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

Jean-François Deconinck, Danny Boué, Francis Amédro, François Baudin, Ludovic Bruneau, Emilia Huret, Philippe Landrein, Jean-David Moreau, Anne Lise Santoni

To cite this version:

Jean-François Deconinck, Danny Boué, Francis Amédro, François Baudin, Ludovic Bruneau, et al.. First record of early Aptian Oceanic Anoxic Event 1a from the Paris Basin (France) - Climate signals on a terrigenous shelf. Cretaceous Research, 2021, 125, pp.104846. 10.1016/j.cretres.2021.104846 . hal-03222734

HAL Id: hal-03222734
https://hal.science/hal-03222734
Submitted on 9 May 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License
First record of early Aptian Oceanic Anoxic Event 1a from the Paris Basin (France) - climate signals on a terrigenous shelf

Jean-François Deconinck¹, Danny Boué¹, Francis Amédro¹², François Baudin³, Ludovic Bruneau¹, Emilia Huret⁴, Philippe Landrein⁴, Jean-David Moreau¹ and Anne Lise Santoni¹

¹ Biogéosciences, UMR 6282, uB/CNRS, Université de Bourgogne/Franche-Comté, 6 Boulevard Gabriel, 21000 Dijon, France.
² 26 rue de Nottingham, 62100 Calais, France.
³ ISTeP, UMR 7193, SU/CNRS, Sorbonne Université, 4 Place Jussieu, 75005 Paris, France.
⁴ Agence Nationale pour la gestion des déchets radioactifs, Centre de Meuse/Haute-Marne, RD 960, 55290 Bure, France.

Abstract

In 2013, Andra (French National Radioactive Waste Management Agency) drilled boreholes to the south-east of the Paris Basin, to characterise Aptian and Albian clayey formations, including the ‘Argiles à Plicatules’ Formation dated as early Aptian. One of these boreholes intersected this formation with an excellent recovery allowing detailed biostratigraphy (ammonites), sedimentology, clay mineralogy, isotope geochemistry ($\delta^{13}$Corg) and Rock-Eval analyses to be performed. The base of the formation corresponds to transgressive dark-grey silty clays with iron oolites and plant debris indicating a coastal environment evolving up-section to upper offshore environments. Higher in the succession, clays with less than 4% CaCO$_3$ and less than 0.8% of organic matter were deposited in lower offshore environments. The occurrence of ammonites can be used to draw a biostratigraphic scheme, and in particular, to recognise the deshayesi and furcata ammonite Zones.
The clay mineral assemblages are composed of illite and kaolinite associated with minor amounts of chlorite, vermiculite and smectite. The $\delta^{13}C_{\text{org}}$ values range between -24 and -25‰ except in a particular interval characterised by a prominent negative excursion of about -3‰, that is recognised worldwide and precedes Oceanic Anoxic Event 1a (OAE1a). This interval is also characterised by an abundance of kaolinite and the absence of smectite suggesting an acceleration of the hydrological cycle and enhanced runoff and hydrolysing conditions over the emerged landmasses just before and during the onset of OAE1a. This climate change is consistent with isotope and palynological data indicating warm and humid climate conditions before and during the onset of OAE1a. Surprisingly, the interval corresponding to OAE1a is not significantly enriched in organic matter and its lithology is not different from the rest of the core suggesting that Tethyan anoxic water masses did not reach the relatively shallow epicontinental environments of the Paris Basin.

