridgian-Tithonian / Boulonnais / organic matter / petroleum source rocks / geochemistry / clay minerals

**Résumé** – Importance des variations latérales discrètes dans les apports détritiques, observées dans des faciès de rampe sédimentaire riches en matière organique (Jurassique supérieur du Boulonnais). La formation des Argiles de Châtillon (Kimméridgien-Tithonien, Boulonnais) est un bon analogue géologique de roche mère pétrolière déposée en contexte de rampe clastique. Ces dépôts se sont mis en place le long d'un transect proximal-distal sur une rampe affectée par des mouvements tectoniques synsédimentaires. Pour mettre en évidence et comprendre la distribution des paramètres sédimentaires en fonction de l'évolution de la profondeur, une étude sédimentologique, minéralogique et géochimique fut entreprise. Il en ressort que la distribution de la smectite au sein du cortège argileux respecte ce gradient, malgré la flottabilité reconnue de ce minéral. Il apparaît également que les Argiles de Châtillon ont pu accumuler des quantités sensibles de matière organique malgré un contexte de dépôt peu favorable à la préservation et à l'enfouissement de celle-ci. En revanche, le fer réactif, quand il était présent en faible quantité dans les sédiments, a pu permettre aux ions sulfures de réagir avec les molécules organiques, plutôt que de former des sulfures de fer. Cette sulfuration a pu accroître la résistance de la matière organique à la dégradation microbienne, ce qui explique la bonne préservation du carbone organique. Ce rôle protecteur de la vulcanisation naturelle (qui s'ajoute à d'autres facteurs favorables) ne peut pas s'exercer si le fer réactif est relativement abondant. Nos résultats (encore fragmentaires) suggèrent également que la smectite

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(qui est un minéral pouvant véhiculer du fer faiblement lié au réseau cristallin) pourrait, dans certains cas, limiter la préservation de la matière organique.

**Mots clés :** Kimméridgien-Tithonien / Boulonnais / matière organique / roches mères d'hydrocarbure / géochimie / minéraux argileux

## 1 Introduction

The Late Jurassic marlstones of the Argiles de Châtillon Formation (Fm.) are well exposed along the coastal cliffs of the Boulonnais area (northernmost France), between the Cap Gris-Nez (or Gris-Nez Cape) and Equihen (south of Boulogne-sur-Mer; Fig. 1). These shelf sediments are lateral time equivalents of the distal organic-rich sediments of the Kimmeridge Clay Fm. deposited in the Wessex Basin (Dorset, UK). The Argiles de Châtillon Formation, though deposited in a clastic-dominated, relatively shallow (sometimes above the storm wave base) ramp environment, is relatively rich in marine organic matter (OM) and is a potential petroleum source rock. Along this ramp, the Argiles de Châtillon deposits recorded a proximal-distal gradient, with the shallowest conditions close to the Cap Gris-Nez, and the more distal conditions close to the cities of Wimereux and Boulogne-sur-mer (Cap de la Crèche section, Fig. 1; Mansy *et al.*, 2007). The Boulonnais area has been experiencing an extensional tectonics regime during the Late Jurassic, expressed through synsedimentary faulting (Hatem *et al.*, 2014, 2016; Mansy *et al.*, 2007). The aim of the paper is to examine the lateral evolution of the depositional conditions of this potential source rock, in order to derive some general force-lines for a better understanding of OM accumulation on continental platforms exposed to relative sea-level variations and synsedimentary tectonics. More specifically, emphasis will be set on the roles of iron and the composition of clay-mineral assemblages in the processes of OM preservation. The present paper is partly grounding upon a synthesis of many papers published during two decades, dealing with the Late Jurassic deposits of the Boulonnais (see below); it also presents new results on the clastic fraction of the Argiles de Châtillon Fm. This work tries to draw some guidelines about OM accumulation that can be transposed from the formation at stake here to other similar platform settings of any age or location.

## 2 Geological framework and previous results

The Kimmeridgian-Tithonian series exposed along the Boulonnais cliffs are part of the northern margin of the Weald-Boulonnais basin (sometimes called also Weald-Boulonnais anticline due to its present structure). This margin, alike the adjacent North Sea and Wessex basin, was affected by a major Late Jurassic- Early Cretaceous rifting event (Minguely *et al.*, 2010 and reference therein) coeval with the general propagation of the Atlantic rift zone, north of the Gibraltar-Newfoundland fracture zone. The related pattern of subsidence and uplift induced the preservation of shallow marine Upper Jurassic and continental Lower Cretaceous (Wealdian) deposits in a restricted fault-bounded Boulonnais embayment upon which the present-day exposure is molded (Fig. 1). Extensive studies of the Boulonnais sections have provided a depositional and sequence stratigraphical framework that may be used to help interpret variations in OM content and composition, in response to

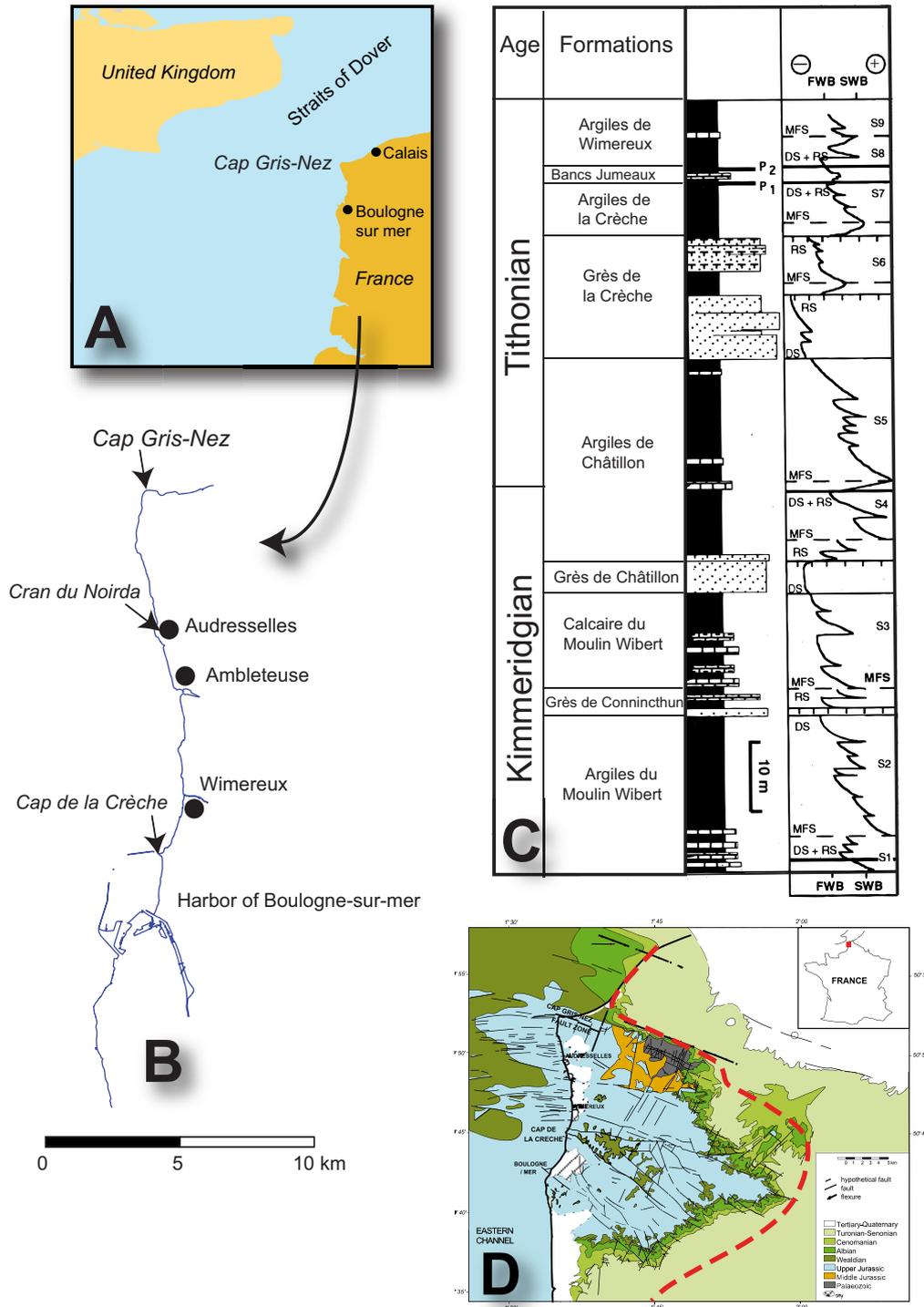
fluctuating relative sea-level (*e.g.*, Al-Ramadan *et al.*, 2005; El Albani *et al.*, 1993; Bialkowski *et al.*, 2000; Braaksma *et al.*, 2006; Deconinck *et al.*, 1996; Herbin *et al.*, 1995; Proust *et al.*, 1995; Schlirf, 2003; Tribovillard *et al.*, 2001; Wignall and Newton, 2001; Williams *et al.*, 2001). The most-studied section is exposed at the Cap de la Crèche, between Wimereux and Boulogne-sur-mer (Fig. 1). There, the 29 m-thick Argiles de Châtillon Fm. (*autissiodorensis* and *elegans* ammonite zones) is well visible, being bracketed between the upper part of the Grès de Châtillon Fm. below (shoreface sandstone formation, *eudoxus* zone), and the base of the Grès de la Crèche Fm. above (another shoreface sandstone formation, *scitulus* zone; Deconinck *et al.*, 1996; Geysant *et al.*, 1993; Herbin *et al.*, 1995; Wignall *et al.*, 1996). The siltstones and shales of the Argiles de Châtillon Fm. represent a low-energy shelf facies deposited below wave base, but revealing some storm influence with some shelly limestone beds (Fürsich and Oschmann, 1986) and thin sandstone bodies showing hummocky cross stratifications. Like the more distal time equivalent shales and mudstones exposed at Kimmeridge on the Dorset coast (Cox and Gallois, 1981; Waterhouse, 1999) or Yorkshire (Ramanampisoa *et al.*, 1992), these sediments are also organic-rich in part (Deconinck *et al.*, 1996; Dunn, 1972; Geysant *et al.*, 1993; Herbin and Geysant, 1993; Herbin *et al.*, 1991, 1995; Proust, 1994; Proust *et al.*, 1993), but their OM has a more mixed origin (El Albani *et al.*, 1993; Herbin and Geysant, 1993; Herbin *et al.*, 1995). The higher pyrite contents, and the depauperate *in situ* macro and microbenthos and reduced bioturbation have long been used to suggest reducing and “stagnant”, but not persistently anoxic, conditions (Ager and Wallace, 1966, 1970; Barnard and Shipp, 1981). Several orders of cyclicity are recorded within the Argiles de Châtillon; the most prominent are:

