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Tracing of variabilities within a geological barrier by molecular organic geochemistry. Case of the Callovo-Oxfordian sedimentary series in the East of the Paris Basin (France)

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Abstract

The Callovo-Oxfordian claystones located at 500 m depth at Bure (Meuse, France) are currently being investigated by Andra (the French National Radioactive Waste Management Agency) for testing the feasibility of long-term and deep geological nuclear waste disposal. In order to evaluate its potential as a geological barrier, it is very important to study, assess and describe its physico-chemical variability. The molecular biomarker composition of 150 samples of these claystones and their surrounding limestones carry diverse information on the sources of the sedimentary organic matter, the chemistry of the depositional environment, the preservation and diagenesis conditions. It also allows assessing the degree of lateral and vertical variability of the organic matter within these sedimentary series. The abundance of unsaturated biomarkers, the distribution of steroids and hopanoids and CPI values >2 prove the thermal immaturity of the organic matter. The co-occurrence of plankton, bacteria and land plant biomarkers indicate that the organic matter is a mixture of marine and continental contributions. The data also reveal that the organic matter was deposited under oxic and open-sea conditions except for a brief event of photic zone anoxia at the beginning of the Middle Callovian. In the claystones, the geosynthesis of diasterenes is favored to the detriment of the formation of steranes, especially in smectite-rich levels, and the organic matter is rapidly isolated from oxidizing then reducing conditions after the deposition due to the protective effect of clays. On the scale investigated, the claystones are characterized by a unique molecular facies and are thus homogenous from their organic content point of view. Yet, detailed investigation of specific molecular families indicates changes related to major claystone–limestone transitions. The homogeneity of these claystones can be explained by the paleogeographic position of their depositional setting and the plane and sub-horizontal paleotopography on which they were deposited. This study demonstrates the efficiency of organic geochemistry in the assessment of the variability of geological barriers.

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1. Introduction

In accordance with the law dated 30 December 1991 on the management of high-level and long-lived radioactive wastes (“Bataille” law), the French government authorized Andra (the French National Radioactive Waste Management Agency) to perform research on the feasibility of long-term and deep geological nuclear waste disposal (Lebon and Mouroux, 1999). With this objective, the Callovo-Oxfordian claystones located at 500 m depth at Bure (Meuse, France) are currently under investigation for testing its confinement properties as required by the French Fundamental Safety Rules. In order to evaluate its potential as a geological barrier between the nuclear waste and the biosphere–atmosphere, it is very important to study, assess and describe its physico-chemical variability. In sedimentary formations, lateral and vertical variabilities are inherited from sedimentologic, diagenetic and structural histories. As organic matter is a very sensitive recorder of the sedimentologic and diagenetic histories of sedimentary series (e.g. Killops and Killops, 2005; Peters et al., 2005), molecular organic geochemistry appears to be adequate for characterizing such variabilities. Characterization of the lateral and vertical variability of another potential geological barrier, the Silty Layer of Marcoule (Cretaceous), has been successfully conducted using organic geochemistry (Fleck et al., 2002). Earlier works on organic matter from the Callovo-Oxfordian claystones were essentially focused on its reactivity under oxidative or alkaline perturbations (Faure et al., 1999; Elie et al., 2000, 2004; Schäfer et al., 2003; Claret et al., 2003) and its interactions with clays (Claret et al., 2004). Geochemical data on the non-altered organic matter provided by Landais and Elie (1999) only include 14 samples from the same well, which is not sufficient to document the variability of the geological barrier. In this work, the molecular composition of the soluble organic matter extracted from 150 samples distributed in five wells is studied. Four of them (MSE 101, HTM 102, EST 312 and EST 342) are arranged on two transects crossing the Underground Research Laboratory (URL) of Bure (Meuse, NE of France) in which Andra performs *in situ* measurements. These two transects are almost perpendicular and are oriented NNW-SSE (15 km long) and NE-SW (30 km long). An additional well, named A 901, was drilled at Montcornet (Aisne, France) at a distance of 170 km to the NW of Bure (Fig. 1a and b).

The present paper discusses the degree of variability of the nature and the distribution of organic matter within the geological barrier. The aims of this study are: (1) to supply additional information about the depositional environment of these sedimentary rocks to those from sedimentological studies; (2) to determine the physico-chemical conditions of the interstitial environment after deposition and

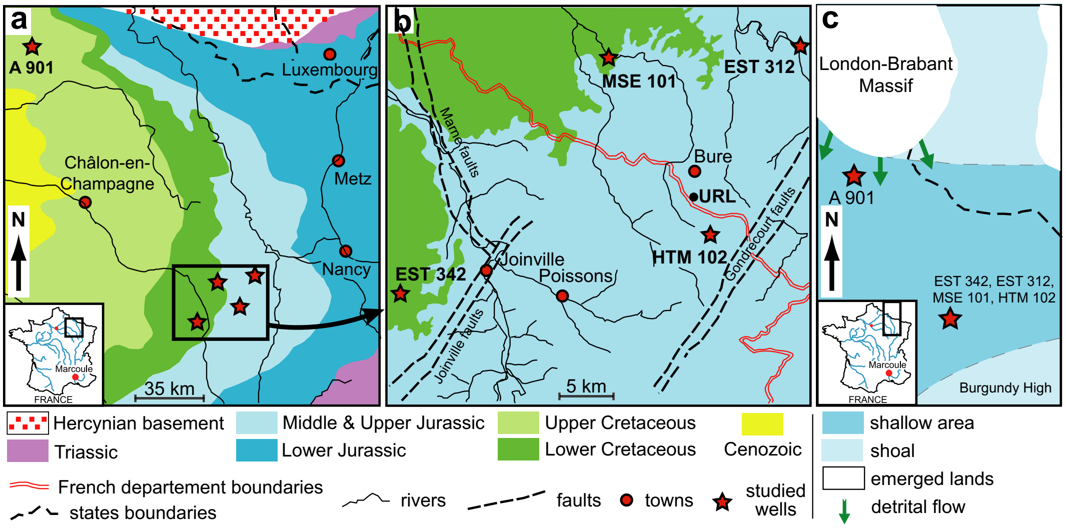

Fig. 1. (a) Geological map of the North-East of the Paris Basin showing the location of the studied wells. (b) Detail of the previous geological map showing the location of the four wells around the Underground Research Laboratory (URL). (c) Paleogeographic map of the Callovian of the North-East of the Paris Basin (drawned after Thierry and Barrier, 2000).

their effects on the chemistry of the sedimentary organic matter; (3) to assess the variability of the organic content within the geological barrier and to determine the processes which control them by comparison of the present results with other available data (stratigraphy, sedimentology, mineralogy, well-logs, etc.).

2. Geological setting

The studied sedimentary series were deposited during the Callovian and the Oxfordian (Dogger/Malm boundary) at the Eastern part of the Paris Basin. They were located at the South of the London-Brabant Massif, the closer emerged land at the time of the deposit (Fig. 1c). The Paris Basin is an intracratonic flexural basin initiated by the post-Hercynian breakdown of Pangea since the Triassic and has accumulated sediments during Meso-Cenozoic times (Guillocheau et al., 2000; Le Solleuz et al., 2004). Carbonate sedimentation predominated during the Jurassic and was periodically interrupted by argillaceous deposits during carbonate platform drownings, which correspond to second order maximum flooding events recorded in the whole of Western Europe (Norris and Hallam, 1995; Jacquin et al., 1998; Guillocheau et al., 2000). Callovo-Oxfordian claystones were deposited during one of these flooding events and are surrounded by two limestone units (Bathono-Callovian and Oxfordian carbonate platforms, Fig. 2). Clay minerals mainly originate from the London-Brabant Massif (Pellenard, 2003). The transition from the Bathono-Callovian platform to the argillaceous deposits is abrupt while the transition to the upper Oxfordian platform is more gradual. Because of the faciologic homogeneity of the monotonous claystones, well-log study appears to be the unique tool able to distinguish three 3rd order depositional sequences *sensu* Vail (Vail et al., 1977). The first sequence starts at the base of the claystones and ends at the Callovian/Oxfordian boundary. Its maximum flooding surface is dated from the Coronatum zone (Middle Callovian). As in most of Callovo-Oxfordian series of Western Europe, the Upper Callovian is condensed and more carbonated. The top of the second sequence is located close to the Lower Oxfordian/Middle Oxfordian transition and corresponds to a more carbonated layer. Its maximum flooding surface is dated from the Mariae zone (Lower Oxfordian) and is superimposed with the second order maximum flooding surface. The third

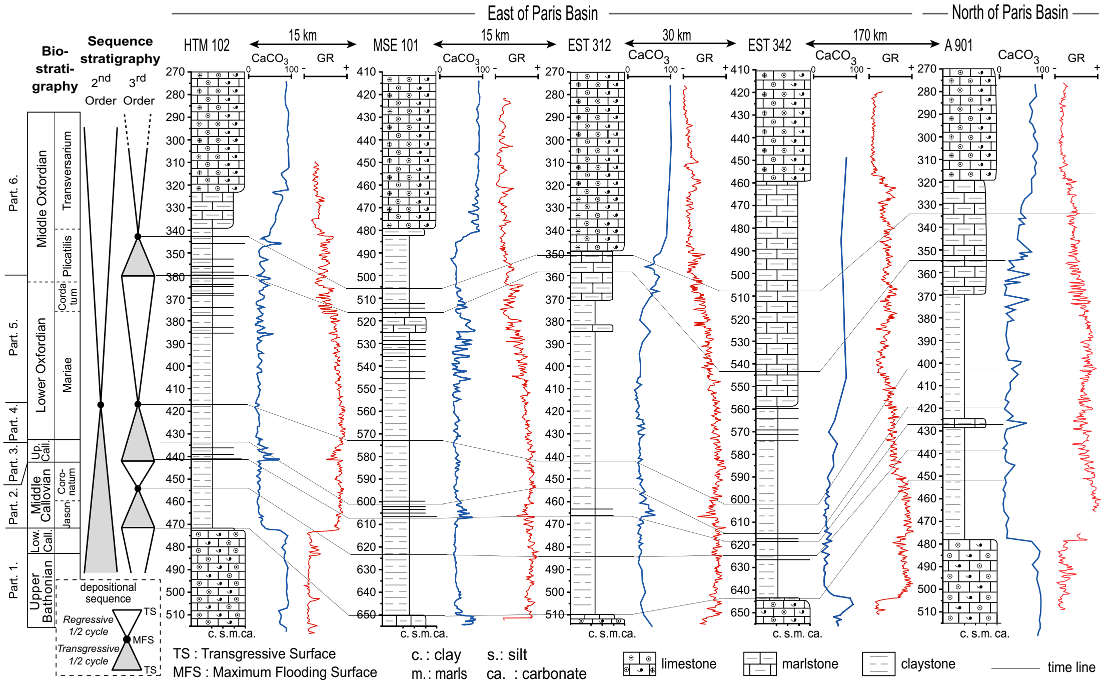

Fig. 2. Litho-, bio- and sequence stratigraphy of the studied wells. The division into the six parts, the carbonate content ($CaCO_3$) and the gamma-ray (GR, well-log) are also reported.

sequence corresponds to the progressive emplacement of the upper carbonate platform (Fig. 2). Dating is based on biostratigraphy of ammonites (Thierry et al., 2006). The mineralogy and the geochemistry have been intensively studied by Andra (Andra, 2005). The claystones are mainly composed of clay minerals (40–60%), calcite (20–40%), quartz (15–35%) and pyrite (0–2%). A major change of clay mineralogy occurs around the second order maximum flooding surface in the four wells to the East of the Paris basin and is characterized by the increase of (1) the proportion of illite/smectite mixed layers to the detriment of illite and kaolinite, (2) the proportion of smectite within the illite/smectite mixed layers (Pellenard et al., 1999). Claystones of EST 342 are more condensed and show two other mineralogical changes in the Callovian claystones. In A 901, a similar mineralogical change occurs earlier during the Calloviense zone (Lower Callovian) (Debrabant et al., 1992). All these mineralogical changes within the Callovo-Oxfordian claystones indicate evolution of the detrital sources (Pellenard et al., 1999). Taking account of this description, the studied sedimentary series were divided into six successive parts. *Part 1* corresponds to the Bathono-Callovian carbonate platform. *Part 2* corresponds to the first 3rd order depositional sequence. *Part 3* is represented by the condensed Upper Callovian. *Parts 4* and *5* constitute the second depositional sequence and are separated by its maximum flooding surface. *Part 6* corresponds to the third sequence and to the progressive installation of the Oxfordian carbonate platform. Isochronous correlations have been established between borehole-cores by well-log study (Andra, 2005) and biostratigraphy (Thierry et al., 2006). The distribution of all samples among the cores and their divisions are given in Table 1.