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

Introduction

Identified for the first time by Schlanger and Jenkyns (1976), Oceanic Anoxic Event (OAE) 1a (early Aptian) is characterised by the worldwide preservation of organic matter in black shales as a consequence of intensification in marine primary productivity under oceanic oxygen-depleted conditions (Cocconi et al., 1987; 1992; Erba, 1994, Erba, 2004; Erbacher et al., 1996; Leckie et al., 2002; Jenkyns, 2010; Föllmi, 2012; Erba et al., 2015). A global perturbation in the carbon cycle is associated with this event, recorded by a prominent negative excursion followed by a shift towards more positive values (Menegatti et al., 1998).
The negative excursion is generally explained by an intense volcanic episode at the origin of the formation of the Ontong-Java oceanic plateau (Tarduno et al., 1991; Larson and Erba, 1999; Méhay et al., 2009; Tejada et al., 2009; Bottini et al., 2012; Erba et al., 2015; Charbonnier and Föllmi, 2017) while the following positive excursion is seen as a consequence of organic matter burial in oceanic sediments. The duration of the negative excursion, first underestimated between 27 and 44 kyr (Li et al., 2008), is likely longer with a duration estimated between 280 and 350 kyr (Lorenzen et al., 2013). The duration of OAE1a itself is estimated between 1 and 1.3 myr (Li et al., 2008). These environmental changes were associated with rising sea surface temperatures (Mutterlose et al., 2014; Bottini et al., 2015) and a calcification crisis in calcareous nannoplankton known as the ‘nannoconid crisis’ (Erba, 1994). Despite its widespread extension and its recognition in numerous sedimentary basins (Bréhéret, 1997; Bellanca et al., 2002; Ando et al., 2008; Vincent et al., 2010; Giraud et al., 2018 among others) and shallow water carbonate platforms (Baudin et al., 1996; Luciani et al., 2006; Najarro et al., 2011; Graziano, 2013; Godet et al., 2014; Pictet et al., 2015; Amodio and Weissert, 2017; Hueter et al., 2019), OAE1a has not yet been described in the Paris Basin mainly because lower Aptian clayey deposits are poorly outcropping. In 2013, several boreholes were drilled by Andra (the French National Radioactive Waste Management Agency) to the south-east of the Paris Basin in order to characterise Aptian and Albian clayey formations including Argiles à Plicatules, a so-called formation because of the occasional occurrence of *Plicatula placunae* Lamarck, 1819, a common warm water bivalve (Squires and Saul, 1997). One of these boreholes (AUB 121) intersected the Argiles à Plicatules Formation with excellent recovery allowing detailed sedimentological, mineralogical and geochemical studies to be performed; it also provided an opportunity to search for a record of OAE1a in the Paris Basin. As a result, facies descriptions as well as mineralogical, Rock-Eval and $\delta^{13}$C$_{org}$ analyses were performed to characterise the Aptian sediments deposited in the Paris
Basin. The main objectives were to precisely describe the whole succession of the Argiles à Plicatules Formation, to highlight the record of OAE1a in the terrigenous shelf environment of the Paris Basin and to specify climatic conditions, notably the fluctuations in the hydrological cycle that prevailed during the Aptian through a high resolution study of the clay minerals.

I - Geological context and biostratigraphy

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

After a long period of continental evolution of the Paris Basin starting at the Jurassic/Cretaceous transition (Purbeckian facies), transgressive marine sediments were deposited above Early Cretaceous variegated continental and deltaic sediments, the so-called Wealden facies (Allen, 1998; Guillocheau et al., 2000; Radley and Allen, 2012). To the south-east of the Paris Basin, the Early Cretaceous continental sedimentation (Berriasian to Barremian) was occasionally interrupted by the deposition of shallow marine sediments including the early Hauterivian “Calcaires à Spathangues” Formation and the early Barremian “Argiles Ostréennes” Formation, as a consequence of transgressions originating from the south-east (Tethyan domain), whereas the late Barremian continental deposits consist of
variegated clays showing common root traces. From the Aptian, a continuous marine
sedimentation took place until the end of the Cretaceous.

I-1. Lithology of the AUB 121 borehole

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

- Unit 1, from 116.76 m to 111.90 m, includes black to grey clays with traces of
palaeosoils at the base. Woody debris and coalified compressions of pteridophytes
are common in this part of the formation (Fig. 4A). Some iron oolites-rich layers
(Fig. 4B) occasionally filling burrows occur at the base of this unit, while the top is
marked by the presence of prominent shelly beds (between 112.40 m and 111.90
m) (Fig. 4C).

