The origin and timing of multiphase cementation in carbonates: Impact of regional scale geodynamic events on the Middle Jurassic Limestones diagenesis (Paris Basin, France)

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A B S T R A C T

The Middle Jurassic carbonates of the eastern part of the Paris Basin display surprisingly low values of porosity and permeability (Φ < 15% and K < 0.5 mD). The main objective of this study is to determine the causes and timing of the cementation that altered the petrophysical properties of these carbonates thereby destroying their potential as oil reservoirs; a fate that did not befall their equivalents in deeper, central parts of the Paris Basin. Using petrographic and geochemical analyses (stable O and C isotopes, Sr isotopes, major elements), we identify six calcitic spar stages, two dolomite stages, and several episodes of fracturing and stylolitization ordered in paragenetic sequence. Cement quantification shows the predominance of two blocky calcite cement stages (75% of total cementation). O and Sr isotopes from these calcite cements suggest that the parent fluids resulted either from a mixing of trapped Jurassic seawater and meteoric water, or from buffered meteoric waters. In the geological history of the Paris Basin, major meteoric water inputs were possible during the Early Cretaceous, when the Middle Jurassic carbonates cropped out at its northern and eastern borders. Lateral meteoric recharge may have occurred as a result of two separate uplift events (Late Cimmerian Unconformity and Late Aptian Unconformity) and the related exposures of carbonates to the north of the study area. This palaeohydrological circulation brought about a significant reduction of porosity (from 40% to 10%) through calcite cement precipitation. The Early Cretaceous events are of great importance in the diagenetic evolution of the sedimentary basins bordering the London-Brabant Massif across all of northwestern Europe. A subsequent dolomite and calcite cementation stage accounts for about 5% of the total cement volumes. This late cementation may have been caused by hydrothermal fluids ascending along permeable fractures during the Late Oligocene extension episode.

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1. Introduction

A great diversity of petrophysical characteristics (porosity, permeability) is commonly reported in neritic carbonates (e.g. Lucia, 1999; Moore, 2001; Ehrenberg and Nadeau, 2005; Ehrenberg et al., 2006). This diversity reflects the variety of depositional processes in shallow environments and the broad spectrum of subsequent diagenetic changes (cementation, dissolution, replacement). In each case study, the challenge is to find ways of detecting patterns within ancient formations from which to predict the distribution of reservoirs and permeability barriers (Montanez, 1997; Heasley et al., 2000; Hendry, 2002). This requires an understanding of lateral and vertical variations of sedimentary facies, of palaeoenvironments, and of diagenetic history and its effects on initial depositional patterns. One of the key points is knowledge of the palaeohydrological system and its evolution; from this, the timing of diagenesis can be reconstructed and the evolution of reservoir properties determined.

Middle Jurassic carbonate formations of the eastern part of the Paris Basin usually display low porosity and permeability (Φ < 15% and K < 0.5 mD) because of extensive cementation (Javaux, 1992; Elion et al., 2005). This is of primary importance because these carbonate formations constitute the basement of the natural clay barrier chosen by the French National Agency for Radioactive Waste Management (Andra) as a study subject for an underground research laboratory investigating the feasibility for deep disposal of radioactive waste.

Our objectives are to determine the causes, the timing and the spatial distribution of the diagenetic phenomena that make for such poor reservoir properties while coeval carbonates in the centre of the
Paris Basin form oil, gas reservoirs, and geothermal resources (Menjoz et al., 1992; Granier, 1995; Bez and Sambet, 1995; Mougenot, 1999). This is a key point for the Andra engineers, who for safety reasons must endeavour to understand as precisely as possible both the palaeohydrological and the present-day hydrological systems (Landais, 2004; Brigaud et al., 2009a). The pore-filling cements are the subject of an integrated petrographical (stained thin sections, cathodoluminescence, SEM), petrophysical (porosity and permeability), and geochemical ($\delta^{18}O$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$) investigation.

2. Location and geological setting

Samples were collected from three Andra cores (HTM102, EST210 and EST433), one oil exploration core at Liffol-le-Grand (L.LI.CD.1) and fifteen outcrops in the eastern part of the Paris Basin (Fig. 1A). Biostratigraphy of the Middle Jurassic carbonates in Burgundy and Lorraine is based mainly on ammonite/brachiopod determinations and on sequence stratigraphic correlations (Thierry et al., 1980; Garcia et al., 1996; Gaumet et al., 1996; Brigaud et al., 2009b).

During the Bajociang–Callovian interval, the Paris Basin was an epicontinental sea in subtropical latitudes (28–32° N), open to the Atlantic, Tethys and Northern Oceans (Fig. 1B; Thierry and Barrier, 2000). The Early Bajociang rocks are composed mainly of bioclastic calcarenites and coral buildups—the Calcaires à polypiers (Fig. 1C)—deposited on a vast carbonate environment extending over almost the entire Paris Basin (Durlet and Thierry, 2000; Fig. 1B). The main components of this carbonate formation include echinoderms, bivalves, corals, bryozoans and Nubecularia oncoids (Purser, 1989).

At the Early/Late Bajociang transition, an abrupt lithological change occurred with the appearance of terrigenous facies above an encrusted bored surface corresponding to the ‘Vesulian Unconformity’ (Fig. 1C). This feature is known in numerous carbonate platforms of

![Fig. 1. A – Location of the 15 study sections and the four study boreholes in the eastern part of the Paris Basin (Lorraine and Champagne–Ardenne regions) on a simplified geological map. B – Palaeogeographic map of the Bathonian (modified after Enay and Mangold, 1980 and Thierry and Barrier, 2000). C – Schematic NE–SW transect illustrating the lithostratigraphic architecture during the Bajociang–Early Callovian interval, modified after Enay and Mangold (1980); Thierry et al. (1980) and Brigaud et al., (2009b).]
the western Tethyan domain (Jacquin et al., 1998; Durlet and Thierry, 2000). As a consequence, mixed carbonate–siliciclastic sedimentation lasted throughout the Late Bajocian. In the south-western part of the study area, it corresponds to interbedded marls and oyster coquina deposits (Marnes à Ostrea acuminata; Fig. 1C). In the northeastern part of the study area, it corresponds to alternating marls (Marnes de Longwy and Oolite à Clypeus ploti) and ooblastic deposits (Oolite miliaire inférieure and Oolite miliaire supérieure). These ooblastic deposits form aggrading and prograding deposits on a ramp dipping gently southwards from the London–Brabant landmass.

During the Bathonian, a carbonate ramp with diversified facies developed in the northeastern part of the Paris Basin (Purser, 1989; Ferry et al., 2007). Three main depositional environments are recognized (Fig. 1C): 1) a typical shoal environment with abundant ooids, peloids, bivalves, bryozoans and gastropods (Oolite Blanche and Oolite de Fréville; Fig. 1C); 2) a protected lagoon behind the shoal with low-energy sedimentation characterized by mudstone facies with oncocoids and large benthic foraminifera, wackestone/packstone with oncocoids, and peloidal grainstone (Calcaires de Chaumont and Calcaires de Neufchâteau); 3) a more proximal lagoon setting with peritidal-to-supratidal muds (fenestral structures and stromatolites) and intraclastic washover deposits forming flat islands bordered by beachrocks (Purser, 1989).

The Early Callovian carbonate formation restricted to the southwestern part of the study area (Pierre de Dijon-Corton and Pierre de Ladoix; Fig. 1C) displays mainly oolitic, bryozoan- and bivalve-rich calcarenites. Northwards, these Callovianshoreface deposits progressively give way to hemipelagic marls interstratified with localised bioturbated biolastic-rich tempestites (upper offshore to lower offshore).

3. Material and methods

3.1. Porosity and permeability

Porosity and permeability were measured on 251 plug samples from EST210, HTM102, EST433 and L.LI.CD.1 cores at Panterra Laboratory, Leiderdorp (The Netherlands). Helium porosity was measured at ambient temperature and pressure. Permeability measurements were made on an unsteady-state air permeameter (lower limit of 0.01 mD) for the other 75 samples. The 251 permeability data were obtained at a confining pressure of 400 psi including the Klinkenberg slip factor.