- the Milankovitch-type (climatic) primary cycles (*ca.* 20 ky, Herbin *et al.*, 1995);
- the superimposed longer-term cycles observed here (*ca.* 500 ky; Herbin *et al.*, 1995; Waterhouse, 1999).

Sequence stratigraphical studies of the Wimereux section (Al-Ramadan *et al.*, 2005; Braaksma *et al.*, 2006; Herbin *et al.*, 1995; Proust, 1994, Proust *et al.*, 1993, 1995) allow us to relate observed variations in organic facies to changes in relative sea-level. Herbin *et al.* (1995) pointed out that relative sea-level rise was not the single cause for OM accumulation. Instead, these authors suggest that three parameters must act in conjunction:

- physiography (concerning the shape of the basin and the volume of sediments available);
- transgression (influencing the size of the area producing the organic material and the water depth);
- climate (governing the quality of the OM and the variation of primary productivity). Note that the climate of this period is reputed to have been warm (Brigaud *et al.*, 2008; Dera *et al.*, 2011).

As detailed descriptions of the lithofacies and stratigraphy of the “reference” section of the Cap de la Crèche have been



**Fig. 1.** A and B: maps showing the location of the study area, between the Gris Nez Cape and the city of Wimereux. C: simplified lithostratigraphic log of the Late Jurassic formations cropping alongshore the Boulonnais (after [Deconinck et al., 1996](#)). FWB and SWB stand for fair-weather wave base and storm-weather wave base, respectively. P1 and P2 stand for the two horizons rich in phosphatized shells. D: geological setting of the Boulonnais area (after [Mansy et al., 2007](#); [Hatem et al., 2016](#)).

given previously in [Proust \(1994\)](#), [Proust et al. \(1995\)](#), [Herbin et al. \(1995\)](#), [Deconinck et al. \(1996\)](#) and [Wignall and Newton \(2001\)](#), only a summary needs be offered here. The Grès de Châtillon consists of brown- to orange-colored sandstones and sandy marlstones with common cross-bedding and wave ripples, and intense bioturbation (especially U-shaped and

*rhizocorallium*, *ophiomorpha* and *thallasinoides* burrows). The formation ends with bioturbated limestone beds that mark the transition to the overlying Argiles de Châtillon Fm. that consists of claystone and siltstone accumulations with some intervals of laminated paper shales ([Fig. 2](#)), and a laterally variable number of local intercalated limestone beds, some of which are

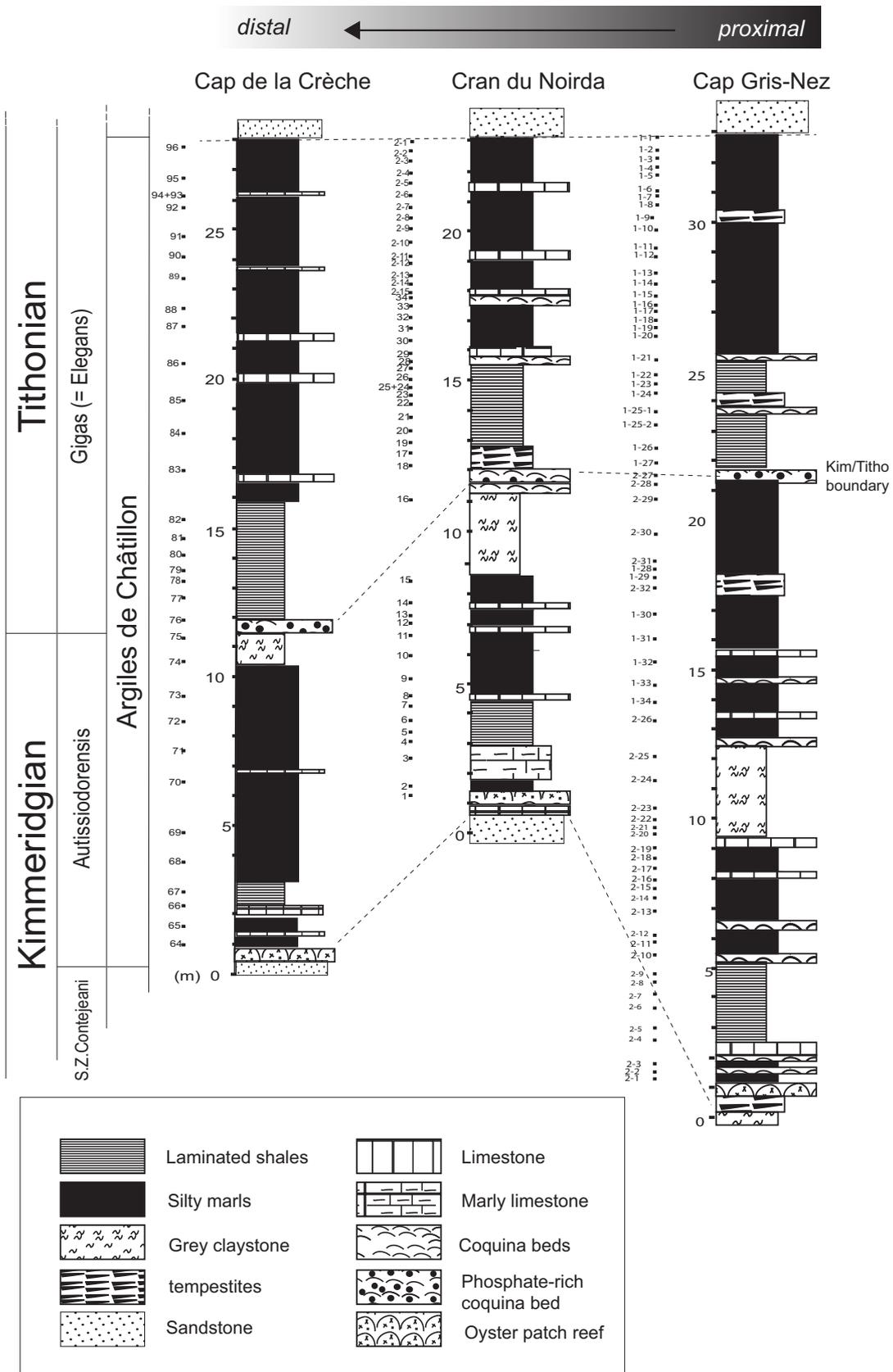


Fig. 2. Simplified logs of the studied three sections. Numbers refer to the samples.

diagenetic in origin (Hatem *et al.*, 2016). The marlstones show a gradual enrichment in silt in the upper part of the formation. The Cran du Noirda section is characterized by the common occurrence of storm beds, notably around the Kimmeridgian-Tithonian boundary (*autissiodorensis-elegans* zone).

