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# **Impact of geodynamics on fluid circulation and diagenesis of carbonate reservoirs in a foreland basin: example of the Upper Lacq reservoir (Aquitaine basin, SW France)**

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## 20 Abstract

21 Orogeny-driven fluids that circulate in foreland basins can have strong impacts on  
22 petroleum systems and reservoir properties. This applies to the Upper Cretaceous Lacq  
23 reservoir of the Aquitaine Basin in southwestern France located north of the Pyrenean  
24 Mountains. We study a drillcore from a 650 m deep oil reservoir to document how the  
25 evolution of a foreland basin, which formed after a hyperextension phase, affected fluid  
26 circulation and eventually reservoir diagenesis. Using drillcore samples, petrographic  
27 observations, fluid inclusion studies coupled with thermodynamic modeling, isotopic and  
28 rare earth element geochemistry, as well as basin modeling were performed to investigate  
29 and describe the fluid types and sources, the pressure-temperature evolution and the  
30 timing of diagenetic fluid flow. Early diagenesis involves some bacterial activity  
31 represented by micrite rims and framboidal pyrites, as well as early dolomitization involving  
32 a mixture of meteoric and formation fluids. During burial, dolomite overgrowth, saddle  
33 dolomites, coarse blocky calcites and anhydrites precipitate. The last products consist of  
34 iron oxide precipitation and meteoric recharge of the reservoir with groundwater. Our  
35 results indicate that after the deposition of the Paleocene flysch formation, Mg-rich, low  
36 salinity, hot, and relatively deep clay-released fluids migrated along thrust faults from  
37 deeper parts of the basin during the climax of the compressional Pyrenean phase  
38 (Eocene). They acted as dolomitizing hydrothermal fluids with a thermal disequilibrium in  
39 the order of 30-40°C hotter than the ambient host rocks. Another orogeny-driven,  
40 hydrothermal and Mg-poor fluid mixed with oil generated by Jurassic-Barremian source  
41 rocks and precipitated calcites and anhydrites. Finally, during uplift, oxidizing fluids were  
42 laterally introduced as the present-day groundwater. Hence, by combining different  
43 petrographic, geochemical and modeling proxies, we document how the Eocene orogenic  
44 phase played a crucial role in basin-scale fluid flow and carbonate diagenesis.

45 *Keywords:* carbonate diagenesis, Pyrenees, Aquitaine foreland basin, Upper Lacq  
46 reservoirs, fluid inclusions, basin modeling, dolomitization, hydrothermal fluids.

48 The geodynamic evolution of basins exerts a major control on the evolution of the  
49 pathways, temperature, pressure and chemistry of circulating fluids (Vilasi et al., 2006;  
50 López-Horgue et al., 2010; Beaudoin et al., 2011; Evans and Fischer, 2012; Vandeginste  
51 et al., 2013; Mangenot et al., 2018a). This in turn influences the diagenesis and  
52 petrophysical properties of petroleum reservoirs. Many dolomitized carbonate reservoirs  
53 worldwide have been interpreted as formed during early diagenesis in shallow peritidal  
54 environments (Koehrer et al., 2010; Moore, 2013; Swart et al., 2005; Walls and Burrowes,  
55 1985). However, several studies demonstrate that processes of pervasive dolomitization  
56 can be linked to the impact of deep hot hydrothermal fluids percolating along structural  
57 pathways (Machel and Anderson, 1989; Boni et al., 2000; Swennen et al., 2003; Davies  
58 and Smith, 2006; Gasparrini et al., 2006; López-Horgue et al., 2010; Gomez-Rivas et al.,  
59 2014; Salardon et al., 2017). In the Aquitaine basin (SW France), several hydrocarbon  
60 fields are located in Jurassic and Cretaceous dolomites, where dolomitization is  
61 interpreted to be the result of early diagenesis (Biteau et al., 2006). First studies of the  
62 Lacq reservoirs, considered as the largest and most strategic hydrocarbon-producing  
63 reservoirs in France (Biteau et al., 2006), date back to the 1950s with the initial drilling of  
64 the Lacq-1 well. Several models were proposed to explain the diagenesis and  
65 petrophysical properties of the reservoir. Initially, dolomitization of the shallow marine  
66 carbonates of the Upper Lacq reservoir was considered to be due to early diagenesis, and  
67 to impact preferentially the more bioclastic facies (Bouroullec et al., 1986). Therefore, in  
68 this initial model fluid circulation, diagenesis, and reservoir properties were mainly  
69 controlled by the distribution of primary sedimentary fabrics. However, even if an early  
70 diagenetic origin for dolomitization was proposed, no clear petrographic or geochemical  
71 evidence were provided by authors and little was known about the nature, timing, and  
72 origin of dolomitization fluids that flowed in these reservoirs. Recently, geodynamic models  
73 of the Pyrenees and the south Aquitaine basin have been revisited and updated to include