3.2. Petrography/diagenesis

Subsurface and field observations focused on the major cementation stages and on other diagenetic stages (fracturing, stylitization, dissolution, neomorphism, mechanical compaction) that characteristically affect the permeability and porosity parameters. Some 267 double-polished thin sections (30 µm) were made from 1-inch core plugs (diameter 2.5 cm) drilled from the three Andra and one oil exploration cores (L.LI.CD.1). Additional thin sections were made from 13 outcrops to complete the petrographic investigation. Depositional facies and diagenesis were studied using optical microscopy on alizarin cores (L.LI.CD.1). Additional thin sections were made from 13 outcrops to systematically establish on the basis of superposition and cross-cutting relationships from thin section observations. The proportion of blocky calcite cement on 229 thin sections (EST210, HTM102, EST433 and L.LI.CD.1 cores) was quantified using a point counting JmircroVision Image analysis system (Roduit, 2008) with a minimum of 100 counts per section. Visual estimations of the different cement stages were carried out on 236 samples (EST210, HTM102 and EST433 cores).

Fluid inclusions are observed on all the double-polished thin sections (30 µm). Doubly polished wafers (100 µm thick) were made from fifteen samples exhibiting massive calcite cements with fluid inclusions. The single liquid phase and the very small size (≤8 µm) of the fluid inclusions observed in the crystalline calcite and dolomite do not permit microthermometric measurements (Goldstein and Reynolds, 1994).

In order to evaluate the importance of stylolites as a potential source of carbonate for blocky calcite during mesogenesis, a mass balance calculation was made by the method described in Finkel and Wilkinson (1990). Five parameters were quantified: grain, cement, and pore volumes, and both stylolite thickness and numbers (Finkel and Wilkinson, 1990). Four characteristic grainstone units of Pierre de Ladoix, Oolite de Fréville, Oolite miliaire inférieure and Calcaires à polypiers were chosen along the Middle Jurassic carbonate cores (EST210 and EST433). For each of them, one representative thin section was point counted to determine grain, cement and pore proportions. The thickness of the units was measured and the number of stylolites and their mean thickness were determined. The present-day grain, cement and pore volumes were calculated from a 1 cm² area. The original pore volume was estimated by adding the present-day pore and cement volumes. The masses of carbonate cement and dissolved grain were calculated using a density of 2.7 and were used to estimate the cement mass balances. The chemical compaction rate of the stylolites (limestone thickness dissolved from stylolite/stylolite thickness) in the study area (HTM102 borehole), based on Al content in insoluble residues within stylolites and close to stylolites, was estimated at between 15 and 30 depending on texture (15 for mudstone, 27 for grainstone and 29 for boundstone; André, 2003). Assimilating this stylolite compaction rate, the amount of carbonate dissolved during stylitization and its potential as a source of cementation was estimated.

3.3. Carbon, oxygen and strontium isotopes

Stable carbon and oxygen isotopes (δ¹³C and δ¹⁸O) were used to ascertain the nature of the palaeohydrological circulation. Sparry calcite and dolomite (~111) filling vugs and fractures in both the cores and the outcrops were sampled using a drilling micro-drill and were analysed for δ¹³C and δ¹⁸O. Before micro-sampling, the selected calcites and dolomites were all checked under cathodoluminescence to select a large crystal zone only and to avoid mixing of calcite stages. In order to reconstruct initial seawater temperatures and δ¹³C values during the Middle Jurassic, additional analyses of oxygen and carbon isotopes (~30) were carried out on micro-drilled non-luminescence areas of well-preserved bivalve calcitic shells (Trichites and oysters).

The δ¹⁸O and δ¹³C values of micro-drilled diagenetic stages and bivalve samples were measured at the Leibniz Laboratory for Radiometric Dating and Stable Isotope Research, Kiel (Germany). Carbonate powders were reacted with 100% phosphoric acid at 75 °C using a Kiel I prototype dual inlet line connected to a ThermoFinnigan 251 mass spectrometer. All isotopic values are reported in the standard δ-notation in per mil relative to V-PDB (Vienna Pee Dee Belemnite) by assigning a δ¹³C value of +1.95‰ and a δ¹⁸O value of −2.20‰ to NBS19. Reproducibility was checked by replicate analysis of laboratory standards and was ±0.05‰ (1σ) for oxygen isotopes and ±0.02‰ (1σ) for carbon isotopes.

Ten samples from HTM102 and EST210 boreholes were chosen for strontium isotope (⁸⁷Sr/⁸⁶Sr) analysis. The Sr isotope analyses were performed at the Geosciences Rennes Laboratory at the University of Rennes. Carbonate powders (~10 mg) were dissolved in 2 N HCl for 1 h. After centrifugation, solutions were evaporated to dryness at 80 to

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100 °C. Residues were dissolved again in 2 N HCl solution and Sr was separated by standard column chromatography methods (BioRad AG 50 W X 8 200–400 mesh H⁺ cation exchange resin). Analyses were performed on a Finnigan MAT262 multiple collector mass spectrometer. Isotope ratios were corrected for mass fractionation using ⁸⁶Sr/⁸⁸Sr = 0.1194. Analytical precision was normalized by analysis of the NBS-987 standard. During analysis of the samples the mean measured value obtained for NBS-987 was 0.710165 ± 0.000003 (n = 3). All sample data have been adjusted to an assumed NBS-987 value of 0.710250.

4. Results

4.1. Petrographic description of the diagenetic stages

The petrophysical measurements of the 251 samples display low porosity and permeability properties (7% average porosity and 0.04 mD median permeability in grainstone, Fig. 2B and data set in Appendix A) because of particularly well-developed cement (20–30% in grainstone). The paragenetic sequence (Fig. 3) described below is established on the basis of superposition and cross-cutting relationships from thin section observations. Sixteen diagenetic events were identified: (1) eogenetic stages (micritization, isopachous fibrous cement, early spar, dissolution of aragonite), (2) burial or mesogenetic stages (mechanical compaction, two blocky calcite cements, two major fracturing stages, two generations of chemical cements are similar to the microstalactitic cements described by Purser (1969) from the Bathonian of the Burgundy platform. They may be of vadose origin, having formed on beach environments in the vicinity of a few ephemeral islands that existed during the Bathonian (Brigaud et al., 1980; Javaux, 1992; Vincent et al., 2007).

4.1.1.3. Microstalactitic and meniscus cements (MC). Asymmetrical crusts several millimetres thick are observed in coarse-grained oncoidal and gastropod grainstone of the Calcaires de Chaumont (Fig. 4). These cements are similar to the microstalactic cements described by Purser (1969) from the Bathonian of the Burgundy platform. They may be of vadose origin, having formed on beach environments in the vicinity of a few ephemeral islands that existed during the Bathonian (Purser, 1969; 1975). LMC cements may form non-luminescent and non-ferroan meniscus cements in ooid facies which may indicate a sea level drop at the top of a stratigraphic sequence during the Late Bathonian (Brigaud et al., 2009b this volume).

Fig. 2. A – Semiquantitative estimation of cementation stage observed on 236 thin sections of the EST210, EST433 and HTM102 boreholes (mean and standard error), B – Porosity mean values and standard deviation on 251 samples. Quantification of blocky calcite cement in 229 Middle Jurassic samples (marls, mudstone, wackestone, packstone, grainstone, boundstone; EST210, EST433, HTM102 and L.L.LCD.1 boreholes), and detailed proportion of blocky calcite cement (Bc1, Bc2 and Bc3) on 203 samples of EST210, EST433 and HTM102 boreholes.
4.1.1.4. Non-ferroan early spar (nfES). This LMC precipitate exhibits two contemporaneous morphologies:

1. Bladed to scalenohedral fringes with elongate inclusion-poor calcite crystals (30–200 µm long).
2. Syntaxial calcite overgrowth cements developed laterally and contemporaneously with the scalenohedral fringes. They precipitated exclusively around echinoderm grains lacking micrite envelopes.