The organic content of the Argiles de Châtillon Fm. (observed from the Cap de la Crèche section) is dominated by amorphous organic matter (AOM; Tyson, 1995). AOM represents the part of the kerogens the origin and nature of which cannot be determined through palynofacies observation alone (Tyson, 1995). Here, AOM is itself dominated by two main varieties distinguished on the basis of their color: orange or brown (see description and microphotographs in Tribovillard *et al.*, 2001). Orange AOM exhibits distinct (and in some cases, almost angular) edges, and has a gel-like texture. Brown AOM has a more heterogeneous “flock” texture, less distinct “fuzzy” outlines, and tends to be less lustrous; in untreated kerogen slides it exhibits a more granular texture and the presence of pyrite crystallites and tiny framboids. It is also associated with lower fluorescence intensities (Bialkowski *et al.*, 2000; Tribovillard *et al.*, 2001). In previous studies of the Kimmeridge Clay, orange AOM has been found to be nanoscopically amorphous, while brown AOM shows an ultralaminar ultrastructure which is thought to represent selectively preserved cell walls of microplankton (Boussafir *et al.*, 1994, 1995a, b; Gelin *et al.*, 1995, 1999). The ratio of the two types of AOM changes with the total organic carbon content (TOC) of the sediments, the proportion of orange AOM increases rapidly as TOC increases from 2 to 7% (Bialkowski *et al.*, 2000; Boussafir and Lallier-Vergès, 1997; Tribovillard *et al.*, 2001). The orange AOM is interpreted as resulting from natural vulcanization, a.k.a. sulfurization (reaction with sulfides and polysulfides, see below), whereas brown AOM is interpreted to result from selective preservation of resistant biopolymers (selective oxidation of metabolizable constituents; Boussafir *et al.*, 1994, 1995a, b; Derenne *et al.*, 1991; Largeau *et al.*, 1990; Mongenot *et al.*, 1997). Natural sulfurization is an early diagenetic process leading to the inter- or intramolecular incorporation of reduced inorganic sulfur species into low-molecular-weight functionalized lipids resulting in the formation of resistant high molecular weight abiotic “geopolymers” (Tegelaar *et al.*, 1989). Recent works suggest that the intramolecular pathway dominates over the intermolecular pathway (Quijada *et al.*, 2016 and references therein).

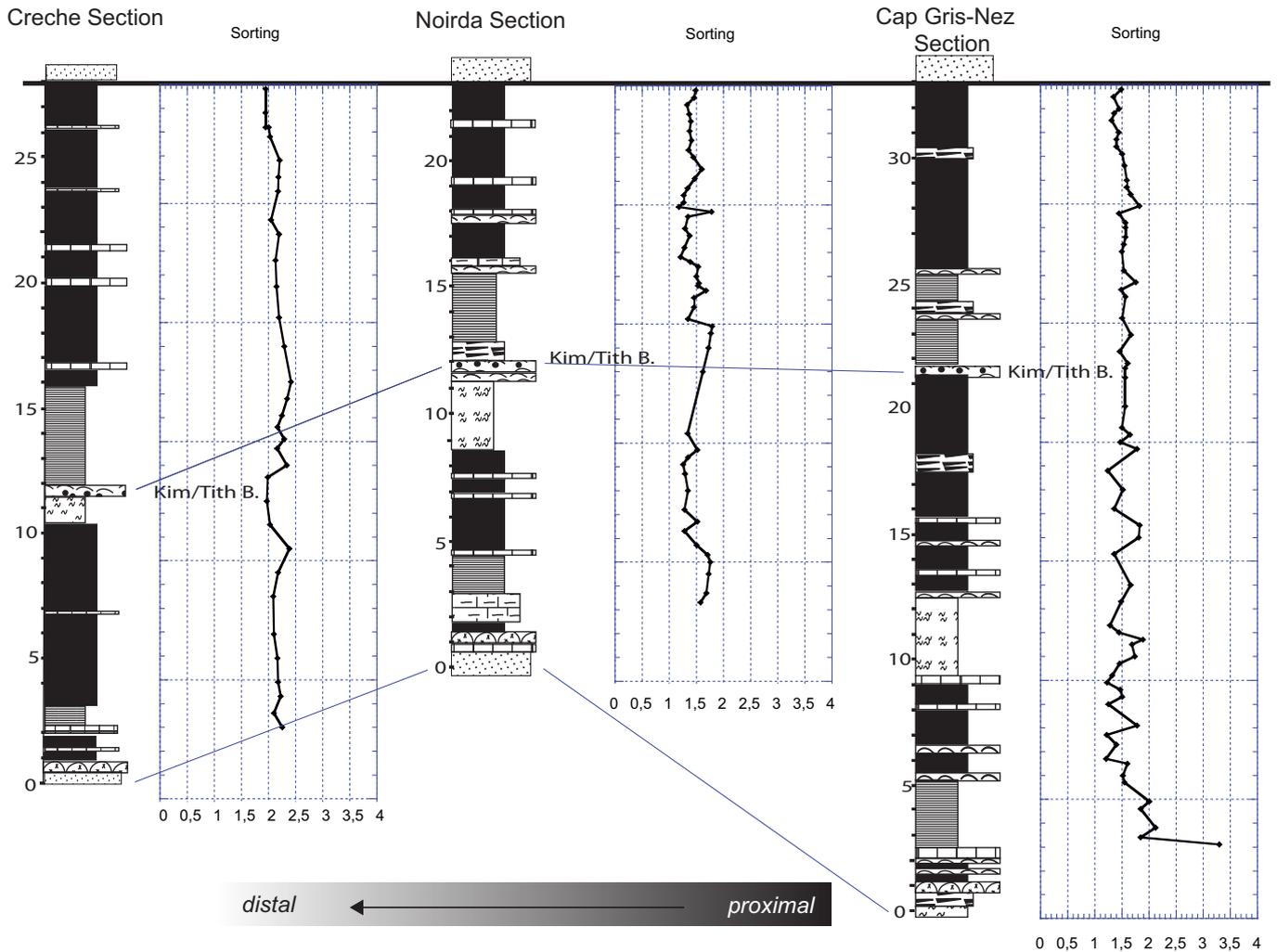
### 3 Material and methods

To study a transect through the area of the Boulonnais where Jurassic formations crop out, namely from Cap Gris-Nez to Equihen, we examined three sections of the Argiles de Châtillon Fm. located, respectively, at Cap Gris-Nez (proximal setting; 68 samples), Cran du Noirda (intermediate setting, north end of Audresselles Village; 51 samples) and Cap de la Crèche (distal setting; 33 samples). The proximal-distal gradient is thus observed over a distance of about 15 km and is not sharp: the facies variations from one section to one another are not strong. Figure 2 illustrates the lithologies observed in the three sections and sampling steps. The same basic facies successions can be observed in the three sections. The main differences consist of some variations in thickness

and a laterally variable number of storm-induced coquina beds (Fig. 2). These tempestites are dominantly made of small oysters (*Nanogyra nana*) and thin levels of sandstones showing hummocky cross stratifications (HCS). The oyster shell beds are dominant in the proximal setting of Cap Gris-Nez whereas the HCS levels are more abundant in the more distal settings of Cran du Noirda (they are not observed in the Cap de la Crèche section, the most distal part of the studied transect). In these sections, we could identify the level that is considered to correspond to the Kimmeridgian-Tithonian boundary (Geysant *et al.*, 1993). This level is rich in phosphatic debris and shells, and lies on top of a thick, shell-rich carbonate bed in the Cran du Noirda section (Proust *et al.*, 1995). Notably, two laminated shale horizons are observed in each section; they are interpreted as deposited during marked elevation of sea-level and begin with a maximum flooding surface. Both laminated shale horizons have a high organic carbon content (up to 9%) and, in the Cap de la Crèche section, are rich in orange-color AOM (Tribovillard *et al.*, 2001).

For the three sections, grain-size distribution of the decarbonated fraction (HCl digestion) was analyzed using a laser-equipped Malvern Mastersizer apparatus, following the protocole of Trentesaux *et al.* (2001). The decarbonated fraction is considered to be representative of the clastic, land-derived component of the sediment, to which the authigenic fractions may be added (mainly pyrite framboids or crystals), as well as organic flocs. Tempestite beds were not taken into consideration for grain-size study. The limit between silt and clay (from a grain size point of view) is 4  $\mu\text{m}$  in the present paper. For all samples, the carbonate content was measured using a Bernard calcimeter (acid digestion followed by CO<sub>2</sub> volume determination; accuracy < 5%). The Rock Eval pyrolysis parameters were determined with a Rock Eval VI apparatus: total organic carbon content (TOC, in wt.%), Tmax (°C), and Hydrogen Index (HI, in mg hydrocarbon per g TOC; see all details about Rock Eval pyrolysis and parameters in Behar *et al.*, 2001; Espitalié *et al.*, 1985; Lafargue *et al.*, 1998).