3. Methodology

The lithologic and sedimentologic characteristics of all samples (≈150 samples) were carefully noted before they were crushed and powdered. Total organic content was measured using a LECO SC144 DRPC on 53 samples. Soluble organic matter was extracted by dichloromethane at 100 bars and 80 °C from 80 to 120 g of powder using an Accelerated Solvent Extractor ASE 200 (Li et al., 1998). Steel cells filled with pulverised samples were carefully solvent prewashed in the ASE 200. The purge gas was N_2, the heating phase and the static extraction times were both 5 min. Two extraction cycles were performed to ensure that the lipidic fraction was completely extracted. Elemental S was removed by introduction of HCl-activated Cu chips in vials containing the solvent and the extract. Dichloromethane was evaporated

Table 1
Distribution of all samples among the cores and their divisions

	HTM 102	MSE 101	EST 312	EST 342	A 901
Part 6. Third depositional sequence					
Position of the base and top (m)	360–300	516–410	358–310	544–460	355–318
Number of samples	4	11	9	0	6
Part 5. Regressive semi-cycle (second sequence)					
Position of the base and top (m)	417–360	574–516	442–358	602–544	403–355
Number of samples	7	8	12	11	7
Part 4. Transgressive semi-cycle (second sequence)					
Position of the base and top (m)	434–417	600–574	454–442	615–602	420–403
Number of samples	2	5	1	3	3
Part 3. Condensed Upper Callovian					
Position of the base and top (m)	441–434	607–600	466–454	618–615	425–420
Number of samples	1	3	4	0	2
Part 2. First depositional sequence					
Position of the base and top (m)	471–441	651–607	511–466	643–618	478–425
Number of samples	5	5	11	5	12
Part 1. Batho-Callovian platform					
Position of the base and top (m)	510–471	670–651	520–511	646–643	490–478
Number of samples	6	2	0	3	2

using a Zymark TurboVap LV then left to dry overnight. The hydrocarbon fraction was separated from the polar fraction by liquid chromatography using an alumina column with successive elutions by dichloromethane then methanol/dichloromethane (50/50 by volume). Hydrocarbons were thereafter fractionated to recover the aliphatic, aromatic and polar fractions on a silica column by successive elutions of pentane, pentane/dichloromethane (65/35 by volume) then methanol/dichloromethane (50/50 by volume). Rock samples, total extracts as well as aliphatic, aromatic and polar fractions were carefully weighted during the procedure. These fractions were diluted in hexane, (4 mg/mL for aliphatic fractions and 8 mg/mL for aromatic and polar fractions) before being analysed by an HP 5890 Serie II Gas Chromatograph coupled with a HP 5971 Mass Spectrometer (GC–MS). The capillary column used was a DB-5 J&W (60 m × 0.25 mm i.d. with 0.1 μm film thickness). The temperature program was 70–315 °C at 15 °C/min up to 130 °C then 3 °C/min followed by an isothermal stage at 315 °C for 15 min. Helium was the carrier gas (1 mL/min flow rate). The mass spectrometer was operated in the electron impact mode (EI) at 70 eV ionization energy and resulting ion fragments were scanned from 50 to 550 Da using a quadrupole detector. Data were acquired and processed using the Agilent ChemStation software. Individual compounds were identified by comparison of their mass spectra with published spectra and by interpretation of mass spectrometric fragmentation patterns.

4. Results

4.1. Total organic carbon

The values of the total organic C content (TOC) are generally low (<1 wt.% of the bulk rock). Higher contents of organic C are located in the Middle Callovian claystones (part 2, Table 2). TOC values decrease after the Upper Callovian and remain low until the top of the claystones. The progressive emplacement of the Oxfordian carbonate platform is marked on the East of the Paris basin by the decrease of TOC values. Only three samples contain higher proportions of organic matter (>1%). The first one is located at the extreme base of the claystones of MSE 101 (TOC = 2.09%), the sample located at 456.87 m depth in A 901 which is dated from the same time interval as the previous sample and finally the sample positioned on the maximum flooding surface of the third depositional sequence of MSE 101 (explaining the high values of the TOC average and standard deviation of Part 6 of MSE 101, Table 2).

4.2. Extraction yields and bitumen composition

Yields of soluble organic matter range between 0.01 and 0.65 mg of organic extract/g of rock. These values are positively correlated to the TOC values. Consequently, as TOC maximum yields (>0.1 mg/g) occur in the lower part of the claystones. Yield values quickly decrease toward the Upper Callovian then remain very low (<0.05 mg/g) during the Oxfordian.

Weight proportions of aliphatic, aromatic and polar fractions are quite similar in all samples (respectively 17%, 13% and 70% in average, Fig. 3) and do not display significant stratigraphic evolution.

4.3. *n*-Alkanes

n-Alkanes (*m*/*z* 57 in the aliphatic fraction) are major components of non-biodegraded sedimentary organic matter. They can be directly synthesized by the living organisms or derived from straight-chain biolipids, which are both ubiquitous in the biosphere. However, despite their ubiquity, *n*-alkane profiles are useful for discriminating marine and continental contributions (Brocks and Summons, 2003). *n*-Alkanes are abundant in all extracts and their distribution ranges in C-chain length from C_{13} to C_{36}.

4.3.1. Callovo-oxfordian claystones

n-Alkane profiles of all claystone samples show a bimodal distribution. The first mode includes *n*-C_{13} to *n*-C_{20} alkanes while the second includes *n*-C_{24} to *n*-C_{34} alkanes (Fig. 4). The first mode is always predominant and is generally attributed to algae and bacteria (Tissot et al., 1977). The carbon preference index (CPI) values, calculated after Bray and Evans (1961), fluctuate between 1.2 and 2.7. This odd-over-even predominance of the *n*-C_{24} to *n*-C_{34} alkanes is typically assigned to epicuticular waxes of continental plants (Eglinton and Hamilton, 1967; Caldicott and Eglinton, 1973). CPI values are higher in the Callovo-Oxfordian claystones (often >2) than in the surrounding limestones (≈1.5) as shown in Table 2.

Table 2
Averages and standard deviations of TOC, CPI, n-C$_{24}^{+}$/n-C$_{24}^{-}$, Pr/Ph, diasterenes/steranes, hopenes/hopanes and ββ C$_{30}$-hopane/αβ C$_{30}$-hopane calculated for each part of each core

	HTM 102	MSE 101	EST 312	EST 342	A 901
Total organic carbon content					
Part 6. Third depositional sequence	0.26 (±0.26)%	0.67 (±0.48)%	0.11 (±0.02)%	–	0.51 (±0.15)%
Part 5. Regressive semi-cycle (second sequence)	0.57 (±0.13)%	0.59 (±0.11)%	0.43 (±0.17)%	0.59 (±0.14)%	0.40 (±0.25)%
Part 4. Transgressive semi-cycle (second sequence)	<0.4%	0.48%	0.59	0.46	0.49
Part 3. Condensed Upper Callovian	<0.4%	0.49 (±0.15)%	0.48 (±0.03)%	–	0.84
Part 2. First depositional sequence	0.78 (±0.20)%	1.18 (±0.62)%	0.81 (±0.19)%	0.74 (±0.09)%	0.77 (±0.48)%
Part 1. Batho-Callovian platform	0.46	–	–	0.58	0.32 (±0.17)%
Carbon preference index[a]					
Part 6. Third depositional sequence	1.59 (±0.29)	1.60 (±0.15)	1.56 (±0.26)	–	2.41 (±0.55)
Part 5. Regressive semi-cycle (second sequence)	1.75 (±0.61)	1.80 (±0.32)	2.08 (±0.38)	1.88 (±0.14)	2.32 (±0.33)
Part 4. Transgressive semi-cycle (second sequence)	2.10 (±0.59)	2.10 (±0.42)	2.60	2.05 (±0.07)	2.22 (±0.27)
Part 3. Condensed Upper Callovian	1.34	1.82 (±0.15)	2.60 (±0.06)	–	2.26 (±0.12)
Part 2. First depositional sequence	2.13 (±0.30)	2.31 (±0.13)	2.42 (±0.13)	1.96 (±0.25)	2.16 (±0.47)
Part 1. Batho-Callovian platform	1.57 (±0.31)	1.46 (±0.08)	–	1.48 (±0.04)	1.46 (±0.34)
n-C$_{24}^{+}$/n-C$_{24}^{-}$[b]					
Part 6. Third depositional sequence	0.30 (±0.16)	0.48 (±0.18)	0.92 (±0.40)	–	0.28 (±0.17)
Part 5. Regressive semi-cycle (second sequence)	0.89 (±0.27)	0.62 (±0.20)	0.69 (±0.28)	0.77 (±0.16)	0.26 (±0.33)
Part 4. Transgressive semi-cycle (second sequence)	0.52 (±0.11)	0.72 (±0.26)	0.76	0.70 (±0.04)	0.28 (±0.15)
Part 3. Condensed Upper Callovian	0.83	0.52 (±0.22)	0.59 (±0.10)	–	0.33 (±0.13)
Part 2. First depositional sequence	0.48 (±0.10)	0.54 (±0.12)	0.60 (±0.10)	0.45 (±0.11)	0.40 (±0.27)
Part 1. Batho-Callovian platform	0.49 (±0.26)	0.31 (±0.11)	–	0.32 (±0.14)	0.15 (±0.10)
Pristane/Phytane ratio					
Part 6. Third depositional sequence	1.13 (±0.27)	1.36 (±0.15)	1.12 (±0.36)	–	1.21 (±0.33)
Part 5. Regressive semi-cycle (second sequence)	1.46 (±0.52)	1.98 (±0.73)	2.41 (±0.92)	4.27 (±0.41)	1.24 (±0.53)
Part 4. Transgressive semi-cycle (second sequence)	1.79 (±0.74)	2.27 (±0.44)	3.08	5.26 (±0.26)	1.18 (±0.24)
Part 3. Condensed Upper Callovian	1.43	2.41 (±0.86)	3.39 (±0.15)	–	1.61 (±0.14)
Part 2. First depositional sequence	2.10 (±0.67)	1.93 (±0.36)	2.28 (±0.10)	3.30 (±1.31)	1.29 (±0.53)
Part 1. Batho-Callovian platform	1.05 (±0.21)	2.08 (±0.59)	–	2.14 (±1.42)	1.22 (±0.46)
Diasterenes/Steranes					
Part 6. Third depositional sequence	2.76 (±4.05)	3.69 (±3.02)	1.39 (±2.02)	–	6.07 (±4.32)
Part 5. Regressive semi-cycle (second sequence)	8.80 (±2.16)	12.52 (±5.92)	11.70 (±9.54)	5.90 (±3.93)	5.16 (±3.04)
Part 4. Transgressive semi-cycle (second sequence)	4.30 (±1.92)	10.78 (±6.58)	11.50	5.34 (±0.85)	4.60 (±0.97)
Part 3. Condensed Upper Callovian	8.29	8.58 (±2.00)	13.88 (±1.49)	–	6.22 (±1.20)
Part 2. First depositional sequence	3.26 (±0.91)	6.27 (±1.93)	7.84 (±2.76)	6.36 (±2.61)	4.31 (±1.39)
Part 1. Batho-Callovian platform	2.15 (±3.74)	3.29 (±1.675)	–	1.93 (±1.65)	<0.1
Hopene/hopane ratio[c]					
Part 6. Third depositional sequence	0.36 (±0.25)	0.53 (±0.23)	0.34 (±0.24)	–	0.37 (±0.09)
Part 5. Regressive semi-cycle (second sequence)	0.78 (±0.10)	0.69 (±0.12)	0.86 (±0.28)	0.26 (±0.10)	0.40 (±0.07)
Part 4. Transgressive semi-cycle (second sequence)	0.66 (±0.07)	0.58 (±0.16)	0.77	0.26 (±0.03)	0.43 (±0.16)
Part 3. Condensed Upper Callovian	0.65	0.86 (±0.01)	1.13 (±0.17)	–	0.36 (±0.03)
Part 2. First depositional sequence	0.86 (±0.21)	0.93 (±0.13)	0.88 (±0.25)	0.64 (±0.125)	0.43 (±0.09)
Part 1. Batho-Callovian platform	0.58 (±0.20)	0.69 (±0.28)	–	0.49 (±0.07)	0.22 (±0.01)