- Unit 2, from 111.90 m to 106.30 m, consists of a grey-brown bioturbated
(Chondrites) clay, which appears to be homogeneous (no cycles can be
distinguished). Some Plicatula occur occasionally and ammonites are common in
the upper part of this unit.

- Unit 3, from 106.30 m to 86.10 m, corresponds to bioturbated khaki clays
(Chondrites) in which the cycles are clearly individualised and limited at the base
by bioturbated surfaces likely corresponding to firmgrounds. This poorly
fossiliferous unit shows scattered Plicatula, some oysters and ammonites which
allow a biostratigraphic division to be established. Coarser quartz grains and glauconite occur at the topmost part of the formation announcing the overlying sandy glauconitic sedimentation (Sables Verts de l'Aube Formation).

I-2. Biostratigraphy

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

The lower three meters of the Argiles à Plicatules Formation did not provide determinable ammonites in the Juzanvigny boreholes and therefore the stratigraphic attribution of the lowermost part of this formation remains uncertain. The occurrence of several *Roloboceras transiens* Casey, 1961 in the neighbouring department of Yonne and *Megatyloceras* at the base of the Argiles à Plicatules Formation (unpublished data) suggests that the interval could be attributed to the *Deshayesites forbesi* Zone, as these ammonites are characteristic of this biozone. The *Deshayesites deshayesi* Zone is undoubtedly recognised from 113.70 m to 105.15 m by the presence of an association including *Aconoceras* (*Aconoceras*) *nisoides* Sarasin, 1893, *Pseudosaynella bicurvata* Michelin, 1838, *Deshayesites deshayesi* d'Orbigny,
1841 and *Lithancylus grandis* J. de C. Sowerby, 1828. The *Dufrenoya furcata* Zone sensu Reboulet compiler (2018) [= the *Tropaeum bowerbanki* Zone described by Casey (1961)] is clearly identified from 102.50 m to 90.60 m by the occurrence of *Dufrenoya cf. formosa* Casey, 1964 and *Dufrenoya cf. furcata* J. de C. Sowerby, 1836.

II – Analytical methods

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

Organic carbon isotope compositions (δ¹³C<sub>org</sub>) and Total Organic Carbon (TOC) were measured on carbonate-free residues of 80 samples at the Biogéosciences Laboratory, Université Bourgogne/Franche-Comté in Dijon. Sample powders were reacted with HCl (2N) at room temperature for 24 h to remove the carbonate phases. Residues were rinsed with deionised distilled water until neutral, centrifuged (4500 rpm for 15 min), and then dried at 50°C overnight. Aliquots of dried decarbonated samples (~7–50 mg) were then weighed in tin capsules. TOC content and δ¹³C<sub>org</sub> measurements were performed at the Biogéosciences Laboratory of the University of Bourgogne/Franche-Comté (Dijon, France) on a Vario MICRO cube elemental analyzer (Elementar, Hanau, Germany) coupled in continuous flow mode to an IsoPrime stable isotope ratio mass spectrometer (Isoprime, Manchester, UK). USGS40 L-Glutamic acid (C = 40.8 wt%; δ¹³C<sub>VPDB</sub> = -26.39 ± 0.04‰) and IAEA-600 Caffeine (δ¹³C<sub>VPDB</sub> = -27.77 ± 0.04‰) certified reference materials were used for calibration. The carbon isotopic composition is expressed in delta notation and reported in per mil (%ε) relative to the Vienna Pee Dee Belemnite (V-PDB) standard; the external reproducibility based on duplicate analyses of the samples is better than ± 0.2‰ (1σ).