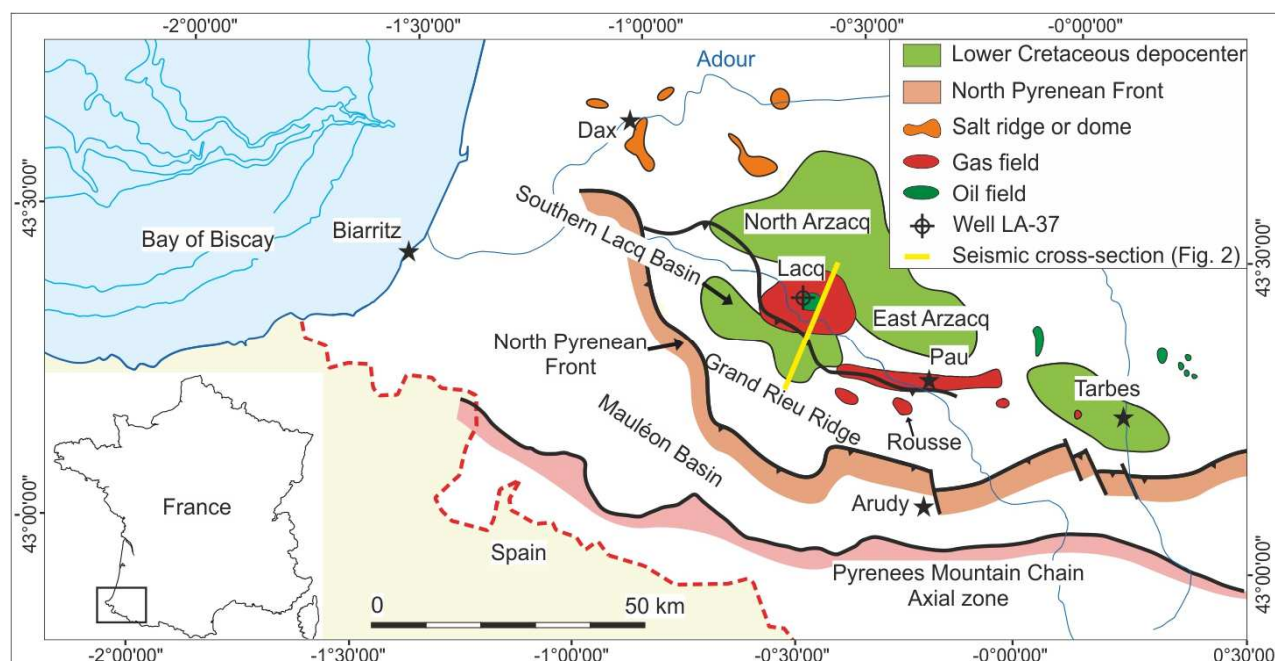
74 the involvement of a late early Cretaceous rifting phase that evolved to extreme crustal  
75 thinning coupled with mantle exhumation (Lagabrielle and Bodinier, 2008; Jammes et al.,  
76 2009, 2010a,b; Roca et al., 2011; Clerc and Lagabrielle, 2014; Masini et al., 2014;  
77 Mouthereau et al., 2014; Tugend et al., 2015; Corre et al., 2016; Teixell et al., 2016;  
78 Vacherat et al., 2016). This event was followed by an inversion and the main Pyrenean  
79 convergence during the late Cretaceous and the Paleogene. This revised model highlights  
80 the possible impact of hydrothermal fluids on the diagenesis of petroleum reservoirs in the  
81 southern Aquitaine Basin (Jammes et al., 2009, 2010; Lagabrielle et al., 2010; Clerc and  
82 Lagabrielle, 2014; Clerc et al., 2015; Salardon et al., 2016; Renard et al., 2019). In this  
83 context a reexamination of the diagenetic evolution of these reservoirs must be performed.  
84 Given its complex geodynamic history and the abundance of subsurface data, the  
85 Aquitaine Basin serves as a natural laboratory to study how the structural evolution of the  
86 Pyrenean foreland domain influenced fluid circulation and eventually reservoir diagenesis  
87 (Moore, 2013; Corre et al., 2018; Haile et al., 2018).