The determination of the major- and trace-element contents was carried out by ICP-OES and ICP-MS by the spectrochemical laboratory of the *Centre de Recherches en Pétrographie et Géochimie* of Vandœuvre-les-Nancy (geochemistry laboratory of the French *Centre National de la Recherche Scientifique*). The samples were prepared by fusion with LiBO<sub>2</sub> and HNO<sub>3</sub> dissolution. Precision and accuracy were both better than 1% (mean 0.5%) for major-minor elements and 5% for trace metals, as checked by international standards and analysis of replicate samples (Carignan *et al.*, 2001). Enrichment factors (EF) were calculated as:  $X_{EF} = [(X/Al)_{\text{sample}} / (X/Al)_{\text{AUC}}]$ , where X and Al represent the weight % concentrations of element X and Al, respectively. Samples were normalized using the average upper crust (AUC) compositions of McLennan (2001). Aluminum normalization is commonly used to minimize the effects of variable dilution by carbonate or biogenic silica, although certain caveats apply to this approach (for a discussion, see Van der Weijden *et al.*, 2002). The convenience of using enrichment factors is that any value larger than 1.0 points to enrichment of an element relative to its average crustal abundance. In practical terms, EFs > 3 represent a detectable enrichment of an element over average crustal concentrations, and EFs > 10 represent a moderate to strong degree of enrichment (Algeo and Tribovillard, 2009).



**Fig. 3.** Compared stratigraphic evolution of the sorting index for the studied three sections.

The  $< 2 \mu\text{m}$  clay fraction was isolated and analyzed using the standard protocol for clay-mineral assemblage determination (a Bruker D4 Endeavour apparatus was used together with the Macdiff software; see detailed protocol in [Bout-Roumazeilles \*et al.\*, 1999](#)).

Lastly, low-field magnetic susceptibility was measured on the dried samples, using a Kappabridge KLY 2 apparatus (three measures per sample) operating at an alternating magnetic field of 300 A/m (frequency 920 Hz). Low-field MS values were normalized with respect to sample mass to allow comparisons between samples of different density.

## 4 Results

The analytical results are gathered in [Tables S1–S3](#) (see on-line supplementary data).

### 4.1 Grainsize analysis

The dominant size fraction is that of silt for the three sections. Consistently with the existence of the proximal-distal gradient, the most remote site of Cap de la Crèche yields a relatively important clay-size fraction (up to 20%), while the most proximal Cap Gris-Nez site shows a relatively important

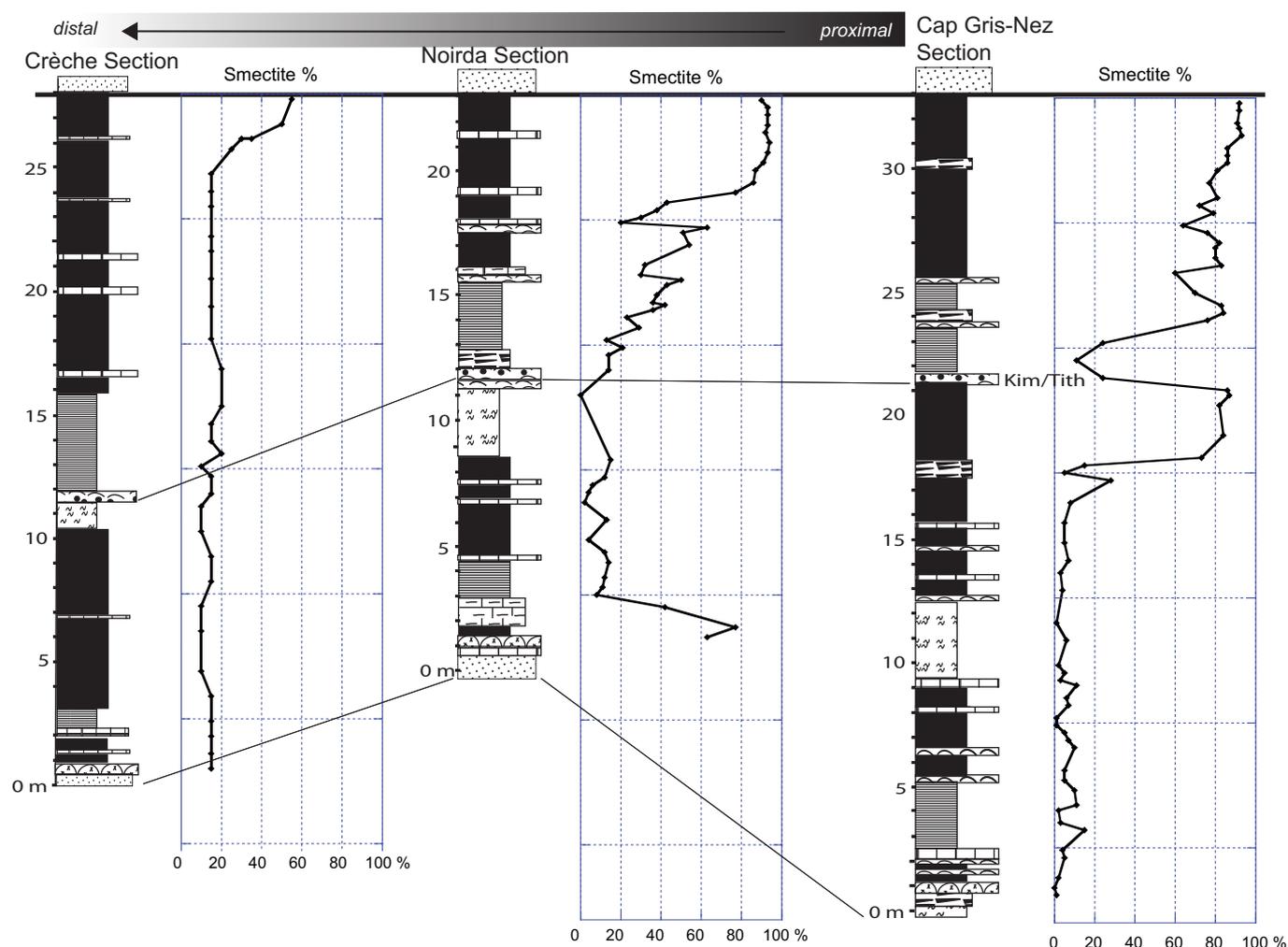
fine-sand fraction (up to 20%). In addition, sorting is smoother at Cap de la Crèche than at Cap Gris-Nez. The sorting index used here is the classic one defined by [Folk and Ward \(1957\)](#), using the  $\Phi$  notation:  $(\Phi_{84} - \Phi_{16}) \div 4 + (\Phi_{95} - \Phi_5) \div 6.6$ . [Figure 3](#) and [Tables S1 to S3](#) (supplementary data) summarize the lateral evolution of grain-size distribution.

### 4.2 Clay-mineral assemblages

The assemblages contain illite, smectite, kaolinite and chlorite in variable proportions. Chlorite is the less abundant clay mineral, and shows smoothed stratigraphic distributions. Smectite distribution is largely opposed to that of illite + kaolinite, which is also the case at the scale of the entire Late Jurassic in the Boulonnais ([Deconinck \*et al.\*, 1996](#)). At the Cran du Noirda and Cap Gris-Nez sites, the smectite content starts increasing from the Kimmeridgian-Tithonian boundary upward, whereas the increase is observed only in the top three meters at Cap de la Crèche ([Fig. 4](#)).

### 4.3 Rock Eval parameters

Organic matter is present in the three sections, with TOC values falling into the 0.1–7.7% range (a maximum of 9% was recorded in the Cap de la Crèche section, as reminded above).



**Fig. 4.** Compared stratigraphic evolution of the proportion of smectite within the clay-sized assemblages for the studied three sections.

Figure 5 illustrates the distribution of the Tmax and HI values, as well as the TOC range and mean, for the three sections. All the samples (but 3) fall in the “immature” zone of the diagram, as determined by Tmax. The HI parameter shows that the samples of the three formations straddle the kerogen Types II and III, which indicates that a mixture of marine and terrestrial OM in variable proportions is present, for the three sites. The Cap de la Crèche samples are scattered between the lowest and highest ends of the sample sets. The Gris-Nez samples do not reach HI values as high as those of the other two sections. For the three sections, the highest TOC values are observed in the laminated shale levels. Lastly, a positive correlation is observed between TOC and HI, as already observed and discussed in Tribouvillard *et al.* (2001).