The proportion of CaCO₃ is deduced by the difference in weight before and after decarbonation.
II–2. Organic matter characterisation

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

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

III – Results

III-1. CaCO\(_3\), Organic matter characterisation and \(\delta^{13}C_{\text{org}}\)

In the Argiles à Plicatules Formation, the proportion of CaCO\(_3\) is very low (around 3%) in all of the samples studied (Fig. 5). The total organic carbon (TOC) content measured on the 34 selected samples using Rock-Eval pyrolysis is also very low, comprised between 0.1 and 0.52% (Table 1). As the quantity of organic matter (OM) is low, the Rock-Eval parameters are only partly reliable. However, some reliable \(T_{\text{max}}\) values lower than 420°C indicate that OM is immature (below the oil window). Organic matter is more abundant in
lithological unit 1 at the base of the section; this was expected since macroscopic woody
debris and fern pinnules preserved as coalified compressions were observed (Fig. 4B).

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

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

III-2. Clay mineralogy

The following main clay minerals were identified: a R0 type illite-smectite mixed-
layer (17 Å based on a glycolated run condition) referred to as smectite for the following
sections; chlorite (14.2 Å, 7.1 Å, 4.7 Å and 3.54 Å peaks); illite (10 Å, 5 Å, 3.33 Å peaks);
kaolinite (7.18 Å and 3.58 Å peaks) and vermiculite (14 Å in air-drying conditions, 14.5-15 Å
after ethylene-glycol solvation and 10 Å peaks after heating). In addition, traces of
pyrophyllite are occasionally suspected by the occurrence of a small peak at 9.3 Å. The clay
mineral assemblages are predominantly composed of illite generally between 40 and 50% and
kaolinite with proportions comprised between 20 and 45%. Minor amounts of chlorite (less
than 10%), vermiculite (around 10%) and smectite (generally less than 10%, except at the top
of the formation where the proportions of this mineral may reach 50%) are associated with
these two clay species (Fig. 6). Traces of pyrophyllite are only identified at the base of the
core. Four stratigraphic intervals can be distinguished according to the clay mineralogy. Interval 1 corresponds to the lowermost part of the formation below the bioclastic accumulation and coincides with lithological unit 1. In this interval, the proportion of vermiculite is relatively high and decreases up-section while the proportion of illite increases. The second interval, from 112 to 104.5 m is characterised by the relative abundance of kaolinite (30 to 45%) notably at the base of this interval where the proportions of this mineral show a maximum (45%), and by the absence of smectite. The third interval from 104.5 m to 87.5 m shows a monotonous clay assemblage without any significant change and is composed of approximately 5% of chlorite, 45% of illite, 10% of vermiculite, 10% of smectite and 30% of kaolinite. The uppermost part of the formation (interval 4) shows a sharp increase in the proportions of smectite balanced by significant decreasing proportions of illite and kaolinite.

IV - Discussion

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

The lowermost part of the formation overlying the continental Wealden facies and consisting of dark grey clays with abundant iron oolites (Fig. 4A) and common terrestrial plant remains (woods and foliar remains, Fig. 4B) likely corresponds to transgressive sediments deposited in coastal environments. Similar facies were described in boreholes drilled close to Soulaines to the east of Juzanvigny (Fig. 2) where transgressive facies are clearly separated by emersion features suggesting, several transgressive events at the beginning of the Aptian transgression (Ferry, 2000). Foliar meso- and macro-remains exclusively consist of fragments of pinnae and isolated fern pinnules preserved as coalified compressions (Fig. 4B). The largest pinna fragment is 22 mm long. The pinnae bear up to 8 mm long and 3 mm wide alternate to subopposite, oblong, thick and leathery pinnules. They are attached by a broad base to the rachis and display a rounded apex and an entire margin.
Sometimes the pinnules are slightly inclined forward. The midrib is straight and ends before the apex of the pinnule. These features as well as the reticulate veins allow to ascribe these specimens to *Weichselia reticulata* (Stokes and Webb) Fontaine which is a common fern in the Early Cretaceous flora from Europe (Blanco-Moreno et al., 2018). In France, *W. reticulata* was previously reported from the Wealden facies of the Nord department (Carpentier, 1927) and the Oise department (Carpentier, 1929). The abundance of plant remains in oolitic facies shows that the depositional environment was influenced by strong terrestrial inputs. Although *Weichselia* mostly occurred in a continental environment in Europe (Blanco-Moreno et al., 2018), this report shows that *W. reticulata* was one of the components of littoral flora during the earliest Aptian.