(*continued on next page*)

Table 2 (*continued*)

	HTM 102	MSE 101	EST 312	EST 342	A 901
ββ C_{30}-hopane/αβ C_{30}-hopane					
Part 6. Third depositional sequence	1.44 (±0.90)	1.09 (±0.76)	0.85 (±0.49)	–	0.42 (±0.16)
Part 5. Regressive semi-cycle (second sequence)	2.13 (±0.25)	1.93 (±0.42)	2.00 (±0.64)	0.96 (±0.16)	0.35 (±0.05)
Part 4. Transgressive semi-cycle (second sequence)	2.38 (±0.20)	2.19 (±0.51)	3.05	1.20 (±0.23)	0.33 (±0.03)
Part 3. Condensed Upper Callovian	2.435698	2.34 (±0.38)	2.73 (±0.26)	–	0.36 (±0.02)
Part 2. First depositional sequence	2.07 (±0.51)	1.82 (±0.30)	2.41 (±0.68)	0.88 (±0.36)	0.41 (±0.07)
Part 1. Batho-Callovian platform	1.60 (±0.93)	2.19 (±0.01)	–	0.89 (±0.48)	0.46 (±0.25)

Total organic carbon of HTM 102 are partially from Landais and Elie (1999).

[a] CPI calculated after Bray and Evans (1961).

[b] $n\text{-}C_{24}^{+}/n\text{-}C_{24}^{-} = \sum(n\text{-}C_{25}\text{–}n\text{-}C_{34})/\sum(n\text{-}C_{17}\text{–}n\text{-}C_{24})$.

[c] Calculated using the ratio 30-norneohop-13(18)-ene/(αβ + ββ) C_{30}-hopanes.

The ratio $n\text{-}C_{24}^{+}/n\text{-}C_{24}^{-}$ is here calculated in order to trace the evolution of the relative proportion of the continental contribution compared to the marine contribution.

$$n\text{-}C_{24}^{+}/n\text{-}C_{24}^{-} = \left(\sum n\text{-}C_i/\sum n\text{-}C_j\right)$$
$$i = 25\text{–}34 \quad \text{and} \quad j = 17\text{–}24$$

At the East of the Paris Basin, this ratio fluctuates between 0.2 and 1.5 and the average values for each well range between 0.6 and 0.7. $n\text{-}C_{24}^{+}/n\text{-}C_{24}^{-}$ values display similar and significant long-term variations in each core from the East of the Paris Basin (Fig. 5). They increase from the bottom of the claystones ($n\text{-}C_{24}^{+}/n\text{-}C_{24}^{-} \approx 0.3$) to the appearance of the first carbonate strata announcing the emplacement of the Oxfordian carbonate platform ($n\text{-}C_{24}^{+}/n\text{-}C_{24}^{-} > 1$) then decrease to values generally lower than 0.5.

The $n\text{-}C_{24}^{+}/n\text{-}C_{24}^{-}$ ratio of A 901 samples are half those in the cores located to the East of the Paris basin and its average value is 0.32 indicating a more important marine contribution. Furthermore, the vertical variation of the $n\text{-}C_{24}^{+}/n\text{-}C_{24}^{-}$ ratio is different

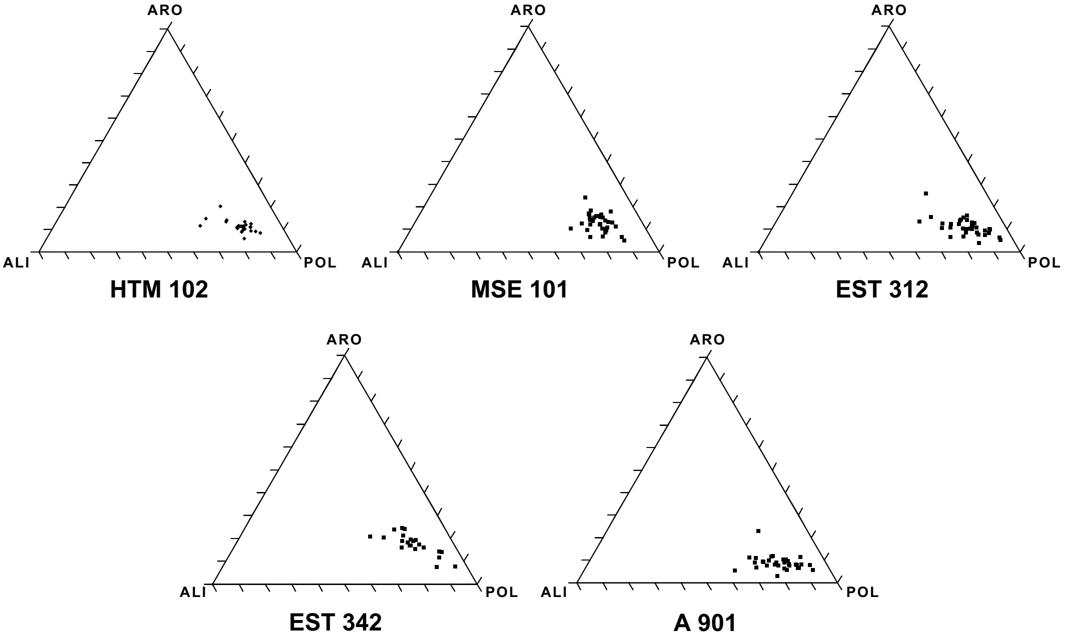

Fig. 3. Ternary plots of the weight proportions of aliphatic (ALI), aromatic (ARO) and polar (POL) fractions for each well.

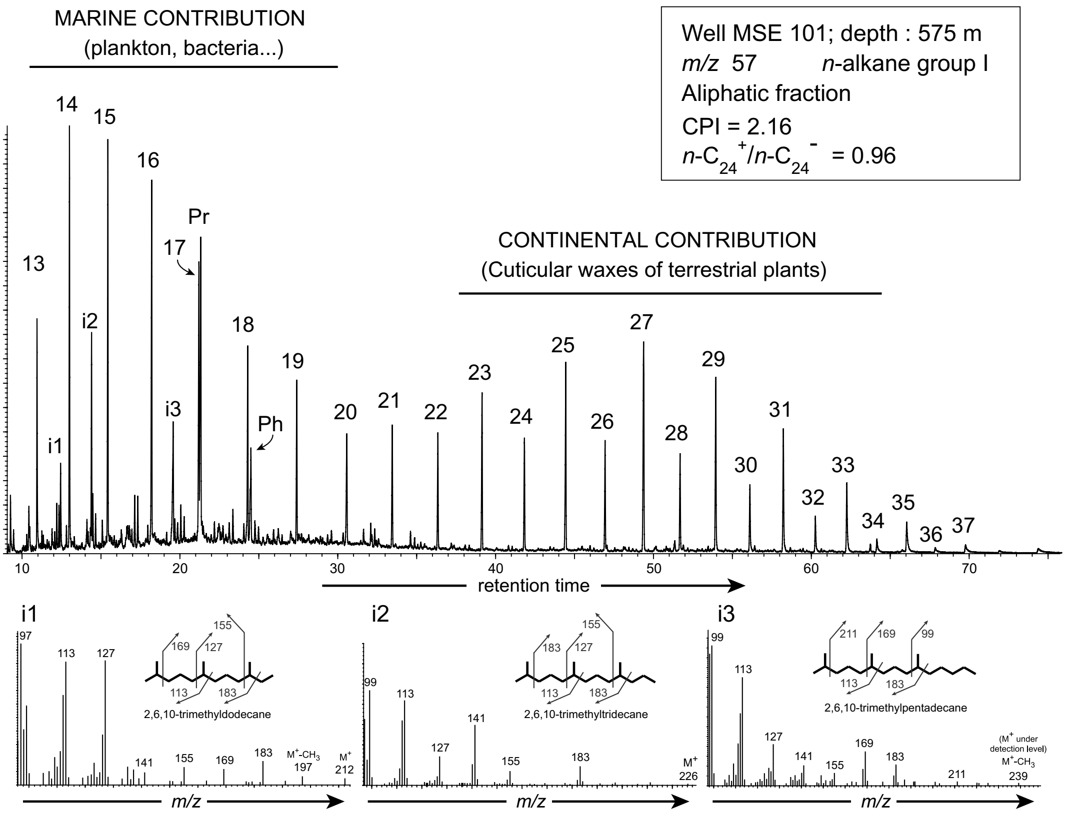

Fig. 4. Typical distribution of *n*-, *iso*- and *cyclo*-alkanes (*m*/*z* 57) of the Callovo-Oxfordian claystones (*n*-alkane group I).

than in the previous wells. The highest values are located near the base of the claystones, between 470 and 450 m depth, then decrease to very low values except for one sample (385.5 m).

4.3.2. Surrounding carbonate platforms

n-Alkane profiles from the limestones are much more diversified than those of the claystones. Indeed, these profiles can be classified into three different groups.

I. Group I has a similar bimodal distribution to those previously described in the claystones (Fig. 4).
II. Group II shows a unimodal distribution with a mode ranging from *n*-C_{24} to *n*-C_{26} (Fig. 6a). This distribution could be related to continental and/or marine precursors (Philp, 1994). This group mainly concerns samples from the Oxfordian limestones of EST 312.
III. Group III is characterized by the low abundance of *n*-alkanes compared to short-chain *iso*- and *cyclo*-alcanes (Fig. 6b).