#### 4.4 Magnetic susceptibility and carbonate content

The stratigraphic distribution of magnetic susceptibility is, by and large, the same for the three sites, with a slight decrease upward in the section. Lastly, the vertical distribution of the carbonate content does not yield specific trends. At the Cap Gris-Nez, the high number of coquina beds induces more “noise” in the stratigraphic distribution.

#### 4.5 Trace metals

A sample subset was analyzed for the elemental composition, 8 samples from the Cap Gris-Nez section, 19 samples from the Cran du Noirda section and 14 samples from the Cap de la Crèche section. The samples were taken below, within and above, respectively, the laminated shale levels, in order to cover a relatively wide array of TOC values. Focusing on the oxygen conditions of the depositional environment, the usual redox proxies, namely, uranium, vanadium and molybdenum (*e.g.*, Algeo and Rowe, 2012; Brumsack, 2006; Scott and Lyons, 2012; Tribouvillard *et al.*, 2006) were observed. These elements show no or modest enrichments. Vanadium shows a clear linear correlation to the aluminum content, which indicates a terrigenous origin. In contrast, Mo and U show poor correlation with Al. Considering enrichment factors (EF), Mo and U show EFs close to the value 1 for the Cap de la Crèche samples, which means that the elements are present in proportions identical to what is observed for the average upper crust of the Earth. In other words, no authigenic enrichment is visible for this distal section. The samples of the more proximal sections (Cap Gris-Nez and Cran du Noirda) show modest enrichments EF

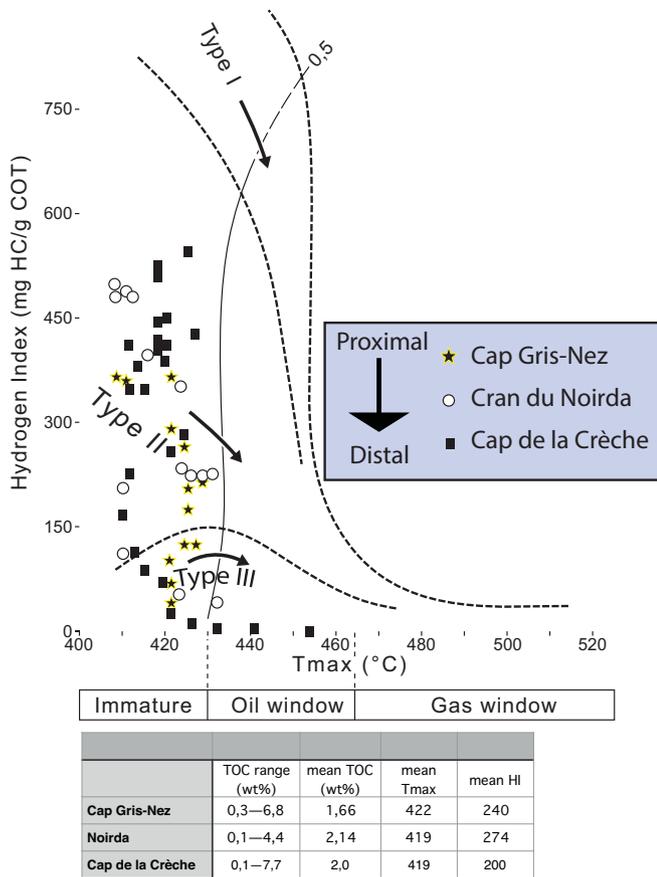


Fig. 5. Rock Eval data.

ranging from 1 to 6 for U and from 1 to 8 for Mo. A crossplot opposing the values of the enrichment factors of U and Mo, respectively, is drawn (Fig. 6) to decipher the oxygenation conditions of the depositional environments (see explanations of such diagrams in Algeo and Tribovillard, 2009; Tribovillard *et al.*, 2012). All samples (mixing the three sections) fall in the “oxic to suboxic” area of the diagram, largely close to the “oxic” zone with both U and Mo keeping with enrichment-factor values below 10.

Regarding proxies for paleoproductivity (Böning *et al.*, 2015; Tribovillard *et al.*, 2006), nickel and copper show enrichment factors below or close to the value 1, that is, no authigenic enrichment.

## 5 Discussion

### 5.1 Smectite abundance and relative sea-level variations

The distribution of clay minerals along the proximal-distal transect at stake here shows that smectite is more abundant in the proximal environments than in the distal one (Fig. 4). This observation is counter-intuitive, in that differential settling of clays usually induces smectite prevalence in remote settings, in relation to its high floatability (Chamley, 1989). However, this unexpected observation was already expressed at least for the deposits ranging from the Oxfordian/Kimmeridgian Boundary

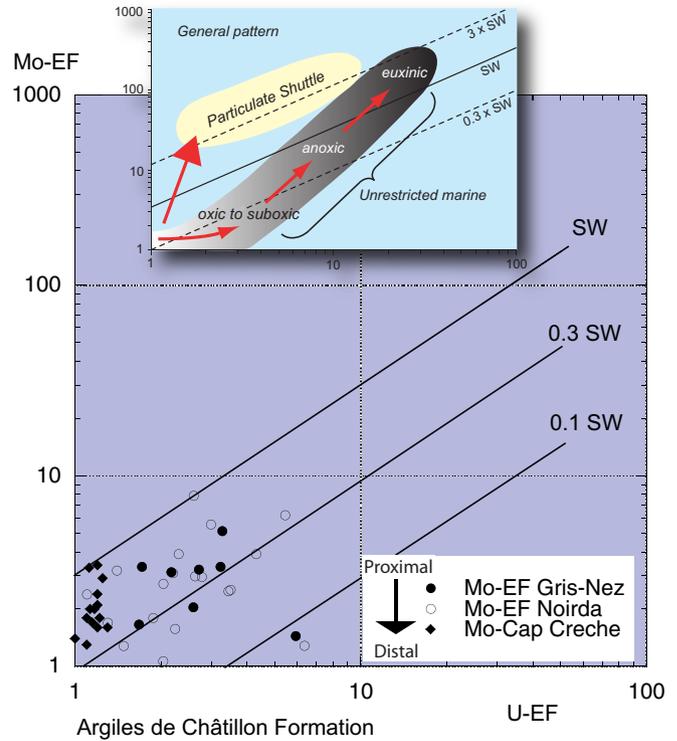


Fig. 6. Cross-plot opposing the respective enrichment factors of U and Mo for the three sections studied, as designed by Algeo and Tribovillard (2009) to derive paleoenvironmental information.

to the end of the Tithonian of the Boulonnais (Deconinck *et al.*, 1982; Hesselbo *et al.*, 2009; Schnyder *et al.*, 2000). These authors, grounding on their own results and those of published works, concluded that the landmass of the London-Brabant Massif was the likely source of detrital particles in the nearshore of the Boulonnais and that the low relief of this landmass would have been favorable to the steady-state erosion of smectite-rich soils. Hesselbo *et al.* (2009) observed the unusual occurrence of smectite in the shallowest environments throughout the Jurassic successions of the Boulonnais, whereas smectite is usually deposited in quiet offshore settings. Their interpretation is that during sea-level lowstand, the London-Brabant Massif was emerged and provided detrital smectite. Contrastingly, during sea-level highstand the massif was submerged and clay sedimentation was dominated by illite, kaolinite and I-S mixed-layer clays originating from more distant areas, including the Central, Armorican and Cornubian massifs.

The same view may apply at the scale of the Argiles de Châtillon Fm. The formation recorded an initial sea-level rise followed by a gradual sea-level fall (Deconinck *et al.*, 1996; Proust, 1994; Proust *et al.*, 1993, 1995). The sea-level fall was accompanied by the release of smectite from the emerged part of the London-Brabant Massif. The supply of smectite was recorded first by the proximal settings (Cap Gris-Nez) and gradually by the more distal settings (Cran du Noirda section and, in the end, Cap de la Crèche section; Fig. 4). What is noticeable here is that such a gradient in smectite distribution is observed on a scale of about 15 km. With such distances, one

would intuitively expect the dispersal of smectite particle inputs to be immediate, from a geological standpoint. As we have no hint that the Kimmeridgian-Tithonian boundary could be wrongly identified, basing on previous works and our own observations, we must conclude that smectite dispersal was gradual. We may suggest that local currents in the Boulonnais embayment could have limited smectite dispersal but this is only conjectural. However, in another geological setting (New Jersey margin), [Deconinck and Vanderaveroet \(1996\)](#) also observed a steep gradient of smectite proportions over a distance of < 50 km, which cannot be ascribed to a change in particle sources or the climate. See also how smectite differential settling and climate influence may be discussed for Cenomanian deposits of France or Morocco (Agadir-Tarfaya area; [Chamley \*et al.\*, 1990](#); [Deconinck and Chamley, 1995](#); [El Albani \*et al.\*, 1999](#); [Gertsch \*et al.\*, 2010](#)). In the case of the Boulonnais, the smectite gradient cannot be accounted for by climatic variations and only sea-level variation coupled to differential settling is put forward (possibly in conjunction with local factors such as currents, seabed topography or mixing of water masses with contrasting salinity that can be evoked in an embayment).