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

Up-section, the deposits increasingly less silty show common bivalves. The first ammonite occurs at 113.70 m indicating open-marine environments. The prominent shell horizon intercalated in the clayey succession at the top of lithological unit 1 between 112.40 m and 111.90 m (Fig. 4C) can be divided into two parts. The first corresponds to a bed comprising pluri-centimetric bivalve shells forming the base of a 30 cm-thick fining up sequence. The top of this bed, which is 112.05 m (Fig. 4C), is bioturbated. Above, a second accumulation of bivalves is associated with centimetric clasts. The succession may
correspond to two successive storm deposits separated by a bioturbated surface. This suggests a deposition above storm wave base in upper offshore environments and a deepening trend of the basin as a consequence of the Aptian transgression. This trend continues up-section from 111.90 m to 106.30 m, as the homogenous faintly bioturbated clays without any sedimentary structure suggest a deposition in a quiet environment, below the storm wave base (lower offshore). Rare calcareous nannofossils observed in smear slides occur in most of the samples and are likely responsible for the carbonate content (close to 3%) of the sediment. From 106.30 m to the top of the formation, the clays contain more silt. Bioturbated surfaces indicate sedimentation breaks that are consistent with the common occurrence of phosphate (carbonate-apatite) nodules.

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

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

Several of the isotopic segments initially distinguished by Menegatti et al. (1998) across the “Livello Selli”, which includes OAE1a, or its equivalent in the Tethys Ocean, and which were subsequently recognised worldwide and used as a reliable tool for chemostratigraphic correlations, are clearly identified in the studied borehole: C2 at the base of the section, C3 corresponding to the negative excursion showing the lowest values of $\delta^{13}$C$_{org}$ between 111.80 and 110 m, C4, C5 and C6 characterised by a shift to higher values and finally C7 (Fig. 5).
The 3‰ negative excursion that occurs immediately before OAE1a and corresponding to the C3 segment is clearly identified. It occurs probably in the deshayesi Zone just above the bioclastic accumulations interpreted as storm deposits, with an amplitude comparable to that observed in many sedimentary basins (Menegatti et al., 1998; Ando et al., 2008). The C3 segment is relatively thick (1.80 m) indicating a relatively high sedimentation rate and shows two distinct negative excursions separated by a positive excursion with a small amplitude, which can also be observed in the $\delta^{13}$C$_\text{carb}$ curves from sections from south-east France (Kuhnt et al., 1998; 2011). This may suggest the existence of, at least, two successive volcanic CO$_2$ pulses at the origin of the emplacement of the Ontong Java-Manihiki-Hikurangi Plateau (Lorenzen et al., 2013; Naafs et al., 2016).

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

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

1) The primary productivity was probably low as suggested by the very low carbonate content of the succession. The carbonate fraction of the Argiles à Plicatules Formation, which does not exceed 4%, is composed of rare nannofossils including the genus *Watznaueria, Zeugrhabdotus, Rhagodiscus, Biscutum, Discorhabdus* and *Cyclagelosphaera* (F. Giraud, in...
Ferry, 2000). The scarcity of fauna and flora suggests that the environment must have been oligotrophic.

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

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

By comparison with several sections from the Tethys ocean, the δ¹³Corg positive excursion is less pronounced than expected, what could be the result of several gaps coeval with the positive excursion like those observed in carbonate platform environments (Wissler et al., 2005). However, except the occurrence of bioturbated surfaces and some scattered phosphate nodules, there is no clear evidence of significant sedimentation breaks.