Together with the few microstalactitic and meniscus early spars of the Calcaires de Chaumont, the scalenohedral and syntaxial non-ferroan spars are the first occurrence of inclusion-free sparry calcites in the paragenesis. Most of them developed below major unconformities where they form m-20 m thick diagenetic horizons (Fig. 4). These cements are cross-cut by borings or hardground abrasion surfaces, thus indicating that they precipitated during sedimentary gaps associated with hardgrounds, as documented in the Bajocian and Bathonian Limestones of Burgundy (Purser, 1969; Durlet et al., 1992; Durlet and Loreau, 1996). The isotopic analyses carried out on these early cements in the Early Bajocian of the Burgundy platform are indicative of a marine origin (Ferry et al., 2007).

4.1.1.5. Bladed ferroan calcite (BFC). These cements exhibit a bladed texture and isopachous fabric with 30–200 µm-long, prismatic LMC crystals. These cements are non-luminescent and strongly ferroan (Fig. 5A–C, F). BFCs are found exclusively in the Oolite miliaire inférieure (Fig. 4). Like the nfES, they are also cross-cut by boring below major unconformities. IFC, MFC, nfES and BFC constitute less than 6% of the total cement volume (Fig. 2) and did not significantly affect the petrophysical properties of the limestone.

4.1.1.6. Dissolution of aragonite shells. Moldic dissolution of the aragonitic skeletal debris (mostly gastropods and corals) was pervasive in the study sections. The moldic voids are progressively filled with BFC or nfES and blocky cements (Fig. 5F), suggesting a very early process. During the Middle Jurassic, in a calcite-sea context (Sandberg, 1983), such early dissolution of aragonite might have occurred either in seawater or under very shallow burial conditions (Palmer et al., 1988; Ferry et al., 2007).

4.1.2. Mesogenetic stages

4.1.2.1. Mechanical compaction. Mechanical compaction features are common other than in a few layers with thick eogenetic cements (Purser, 1969; Javaux, 1992). Three mechanical compaction fabrics are observed: (1) compressed grains with tangential and concave–convex contacts, (2) spalling of oolite cortex and thin isopachous cements; and (3) microfractures (<10 µm) affecting bioclasts, lithified micrites and some early spars.

4.1.2.2. First stage of blocky calcite (Bc1). The first blocky calcite cements are observed in the inter-granular and intra-granular pores and in overgrowths on early syntaxial calcite cements. These cements are present throughout the study sections, except in clay-rich intervals. This stage includes coarse scalenohedral LMC crystals (100 µm–3 mm) and LMC syntaxial overgrowths. Crystals are limpid, non-ferroan, and display a bright orange luminescence with a faint concentric zoning (Fig. 5A–F, H). In this stage, fluid inclusions are very small (<10 µm) and all-liquid. Bc1 cement is cut by all stylolites. This blocky calcite represents about 35% of the total cement volume in the Middle Jurassic calcarenites (Fig. 2), and may represent more than 80% of the cement volume in the Oolite miliaire inférieure and in the Calcaires de Chaumont (Fig. 4).

4.1.2.3. Pyrite. Cubic pyrite crystals are common but located mainly below and above the drowning surfaces. Cathodoluminescence observations clearly reveal that pyrite crystals precipitated after Bc1 but before Bc2 (Fig. 5B).

4.1.2.4. Silica cementation and replacement. Silicification is located mainly in the limestone layers interbedded in the Marnes de Longwy, which contained abundant siliceous sponge spicules. Silica replacements (chalcedony or micro-quartz) occur within bivalve, bryozoan and brachiopod shells. In a few beds, LMC bioclasts are cemented by thin rims (100 µm–1 mm) of chalcedony and megaquartz. Superposition and cross-cutting relationships indicate that silica replacement and cementation episodes occurred between Bc1 and Bc2 cement stages and were associated with chemical compaction processes.

Fig. 3. Paragenetic sequence of the Bajocian–Callovian carbonate formations. The diagenetic stages are composed of: one micritization stage; seven calcite cementation stages (IFC: Isopachous Fibrous Cement; nfES: non ferroan Early Spar; MFC: Microstalactitic and Meniscus Fibrous cements; BFC: Bladed Ferroan Calcite; Bc1: first stage of Blocky calcite; Bc2: second stage of Blocky calcite; Bc3: third stage of Blocky calcite); two dolomitization stages (D1 and D2); one pyritisation stage; one silicification stage; early dissolution of aragonite shells; mechanical compaction (microfracturing); two fracture episodes (fractures 1 and 2); and two stylolite stages.
4.1.2.5. Fracture 1 (F1). Cored and outcropping limestones display two episodes of poorly-developed fracturing. The first stage displays 0.5–3 mm wide fractures cross-cutting the early cements and Bc1 spars, and filled with the late Bc2 cement.

4.1.2.6. Dolomite (D1). This consists of 50–100 µm planar-e crystals with turbid, brightly luminescent rhombohedral cores, and limpid non-luminescent rims with a single bright subzone (Fig. 4E, F, H, I). EDX analyses also reveal that the non-luminescent substages contain iron (on average 5.5 mol% FeCO3). D1 crystals precipitated after Bc1 cement and typically located within and immediately around stylolites, mainly in the Oolite à Clypeus ploti and in the other clay-rich levels disseminated in the Calcaires de Chaumont, Calcaires de Neufchâtel and Oolite Miliare (Figs. 5E, 6A).

4.1.2.7. Second stage of blocky calcite (Bc2). This ferroan calcite cement is coarse crystalline (100 µm–3 mm) and displays a dull brown luminescence (Figs. 5A–F, H and 6A). This cement fills the F1 fractures and part of the remaining intergranular pore-space. Bc2 affects all of the Middle Jurassic carbonate (Fig. 2). It corresponds to the most important cement in volume in the Calcaires à polypiers, Oolite Miliare inférieure and Oolite de Fréville (about 35% on average within the Middle Jurassic limestones), (Fig. 4). Fluid inclusions are all-liquid and small (<10 µm) in these sparry calcite cements.

Table 1
Summarized petrographic characteristics of diagenetic carbonate cements in the Middle Jurassic limestones.

<table>
<thead>
<tr>
<th>Diagenetic phases</th>
<th>General characteristics</th>
<th>Cathodoluminescence</th>
<th>Proportion of cements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopachous Fibrous (IFC) Cement</td>
<td>Fibrous crystals – (10–50 µm) Initially in HMC, recrystallized during burial in LMC; Pink stained non-ferroan calcite</td>
<td>Turbid luminescence</td>
<td>&lt;2% - below discontinuities</td>
</tr>
<tr>
<td>Microstellatatic and Meniscus cements (MC)</td>
<td>Asymmetrical crusts of laminated layers (fibrous and/or drusy mosaic crystals to bladed) – several nm-thick; Pink stained</td>
<td>Non-luminescent</td>
<td>&lt;2% - in the Calcaires de Chaumont and below the Calcaires de Chaumont/ Oolite Miliare supérieure unconformity</td>
</tr>
<tr>
<td>Non-ferroan Early Spar (nES)</td>
<td>Bladed to scalenohedral fringes (length: 30–200 µm); Syntactical calcite overgrowth cement; inclusion-poor; pink stained</td>
<td>Non-luminescent with occasional thin yellow luminescent band</td>
<td>&lt;3% - present in the major part of the studied section except in the Oolite Miliare inférieure.</td>
</tr>
<tr>
<td>Bladed Ferroan Calcite (BFC)</td>
<td>Bladed isopachous crystals (30–200 µm); Blue stained</td>
<td>Non-luminescent</td>
<td>&lt;5% - cement present in the Oolite Miliare inférieure.</td>
</tr>
<tr>
<td>First Blocky calcite (Bc1)</td>
<td>Medium–coarse crystalline (100 µm–3 mm) Pink stained</td>
<td>Bright to moderate luminescence, unzoned to concentric zoned</td>
<td>35% - affected all the Middle Jurassic limestone</td>
</tr>
<tr>
<td>Pyrite</td>
<td>Crystals cubic or octahedral</td>
<td>Non-luminescent</td>
<td>Common below hardground</td>
</tr>
<tr>
<td>Dolomite (D1)</td>
<td>Euhedral core, zoned crystal (50–100 µm)</td>
<td>Bright luminescence euhedral core/surrounded by a non-luminescent subzone containing a very fine bright subzone</td>
<td>7% - Dominant in Oncoids facies of the Oolite à Clypeus ploti and the Upper part of the Oolite Miliare inférieure.</td>
</tr>
<tr>
<td>Second Blocky calcite (Bc2)</td>
<td>Coarse crystalline-Length (100 µm–3 mm)</td>
<td>Dull brown luminescence</td>
<td>35% - Dominant in the Oolite de Fréville Oolite Miliare inférieure, Calcaires à polypiers</td>
</tr>
<tr>
<td>Saddle Dolomite (D2)</td>
<td>Intense mauve-blue stained</td>
<td>Non-luminescent (npD2)</td>
<td>&lt;5% - filling residual porosity and fractures npD2 in lower part of the studied section (Oolite Miliare inférieure and Calcaires à polypiers)</td>
</tr>
<tr>
<td>Third Blocky calcite (Bc3)</td>
<td>Dark brown luminescence, concentric zoned</td>
<td>fluorescent blue</td>
<td>npD2 dominant in the Calcaires de Chaumont 6% - filling major fracture and residual porosity</td>
</tr>
<tr>
<td>Fluorine (F)</td>
<td>Coarse crystalline (100 µm–3 mm); Pink stained</td>
<td>up to 20% in the Calcaires de Chaumont</td>
<td></td>
</tr>
</tbody>
</table>
4.1.2.8. Fracture 2 (F2). The second episode of fracturing displays 0.5 mm–1 cm wide fractures cross-cutting the Bc1 and Bc2 cements, and the D1 stages (Fig. 6F). These fractures are filled with a few dolomite (pD2) crystals and by the non-ferroan Bc3 cement (Figs. 5G and 6F).