4.4. Iso- and cyclo-alkanes

Pristane (Pr) and phytane (Ph) are two isoprenoids derived essentially from phytol which can be free in phytoplankton or bound to a tetrapyrrole to form chlorophylls. In oxic conditions, phytol is degraded into pristane while it is degraded into phytane in anoxic/reducing conditions (Dydick et al., 1978). The Pr/Ph ratio is thus often used as a marker of redox conditions of the depositional and the interstitial environments. $Pr/Ph < 1$ indicates reducing/anoxic conditions while $Pr/Ph > 1$ indicates oxic environments. However, because the Pr/Ph ratio is also source and maturity dependent, it must be used with caution notably when the values ranged between 1 and 4 (Volkman and Maxwell, 1986).

In this study, Pr/Ph values usually range between 1 and 3, and do not show significant vertical variation except for EST 342 in which they can be significantly higher, up to 5.5 (Table 2). EST 342 has (1) low values ($Pr/Ph \approx 1$–2) at the top of the Bathono-Callovian platform and the regressive semi-cycle of the first

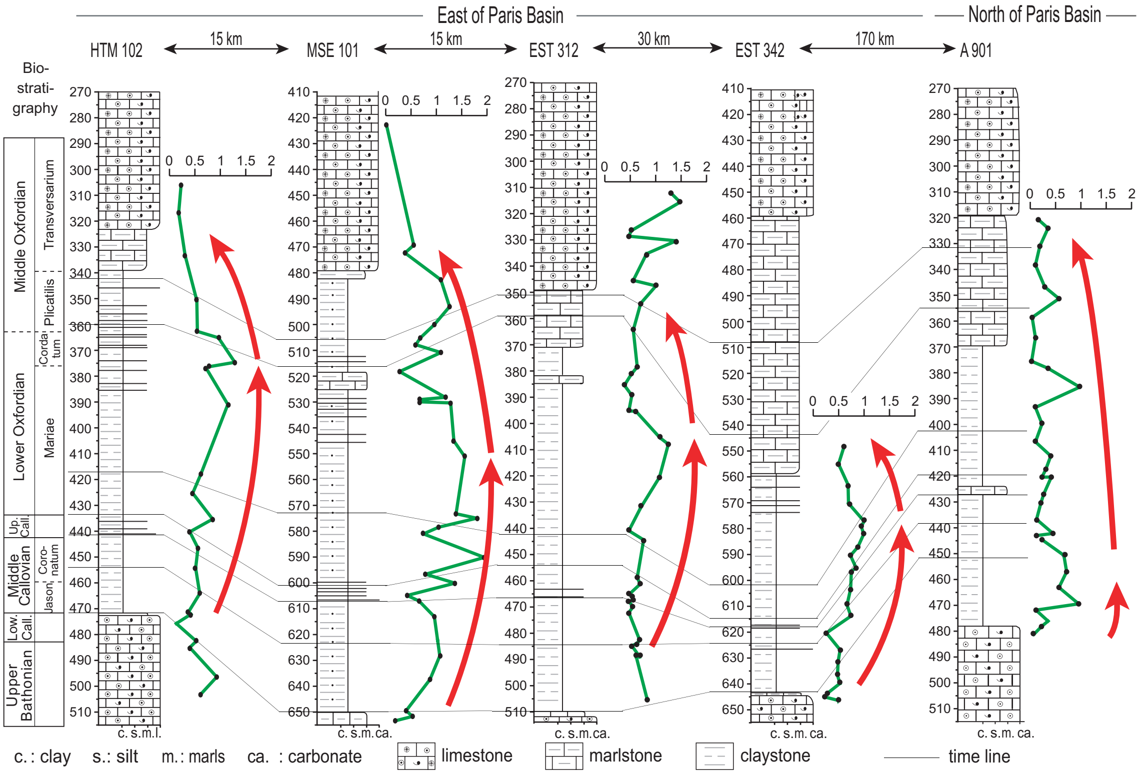

Fig. 5. Long-term (arrows) and short-term (curves) evolution of the $n\text{-}C_{24}^{+}/n\text{-}C_{24}^{-}$ ratio for each well.

depositional sequence, (2) high values (Pr/Ph > 4) in the transgressive semi-cycle of the first depositional sequence (which explain the high standard deviation observed in part 2 of this well) and the second depositional sequence.

Aliphatic fractions sometimes show a unresolved complex mixture (UCM) ranging from n-C_{14} to n-C_{22} due to a great diversity of low molecular weight *iso*- and *cyclo*-alkanes. The UCM is generally slight or absent in argillaceous deposits but is much more important in many samples of the Oxfordian carbonate platform. This UCM could be linked to degraded organic matter or to bacteria/algae input. Three isoprenoids, 2,6,10-trimethyldodecane, 2,6,10-trimethyltridecane and 2,6,10-trimethylpentadecane, are abundant whatever the intensity of the UCM (Fig. 4). These compounds probably originate from the same precursors as pristane and phytane (Volkman and Maxwell, 1986). The *iso*-alkanes characterizing the *n*-alkane group III are mainly composed of short-chain monomethylalkanes with the methyl group at position C(3) and short-chain alkanes including one or two quaternary carbons (BAQCs) as shown in Fig. 6b. The presence of the short-chain monomethylalkanes seems to be typical of cyanobacteria (Kenig et al., 1995, 2005).

4.5. Sesqui- and diterpenoids

The main sources of geosesquiterpenoids are land plants because they are major compounds of resins and essential oils (Simoneit, 1986). In the aliphatic fractions, $C_{14}H_{26}$ (M^{+} 194), $C_{15}H_{24}$ (M^{+} 204) and $C_{15}H_{28}$ (M^{+} 208) undetermined sesquiterpanes (key ion m/z 161) as well as drimanes (key ion m/z 123) are present in relatively low amounts in all samples. In aromatic fractions, sesquiterpenoids seem to be restricted to the cadinane and curcumane classes.

Diterpenoids are typically assigned to vascular plants and more particularly to conifers (Simoneit, 1986). They are generally below the detection limit or in low proportion in claystones while their proportion increase synchronously with the progressive installation of the carbonate Oxfordian platform. This important change of the distribution of vascular

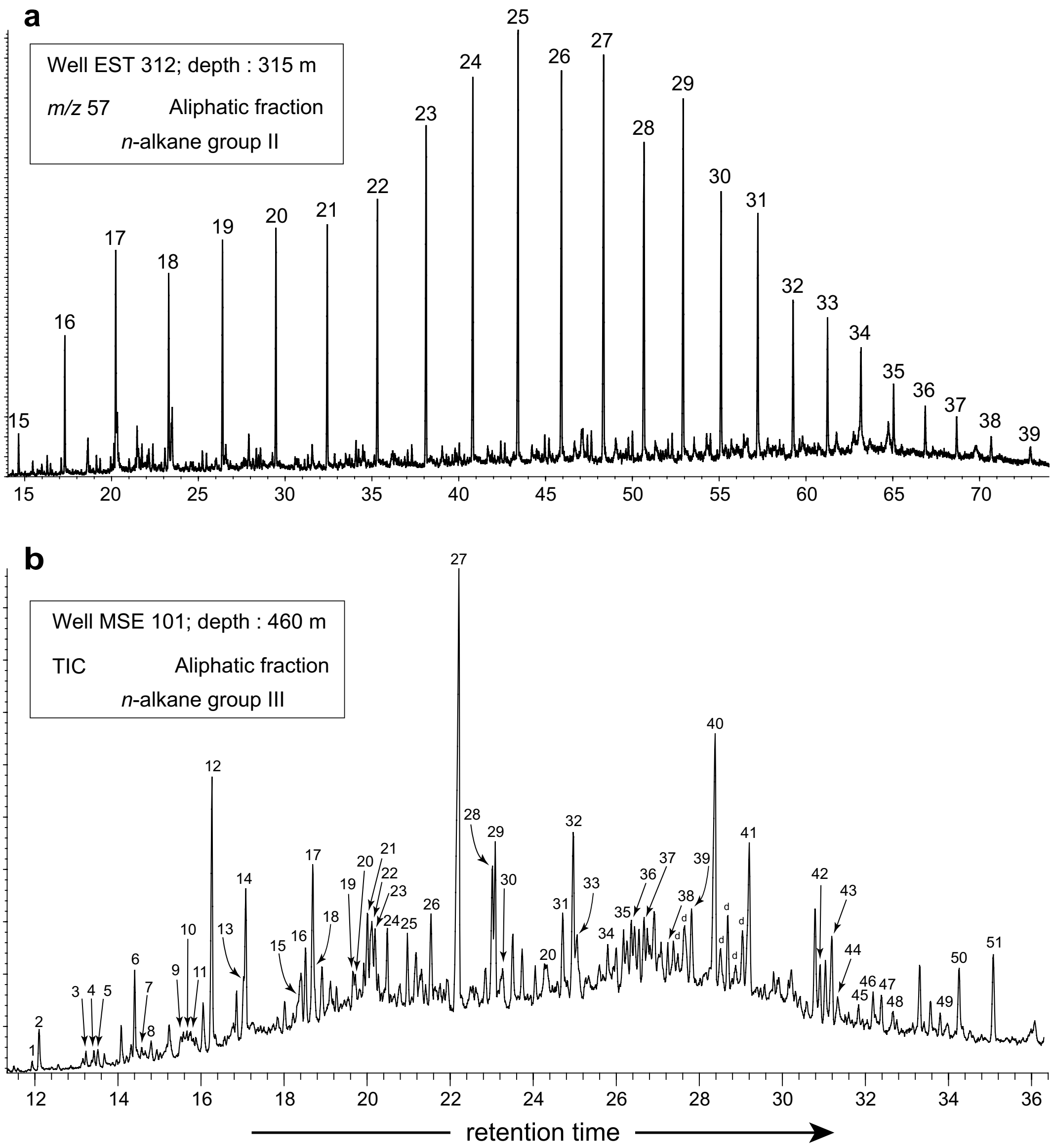

Fig. 6. (a) *n*-Alkane profile of limestone samples presenting an unimodal distribution (*n*-alkane group II). (b) Partial chromatogram of the aliphatic fraction of limestone samples presenting high content of *iso*- and *cyclo*-alkanes (*n*-alkane group III). Peak assignments are given in Table 3; d: diterpanes.

plant biomarkers is interpreted as a paleoflora change induced by a paleoclimatic change (Hautevelle et al., 2006).