88 This study focuses on the Upper Cretaceous reservoirs (from Coniacian to Campanian in  
89 age) and aims to reappraise the diagenetic model by combining results from recent  
90 analytical methods (e.g. fluid inclusion modeling, clumped isotope thermometry...) and to  
91 identify the different fluid types involved at different phases of the geologic history. The  
92 final objective is to correlate the timing of fluid circulations with the geodynamic evolution  
93 of the basin.

## 94 2 Geological setting and stratigraphic framework

95 The Lacq petroleum system is one of the largest petroleum fields in the Arzacq sub-basin,  
96 of the Aquitaine basin (Fig. 1). It consists of a salt-cored anticline whose axis is oriented  
97 NW-SE (Fig. 2). This anticline is an elevated structure relative to the surrounding Lower  
98 Cretaceous sub-basins (Southern Lacq, North Arzacq and East Arzacq basins (Fig.1) that  
99 were formed during the major rifting phase that created the V-shaped Bay of Biscay to the  
100 west (Biteau et al., 2006). These rift basins formed part of the European rifted margin. The

101 proximal Arzacq rift was separated from the hyper-extended Mauléon rift basin to the  
 102 south by the Grand Rieu Ridge, a tilted basement block (Figs 1 and 2) (Masini et al.,  
 103 2014).



104  
 105 Figure 1. Structural sketch map of the SW Aquitaine basin, showing the principal structural  
 106 elements, Cretaceous rift basins and hydrocarbon fields (modified after Biteau et al.,  
 107 2006).

108 The petroleum system encompasses two economically important reservoirs. The first is  
 109 the Upper Lacq reservoir located at 650m depth and sealed by the overlying Paleocene  
 110 Flysch (Fig. 2). The reservoir produced heavy oil from Upper Cretaceous (Coniacian to  
 111 Campanian) fractured dolomites. The second is the Deep Lacq reservoir, which is located  
 112 at a depth of 3700m and is capped by the overlying early Aptian Sainte Suzanne marls  
 113 (Figs 2 and 3) (Le Marrec et al., 1995). Here, Jurassic to Barremian limestones and  
 114 dolomites produce mainly dry gas.