Such a smectite gradient over relatively short distances (here, ca. 15 km) is an interesting indication for all those using the composition of clay-mineral assemblages as a paleoclimatic or paleo-environmental tool. Variations in the abundance of smectite in an ancient sedimentary succession must be questioned in terms of sea-level variations, as well as in terms of evolution of on-land clay sources, even in small-dimension basins.

## 5.2 potential oil source-rock despite lowly favorable conditions

The second point to comment is that the Argiles de Châtillon Fm. has some of the characteristics of a potential petroleum source rock, as well as its lateral, time-equivalent counterpart of the Kimmeridge Clay Fm. in UK ([Herbin \*et al.\*, 1995](#); [Tribovillard \*et al.\*, 2005](#)). However, the Argiles de Châtillon Fm. was deposited above the storm wave base, where sediment accumulation was overwhelmed by silt-sized particles, and not clay-sized ones. The Cap de la Crèche section was probably close or sometimes below the shoreface/lower offshore limit. The most-OM-rich levels, namely, the laminated shales, are – unexpectedly – not enriched in clay-sized fraction relatively to the other shales of the sections. In other words, the grain size itself of the clastic fraction of the sediment (clay vs. silt, which relates to pore-water and dissolved-oxidant circulation and replenishment) did not preside directly over OM accumulation. However, this must be replaced in the light of the works by [Macquaker \*et al.\* \(2010\)](#); [Schieber and Southard \(2009\)](#); [Schieber and Yawar \(2009\)](#) and [Schieber \*et al.\* \(2007\)](#) who studied the way organic-mineral aggregates may accumulate in silt-rich deposits.

As far as redox conditions of deposition are concerned, the redox-proxying trace metals show that depositional conditions were not particularly prone to the development of oxygen limitation. The redox conditions may thus be termed as “normal marine” for many of the samples, according to the seminal sense of the term defined by [Raiswell and Berner](#)

(1985). “Normal marine” must be used to refer to oxygenated conditions within the water column and at the sediment-water interface, with suboxic to anoxic conditions developing at shallow depth below this interface. Here, the relative enrichments in U and Mo observed for the proximal and intermediate sections (namely, Cap Gris-Nez and Cran du Noirda) indicate that the water column as well as the interface must have kept oxic, but for the samples yielding a detectable enrichment, reducing conditions must have got close to the sediment-water interface, inducing some diffusional capture of U and Mo ([Algeo and Tribovillard, 2009](#); [Scott and Lyons, 2012](#); [Tribovillard \*et al.\*, 2012](#)). These redox conditions, inferred from trace metal concentrations, are corroborated by the presence of benthic foraminifers (A. Teresina, unpublished Master thesis). Benthic foraminifer assemblages are observed in various facies of the Argiles de Châtillon Fm., including the laminated shales. The assemblages are dominated by the genus *Lenticulina* ([Kandel, 1969](#)). However, it is known that some benthic foraminifers may be present in oxygen-poor environments.

The trace elements referred to as proxies to paleoproductivity, *i.e.*, Ni and Cu (see discussion in [Böning \*et al.\*, 2015](#); [Tribovillard \*et al.\*, 2008](#)), do not show any enrichment, thus suggesting that productivity was not high (we will not mention barium that cannot be used as a paleoproxy in the case of such relatively shallow environments). This conclusion is consistent with the one derived independently from organic parameters in the study by [Tribovillard \*et al.\* \(2001\)](#). The latter study concluded to productivity levels being of the same order of magnitude as that observed on today’s marine platforms.

The predominance of silt over clay-sized minerals indicates that the depositional settings were not far away from shore, in turn suggesting that the sedimentation rate may have been relatively important, compared to common, clay-dominated, source rocks deposited in distal environments. In addition, the Argiles de Châtillon Fm. is (sometimes heavily) bioturbated (except for the laminated shales), which of course is not known to be a factor favorable to OM burial.

The distal-proximal gradient is observed within the Argiles de Châtillon Fm. and is best recorded by the lateral grain-size distribution. The organic content is only moderately impacted by the gradient. The land-derived, Type III, OM is expectedly a little more abundant at the Cap Gris-Nez as indicated by Rock Eval parameters ([Fig. 5](#)), but marine, Type II, OM is also present in the more proximal part of the basin. IH values appear not very different when comparing Cran du Noirda and Cap Gris Nez section, despite the proximal-distal gradient, whereas the Cap de la Crèche section shows relatively lower IH and higher Tmax values. [Wignall and Newton \(2001\)](#), basing on detailed facies observation, reported that oxygen levels were (at least episodically) lower in proximal settings of the Boulonnais than in more distal environments. An echo of this observation may be found in the redox-proxy distribution, since the Cran du Noirda and Cap Gris-Nez sections recorded slightly higher enrichment in Mo and U, compared to the Cap de la Crèche section (but not reaching anoxic conditions; [Fig. 6](#)). This can help explaining the somewhat lower HI/higher Tmax values of the Cap de la Crèche section.

Thus, the first conclusion is that one may encounter potential source rocks even in settings that are not *a priori* prone to OM preservation and storage: relatively shallow

environments dominated by deposition of silt-sized clastic particles, where sediment showing evidence of bioturbation and bio-irrigation were accumulated under normal-marine redox conditions. In addition, productivity was not high, but probably just comparable to what is observed on present platforms. The fact that the proximal-distal gradient did not impact significantly OM accumulation suggests that particle size distribution seems not to be a first-order parameter for OM accumulation, but, as evoked above, the fact that silt-rich deposits may trap organic-mineral aggregates must be kept in mind.

Despite environmental conditions that may be judged as unfavorable, or at least lowly favorable to OM preservation, the sediments studied here contain OM in noticeable abundance. The discrepancy must be explained.

### 5.3 Iron limitation, enhancing OM sulfurization, then OM preservation

Within the Cap de la Crèche section, one can observe a marked enrichment in organic S-rich OM (sulfurized amorphous OM) in sediments deposited under normal marine conditions: the sediments accumulated up to several weight percents of vulcanized OM, whereas trace-metal distribution (together with the presence of benthic foraminifers and bioturbation) shows that bottom conditions were not reducing nor oxygen-deprived (except perhaps for the laminated intervals but they contain benthic forams, *i.e.*, lenticulina), reminding the Cap de la Crèche section has the lowest enrichment-factors values for U and Mo (see Tribouvillard *et al.*, 2001 for detail about the abundance of AOM in this section). The other two sections studied shows lower TOC values. In addition, the strong S-rich OM accumulation of the Cap de la Crèche took place under conditions of moderate productivity. This observation is not common, since accumulation of abundant, sulfurized OM has been attributed hitherto for paleo-environments characterized by high productivity and/or low terrigenous supply (review in Vandenbroucke and Largeau, 2007). In a few words, OM sulfurization takes place when sulfide ions can react with functionalized organic molecules, which implies that all the sulfide ions are not monopolized by Fe(II). An iron deficiency, either relative or absolute, will favor sulfide-OM interactions. If reactive iron is little or not supplied to the depositional environment, the iron deficiency will be termed as absolute. If reactive iron is actually supplied, but if a high organic flux is also present (in case of high productivity), the large pool of sulfide ions generated through bacterial sulfate reduction (at the expense of OM) will exhaust the reactive iron pool. As a consequence, sulfide will be available for sulfurization (Tribouvillard *et al.*, 1994; Zaback *et al.*, 1993).