4.1.2.9. Dolomite (D2). This takes on two distinct forms. The first occurs in the Bajocian limestones and exhibits non-planar crystals (1–2 mm; npD2; Fig. 6B, E). Cathodoluminescence reveals non-luminescent and turquoise-stained crystals indicating an iron-rich dolomite (Fig. 6B). EDX analyses indicate a non-stoichiometric (on average 55.5 mol% CaCO_3 and 38 mol% MgCO_3) and iron-rich dolomite (on average 6.5 mol% FeCaCO_3; Fig. 6H).

The second form occurs in the upper reaches of the study limestones (above the Oolite à Clypeus ploti and is characterized by planar dolomite (pD2) with a red luminescence (Figs. 5G and 6C, D, F). pD2 is observed in overgrowth on D1 (Fig. 6C, D, F) and alone in fracture 2 (F2; Fig. 5G). EDX analysis indicates a non-stoichiometric dolomite (on average 60 mol% CaCO_3 and 40 mol% MgCO_3 (Plate 3H)).

D2 is scarce and not very abundant, except in porous layers in the Calcaires de Chaumont (pD2) and in the Calcaires à polypliers (npD2), where it may fill up to 50% of the vugs and intergranular porosity (Fig. 4). D2 is a saddle dolomite fracture at the base of the Middle Jurassic series and evolves into a planar dolomite at the top of the Middle Jurassic carbonate.

4.1.2.10. Third stage of blocky calcite (Bc3). These non-ferroan calcite coarse, limpid LMC crystals (100 μm–3 mm) exhibit a dark brown luminescence (Fig. 5D). They fill part of the residual pores and the second generation of fractures F2, and post date D2 (F2; Fig. 5G). Primary fluid inclusions are small (<10 μm) and all-liquid. Bc3 occurs from the base to the top of the study interval, but it makes up a small proportion (mean ~5%) of the total cement volume (Fig. 2).

4.1.2.11. Fluorite (F). CL observations display blue luminescent cubic crystals within porous levels of the Calcaires de Chaumont (Figs. 5H and 6F). EDX analyses show 71 mol% Fluorine and 29 mol% Calcium. Fluorite crystals precipitated in pores and replaced micritic matrix, allochems and all other cement stages (Bc1, D1, Bc2, D2 and Bc3; Fig. 5H).

4.1.2.12. Chemical compaction. Pressure-solution features are (1) sutured grain contacts (microstylolites) or multi-grain seams in clayey matrix-dominated facies and (2) stylolites. Two distinct types of stylolites are distinguished (André, 2003): (1) high-frequency stylolite with peaks of relatively low vertical amplitude (0.1–0.5 mm), and (2) columnar stylolite with high vertical amplitude peaks (0.5 mm–1 cm). The first type represents about 95% of all stylolites and occurs throughout the study section with an estimated average frequency of 5 per metre in grainstone facies. Bc2 cement stage occurs in gash fractures associated with this first generation of stylolites (Fig. 6G), indicating that stylolithization occurred meanwhile and after Bc2 precipitation. F2 fractures filled by pD2 dolomite crystals cross-cut these first-generation stylolites (Fig. 6F). The second stage of stylolithization is uncommon and is confined to the Calcaires de Chaumont. It cross-cuts the first stylolites, indicating the order of events. These characteristics suggest that pressure-solution operates during and after Bc2 precipitation. Gash fractures associated with the second-generation stylolites may be partially filled with Bc3 spar and pD2 dolomite crystals.

4.2. Geochemical analysis

Geochemical data are listed in Appendix B, including the sample name, location, cement type, δ¹⁸O, δ¹³C and ⁸⁷Sr/⁸⁶Sr values.

4.2.1. Oxygen and carbon isotopes

Oxygen and carbon isotopic values of the micro-sampled LMC bivalve shells (n = 30), micritic ooids (n = 6) and cements (early spars, blocky calcite cements and dolomite, n = 105) range from −12.9 to +0.5‰ V-PDB for δ¹⁸O and from −0.5 to +4.2‰ V-PDB for δ¹³C (Figs. 3 and 5). The range of δ¹³C values fits with the bulk rock data from Bajocian–Kimmeridgian carbonates already available in the study area (Buschaert et al., 2004; Fig. 7). The δ¹³O and δ¹³C of bivalve shells range respectively from −2.2 to −0.5‰ and +2.3 to +4‰ V-PDB. These bivalve shell values are similar to previously published Mid-Jurassic oyster data (Anderson et al., 1994; Wierzbowksi and Joachimski, 2007; Brigaud et al., 2008). Early bladed ferroan calcite cements show slightly lower δ¹³O values (from −3.3‰ to −1.6‰ V-PDB) and significantly lower δ¹³C values (from +1.3‰ to +1.9‰ V-PDB). The six micritic ooids range from −5.4‰ to −3.5‰ V-PDB in δ¹³C and display a significant scatter of δ¹³C from −1 to +2‰ V-PDB (Fig. 7). The δ¹³O of dolomite (D1) ranges between −4 and −2‰ V-PDB and the δ¹³C between +2.5 and +3‰ V-PDB (Fig. 7).

The three stages of blocky calcite cements are distinguished by their δ¹³O values alone, while their δ¹³C values are similar (+1 to +3‰; Fig. 7). δ¹³O values change from −3.3‰ for the heaviest Bc1 blocky calcite stage to −12.5‰ for the lightest Bc3 blocky calcite stage (Fig. 7). The Bc1 stage δ¹³O values (n = 22) range from −6.2‰ to −3.3‰ V-PDB with a mean value of −4.9‰ and a standard deviation of 0.9‰. This set of values seems to be homogeneous throughout the stratigraphic column of EST210 (Fig. 4). The Bc2 blocky calcite stage δ¹³O values (n = 34) fluctuate between −8.2‰ and −5.1‰ V-PDB with a mean value of −6.7‰ and a standard deviation of 0.7‰. Bc1 and Bc2 δ¹³O values are significantly different (T-test; p < 0.01). The Bc3 blocky cement stage δ¹³O values (n = 37) range from −12.9‰ to −8.6‰ V-PDB with a mean value of −9.9‰ and a standard deviation of 0.9‰. Bc3 cement also appears relatively homogeneous along the studied EST210 and HTM102 core (Fig. 4). Contrary to Bc1, the δ¹³O of Bc3 are lowest at the base of EST210 core, with a difference of about 1–2‰ from the base to the top of the 200 m-thick study interval. The δ¹⁸O of Bc3 are similar to the δ¹⁸O of calcite cements filling Oligocene-age fractures in Jurassic strata from the study area (Buschaert et al., 2004).