4.6. Steroids

Geosteroids, ubiquitous in sedimentary organic matter, derive from sterols which act as rigidifiers in the cell walls of eucaryotes (Volkman, 1986). In the biosphere, they essentially contain 27, 28 and 29 C atoms. C_{27}-sterols are common in animals and red algae. C_{28}-sterols are essentially produced by microalgae (as diatoms) and fungi while C_{29}-sterols are mostly synthesized by land plants (Huang and Meinschein, 1979; Volkman, 1986). 4-Methylsterols and C_{30}-demethylsterols as dinosterol are synthesized by marine organisms, and more particularly dinoflagellates (Volkman et al., 1999; Volkman, 2003). Because the number of C atoms is often preserved during diagenesis, steroid biomarkers from ancient sediment are potentially good source indicators. Furthermore, many transformations

Table 3
Peak assignments for *n*-, *iso*- and *cyclo*-alkanes of the *n*-alkane group III represented in Fig. 6

Peak #	Compound name
1	*n*-Nonylcyclopentane or *n*-octylcyclohexane
2	*n*-Tetradecane
3	*n*-Nonylcyclopentane or *n*-octylcyclohexane
4	2,6,10-Trimethyltridecane
5	3-Ethyltridecane or 2-methyltetradecane
6	*n*-Pentadecane
7	5-Ethyl-5-methyltridecane
8	2,2-Dimethyltetradecane
9	5-Butyl-5-ethylundecane
10	3-Ethyl-3-methyltridecane
11	*n*-Nonylcyclohexane
12	3-Methylpentadecane
13	5,5-Diethyltridecane
14	*n*-Hexadecane
15	2,6,10-Trimethylpentadecane
16	3,3-Diethyltridecane
17	*n*-Undecylcyclopentane or decylcyclohexane
18	*n*-Undecylcyclopentane or decylcyclohexane
19	6,6-Diethyltetradecane
20	Methylalkylcyclohexane ?
21	*n*-Heptadecane
22	Phytane
23	5-Ethyl-5-methylpentadecane
24	2,2-Dimethylhexadecane
25	5-Butyl-5-ethyltridecane
26	3-Ethyl-3-methylpentadecane
27	3-Methylheptadecane
28	5,5-Diethylpentadecane
29	*n*-Octadecane
30	Phytane
31	3,3-Diethylpentadecane
32	Tridecylcyclopentane
33	3-Ethylheptadecane + dodecylcyclohexane
34	6,6-Diethylhexadecane
35	*n*-Nonadecane
36	5-Ethyl-5-methylheptadecane
37	2,2-Dimethyloctadecane
38	5-Butyl-5-ethylpentadecane
39	3-Ethyl-3-methylheptadecane
40	3-Methylnonadecane
41	5,5-Diethylheptadecane
42	3,3-Diethylheptadecane
43	*n*-Pentadecylcyclopentane
44	Tetradecylcyclohexane
45	6,6-Diethyloctadecane
46	*n*-Henicosane
47	5-Ethyl-5-methylnonadecane
48	2,2-Dimethylicosane
49	3-Ethyl-3-methylnonadecane
50	3-Methylhenicosane
51	5,5-Diethylnonadecane

Identifications were made after Kenig et al. (2005).

(rearrangements, isomerization, aromatisation, etc.) can occur during diagenesis depending on the post-depositional conditions, making them also good markers for diagenetic conditions (MacKenzie et al., 1982; De Leeuw and Baas, 1986).

In the studied sedimentary series, steroid biomarkers are very diversified due to their number of C atoms and their different structures.

In the aliphatic fractions of the four wells from the East of the Paris basin, C_{27}-, C_{28}- and C_{29}-steranes are present together with much less common steranes having from 23 to 26 C atoms (key ions m/z 203 and 217, C_{23}- and C_{26}-steranes, respectively, identified after the mass spectra published by Philp, 1985 and Moldowan et al., 1991). It is also possible that these C_{23}- to C_{26}- steranes are de-A-diasterenes as proposed by Peakman et al. (1986). Low proportions of dinosterane (identified after the mass spectrum published by Summons et al., 1987) and 4-methylsteranes (key ion m/z 231) are also present (Fig. 7a). The distribution of C_{23}- to C_{30}-steranes is remarkably stable in the claystones while it is more variable in the limestones. Diasterenes (rearranged sterenes; key ion m/z 257) are much more abundant than steranes (Fig. 7b), except in a few carbonate samples in which they are absent or in low proportion. As with the steranes, their distribution is remarkably constant in the whole sample set. Fig. 8 points out the relationship between the diasterenes/steranes ratio, the lithology and the clay mineralogy. This ratio is low in limestone samples and higher in the claystones. Within the argillaceous deposits, the diasterenes/steranes ratio shows some evolution, which seems to be correlated to the clay mineralogy. Indeed, the relative proportion of diasterenes compared to steranes increases significantly and systematically through the clay mineralogy change which is mainly expressed by an increase in the smectite content.

Aromatic fractions show a complex mixture of aromatic steroids composed of many isomers of desmethylmonoaromatic (C-ring) steroids ranging from C_{27} to C_{29} with minor amounts of C_{21} and C_{22} (key ions m/z 239, 253), methylmonoaromatic (C-ring) steroids ranging from C_{28} to C_{30} (key ion m/z 267), desmethyl and methyltriaromatic steroids (key ions m/z 231, 245, respectively; Fig. 7c). The distribution of aromatic steroids is identical in all samples.

The distribution of steroids in A 901 is relatively similar. C_{27}-steranes generally have similar relative proportion to C_{29}-steranes and C_{23}- to C_{26}-steranes are less abundant than in the East of the Paris Basin. Dinosterane and methylsteranes are still in low abundance.

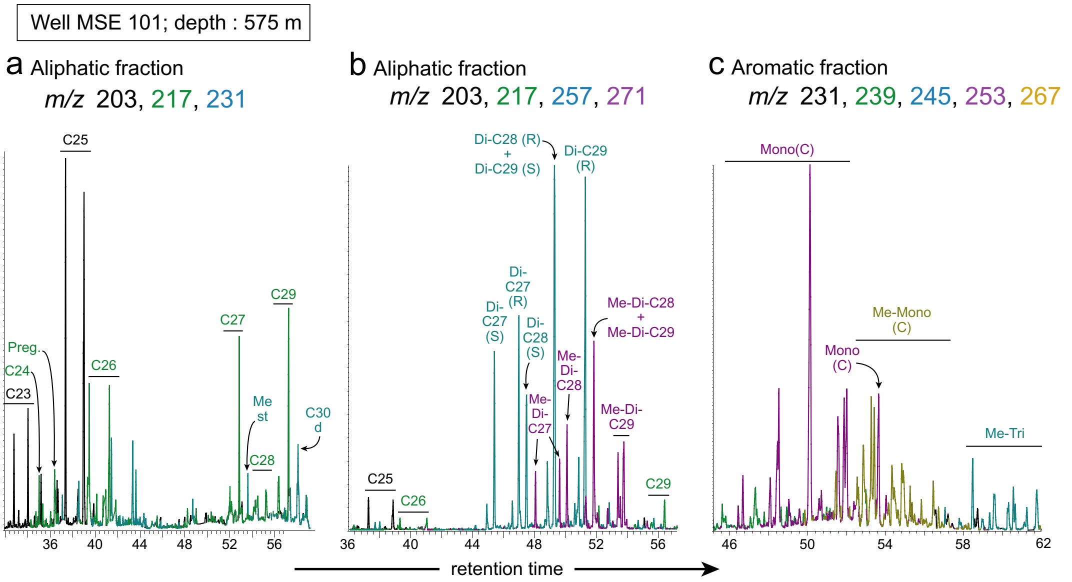

Fig. 7. (a) Distribution of steranes and methylsteranes (*m*/*z* 203, 217, 231). (b) Distribution of steranes, diasterenes and methyldiasterenes (*m*/*z* 203, 217, 257, 271). (c) Distribution of aromatic steroids (*m*/*z* 231, 239, 245, 253, 267). Preg., pregnane; C23–C29: regular steranes having from 23 to 29 C atoms; C30d: dinosterane; Mest: methylsterane; Di-C27–Di-C29: diasterenes having from 27 to 29 C atoms; Me-Di-C27 to Di-C29: methyldiasterenes having from 27 to 29 C atoms; Mono(C): monoaromatic steroids; Me-Mono(C): monoaromatic methylsteroids; Me-Tri: triaromatic methylsteroids.

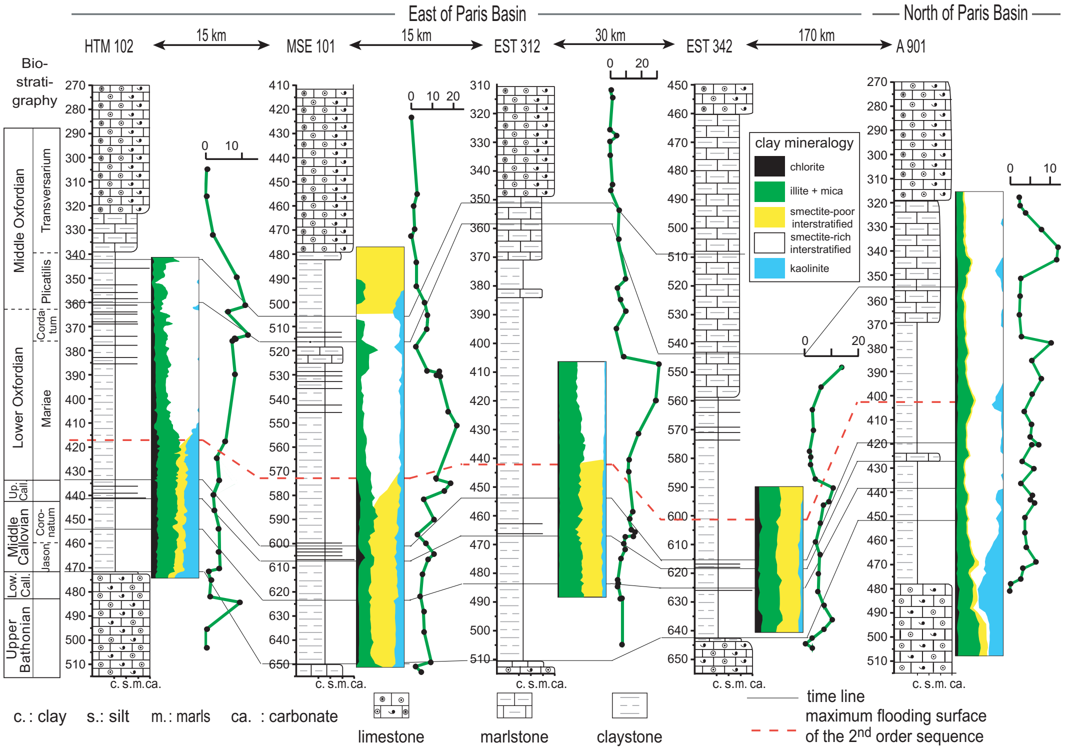

Fig. 8. Stratigraphic evolution of the diasterenes/steranes ratio in relation to the lithology and the clay mineralogy.

4.7. Hopanoids

Hopanoids are triterpenoids derived from bacteriohopanepolyols, diplopterol and diploptene which mainly act as rigidifiers in the cell walls of procaryotes and are degraded during diagenesis into saturated, unsaturated and aromatic hopanoids (Ourisson et al., 1979). The distribution of hopanoids in