In the case of the Argiles de Châtillon, according to the information gathered from previous studies about the Cap de la Crèche section (Tribouvillard *et al.*, 2015), the Fe/Al ratio is most of the time close to the “stoichiometric” value of the averaged upper crust (0.44; McLennan, 2001) or slightly above it (mean Fe/Al=0.53; n=63). In the previous studies evoked above (Tribouvillard *et al.*, 2015), the part of the Fe content that is postulated to be in excess relative to the clastic fraction-associated part of the iron inventory (called  $Fe_{xs}$ ) was

calculated: taking into consideration the long diagenetic history of the sediments deposited about 152 millions years ago, as well as the detrital nature of the studied sedimentary rocks, it is considered that the chemically-inert fraction of the iron content was the part incorporated into the lattices of alumino-silicates; this non-reactive, or detrital part is calculated according to the following formula:

$$Fe_{\text{detrital}} = [Al]_{\text{sample}} \times [Fe]/[Al]_{\text{upper crust}}, \text{ with } [Fe]/[Al]_{\text{upper crust}} = 0.44 \text{ (McLennan, 2001).}$$

The iron content in excess to the detrital part then derived using the formula:

$$Fe_{xs} = Fe_{\text{total}} - Fe_{\text{detrital}}.$$

This fraction  $Fe_{xs}$  is considered to give a good estimate of the “paleo” reactive-iron proportion, regardless of its present mineralogical carrier phase, after the successive steps of long-term diagenesis (see Scholz *et al.*, 2014). In the case of the Cap de la Crèche section,  $Fe_{xs}$  represents 16% on average of the total Fe inventory (Tribouvillard *et al.*, 2015). Thus, it is inferred that the amount of reactive iron was relatively limited in the sediments of this section, compared to the other sections studied here. It is concluded that sulfate-reducing reactions, induced by bacterially-mediated OM remineralization, operated with sediments rich in land-derived, clastic fractions, but limited in reactive iron (despite abundant silt and clay fractions). Consequently, in the Cap de la Crèche section, OM could react with free (“unemployed”) sulfide ions and accumulate organic sulfur. This sulfurization protected OM against further bacterial remineralization and permitted its accumulation in relatively large proportions. The important point is that reactive-iron limitation triggered OM sulfurization in spite of a relatively low supply of OM: remineralizing a large pool of OM producing enough sulfide to immobilize all the reactive iron ions was not required, since the reactive iron pool was limited. Consequently, although the OM flux must have been moderate (moderate surface productivity), OM was protected through sulfur incorporation and thus stored in relatively large amounts.

Comparatively, excess iron is significantly more abundant in the other two sections that are more proximal than the Cap de la Crèche section.  $Fe_{xs}$  represents 32% on average of the total Fe inventory in the Noirda section, and 30% in the Cap de la Crèche section. For these two sections that are poorer in organic carbon than the Cap de la Crèche section, TOC values seem to be negatively correlated to the relative abundance of excess iron. The determination coefficient is of only 0.04 (n=12) for the Gris Nez samples but is 0.61 (n=14) for the Noirda samples. These results suggest that an increased amount of reactive iron may be associated to a decreased preservation of OM, but our data set does not allow us evidencing any clear-cut linear relation.

Iron, as an agent favoring OM remineralization was extensively discussed by Meyers *et al.* (2005) and Meyers (2007). For these authors, a relatively abundant flux of reactive iron will allow buffering dissolved sulfide *via* iron sulfidization (Canfield *et al.*, 1992; Raiswell and Canfield, 1996). The toxic dissolved sulfide is thus put “harmless”, which will stop preventing the presence of in-fauna. The possible presence of in-fauna will increase bioturbation and bio-irrigation, required to maintain oxidants such as dissolved oxygen and nitrate in pore waters, and hence enhance OM remineralization. Furthermore, active bioturbation and bio-irrigation can expand

the thickness of the zone of aerobic OM degradation, thus increasing the exposure time of OM to dissolved oxygen. Reversely, these factors fostering OM degradation will be much tempered in case of reactive-iron limitation (Meyers, 2007). Our work adds one positive effect of iron limitation regarding OM accumulation: the sulfide ions, maintained at relatively high concentration in the dissolved state (if no iron-induced buffering takes place), as is the case for the Cap de la Crèche samples, will induce OM sulfurization, thus fostering OM preservation and hence, its burial. This OM accumulation is possible even in the case when OM is not particularly abundant, as is the case here.

Now an additional question is about the reason(s) why a relative iron deficiency may be observed in the case of the Cap de la Crèche, because the sediments are rich in fine-grained particles (silts and clays), which is *a priori* favorable to the presence of adsorbed iron ions (Burdige, 2006).

#### 5.4 The causes of the reactive-iron deficiency or presence

The Argiles de Châtillon Fm. was deposited under relatively distal conditions accompanied by occasionally-reduced sedimentation rates, in a general context of sea-level rise (see Proust *et al.*, 1995 or Wignall and Newton, 2001 for a detailed sequence stratigraphy description). Generally speaking, the reactive-iron supply to a basin may be conditioned by several factors:

- the relative width of the platform being flooded during sea-level rise. The larger the transgression, the larger the volume of reworked and remobilized sediments, which will impact the possible release of iron, coating fine particles;
- the flux of river-borne (Severmann *et al.*, 2010) or air-borne (*e.g.*, Baddock *et al.*, 2013; Buck *et al.*, 2013) iron-coated particles;
- the flux of OM possibly associated with reactive iron (*e.g.*, Barber *et al.*, 2014; Bressac and Huieu, 2013; Krachler *et al.*, 2012; Shigemitsu *et al.*, 2013). Notably, Krachler *et al.* (2012) indicated that peatland-derived iron-bearing lignin particles may have a sufficiently long half-life in ocean water to sustain iron concentration in extended regions of the ocean;
- the offshore discharge of anoxic ground waters may generate O<sub>2</sub>-undersaturated bottom water masses that can be advected into nearshore waters (Peterson *et al.*, 2016). These anoxic water masses may thus carry dissolved iron.

In parallel, iron may be redistributed with the marine environment itself. The current model (Anderson and Raiswell, 2004; Lyons and Severmann, 2006; Owen *et al.*, 2012; Poulton and Canfield, 2005; Poulton and Raiswell, 2002; Raiswell and Canfield, 2012; Rickard, 2012; Scholz *et al.*, 2013, 2014) explains how detrital iron deposited on the shelf may undergo suboxic diagenesis, thus releasing dissolved Fe (II). This aqueous iron may diffuse out of the sediment through the sediment-water interface where it is oxidized and trapped as reprecipitated Fe(III) oxyhydroxides. Nevertheless, a fraction of the dissolved iron thus released may be transported to the deeper (possibly euxinic) parts of the basin where it will

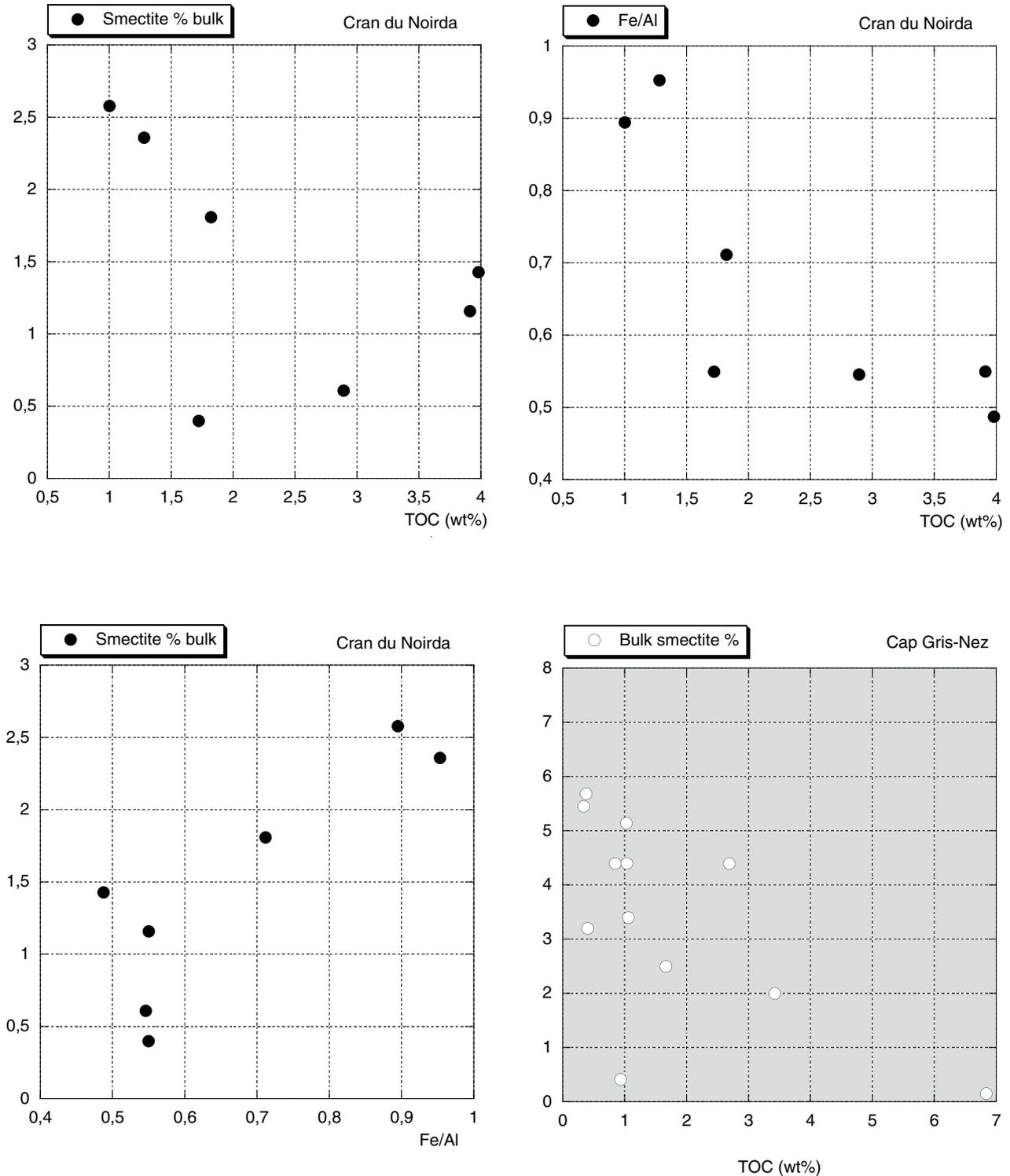
be sequestered as iron sulfide (see discussion in Little *et al.*, 2015).