4.2.2. Strontium isotopes

The ⁸⁷Sr/⁸⁶Sr value of a well-preserved calcitic shell of Trichites bivalve from the Sommécourt outcrop (Oncolite cambiana; humphriesiana Zone) is 0.70714. The strontium isotope value of BFC from the EST210 core (Oolite miliare inférieure, garantiana Zone) is also similar to the Bajocian seawater value (0.70714). These two values fit well with the seawater curve of Jones et al. (1994), which is consistent for an Early to Late Bajocian age (Fig. 8A–B). The Bc1 cement has a slightly higher ⁸⁷Sr/⁸⁶Sr ratio (0.70729) and Bc2 ranges from 0.70722 to 0.70723. One D1 value is available from a Calcaires de Chaumont sample, and is close to the Bc1 and Bc2 values (0.70721). A second value for D1 located just below the Oolite à Clypeus ploti deposits is more radiogenic (0.70780). D2 and Bc3 values ranging from 0.70743 to 0.70773 are higher than the values of the previous constituents. Bc3 values from F2 fractures are consistent with the values measured on
similar blocky calcite spars filling fractures of the Gondrecourt faulted area (0.70767 to 0.70805), and fractures in the Calcaires de Chaumont in the HTM102 borehole (0.70742 to 0.70769; Maes, 2002 and Fig. 8A). The measured value in this study from the Calcaires de Chaumont fracture (0.70743; 484.5 m; HTM102 borehole) is similar to previous measurements; (0.70742; 484.82 m; HTM102 core; Maes, 2002). The $\delta^{18}O$ versus $^{87}Sr/^{86}Sr$ cross-plot displays a coeval increase of $^{87}Sr^{86}Sr$ values and decrease of $\delta^{18}O$ values from bivale to Bc3 (Fig. 8C).

5. Discussion

5.1. Thermal evolution of the carbonate rock

In order to estimate the possible parent fluid composition from the $\delta^{18}O$ values, we need to assess the thermal evolution of the carbonate under study. The lower temperature corresponds to the seawater temperature recorded in well-preserved oyster shells. The maximum temperature, reached during burial at the end of Cretaceous sedimentation (Vincent et al., 2007), is estimated from maturation of organic matter, fluid-inclusion microthermometry analyses and detailed studies of clay mineral assemblages (Pellenard et al., 1999; Buschaert et al., 2004; Elion et al., 2005; Clauer et al., 2007). Two burial curves, constrained by the palaeotemperature proxies, are constructed for the Early Bajocian and Early Callovian (the lower and upper stratigraphic boundaries of the studied interval, respectively; Fig. 9) following the burial evolution proposed by Vincent et al. (2007).

5.1.1. Depositional seawater temperature

Previous studies have shown that marine bivalves precipitate their shells in isotopic equilibrium with seawater (Lécuyer et al., 2004), and their $\delta^{18}O$ values have been successfully used to reconstruct palaeotemperatures of past oceans (Steuber, 1996; Brigaud et al., 2008). Temperatures were calculated using the equation given by Anderson and Arthur (1983):

$$T = 16 - 4.14(\delta^{18}O_{\text{calcite}} - \delta^{18}O_{\text{seawater}}) + 0.13(\delta^{18}O_{\text{calcite}} - \delta^{18}O_{\text{seawater}})^2$$

in which $T$ is the temperature in degrees Celsius, $\delta^{18}O_{\text{calcite}}$ the oxygen isotope composition of calcite (relative to V-PDB) and $\delta^{18}O_{\text{seawater}}$ the oxygen isotope composition of seawater (relative to V-SMOW).

Palaeotemperature calculation requires an assumption for the $\delta^{18}O$ of Jurassic seawater. The oxygen isotope composition of surface seawater depends on (i) the evolution of continental ice sheets that modifies the $\delta^{18}O$ of the global ocean by preferentially storing $^{18}O$ in high latitude ice caps, (ii) the local evaporation/precipitation ratio, and, (iii) continental runoff. The Jurassic has often been considered as
an “ice-free” time period because of the absence of glacial deposits for most of it (Sellwood et al., 2000). For an ice-free period, a sea water δ¹⁸O value of −1‰ SMOW is generally assumed (Shackleton and Kennett, 1975). However, the Paris Basin was located at subtropical latitudes that may have been characterized by intensified evaporation, resulting in increased salinity and a higher δ¹⁸O value of surface waters (Pucéat et al., 2003; Lécuyer et al., 2003; Roche et al., 2006; Brigaud et al., 2008). Both the dominance of evaporation over precipitation in shallow marine reservoirs and the potential occurrence of limited ice-sheets during the Jurassic led some authors to use a δ¹⁸O value of 0‰ SMOW for calculating palaeotemperatures (Hendry, 1993; Pucéat et al., 2003; Lécuyer et al., 2003). Consequently, a δ¹⁸O of 0‰ V-SMOW is considered valid for Jurassic surface waters in the Paris Basin. With this assumption, the seawater palaeotemperatures during precipitation of the bivalve shells range 20 °C to 24 °C (mean value = 22 °C ± 2 °C). This is consistent with palaeotemperature ranges inferred from bivalve shells in Middle Jurassic carbonate deposits at similar latitudes (Anderson et al., 1994).

5.1.2. Burial temperatures

The maximum burial temperatures inferred from the maturation of organic matter located in the lower part of the Callovian–Oxfordian clays (20 m above the top of the Middle Jurassic carbonate formation) range from 35 °C to 40 °C (Elion et al., 2005; Clauer et al., 2007).

Burial diagenesis is responsible for the progressive illitization of original smectite, followed by the progressive decrease of kaolinite replaced by illite and chlorite (Lanson and Meunier, 1995). On the borders of the Paris Basin, Toarcian to Kimmeridgian sections do not exhibit a progressive decrease in smectite and kaolinite with depth (Uriarte, 1997; Pellenard et al., 1999; Pellenard and Deconinck, 2006; Dera et al., 2009), which suggests only slight burial-related modification. The smectite-rich composition of a bentonite layer, detected in the Callovian–Oxfordian clays 100 m above the top of the Middle Jurassic neretic carbonates in the HTM102 borehole, also confirms the negligible influence of burial diagenesis (Pellenard et al., 1999; Pellenard et al., 2003; Pellenard and Deconinck, 2006).

The fluid inclusions observed in different generations of cements (Bc1, Bc2, Bc3 and D2) are all one-phase liquid, indicating trapping temperatures of below 40–50 °C (Goldstein and Reynolds, 1994). Studies of the maturation of organic matter, clay mineral evolution, and fluid inclusions all argue for a maximum burial temperature in the eastern part of the Paris Basin of less than 50 °C. According to the geological history of the Paris Basin, the maximum burial was reached at the end of the Late Cretaceous after chalk deposition (Guillocheau et al., 2000; Vincent et al., 2007; Gonçalvès et al., in press; Fig. 9). Due to the subsequent erosion of Cretaceous chalk in the eastern part of the Paris Basin, its original thickness is inferred from regional knowledge of the Late Cretaceous palaeogeography. Assuming a thermal gradient of 30 °C/km and a surface temperature of 10 to 15 °C.
Fig. 9. Burial curves of the Bajocian–Callovian sediments in the study area for the EST210 borehole until the Kimmeridgian, (after the data of Vincent et al., 2007, Thierry et al., 1980 and Magniez et al., 1980).

(Fig. 9), the estimated thickness of overburden (400 m) is in accordance with the various maximum burial temperatures detailed above.

5.2. Oxygen and strontium isotope composition of parent fluids

As oxygen isotopes fractionated during calcite precipitation, an equilibrium fractionation diagram relating calcite $\delta^{18}O$ V-PDB to precipitation temperatures is constructed using the Anderson and Arthur (1983) equation (Fig. 10) to estimate parent fluid composition(s). No fractionation of $^{87}$Sr/$^{86}$Sr ratios takes place during calcite precipitation.