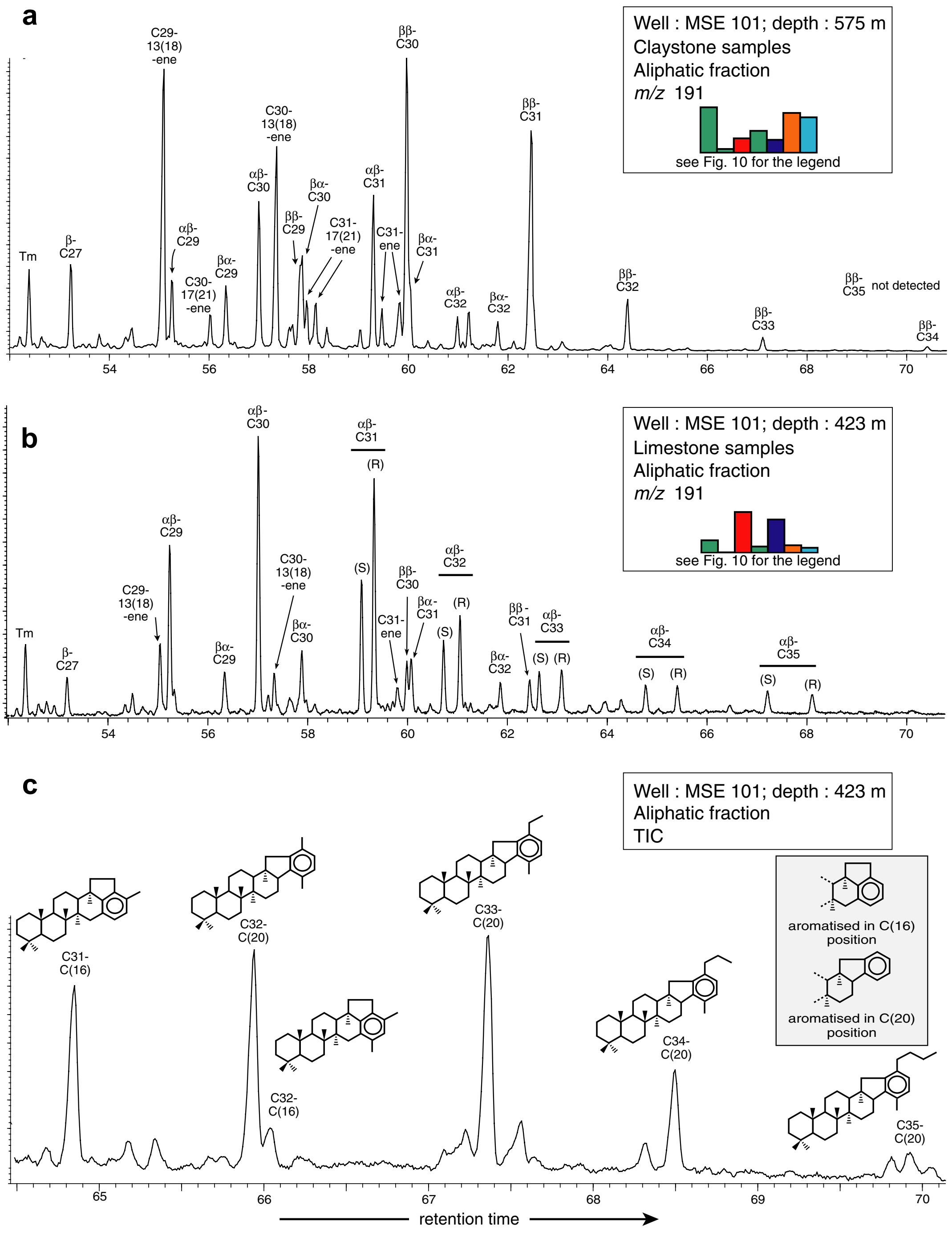

Fig. 9. (a) Distribution of hopanes and hopenes (*m*/*z* 191) in the aliphatic fraction of the claystone samples. (b) Distribution of hopanes and hopenes (*m*/*z* 191) in the aliphatic fraction of limestone samples. (c) Distribution of benzohopanes (*m*/*z* 191) in aromatic fractions of all samples. Histograms in (a) and (b) represent the distribution of hopanes and hopenes of the corresponding samples (see legend of histograms in Fig. 10). Peak assignments are given in Table 4.

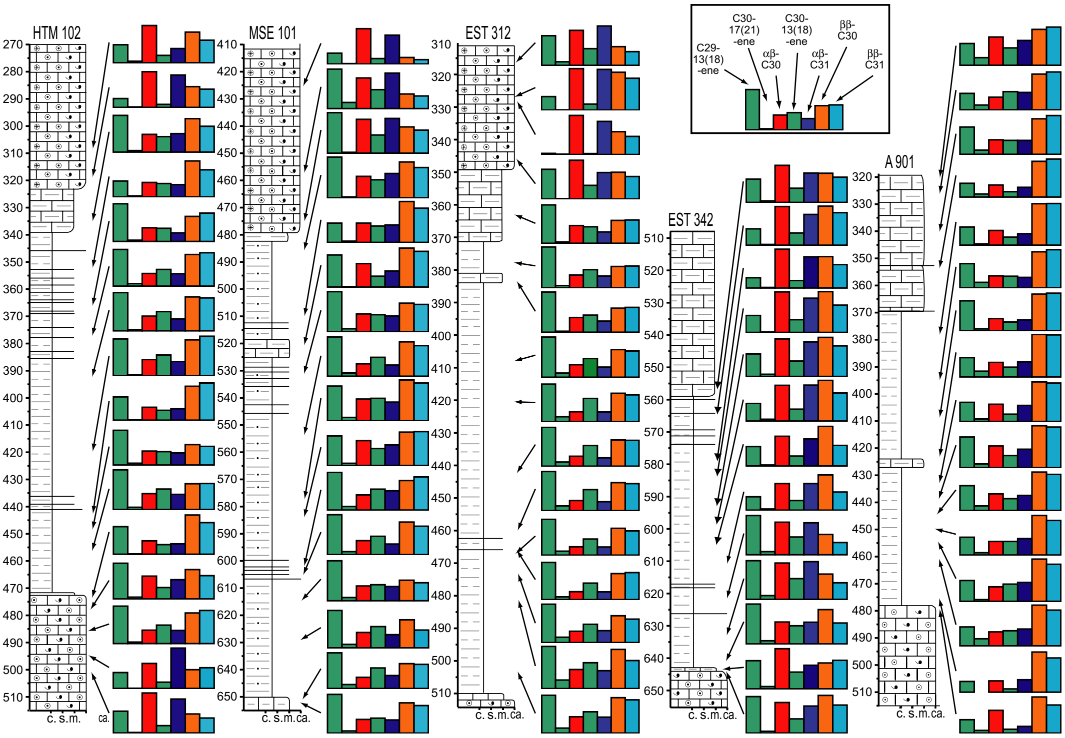

Fig. 10. Vertical and lateral evolutions of the distribution of hopenes and hopanes.

the aliphatic fractions (key ion m/z 191) of the Callovo-Oxfordian claystones is shown in Fig. 9a. This distribution is characterised by the abundance of hopenes and the predominance of hopanes, which have still kept their biological stereochemistry (ββ hopanes) over hopanes showing geological stereochemistry (αβ hopanes). Moretanes (βα hopanes) are present in low proportion. This distribution is also characterized by the exponential decrease of the abundance of homohopanes as a function of their number of C atoms. C_{33}- and C_{34}-homohopanes are in low proportion and C_{35}-homohopanes are generally below the detection limit. Most of the samples from the carbonate platforms, especially the Oxfordian platform which is the most carbonated, display a more "mature" distribution. Indeed, hopenes are in a lower relative abundance than in the claystones, the two epimers 22S and 22R of homohopanes are present in similar proportion and the αβ hopanes (geological stereochemistry) are predominant over the ββ hopanes (biological stereochemistry) as shown in Fig. 9b. This is also indicated by lower values of hopenes/hopanes and ββ hopane/αβ hopane ratios in Part 6 (transition of the Oxfordian platform) of all wells (Table 2). The transition from claystones to the surrounding limestones is thus expressed by a significant change in the distribution of hopanes and hopenes (Fig. 10). Furthermore, the hopanes distribution of EST 342 is slightly different from those of the previous wells since ββ hopanes have similar relative proportions to αβ hopanes and hopenes are less abundant in the Oxfordian than in the Callovian. A 901 also displays lower abundances of hopenes and its Part 6, which is less carbonated than the other wells, does not display a predominance of αβ hopanes over ββ hopanes (Fig. 10).

Every aromatic fraction of the claystones and the carbonate platforms show a similar distribution of benzohopanes (key ion m/z 191). These benzohopanes are aromatised in C(16) and C(20) positions and range from C_{31} to C_{35} (Fig. 9c).

Other aromatic hopanoids as well as the seco- and des-A(or E)-hopanoids are not detected.

4.8. Tetraterpenoids and other pigments

Most of the tetraterpenoids of the geosphere are carotenoid pigments. These pigments are synthesized by most organisms and many of them are more or less specific (Killops and Killops, 2005). These compounds are generally unsaturated in living organisms and have a long hydrocarbon chain, which is often fragmented during diagenesis. In sedimentary organic matter, they are found either as the saturated hydrocarbon counterparts of bio-carotenoids (as lycopane, β-carotane and isorenieratane) or as their fragmentation products (as trimethylalkylcyclohexanes and trimethylalkylbenzenes, respectively, derived from β-carotane and isorenieratane). In the cores from the East of the Paris basin, tetraterpenoid derivatives, as trimethylalkylbenzenes (m/z 133, 134 in aromatic fractions), were detected in significant proportion in one sample only, located at the extreme bottom of the claystones of MSE 101. Their distribution is shown in Fig. 11 and is remarkably similar to those published by Schwark and Püttmann (1990) who linked these aryl-isoprenoids to isorenieratene-type carotenoids synthesized by *Chlorobiaceae* (green sulphur bacteria). In A 901, trimethylalkylbenzenes are also found in significant amount with the same distribution between 463 and 440 m. Their relative abundance decreases during this interval, which is the stratigraphic counterpart of the bottom of the claystones in the East of the Paris basin. The samples characterized by the presence of these carotenoid moieties are those displaying high TOC values.

All the polar fractions contain maleimides (1-*H*-pyrrole-2,5-diones). Their distribution is largely dominated by 3-methyl-4-ethyl-, 3,4-methyl- and 4-methyl-maleimides, which are derived from chlorophyll-*a*, the major chlorophyll of the biosphere synthesized by land plants and phytoplankton (Grice et al., 1996).

4.9. Other biomarkers

Non-alkylated polycyclic aromatic hydrocarbons (PAH) ranging from 3 to 7 aromatic cycles are detected in relatively low proportion except for phenanthrene (P), pyrene and fluoranthene which are major compounds of the aromatic fractions. Their proportions are strongly predominant over their methylated counterparts indicating a pyrolytic origin as paleovegetation fires (Jiang et al., 1998). PAH profiles of the present samples are all similar.

Sulphur is incorporated into kerogen and low molecular weight compounds during early diagenesis when the availability of Fe (II) ions is limited to form Fe sulphides such as pyrite (Hartgers et al., 1997). Organo-S compounds are only reported as dibenzothiophene (DBT) and methylated dibenzothiophenes (key ions m/z 184, 198, 212, 226 in aromatic fraction). Dibenzothiophene is the most abundant organo-S compound but remains in much lower abundance than phenanthrene (DBT $\ll$ P) which indicates that reduced S is preferentially associated with Fe in inorganic matrices than incorporated into organic matter during early diagenesis (Hughes et al., 1995).This is consistent with the relatively high content of pyrite (1–2%) in Callovo-Oxfordian claystones which sequester the major part of the S (Andra, 2005).