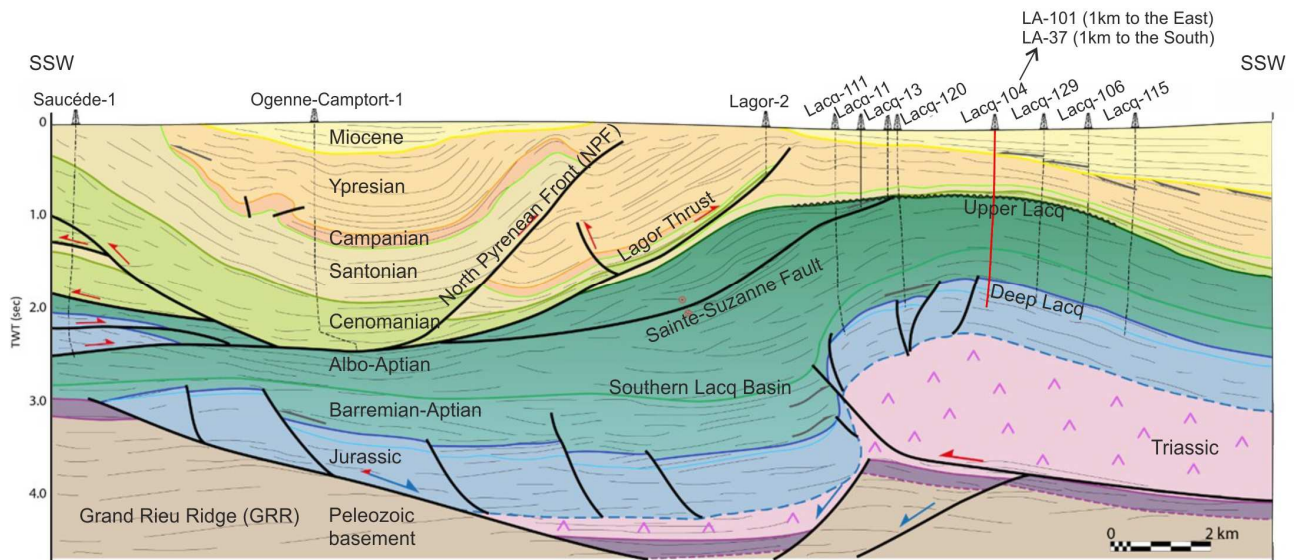
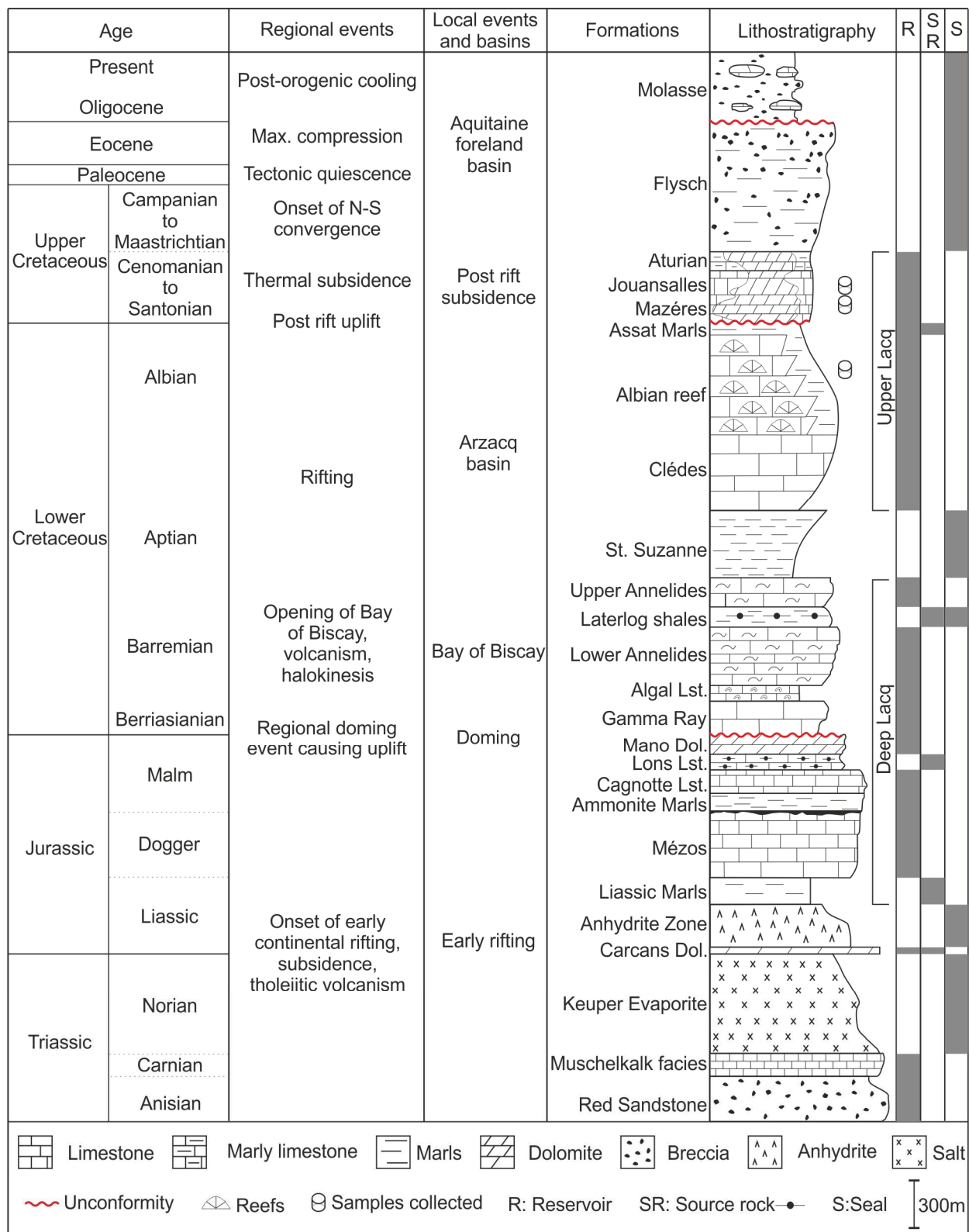


Figure 2. Interpreted NNE-SSW seismic cross-section through the Lacq structure in the Arzacq basin (See Figure 1 for location). Due to the lack of a reliable velocity model the vertical scale is in two-way time (TWT). For equivalent depth estimations, well LA-104 (red line), reaches a true vertical depth (TVD) of 4346 m.

The structural and sedimentary history of the Lacq area is closely linked to the relative motion between the Iberian and European plates during the Mesozoic and Cenozoic eras that first generated the Arzacq rift basin and the subsequent Pyrenean orogeny and associated Aquitaine foreland basin. Initial crustal architecture was partly inherited from the Paleozoic Variscan orogeny (Kroner and Romer, 2013).

A simplified lithostratigraphic section of the southern Aquitaine basin with the timing of the main geodynamic events are compiled in figure 3.