5.2.1. Marine water

A local $\delta^{18}O$ seawater value of 0‰ V-SMOW is assumed in palaeotemperature reconstruction (cf. Section 5.1.1). It is reasonable to assume that pore fluid temperature during the formation of these early cements equaled seawater temperature. With a temperature of 20–24°C, these early cements precipitated from pore fluids of about 0‰ V-SMOW (Fig. 10). The $^{87}$Sr/$^{86}$Sr ratio of BFC cement is similar to the seawater values for the Bajocian interval suggesting a marine cementation.

5.2.2. Mixed marine-meteoric waters or buffered meteoric waters

The temperature range during burial being constrained (20–50 °C), the pore fluid compositions of the Bc1 cements, whose $\delta^{18}O$ is $-4.9 \pm 0.9$‰ V-PDB, range from $+2$‰ V-SMOW to $-4.5$‰ V-SMOW (Fig. 10). A Middle Jurassic seawater heated with increasing burial implies temperatures in excess of 40 °C to originate Bc1, with oxygen isotope composition restricted to between $-4$‰ and $-5.8$‰ V-PDB. Optical observations show that Bc1 cements predate the beginning of chemical compaction, and so they crystallized before the maximum burial (cf. Section 4.1.1.2, Figs. 2 and 7). As the 40–50 °C maximum temperature is reached at the end of the Cretaceous during the maximum burial (Fig. 9; Vincent et al., 2007), it appears unrealistic that Middle Jurassic marine seawater fluids originated the Bc1 cements.

The parent fluid compositions for Bc1 (up to $-4.5$‰ V-SMOW) are slightly depleted compared with the Jurassic seawater composition.
Two hypotheses can be proposed: (1) the parent fluids result from mixing between trapped Middle Jurassic seawater and later introduced isotopically depleted meteoric water, or (2) meteoric water buffered during percolation through the Jurassic carbonate.

The δ18O and Sr isotope values of the Bc2 cements also illustrate a likely meteoric or mixed-water origin. The parent fluid composition of the Bc2 cement, with δ18O values of −6.7‰ ± 0.7‰ V-PDB, ranges from 0‰ to −6‰ SMOW (Fig. 10). A seawater origin would imply burial temperatures of more than 50 °C to originate blocky calcite ranging between −6‰ and −7.4‰ V-PDB. This appears unrealistic given the maximum temperature inferred from the burial curve of the study area (Fig. 9; Vincent et al., 2007) and the palaeothermicity indicators (cf. Section 5.1.2). Here, there is a clear influence of meteoric water influx into the Middle Jurassic carbonates. The parent fluids are either (1) a mixing between trapped marine waters, or pressure-solution-related fluids, and meteoric waters flushing into the aquifers, or (2) meteoric waters buffered during their flow through the Jurassic marine carbonates. Sr isotope ratios of Bc1 and Bc2 are close to the ratio of the initial sediment, indicating that limestone may have buffered the meteoric fluid (Maes, 2002).

5.2.3. Meteoric water

The third stage of blocky calcite (Bc3) displays the lowest δ18O values (−9.9‰ ± 0.9‰ V-PDB) of the cement set. The estimated burial temperatures of 20 °C to 50 °C suggest that these cements precipitated from isotopically depleted fluids with values ranging between −3‰ V-SMOW and −9‰ V-SMOW (Fig. 10). A seawater origin would imply temperatures of about 80 °C which is unlikely judging from palaeothermicity indicators and the burial history (cf. Section 5.1.2 and Fig. 9).

5.3. Timing and origin of main cements

5.3.1. Bc1 age and origin

As demonstrated above, Bc1 blocky calcite precipitated from mixed waters or buffered meteoric waters. Given the 87Sr/86Sr ratio (0.70729), a Late Bathonian to Early Callovian age for an extensive meteoric recharge is unlikely from low-relief emergent island. Similarly, there is no evidence for significant synsedimentary freshwater influx in the Late Jurassic limestones (Brigaud et al., 2008). Localized and non-permanent islands may have existed during this period (Vincent et al., 2006) but the underlying fresh water lenses were probably limited in extent and could not account for cements laterally distant from the recharge zone (Hendry, 1993).

The first evidence of widespread sub-aerial exposure, soil development and karstification of the Jurassic limestones appears during the lowermost Cretaceous (Corroy, 1925; Magniez et al., 1980; Guillocheau et al., 2000; Quesnel, 2003; Thiry et al., 2006; Vincent et al., 2007; Thiveniaut et al., 2007). This emergence corresponds to the amalgamation of two unconformities (the Jurassic/Cretaceous and Lower/Upper Berriasian boundaries) known as the Late Cimmerian Unconformity (LCU; Guillocheau et al., 2000). This unconformity is the expression of the uplift of the Paris Basin margins during the Bay of Biscay rifting, the North Sea oceanic accretion and the Ligurian oceanic accretion (Guillocheau et al., 2000). During the LCU, this uplift also occurred in the Wessex–Weald Basin (Lake and Karner, 1987). The Middle Jurassic limestone aquifer may have recharged at this time but vertical flows were unlikely because the thick Caledonian–Oxfordian clay (150 m) and Upper Kimmeridgian marls probably acted as permeability barriers (Vincent et al., 2007; Fig. 12B). Middle Jurassic limestones were directly exposed in the vicinity of the London–Brabant Massif (in the ‘Pays Haut’ – 100 km from the study area; Fig. 13). Ferricrete soils overlying karstified Bajocian limestones have formed during the Early Cretaceous (Thiry et al., 2006; Thiveniaut et al., 2007). Lateral recharge of meteoric waters in the Middle Jurassic limestones may have occurred since a dip of the Jurassic carbonate formation has been demonstrated between the study area and the potentially exposed Paris Basin edge during the Early Cretaceous (Vincent et al., 2007; Fig. 12B). A lateral meteoric recharge responsible for cementation of Middle Jurassic limestone during the LCU has already been demonstrated in the Wessex–Weald Basins (Sellwood et al., 1989; Hendry, 1993; Hendry, 2002). The same process has been suggested for the Late Jurassic limestone cementation of the study area (Vincent et al., 2007). In the Wessex and Weald Basins, cementsations are also attributed to a mixed water with a marine component (Hendry, 1993; Hendry, 2002). In the study area, the Early Cretaceous cementation of the Late Oxfordian limestones is attributed to buffered meteoric water where blocky calcite has lower δ18O (−7‰ to −10‰) than the Bc1 observed in the Middle Jurassic formations (Vincent et al., 2004; Vincent et al., 2007). This difference may arise from distinct lateral sedimentological drainage properties. Firstly, the exposed Late Jurassic limestones were closer to the study area during the LCU than the exposed Middle Jurassic limestones (Figs. 12B and 13). Then, there are no marly deposits towards the recharge area in the Late Jurassic limestones (Lorraine and Meuse; Magniez et al., 1980; Vincent et al., 2007) compared with the marly deposits (Marnes à Rhynchochelle; Bathonian) in the western part of the Souabe Basin during the Bathonian (Figs. 1B and 12B). This marly formation located between the study area and the potential meteoric water recharge area may have limited meteoric inputs compared with what occurred in the overlying Late Jurassic limestones (Fig. 12B). With this Early Cretaceous timing for the first well-developed cementation, the burial curve (Fig. 9) indicates an estimated burial temperature of 25–35 °C during precipitation allowing the parent fluid composition to be better constrained around −2‰ V-SMOW (Fig. 10).

5.3.2. D1 age and origin

With the return of marine environments in the Paris Basin and on its borders during Hauterivian, Barremian and Early Aptian times, meteoric recharge was interrupted for approximately 20 My. Stagnant waters in the Mid-Jurassic aquifer might have led to water anoxia favouring pyritization and silification. Petrographic observations clearly show that euhedral dolomite (D1) precipitated after Bc1 blocky calcite, in relation with the first generation of stylolites and in spatial relation with marl levels. Magnesium is abundant in the smectite minerals contained in the Oolite à Clypeus platy and Marnes de Longwy (Appendix C). Dewatering during compaction of clay-rich formations
and expulsion of Mg$^{2+}$ may have originated dolomite crystal precipitation with radiogenic strontium, similar to the radiogenic ratio of clays (Fig. 11). The strontium isotope values of D1 from the Calcaires de Chaumont is similar to the whole rock value (0.70712; Maes, 2002) suggesting intense water–rock interaction during compaction.