Table 4
Peak assignments for hopanes, hopenes and benzohopanes (m/z 191) represented in Fig. 9

Peak name	Name
Tm	17α(H)-22,29,30-trisnorhopane
β-C27	17β(H)-22,29,30-trisnorhopane
C29-13(18)-ene	30-Norneohop-13(18)-ene
αβ-C29	17α(H)-21β(H)-30-norhopane
C30-17(21)-ene	Hop-17(21)-ene
βα-C29	17β(H)-21α(H)-30-normoretane
αβ-C30	17α(H)-21β(H)-hopane
C30-13(18)-ene	Neohop-13(18)-ene
ββ-C29	17β(H)-21β(H)-30-norhopane
βα-C30	17β(H)-21α(H)-moretane
C31-17(21)-ene	Homohop-17(21)-ene
αβ-C31	17α(H)-21β(H)-homohopane
C31-ene	Non-identified homohopenes
ββ-C30	17β(H)-21β(H)-hopane
βα-C31	17β(H)-21α(H)-homomoretane
αβ-C32	17α(H)-21β(H)-bishomohopane
βα-C32	17β(H)-21α(H)-bishomomoretane
ββ-C31	17β(H)-21β(H)-homohopane
ββ-C32	17β(H)-21β(H)-bishomohopane
αβ-C33	17α(H)-21β(H)-trishomohopane
ββ-C33	17β(H)-21β(H)-trishomohopane
αβ-C34	17α(H)-21β(H)-tetrakishomohopane
ββ-C34	17β(H)-21β(H)-tetrakishomohopane
αβ-C35	17α(H)-21β(H)-pentakishomohopane
ββ-C35	17β(H)-21β(H)-pentakishomohopane
C31–C(16)	C31-benzohopane aromatised in position C(16)
C32–C(20)	C32-benzohopane aromatised in position C(20)
C32–C(16)	C32-benzohopane aromatised in position C(16)
C33–C(20)	C33-benzohopane aromatised in position C(20)
C34–C(20)	C34-benzohopane aromatised in position C(20)
C35–C(20)	C35-benzohopane aromatised in position C(20)

5. Discussion

5.1. Thermal maturity

Organic matter is very reactive to thermicity and its effects can be efficiently evaluated using hydrocarbon

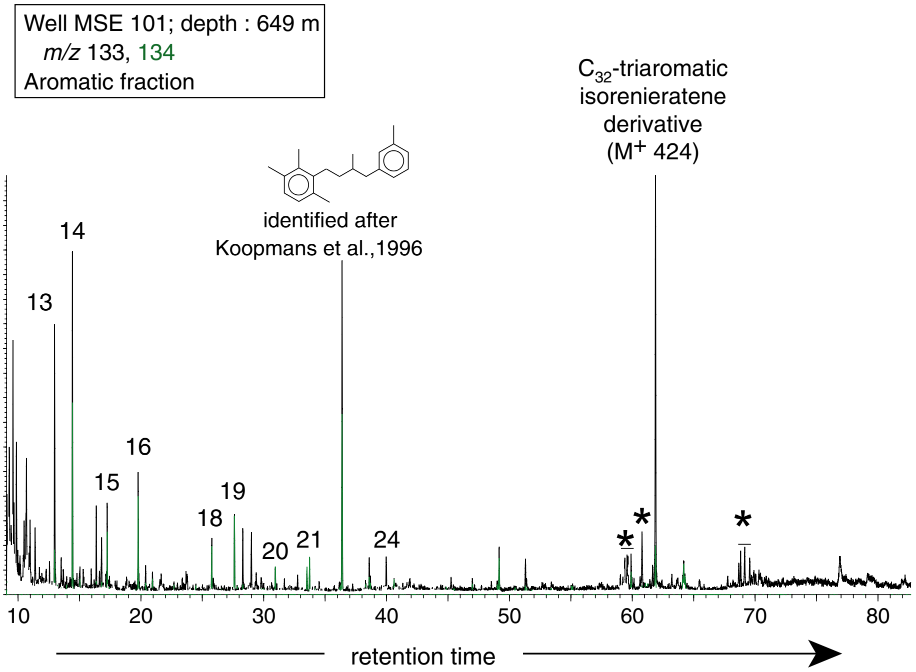

Fig. 11. Distribution of trimethylalkylbenzenes (*m*/*z* 133, 134) at the extreme bottom of MSE 101. Numbers indicates the number of C atoms of the trimethylakylbenzenes. *: other diagenetic products of isorenieratene.

geochemical parameters. The organic extracts of the claystone samples show several features which are typical indicators of a thermal immaturity of the sedimentary organic matter.

(1) Unsaturated biomarkers (sesquiterpenes, diterpenes, diasterenes, hopenes) are major compounds in the aliphatic fractions of the Callovo-Oxfordian claystones. Because unsaturated compounds are rapidly hydrogenised or aromatized during the diagenesis and the catagenesis, their occurrence is a first argument for the immaturity. (2) The distribution of hopanoids in the claystones is typical of immature organic matter. Indeed, the predominance of the thermodynamically unstable ββ hopanes over the stable αβ hopanes, the low abundance of moretanes (βα hopanes) and the large predominance of 22R-homohopanes epimers over the 22S epimers are well known features of immaturity. Furthermore, benzohopanes aromatized at the C(16) position are thermally unstable and their occurrence is an additional argument in favor of the immaturity (Schaeffer et al., 1995). (3) The long-chain *n*-alkanes display an odd-over-even predominance (CPI often higher than 2). (4) The monoaromatic steroids predominate over the triaromatic steroids, which is also characteristic of immature organic matter (Peters et al., 2005).

All these data are consistent with previous studies on the thermal history of Callovo-Oxfordian claystones which show that the maximum temperature experienced by the Callovo-Oxfordian sediments did not exceeded 50 °C (Landais and Elie, 1999). Although immature, the organic matter of EST 342 shows a more mature distribution of hopanes than other wells, characterized by the lower abundance of hopenes and a similar proportion or a slight predominance of the αβ hopanes over the ββ hopanes. This may be explained by the paleogeographic position of this well, which is closer to the area of maximum subsidence of the Paris Basin. Sedimentary rocks from this core have been buried deeper or were subjected to higher heat flux during the Paris Basin history than those from the other cores.

5.2. Paleoenvironment

5.2.1. Source of sedimentary organic matter

The molecular composition of the organic extracts indicates that the organic matter of the studied sedimentary series is a mixture of:

(1) Autochthonous organic matter derived from marine biomass. This marine contribution originates from two types of organisms.
  (a) Algae and plankton living in the water column, mainly in the photic zone, as indicated by the presence of C_{27}- and C_{28}-steroids. The presence of dinosterane and 4-methyl-steroids can be imputed more specifically to dinoflagellates (Summons et al., 1987).
  (b) Bacteria living within the sediment as indicated by the presence of hopanoids. Furthermore, few samples from the Oxfordian platform are characterized by the presence of short-chain alkanes including one or two quaternary C atoms (BAQCs) and 3-methylalkanes, which are typically assigned to cyanobacteria (Kenig et al., 1995, 2005).

(2) Allochthonous organic matter initially synthesized by terrestrial plants as indicated by the presence of n-C_{24} to n-C_{34} alkanes with an odd-over-even predominance, C_{29}-steroids, sesqui- and diterpenoids. Most of these organisms probably lived on the London-Brabant Massif, the nearest emergent land and the main source of detrital clays (Pellenard et al., 1999).

5.2.2. *Chemistry of the depositional environment*

Several biomarker families are sensitive to redox and salinity conditions of the depositional environment. The most used are the Pr/Ph ratios, the distribution of hopanes, the abundance of degradational products of carotenoids, gammacerane, perylene and S compounds (Peters et al., 2005).

Among them, hopanes have the advantage of carrying information on the redox conditions of the interstitial environment since they are primarily derived from bacteria living within the sediment. In all samples, the hopane distribution is characterised by the exponential decrease of the abundance of homohopanes as a function of their number of C atoms coupled to the very low preservation of C_{35}-homohopanes. This distribution indicates oxic conditions within the sediment during deposition (Philp and Mansuy, 1997).

In contrast, gammacerane and the derivative products of isorenieratane-type carotenoids carry information on the redox conditions restricted to the water column because their source organisms lived in O_2-depleted photic zones (Sinninghe Damsté et al., 1995; Koopmans et al., 1996). Trimethylalkylbenzenes are only significantly present at the extreme bottom of MSE 101 as well as its stratigraphic counterpart on A 901 and are absent in all other samples. This implies that the photic zone of the water column was oxic during the whole of the deposition of the Callovo-Oxfordian series.

The oxic conditions in the soft sediment as well as in the photic zone strongly suggest that the water column was well mixed and thus opened to the deeper area located to the SW. This is also consistent with the absence of gammacerane, a marker of stratified water derived from tetrahymanol synthesized by ciliates. Generalised oxic conditions are also supported by other markers such as Pr/Ph ratios higher than 1, perylene content close to those of other PAHs and low-organic C content ($<1\%$), which, in regard to the clayey nature of the sediment suggests that the major part of the sinking organic matter was oxidized.

The thin interval characterized by a significant content of trimethylalkylbenzenes (green sulphur bacteria biomarkers) could correspond to a brief development of photic zone anoxia at the beginning of the Jason zone during which higher contents of organic matter were preserved within the sediment. The absence of gammacerane in this interval can be explained by the absence of ciliates in the photic zone or by anoxia which was not too severe allowing the development of microalgae, which inhibit the biosynthesis of tetrahymanol by ciliates. Similar euxinic-anoxic events were described in the Central Atlantic (Unnamed Formation of the site DSDP 534, Leg 76) and in South-central England (Peterborough member, Oxford Clay) during the Middle Callovian (Herbin et al., 1983; Kenig et al., 2004). This supports the occurrence of a generalised euxinic-anoxic event on the Western European scale having variable duration according to the localities. This important temporary change of the water chemistry could have induced an increase of the organic C burial which may be responsible for a drastic cooling event of the late Callovian (Dromart et al., 2003).

Gammacerane and S organic compounds are widespread within sediments deposited in hypersaline environments. Thus, the present data do not indicate hypersaline conditions which is consistent with the lack of evaporitic minerals (halite, gypsum, etc.) or their residual structures in the studied sedimentary series as well as with open-sea conditions suggested by biomarker distributions as described above.

5.3. Preservation conditions and diagenesis

5.3.1. Catalytic effect of clays

The mineralogy of the matrix embedding the sedimentary organic matter clearly has an influence on the distribution of steroids and more particularly on the relative proportion of the diasterenes compared to steranes. The fact that the lower values of the diasterenes/steranes ratio occur in the limestones while the higher ones are encountered in the claystones is consistent with the observations reported by van Kaam-Peters et al. (1998) who indicate that this ratio is positively correlated to the clay/TOC ratio. Indeed, limestones display a clay/TOC ratio fluctuating between 8 and 50 (considering clay content = 2.5–5% and TOC = 0.1–0.3%) while claystones samples have a clay/TOC ratio fluctuating between 55 and 160 (considering clay content = 40–60% and TOC = 0.4–0.7%).

Furthermore, the relation between the diasterenes/steranes ratio and the clay mineralogy – and more precisely the smectite content – can be explained by the catalytic effect of this mineral during diagenesis. Indeed, the surface of smectite crystals bears superacid sites which favor the geosynthesis of rearranged steroids to the detriment of the formation of regular steroids (Sieskind et al., 1979).

5.3.2. Physical protection by clays

The distribution of saturated hopanoids is drastically different between the claystones and the limestones. Claystones show a thermally immature distribution while limestones have a more "mature" distribution (Figs. 9a and b and Fig. 10). However, thermicity can not explain this last distribution because the Oxfordian limestones lie above the claystones and its temperature has not exceeded 50 °C since deposition (Andra, 2005). In addition, Faure et al. (1999) then Elie et al. (2000) demonstrated by experimental studies on powdered Callovo-Oxfordian claystones that oxidation has a similar effect to thermicity on the relative abundance of hopenes and ββ hopanes. Consequently, it can be expected that the "mature" distribution characterizing the limestones can be related to a more intense post-depositional oxidation. In contrast, the hopane distribution indicates that the organic matter of the claystones was not oxidized although the deposit conditions were oxic. This can be explained by a protective matrix effect of clay minerals. Many studies point out that the minerals can physically protect their associated organic matter from degradation, especially clay minerals (Hedges and Oades, 1997; Nelson et al., 1999). Indeed, organic matter is more efficiently isolated from oxidative agents in the depositional environment than in carbonate sediments which are generally coarser and better oxygenated.