IV-3. Significance of clay mineral assemblages

IV-3-1. Diagenetic influences

Before examining the significance of clay mineral assemblages in terms of the palaeoclimate and palaeoenvironment, it is essential to ensure that they are predominantly detrital in origin without any significant influence of burial diagenesis, thermal influences or authigenic growth during early or late diagenesis. The post-Aptian sedimentary successions
probably never exceeded 1100 m (Robaszynski et al., 2005), which is consistent with a weak thermal impact (Torelli et al., 2020) compatible with the occurrence of smectite and immature organic matter. Consequently, it is unlikely that clay minerals may have been transformed during burial diagenesis. This conclusion is consistent with many studies performed to the east of the Paris Basin on upper Jurassic deposits showing that the thermal influences remain very weak even when these deposits are more deeply buried (Pellenard et al., 1999; Pellenard and Deconinck, 2006; Blaise et al., 2014; Mangenot et al., 2018).

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

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

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

Primary minerals, including illite, chlorite and pyrophyllite constitute more than half of the clay fraction. The abundance of these minerals suggests a relatively intense erosion on the continental areas bordering the Paris Basin. Although clay minerals may be transported over long distances, they likely originated from the Palaeozoic massifs surrounding the Paris Basin. Illite, chlorite and pyrophyllite originated from the erosion of igneous and metamorphic rocks from the AM/MC and from the low grade metamorphic rocks from the
LBM. Vermiculite is also common, notably at the base of the formation. This mineral also occurs in lower to middle Albian clayey strata of the Paris Basin and likely originated from the north, i.e. from the LBM (Gale et al., 1996; Corentin et al., 2020). Vermiculitic clays corresponding to illite/vermiculite mixed-layers were also identified together with illite and kaolinite in the Aptian deposits of the Lower Saxony Basin of Germany (Benesch et al., 1998) and likely originate from the moderate weathering of chlorite.

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

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

A comparison of $\delta^{13}C_{\text{org}}$ and the mineralogical data shows that the C3 segment corresponding to the negative excursion recorded prior to the OAE1a is characterised by an
increase in the proportions of kaolinite (Fig. 7) at the same time as a decrease in the proportions of smectites. This suggests the installation of a more humid climate as a consequence of an acceleration of the hydrological cycle induced by the warming triggered by the increase in pCO$_2$ (Keller et al., 2011; Bodin et al., 2015; Naafs and Pancost, 2016). There are several lines of evidence for such a climatic change. Wortmann et al. (2004) suggested that the widespread occurrence of sandstones in the Tethys-Atlantic seaway was a consequence of increasing erosion rates due to the acceleration of the hydrological cycle in the wake of the early Aptian carbon cycle perturbation. Increasing global weathering intensity coeval with OAE1a is also suggested by calcium isotopes (Blättler et al., 2011) measured in carbonate deposits from several areas including southern England, Italy and Resolution Guyot from the mid-pacific mountains. Hochuli et al. (1999) also describe global warming resulting in increasing riverine fluxes. The warming is evidenced by a drop in δ$^{18}$O, TEX$_{86}$ data and by pollen records. The δ$^{18}$O data from many sedimentary basins including the South Pacific shows, that the ocean waters warmed strongly during the negative excursion and that temperatures then decreased probably due to the storage of organic matter in the sediments (Ando et al., 2008; Stein et al., 2011; Zakharov et al., 2013). These observations are in agreement with the maximum proportions of kaolinite and the decrease in the proportion of Classopollis, (xerophytic pollen) in the Maestrat Basin (eastern Spain) during OAE1a (Cors et al. 2015). Tex$_{86}$ data obtained in the Selli level (or other equivalents of the OAE1a) also indicate particularly warm sea-surface temperatures (Schouten et al., 2003; Dumitrescu and Brassel, 2006; Mutterlose et al., 2010, 2014).