Discussing these factors is rather hypothetical in the case of the Argiles de Châtillon, even if each of them can apply to the situation. That is why the attention will be instead focused on the composition of clay-mineral assemblages.

##### 5.4.1 Iron and clay-mineral assemblages

The clay-mineral assemblages observed in the Boulonnais are composed of illite and kaolinite opposed in abundance to smectite, plus illite-smectite mixed-layer minerals and chlorite, the latter being negligible (Deconinck *et al.*, 1982, 1996). Smectite is a potential carrier phase for reactive iron, whereas illite and kaolinite are less prone to be coated by reactive iron (Canfield *et al.*, 1992; 1996; Chamley, 1989). Structural iron, relatively abundant in illite, cannot be considered to be reactive as long as it is part of the mineral lattice. Thus, attention must be paid to the relations between smectite abundance and iron proportions. Concerning the Cap de la Crèche section, the decarbonated fraction of the rocks of the entire section contain between 7 and 25% of clay-sized fraction (< 4 μm), and within the clay fraction itself, smectite amounts to less than 25% all along the section but the top three meters, inducing that smectite represents between 1 and 4% of the clastic fraction of the rock, which is negligible. Contrastingly, in the Cran du Noirda section with 5–17% clay fraction, and with 0–93% of smectite in the clay assemblage, smectite represents between 0 and 11% of the clastic fraction of the rock composition. In the proximal Cap Gris-Nez section with 5–25% clay fraction, and with 0–93% of smectite in the clay assemblage, smectite represents between 0 and 7% of the clastic fraction of the rock composition. For the sample subsets for which data about both the clay-mineral assemblages and geochemical composition are available, one can observe a positive correlation between the proportion of smectite within the bulk decarbonated fraction of the rock and the relative reactive-iron abundance, as well as a negative relationship between bulk smectite and TOC in the case of the Noirda section (Fig. 7). In the case of the Cap Gris-Nez section, a clear negative correlation is drawn between bulk smectite content and TOC.

With this small sample set, we cannot be too ambitious in our interpretations, but we suggest that first, smectite could be associated with reactive iron (as may be observed in lacustrine or marine depositional environment; Mahamat Ahmat *et al.*, 2016, 2017) and, second reactive iron could be associated with reduced OM preservation. The inference is twofold. First, if true, a correlation between reactive iron and smectite indicates that the amount of clay, even when present in relatively low proportions in the sediments of rocks, may have a significant impact on bulk-rock chemical composition. Second, and maybe more crucial, the correlation indicates that smectite may govern (at least partly) the amount of reactive iron of the sediment, which in turn impacts OM preservation (Mahamat Ahmat *et al.*, 2016 and references therein). A higher abundance of reactive iron, capturing free sulfide and hence hampering OM sulfurization, may limit OM preservation. It is thus suggested that the amount of smectite may have a negative imprint on OM preservation and accumulation.



**Fig. 7.** Cross-plots illustrating the relationships between the Fe/Al ratio, TOC values and the proportion of smectite within the carbonate-free fraction of the bulk rock.

This interpretation is in partial contradiction with usual interpretations. Clay minerals, especially smectite, are considered to have a positive effect regarding OM accumulation (Keil and Mayer, 2014; Mahamat Ahmat *et al.*, 2016, 2017; Zhang *et al.*, 2014 and references therein): OM is frequently associated with fine-grained clay minerals, due to

their high specific surface area, cation exchange capacity and hence their strong adsorption capacity. In clay-rich sediments, OM abundance is commonly correlated with smectite abundance. This correlation suggests that the expandable internal surface of smectite (*i.e.*, interlayer region) can sequester large amounts of molecular-scaled OM (Keil and

Mayer, 2014; Kennedy and Wagner, 2011; however, see discussion in Mahamat Ahmat *et al.*, 2016). Indeed, it has been suggested that enhanced organic matter preservation in sediments is largely due to increased smectite abundance in sedimentary record through geological time (Kennedy *et al.*, 2006): organic matter, once associated with smectite-rich sediments, would be physically protected against microbial oxidation (see details in Keil and Mayer, 2014; Mahamat Ahmat *et al.*, 2016, 2017; Zhang *et al.*, 2014). However, as reminded above, smectite can also bring reactive iron, which will impact OM preservation: first, iron oxi-hydroxides are electron acceptors used by bacteria during OM remineralization; an input of reactive iron may thus fuel OM-consuming bacteria. Second, iron may impede sulfurization, as already mentioned. In other words, smectite is susceptible to convey both OM (organic molecules, *i.e.*, dissolved organic carbon) and reactive iron, that is, the organic substrate and the iron used to consume the organic substrate.

All the studies showing a link between the abundance of smectite and the organic-molecule supply (see above) refer to present-day sediments or settling-particle fluxes; here we study ancient sediments. One hypothesis is that iron conveyed by smectite and progressively released during sediment (early) diagenesis, may have a deleterious effect on OM on the long run. Thus our preliminary results and interpretations bring new and complementary views about what is currently known regarding the role of smectite played in OM accumulation. However, our results are obviously too fragmentary and need further testing on other geological formations.

## 6 Conclusions

This work, synthesizing several previously published results and bringing new data about the detrital fraction of the rocks of the Argiles de Châtillon Fm., allows us having a consistent, multi-parameter, view of the depositional conditions that favored OM accumulation. Some of our conclusions are neither restricted to the Argiles de Châtillon Fm., nor to the Boulonnais region, but may be extended to many other clastic-dominated, relatively shallow, platform environments where black shales or even possible oil source-rocks were accumulated. However, we do not consider the factors favoring OM accumulation discussed here, grounding on the central role of reactive iron, as being exclusive. Vulcanization is one processus among some (many?) other ones allowing for OM preservation. The first “take-home” message of the present work is that OM may be accumulated up to a few weight percents of organic carbon in rocks largely dominated by silt and with only < 20% clay-sized minerals, and showing evidence of bioturbation, and deposited under conditions of moderate productivity. In other words, a significant OM enrichment may be observed in ancient sediments deposited under environmental conditions that were not specifically prone to OM preservation. The second teaching is that our results suggest that the clay-mineral assemblages may have a significant impact on reactive iron abundance even when the clay fraction is present in modest proportions compared to silt. The third message is that smectite, usually considered to have a positive influence on OM adsorption and preservation, may also have a negative

impact when this mineral can carry and release reactive iron during diagenesis. This iron may in turn react with sulfide ions released from OM decay mediated by sulfate-reducing bacteria, which prevents free sulfide to react with OM. OM sulfurization being limited by capture of free sulfide by reactive iron, OM preservation and accumulation will be hampered. However, this third message is suggested by our (quite simplistic) observations but still needs to be tested with other geological settings. Furthermore, even if our hypothesis is further confirmed, the exact mechanism is still to be determined: is reactive iron release by desorption from clay-mineral surface or by structural iron being reduced and solubilized through bacterial activity or clay-mineral diagenesis? Lastly, this study shows that a gradient in smectite distribution may be observed on a scale even as small as about 15 km, resulting from the way sea-level variations (re-) mobilize the on-land clay-mineral inventories. The more-or-less important abundance of smectite in an ancient sedimentary succession must be questioned in terms of sea-level variations, as well as in terms of evolution of on-land clay sources, even in small-dimension basins.

## Supplementary material

Table S1 Grainsize parameters, carbonate content, composition of the clay-mineral assemblages and magnetic susceptibility of the analyzed samples from the Cap de la Crèche section.

Table S2 Grainsize parameters, carbonate content, composition of the clay-mineral assemblages and magnetic susceptibility of the analyzed samples from the Noirda section.

Table S3 Grainsize parameters, carbonate content, composition of the clay-mineral assemblages and magnetic susceptibility of the analyzed samples from the Cap Gris-Nez section.

The supplementary material is available at <http://www.bsgf.fr/10.1051/bsgf/2017193/olm>.

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