A similar change in the hopane distribution was also observed within the Silty Layer of Marcoule but was related to bioturbation intensity instead of lithologic changes (Fleck et al., 2002). In this last study, bioturbated strata were systematically associated with "mature" hopane distributions. The intense disturbance of the sediment by bioturbation certainly alters its protective effect and favors oxygenation of the sediment. In Callovo-Oxfordian claystones, no relation was found between the intensity of the bioturbation and the hopane distribution. The bioturbations encountered in these claystones are pyritised and belong to the *Chondrites* ichnogenera. This ichnogenera as well as the presence of pyrite indicates slightly reducing conditions in the sediment at the time of bioturbation (Bromley, 1996). At first sight, this contrasts with the data indicating oxic conditions within the sediment just after deposition. However, careful observations of the pyritised burrows show that they do not have any significant deformation which could be induced by the compaction and that their walls are sharp. This indicates that these bioturbations were made in a firm sediment and that the interstitial environment became reducing tardily after deposition. This means that the organic matter was already protected at this diagenesis stage explaining why it did not record any reducing condition.

5.4. Variability of the distribution of organic matter

5.4.1. Intrinsic variability within the claystones

The organic matter from the Callovo-Oxfordian claystones can be considered as homogenous on the regional scale around the hosted Underground Research Laboratory (URL). Claystones are actually characterized by only one molecular facies without important changes related to major evolution of the depositional environment and/or diagenetic conditions even with the most pronounced sedimentological changes. Indeed, bioturbated and non-bioturbated levels do not display systematic differences in their molecular composition. The more carbonated and condensed Upper

Callovian strata have the same molecular facies as their surrounding clayey and dilated deposits and finally no significant evolution is reported through the mineralogical transition except an increase of the relative proportion of diasterenes. This last variability remains slight because diasterenes are much more abundant than steranes whatever the clay mineralogy.

Some nuances have to be pointed out concerning the homogeneity of the claystones. From a quantitative point of view, the organic matter content is significantly higher in part 2 (Middle Callovian claystones) than in the upper parts. Then, from a qualitative point of view, some parameters such as the $n\text{-C}_{24}^{+}/n\text{-C}_{24}^{-}$ also show vertical variations. These vertical changes in the molecular composition remain slight (TOC remains low except for a few samples associated with a brief anoxic event and $n\text{-C}_{24}^{+}/n\text{-C}_{24}^{-}$ only fluctuates between 0.5 and 1) and are laterally well correlated between the wells located around the URL. Similar vertical evolution in many wells located several kilometres away is indicative of a good lateral homogeneity of the organic matter within the geological barrier. These data support many previous geochemical, mineralogical, geomechanical and sedimentological studies demonstrating the good lateral homogeneity of the Callovo-Oxfordian claystones (Andra, 2005).

Significant lateral evolution of the molecular composition appears on a larger geographic scale, when the molecular facies of the claystones from the East of the Paris basin is compared to those of A 901. While these two molecular facies show many similarities, the marine contribution is significantly higher in A 901. This evolution is imputed to a paleoenvironmental change because A 901 claystones were deposited relatively close to the paleocoasts of the London-Brabant Massif while those from the East of the Paris basin lay in a distal position (Fig. 1c). Coastal environments are characterized by a higher marine contribution because the supply of nutrient coming from emerged lands favors the development of marine organisms.

5.4.2. Variabilities through the transitions to the surrounding limestones

The transitions from the claystones to the limestones are characterized by noticeable changes of the molecular composition of organic extracts. These changes are induced by the evolution of:

1. The source of the sedimentary organic matter. Indeed, the progressive emplacement of the Oxfordian platform is marked by a change and a diversification of the source organisms as indicated for instance by the appearance of a cyanobacterial contribution and a change of land plants input induced by a paleoclimatic shift (Hautevelle et al., 2006). Because the nature of the source organisms is directly linked to paleoenvironmental conditions, its change and its diversification through the transitions to the limestones indicate an evolution and a diversification of the paleoenvironments. This is consistent with the facts that the claystones were deposited in a unique offshore environment while the limestones are characterized by many sedimentological facies (more or less argillaceous, bioclastic, oolitic, bioconstructed, etc.) which reflect a wider range of shoreface environments. This is also supported by sedimentological and geochemical studies which highlight the wide diversity of paleoenvironments and diagenetic conditions encountered in the Oxfordian carbonate platform (Carpentier, 2004; Vincent et al., 2004).
2. The quality of the preservation and of the diagenetic conditions. Indeed, the claystone/limestone transitions are marked by major changes in the distribution of the steroids and hopanoids due to a decrease of the catalytic effects and the physical protection by clay minerals. These conditions are thus clearly influenced by the nature of the mineral matrix, and more especially by the clay content.

5.5. Primary factors controlling variabilities of the composition of organic matter in sedimentary series

This study highlights that the lateral and vertical variability of the molecular composition of the organic matter within the studied sedimentary series is related to:

1. the spatio-temporal evolution of depositional environments during the sedimentation, which controls the changes of the sources of the organic matter.
2. the lateral and vertical variabilities of the sedimentological facies because the mineral matrix has a major influence on the preservation and the diagenesis of the organic matter after its deposition.

More generally, these paleoenvironmental and faciological changes are strongly correlated and are both mainly controlled by the paleogeographic position and the morphology of the depositional setting.

5.5.1. Paleogeographic position of the depositional setting

The paleogeography, and more especially the distance between the depositional setting and the paleocoasts, has a major influence on the variability of the distribution of organic matter within sedimentary series. Indeed, in coastal environments, the quantity and the quality of organic matter preserved in sediments is very variable as well in space and time. The spatial variability of organic matter in coastal environments depends on the proximity of river mouths, on the characteristics of the watersheds and on the sea currents (Fernandes and Sicre, 2000). Its temporal variability occurs as well at the season-scale (Lambert et al., 1999), at the secular and millennium-scale (Kong et al., 2006) and in relation to sudden catastrophic events such as cyclones or tsunamis (Shiah et al., 2000). In contrast, in offshore environments, the composition of organic matter is much less dependent on these sources of variabilities. Therefore, the sedimentary organic matter is more likely to be heterogeneously distributed within sedimentary series deposited in coastal than in offshore environments. This is supported by many studies of the organic matter in recent sediments along proximal–distal transects (e.g. Tselepides et al., 2000) and was confirmed by the study of another potential geological barrier (Fleck et al., 2002). In the present case study, the geological barrier is located far away from the paleocoasts of the massifs surrounding the Paris basin, which partly explains its homogeneity. On the other hand, some variabilities appear between the wells from the East of the Paris basin and A 901 because this last well was located in a more proximal position.

5.5.2. Morphology of the depositional setting

The sequence stratigraphic concepts describe the 3D distribution of sedimentological facies within depositional sequences. They also highlight the major influence of the morphology of the depositional setting, and more particularly the topography on which the deposition takes place, on the vertical and lateral evolution of the sedimentary facies within the deposits. The classic and frequently used model proposed by the EXXON Group concerns sequences deposited in passive margin basins, which are characterised by a shelf-break topography (Vail et al., 1977). In such a model, the sigmoidal geometry of the initial topography produces an abrupt deepening from upslope to downslope which induces a rapid evolution of paleoenvironments and sedimentological facies

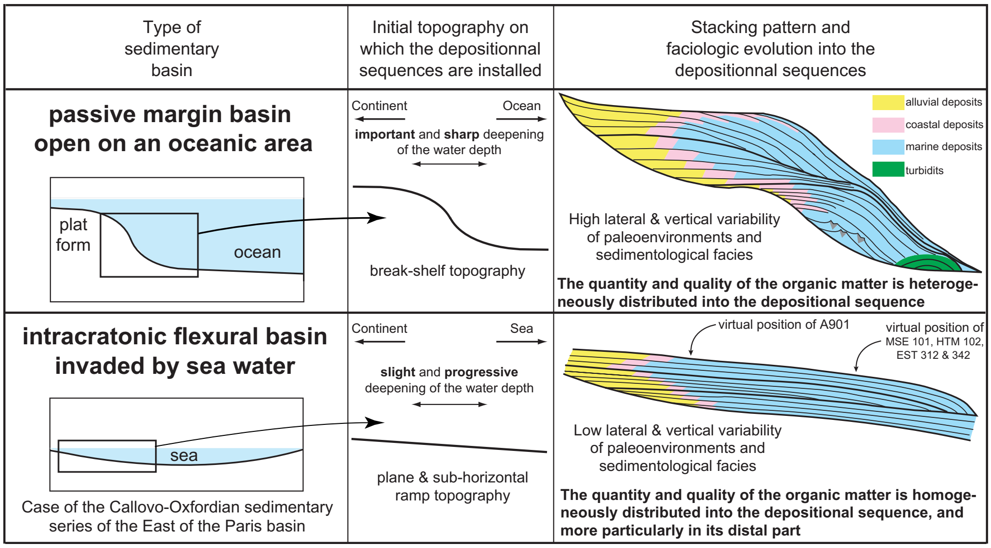

Fig. 12. Comparison of the stacking pattern and distribution of the sedimentological facies within depositional sequences deposited on a shelf-break topography and those deposited on a plane and sub-horizontal ramp.

along the proximal–distal transect. Consequently, depositional sequences settled on a shelf-break topography present an important vertical and lateral variability of its sedimentological facies which should undoubtedly induce a high degree of variability of the composition of the organic matter within the deposits (Fig. 12).

In contrast, the claystones constituting the geological barrier were not deposited within a passive margin basin but on a side of a flexural intracratonic basin. They are thus deposited on a plane and slightly-tilted ramp (Dromart et al., 1996; Robin et al., 2000). With this type of initial topography, the deepening from upslope to downslope remains slight and the evolution of paleoenvironments and sedimentological facies are therefore much more progressive than in the case of a sigmoidal topography. Because the paleoenvironments and the facies do not change in an important way in third order sequences deposited on slightly-tilted and plane ramp, their sedimentary organic matter should be more homogenous on a regional scale (Fig. 12).

6. Conclusion

The molecular biomarker composition of the Callovo-Oxfordian claystones and their surrounding limestones located to the NE of the Paris basin indicates that the sedimentary organic matter is thermally immature and is a mixture of marine (algae, plankton, bacteria) and continental (terrestrial plants) contributions. The data also indicate that the organic matter was deposited under oxic and open-sea conditions except for a brief event of photic zone anoxia during the deposition of the very first argillaceous sediments to the East of the Paris basin.

These claystones, which may constitute a geological barrier in the case of the realization of an in-depth storage of nuclear wastes, display a unique molecular facies without major lateral and vertical change of the biomarker distribution. These results suggest no important evolution of paleoenvironmental and/or diagenetic conditions. In contrast, the transitions to the surrounding limestones are marked by many changes in the distribution of biomarkers reflecting both paleoenvironmental and diagenetic evolution. Limestones are characterised by a higher variability of biomarker distribution than the claystones, thus reflecting the greater diversity of paleoenvironments which can be encountered in shoreface domains. The data also indicate a noticeable evolution of the molecular facies between the four wells of the East of the Paris basin and A 901. The higher marine contribution recorded in A 901 can be explained by a large nutrient supply coming from the London-Brabant Massif supporting the development of marine organisms.

More generally, the obvious homogeneity of the organic content of the Callovo-Oxfordian claystones from the East of the Paris Basin can be explained by:

- the paleogeographic position of their depositional setting. The deposition took place in a distal offshore domain, which was not under the influence of coastal phenomena which are very variable in space and time.
- the morphology of the Paris basin. Because the Paris basin is a flexural intracratonic basin, the deposition of the studied sedimentary series took place on a plane and sub-horizontal ramp. Such a paleotopography favors a homogenous distribution of organic matter within the deposits.

This study combined with the results of Fleck et al. (2002) on the potential geological barrier of Marcoule demonstrates the efficiency of organic geochemistry in the assessment of the heterogeneity of geological barriers.

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