5.3.3. Bc2 age and origin

Bc2 cement reveals a relatively 18O-depleted parent fluid (−3‰ SMOW) indicative of a meteoric water influx. A second major unconformity occurring at the Aptian/Albian transition (Late Aptian unconformity LAU; Guillocheau et al., 2000) is associated with erosion, ferricrete soils development and karstification of the Paris Basin borders (Figs. 12D and 13). As for the LCU, meteoric recharges occurred in exposed carbonates on the northern edge of the Paris Basin (Fig. 12D). The ferroan Bc2 can reveal weathering of these ferricrete soils, which could have contributed to enrich the meteoric fluid in iron. The $^{87}$Sr/$^{86}$Sr isotope ratios of Bc2 (0.70722 and 0.70723) reveal a possible rock–water interaction influence, the Middle Jurassic limestones buffered the fluid.

Since Bc1 and Bc2 represent more than 75% of the total cement volume, the Middle Jurassic carbonates were largely plugged after the Early Cretaceous events and before the Late Cretaceous maximum burial.

5.3.4. D2, Bc3 and fluorite origins

The Early Cretaceous marl deposits (the Early Barremian oyster clays, the Aptian clays and the thick Brienne Marls and ‘Gault’ formation of the Albian) and the development of the chalk sea over Western Europe during the Late Cretaceous prevented lateral meteoric water recharges. The non-renewal of fluid by lateral recharges may be the cause of the absence of extensive calcite cementation during this period of about 45 My. In the Paris Basin, the Palaeocene and Eocene period is mainly characterized by low accumulation rates (Guillocheau et al., 2000). A change to sediment by-pass occurred in the Late Oligocene and lasted until the Pleistocene (Guillocheau et al., 2000). During the Early Cenozoic, the main terrestrial erosion was emplaced in the northeast Paris Basin (Le Roux and Harmand, 2003). The Pyrenean episode (Bergerat, 1987; Guillocheau et al., 2000; Bergerat et al., 2007) peaked at the end of the Eocene and the Cretaceous chalk on the London–Brabant Massif may have been eroded. During the Oligocene, a major extension episode occurred in the Paris Basin in particular in the study area, where major faults were created (Guillocheau et al., 2000; Bergerat et al., 2007). The Alpine uplift episode with its NW–SE compression started at the Early/Middle Pliocene transition (Bergerat, 1987; Guillocheau et al., 2000; Bergerat et al., 2007) and the eastern part of the Paris Basin was subjected to intense erosion (30 m/100000 y; Guillocheau et al., 2000). However, it is difficult to estimate when the Early Cretaceous marls were removed from the study area. Thick Early Cretaceous marls still exist in the proximity of the study area (in the Marne and Aube departments; Magniez et al., 1980), and it is likely that this marl seal and the Cretaceous chalk prevented vertical and lateral meteoric recharge. Nevertheless, vertical circulation could have occurred during the Oligocene fracturing, triggering a cementation stage (Matray et al., 1989; Matray and Fontes, 1990; Matray et al., 1994; Worden and Matray, 1995; Buschaert et al., 2004). In the study area several normal faults were created or re-activated during this extension episode, for example the ‘Gondrecourt faults’ and ‘Marne faults’ (Fig. 12E; Bergerat et al., 2007). Downward percolating meteoric waters and/or upward migrating hydrothermal fluids could have circulated along these faults favouring exchanges with the Middle Jurassic aquifer (Fig. 12E), as has been demonstrated for the centre of the Paris Basin (Matray et al., 1989; Matray and Fontes, 1990; Matray et al., 1994; Worden and Matray, 1995).

The occurrence of saddle dolomite (npD2) in the lowermost limestone under study (Bajocian), also observed in Mid-Jurassic limestones of England (Sellwood et al., 1985; Sellwood et al., 1987), suggests a precipitation temperature in excess of 50 °C (Davies and Smith, 2006). Hydrothermal dolomitizations are common in carbonate rocks, and are often related to major faults (Nader et al., 2007). Hydrothermal dolomitization is defined as dolomitization by fluids at temperatures above the ambient temperature of the host formation (Davies and Smith, 2006). A precipitation temperature of more than 50 °C could not be fully explained by the Oligocene burial thermal gradient (30–42 °C; Fig. 9; Matray et al., 1989). The rising fluid was in thermal disequilibrium with the Middle Jurassic host carbonates. The

![Fig. 11. Dolomitization model affecting the Middle Jurassic limestone of the eastern part of the Paris Basin.](image-url)
A. Study Area

B. Late Jurassic (150 My)
   - Lateral meteoric water recharge
   - Uplift
   - Jurassic-Cretaceous transition to Bernasian (145 My to 140 My)

C. Late Cimmerian Unconformity
   - Valanginian to Late Aptian (140 My to 112 My)

D. Late Aptian Unconformity
   - Aptian/Albian transition (112 My)
   - Mixed fluids

E. Vertical Circulation
   - London-Brabant Massif
   - Extension
   - Oligocene (33 My to 23 My)
   - Meteoric fluids

Legend:
- CI: Late Cretaceous
- AL: Late Aptian-coastal sandstone
- AE: Early Aptian
- BI: Late Barremian (sandstone)
- HB: Hauterivian + Early Barremian (marine clays)
- Va1: Valanginian (marine limestone)
- Va2: Wealden facies
- T: Tithonian limestone
- K: Kimmeridgian marls
- OX: Oxfordian - Kimmeridgian limestone
- CO: Callovian-Oxfordian marls
- JM: Middle Jurassic (Marls)
- Je: Early Jurassic
- Variscan basement

Porosity:
- 30%
- 20%
- 10%
- <10%

Isotopic Composition:
- δ18O = -2.5‰ PDB
- δ18O = -5‰ PDB
- δ18O = -6.5‰
- δ18O = -10‰
radiogenic strontium values on npD2 crystals (Fig. 8B) are compatible with fluids ascending along faults from Triassic formations, which contain numerous evaporite (anhydrite and salt) levels, and water formation enriched in radiogenic strontium (Fontes and Matray, 1993a; Fontes and Matray, 1993b; Worden and Matray, 1995).

The petrographic characteristics, isotope signature ($\delta^{18}$O and $\frac{87}{86}$Sr/$\frac{86}{86}$Sr) and occurrence of Bc3 in fractures (F2) argue for meteoric fluid circulating along fault systems during the Oligocene active fracturing episode. In the present study, the meteoric parentage of parent fluids is inferred from Bc3 $\delta^{18}$O (about $-10\%$ V-PDB) in fractures and vugs (Fig. 10). The similar $-10\%$ V-PDB isotopic composition of fracture cement of the Late Jurassic limestone (Buschaert et al., 2004) argues for an Oligocene cementation stage in Late and Middle Jurassic limestone. However, the cement quantification reveals a minor influence of this blocky calcite cement stage ($5\text{--}10\%$ of cement volume; Fig. 2A) compared to the Early Cretaceous blocky calcite cements Bc1 and Bc2 ($75\%$ of cement volume; Fig. 2A). Sr-isotope values of Bc3 (on average $0.7076$; Fig. 8C) support the model of fluid migration through vertical circulation.

Fig. 13. Palaeogeographic reconstructions of the Late Cimmerian Unconformity (LCU) in the Paris Basin and the Wessex–Weald Basins (Hendry, 1993; Guillocheau et al., 2000; Hendry, 2002, Thiry et al., 2006 and Vincent et al., 2007). A subcrop map beneath the LCU illustrates the location of the potential exposure and erosion areas of the Jurassic limestones. The truncation of the Bathonian limestone onlaps the Palaeozoic basement of the London–Brabant Massif in central England and in the northern part of the Paris Basin. The Middle Jurassic Limestone exposure (karstifications, palaeosols) during the Early Cretaceous on the northern edge of the Paris Basin (Pays Haut and Ardennes) allowed the aquifers to be recharged with meteoric water, leading to blocky calcite cementation. The same sketch is applicable for the Late Aptian Unconformity (LAU).
fractures (Matray et al., 1989; Matray and Fontes, 1990; Matray et al., 1994; Worden and Matray, 1995; Maes, 2002) as the origin of radiogenic strontium-enriched water in the Middle Jurassic limestones. The decrease in Mg²⁺ content of the fluids due to dolomitization and their fall in temperature during their ascending flow could have favoured Bc3 calcite precipitation after D2 precipitation.