The global warming that occurred prior to OAE1a is therefore likely responsible for an acceleration of the hydrological cycle and for the increase of kaolinite because of increasing runoff and hydrolyses on the continental areas bordering the Paris Basin. The high proportions of kaolinite in Aptian deposits of the Paris Basin could be explained by the
formation of kaolinite in soils, but the duration of the climatic perturbation is relatively short, between 280 and 350 kyr (Lorenzen et al., 2013), while the formation of kaolinite in soils required a longer time estimated at least to 1 myr (Thiry, 2000). It is more likely that kaolinite was principally reworked from kaolinite-rich weathering profiles developed over the Palaeozoic massifs during the Early Cretaceous (Jurassic-Cretaceous transition to Barremian) (Meyer, 1976; Gilg, 2000; Quesnel, 2003; Yans, 2003; Thiry et al., 2005, 2006; Corentin et al., 2020). As detrital clays including kaolinite may be reworked from older rocks or from palaeo-alterations, their climatic significance may be questioned (Jeans et al., 2001), but overall, illite and kaolinite dominated clay assemblages of the Aptian in the Paris Basin point to a significant runoff and consequently to humid climate conditions. It is probable, that fluctuations in the hydrological cycle controlling fluvial inputs occurred before and during OAE1a as evidenced by changing environmental conditions in terms of anoxia/dysoxia (Socorro and Maurasse, 2018; 2020).

Although the reliability of δ¹⁸O data has recently been confirmed (O’Brien et al., 2017), the acceleration of the hydrological cycle following the very hot episode preceding OAE1a can be used to address the question of the significance of the low δ¹⁸O values recorded prior to OAE1a. δ¹⁸O-values may also be a result of a slight decrease in ocean salinity. This question, already addressed for other periods, shows that it is essential to take better account of the fluctuations in the hydrological cycle in the context of climatic reconstructions. In addition, higher runoff may increase thermohaline stratification that may be involved in the development of an OAE (e.g. Erbacher et al., 2001; Van Helmond et al., 2015).

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

Acknowledgements: We would like to thank Claude Aurière, who is in charge of storing Andra's cores, for his help in studying the boreholes. We would like to warmly thank the two reviewers, Jochen Erbacher and Helmut Weissert for their constructive and helpful comments on the initial version of the manuscript.

References


Méhay, S., Keller, C. E., Bernasconi, S. M., Weissett, H., Erba, E., Bottini, C., Hochuli, P. A.,


sequence, Organyà Basin, northeast Spain. Depositional record, DOI: 10.1002/dep2.111.


Figure captions

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


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

Fig. 3. Lithology of the AUB 121 borehole from the lower Barremian “Argiles ostréennes” Formation to the lowermost part of the “Argiles tégulines de Courcelles” Formation (lower Albian) (modified after Amédro et al., 2017). The lower Aptian Argiles à Plicatules Formation comprises three distinct lithological units and are dated by ammonites. The deshayesi and furcata ammonite Zones are clearly identified while the
lowermost part of the formation may belong to the forbesi Zone (see text). (A.P. = Argiles à Plicatules).

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

Fig. 5. CaCO$_3$ content, $\%C_{org}$ and $\delta^{13}C_{org}$ stratigraphic trends along the “Argiles à Plicatules” Formation. The prominent $\delta^{13}C_{org}$ negative excursion occurring prior to the OAE1a is compared with the $\delta^{13}C_{org}$ of the Roter Sattel reference section. Most of the segments (C2 to C7) defined by Menegatti et al. (1998) are recognised in the Argiles à Plicatules Formation.


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

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

MFS = Maximum Flooding Surface, TST = Transgressive System tract, HST = Highstand system tract.
Fig. 7. Early Aptian climate trends deduced from $\delta^{13}C_{org}$ and kaolinite content through the Argiles à Plicatules Formation.

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

Table 1. Rock-Eval data of the studied samples (TOC = Total Organic Carbon, OI = Oxygen index, HI, Hydrogen index).
<table>
<thead>
<tr>
<th>Sample (depth m)</th>
<th>reliable Tmax (°C)</th>
<th>TOC(%)</th>
<th>HI (mgHC/g TOC)</th>
<th>OI (mgCO2/gTOC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>86.45</td>
<td></td>
<td>0.13</td>
<td>54</td>
<td>208</td>
</tr>
<tr>
<td>87.12</td>
<td></td>
<td>0.1</td>
<td>70</td>
<td>250</td>
</tr>
<tr>
<td>88.15</td>
<td></td>
<td>0.18</td>
<td>67</td>
<td>233</td>
</tr>
<tr>
<td>89.15</td>
<td></td>
<td>0.18</td>
<td>33</td>
<td>139</td>
</tr>
<tr>
<td>90.15</td>
<td></td>
<td>0.13</td>
<td>54</td>
<td>269</td>
</tr>
<tr>
<td>91.15</td>
<td></td>
<td>0.18</td>
<td>39</td>
<td>144</td>
</tr>
<tr>
<td>92.15</td>
<td></td>
<td>0.15</td>
<td>33</td>
<td>233</td>
</tr>
<tr>
<td>92.90</td>
<td></td>
<td>0.12</td>
<td>52</td>
<td>300</td>
</tr>
<tr>
<td>94.42</td>
<td></td>
<td>0.23</td>
<td>43</td>
<td>135</td>
</tr>
<tr>
<td>96.42</td>
<td></td>
<td>0.22</td>
<td>45</td>
<td>132</td>
</tr>
<tr>
<td>97.00</td>
<td></td>
<td>0.22</td>
<td>45</td>
<td>132</td>
</tr>
<tr>
<td>97.50</td>
<td></td>
<td>0.21</td>
<td>33</td>
<td>133</td>
</tr>
<tr>
<td>98.13</td>
<td></td>
<td>0.17</td>
<td>53</td>
<td>194</td>
</tr>
<tr>
<td>98.63</td>
<td></td>
<td>0.17</td>
<td>53</td>
<td>218</td>
</tr>
<tr>
<td>99.13</td>
<td></td>
<td>0.18</td>
<td>44</td>
<td>172</td>
</tr>
<tr>
<td>99.63</td>
<td></td>
<td>0.18</td>
<td>36</td>
<td>180</td>
</tr>
<tr>
<td>100.13</td>
<td></td>
<td>0.18</td>
<td>44</td>
<td>128</td>
</tr>
<tr>
<td>101.10</td>
<td></td>
<td>0.17</td>
<td>41</td>
<td>135</td>
</tr>
<tr>
<td>102.10</td>
<td>398</td>
<td>0.21</td>
<td>100</td>
<td>152</td>
</tr>
<tr>
<td>103.23</td>
<td></td>
<td>0.17</td>
<td>47</td>
<td>141</td>
</tr>
<tr>
<td>104.23</td>
<td></td>
<td>0.2</td>
<td>50</td>
<td>150</td>
</tr>
<tr>
<td>105.23</td>
<td></td>
<td>0.19</td>
<td>63</td>
<td>221</td>
</tr>
<tr>
<td>107.07</td>
<td></td>
<td>0.21</td>
<td>48</td>
<td>190</td>
</tr>
<tr>
<td>108.00</td>
<td></td>
<td>0.16</td>
<td>59</td>
<td>256</td>
</tr>
<tr>
<td>110.00</td>
<td>418</td>
<td>0.23</td>
<td>83</td>
<td>148</td>
</tr>
<tr>
<td>111.00</td>
<td></td>
<td>0.17</td>
<td>53</td>
<td>229</td>
</tr>
<tr>
<td>111.80</td>
<td></td>
<td>0.13</td>
<td>77</td>
<td>277</td>
</tr>
<tr>
<td>112.35</td>
<td></td>
<td>0.26</td>
<td>38</td>
<td>92</td>
</tr>
<tr>
<td>112.92</td>
<td>384</td>
<td>0.52</td>
<td>56</td>
<td>29</td>
</tr>
<tr>
<td>113.52</td>
<td>419</td>
<td>0.44</td>
<td>34</td>
<td>139</td>
</tr>
<tr>
<td>114.52b</td>
<td>365</td>
<td>0.38</td>
<td>53</td>
<td>216</td>
</tr>
<tr>
<td>114.52a</td>
<td>394</td>
<td>0.4</td>
<td>55</td>
<td>258</td>
</tr>
<tr>
<td>115.50</td>
<td></td>
<td>0.42</td>
<td>26</td>
<td>129</td>
</tr>
</tbody>
</table>