The fluorite cross-cut all the blocky calcite and dolomite cements, including Bc3 and D2. It is found only in present-day porous horizons. Fluids containing fluorine may have percolated within crystalline formations of the Hercynian basement or from fluorite mineralization in the lower part of the Mesozoic deposits (Soulé de Lafont and Lhégu, 1980). Fluids from this basement could have circulated along faults through the Triassic and Early Jurassic marls.

These dolomite, Bc3 cements and fluorite deposits suggest a Fe-, Mg- and F-rich fluid circulating along vertical faults, as has been demonstrated for the centre (Worden and Matray, 1995) and the eastern part (Buschaert et al., 2004) of the Paris Basin.

5.3.5. Source of carbonate, cementation and its impact on porosity

A mass balance calculation has been made to evaluate the importance of pressure-solution as a source for cement (Finkel and Wilkinson, 1990). For the four grainstone sedimentary units detailed, the estimation shows that 13–22% of the initial carbonate is dissolved, which is in the range of estimation found in Late Jurassic limestones of the study area (5–20%, André, 2003). Thus, depending on the grain and cement content, chemical compaction can be a source of carbonates for cementation (21–45%) in the immediate vicinity of the stylolites in ooidal and skeletal grainstone (Table 2). According to the models of porosity reduction by pressure solution in limestone (Heydari, 2000), the maximum vertical shortening (20%) of the Middle and Late Jurassic limestones have reduced the porosity of ooid grainstones from 40% initially to about 30% (Heydari, 2000; Moore, 2001). The cement possibly generated by dissolution of carbonate may have reduced the porosity by an additional 5%, from 30% to 25% (Heydari, 2000). These results suggest that pressure solution released insufficient calcium carbonate to precipitate the cement observed in the Middle Jurassic limestone (23% on average). An outside source of carbonate is necessary to generate at least 10% of cement in grainstone samples (45% of about 23% of blocky calcite). In the case of meteoric fluid recharges from sub-aerial terrains on the Paris Basin borders during the LCU and LAU (Figs. 11 and 12), karst-related dissolution enriched the fluids in calcium carbonate. The pressure solution-derived fluids and the karst-related dissolution of marine carbonates may have buffered the initial meteoric fluid with regard to its strontium and oxygen isotope signature. Besides porosity loss by intergranular pressure dissolution (from 40% to 30%), the Bc1 and Bc2 cements (representing about 20% of the total volume in grainstone; Fig. 2B) reduced porosity from 30% to 10% during the Early Cretaceous (Fig. 11). The late Bc3 cement (3% of the total volume in grainstone; Fig. 2B) caused the final loss porosity in grainstone (from 10% to 7%) and is responsible for the present-day porosity value (7% on average in grainstone; Figs. 2B and 11).

6. Conclusion

In the Middle Jurassic limestone of the Eastern Paris Basin, extensive developments of blocky calcite cements are responsible for poor reservoir properties (4–15% and K<0.1 mD). Optical observations of 267 thin sections from cores reveal three major stages of blocky calcite cements formed during burial, after eogenetic cementation that appears to have been negligible (less than 10%) compared with the mesogenetic cement volumes (about 90%). Strontium isotope and δ¹⁸O measurements of all the calcite cements allow us to reconstruct the isotopic compositions of the parent fluids. The early spar δ¹⁸O and strontium isotope values attest to the marine origin of the poorly-developed eogenetic cements. The strontium isotope and the recalculated δ¹⁸O values for the parent fluids of the three major stages of blocky calcite cements reveal precipitation from mixed marine/meteoric water or buffered meteoric water. Judging from the geodynamic record of the eastern part of the Paris Basin, a multiphase palaeohydrological system with lateral meteoric water recharge is in evidence. The Middle Jurassic limestones were exposed on the southern border of the London–Brabant Massif during two Early Cretaceous uplift episodes (Late Cimmerian Unconformity – LCU and Late Aptian Unconformity – LAU). These two separate palaeohydrological circulation systems caused a significant reduction in porosity (from 40% to 10%) through two extensive calcite cementation stages. A third calcite cementation stage occurred following the Oligocene fracturing connecting the aquifers of the Triassic formations and the Middle Jurassic formations, and engendered upward-migrating basinal fluid flows. This process was less developed, though, than in the centre of the Paris Basin. A mass balance between dissolved carbonate during stylolite formation and

Table 2

<table>
<thead>
<tr>
<th>Mass balances on 1 cm³ Middle Jurassic grainstone columns.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EST433 core (692–695 m)</td>
</tr>
<tr>
<td>Pierre de Ladoix</td>
</tr>
<tr>
<td>Oolitic/bioclastic grainstone</td>
</tr>
<tr>
<td>EST433 core (721–723 m)</td>
</tr>
<tr>
<td>Oolite de Fréville</td>
</tr>
<tr>
<td>Micritic ooids grainstone</td>
</tr>
<tr>
<td>EST210 core (660–661 m)</td>
</tr>
<tr>
<td>Oolite hylaé sup.</td>
</tr>
<tr>
<td>Micritic ooids grainstone</td>
</tr>
<tr>
<td>EST210 core (753–758 m)</td>
</tr>
<tr>
<td>Calcaires à polyiers</td>
</tr>
<tr>
<td>Bioclastic grainstone</td>
</tr>
<tr>
<td>Thickness (cm) A</td>
</tr>
<tr>
<td>Present grain content (%) C</td>
</tr>
<tr>
<td>Present cement content (%) C</td>
</tr>
<tr>
<td>Present pore content (%) C</td>
</tr>
<tr>
<td>Present grain volume (cm³) E</td>
</tr>
<tr>
<td>Present cement volume (cm³) F</td>
</tr>
<tr>
<td>Present pore volume (cm³) G</td>
</tr>
<tr>
<td>Original grain content (%) H</td>
</tr>
<tr>
<td>Original pore content (%) I</td>
</tr>
<tr>
<td>Average stylolite amplitude (cm) J</td>
</tr>
<tr>
<td>Number of stylolites K</td>
</tr>
<tr>
<td>Compaction rate in grainstone L</td>
</tr>
<tr>
<td>Dissolved carbonate (cm³) M</td>
</tr>
<tr>
<td>Dissolved carbonate (%) N</td>
</tr>
<tr>
<td>Dissolved grains (cm³) O</td>
</tr>
<tr>
<td>Cement mass balances P</td>
</tr>
<tr>
<td>Cement carbonate mass (g) Q</td>
</tr>
<tr>
<td>Dissolved grain mass (g) R</td>
</tr>
<tr>
<td>Cement from stylolites (%) S</td>
</tr>
</tbody>
</table>

Proportion of stylolite dissolution as a source of carbonate for cementation.
precipitated cements indicates there must have been another source of carbonate. The main source of carbonate for cementation was the chemical weathering of sub-aerially exposed limestones to the north of the study area during the Early Cretaceous. More broadly, at the scale of northwestern Europe, the Early Cretaceous unconformities appear to govern the petrophysical properties of the Jurassic carbonates in the sedimentary basins bordering the London–Brabant Massif. Their role, previously demonstrated in the Jurassic carbonates of both the Weald and Wessex basins, is now well-constrained in both the Upper and Middle Jurassic carbonates of the eastern part of the Paris Basin. The Oligocene cementation seems, on the contrary, more restricted in the Paris Basin geodynamics and localized in the vicinity of vertical fracture areas (e.g. Marne and Gondrecourt fracture network, Bray Fault, St Martin-de-Bossey Fault).

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Appendices A, B and C. Supplementary data

Supplementary data for this article can be found in the online version at doi:10.1016/j.sedgeo.2009.09.002.

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