128

129 Figure 3. Lithostratigraphic column of the Arzacq and SW Aquitaine Basins including  
 130 elements of the Lacq petroleum system and a summary of main geodynamic events,  
 131 which impacted the area since the Triassic.

132 Triassic to Jurassic times marked the onset of continental rifting between the European  
 133 and Iberian plates associated with the breakup of Pangea. Early rifting resulted in tholeiitic  
 134 volcanism and evaporitic sedimentation (Bilotte et al., 2001; Biteau et al., 2006). Triassic  
 135 formations consist of basal fluvial sandstones (Red sandstone), limestones and dolomites



136 (Muschelkalk) and evaporites (Keuper) (Lucas, 1985; Fréchengues et al., 1990; Le Marrec  
137 et al., 1995). The Lower Jurassic begins with the deposition of the Carcans Dolomites  
138 followed by the Liassic anhydrite unit (Curnelle et al., 1982; Curnelle and Dubois, 1986).  
139 The Middle Jurassic is represented by the clay-rich to peloidal limestones of the Mézos  
140 Formation (Canerot, 1991; Le Marrec et al., 1995). Upper Oxfordian Ammonite Marls  
141 cover a condensed ferruginous crust (Canérot et al., 1990) corresponding to the Callovo-  
142 Oxfordian subaerial exposure. During the Kimmeridgian, shelf carbonates were deposited  
143 (Cagnotte Formation) followed by the Lons Formation (Upper Kimmeridgian) consisting of  
144 marly limestones and dolomites, which is the main source rock for most of the petroleum  
145 systems in the Aquitaine basin (Connan and Lacrampe-Couloume, 1993; Le Marrec et al.,  
146 1995). The dolomitized oolitic limestones of the Mano Dolomite Formation (Fig. 3)  
147 represent the end of the Jurassic. During the Early Cretaceous the opening of the Bay of  
148 Biscay dissected the Aquitaine platform into two subsiding rifts: the Parentis basin to the  
149 north and the Arzacq basin to the south (Jammes et al., 2010). In the Arzacq basin the  
150 Hauterivian-Barrémien deposits are subdivided into four formations, from bottom to top  
151 (Fig. 3): Algal Limestones, Lower Annelids Limestones, Laterlog shales, and Upper  
152 Annelids Limestone Formations.

153 The Aptian records the onset of the main episode of rifting between the European and  
154 Iberian plates, characterized by an extreme crustal thinning leading to mantle exhumation  
155 (Clerc et al., 2015; Clerc and Lagabriele, 2014; Jammes et al., 2010; Lagabriele et al.,  
156 2010; Vacherat et al., 2016, 2014). Increased subsidence during the Early Aptian resulted  
157 in the deposition of 600 m of silty marls of the Sainte Suzanne Marl Formation (Biteau et  
158 al., 2006; Le Marrec et al., 1995). During the Middle Aptian, marly sediments of the Lower  
159 Cludes Formation were deposited while the Late Aptian to Late Albian is characterized by  
160 patch-reefs known as the Albian facies on the uplifted salt-cored Lacq structure (Biteau et  
161 al., 2006). The laterally equivalent and overlying Assat Marl Formation covered the entire  
162 basin (Fig. 3). Because of the crustal asymmetry at the base of the Mauléon and Arzacq

basins, Masini et al. (2014) distinguished a lower “plate” of the rift system and an upper plate separated by a detachment surface. The deformation migrated along the detachment surface between the Arzacq and Mauléon basins during the Albo-Aptian. Major faults developed in the lower plate and formed the Mauléon basin while passive sagging characterized the Arzacq basin on the upper plate section (Masini et al., 2014). The base Cenomanian is a regional unconformity, linked to the post rift uplift (Lagabrielle et al., 2010). The Cenomanian is marked by the deposition of shallow platform carbonates of the Mazères Formation, constituting the main reservoir of Upper Lacq (Biteau et al., 2006). The micritic and rudist-bearing Jounsalles Formation represent the Coniacian to Early Campanian in the Lacq area. By the end Santonian the tectonic regime in the Pyrenean domain started to change with the onset of N-S closure of the exhumed mantle domain (Lagabrielle et al., 2010; Mouthereau et al., 2014; Plaziat, 1981; Teixell et al., 2016; Vacherat et al., 2014). All subsequent units were deposited in the Aquitaine foreland basin. The Middle and Upper Campanian is represented by the marly limestones of the Aturian Formation. The Paleocene to Eocene times recorded the deposition of the Flysch Formation characterized by debris flows, turbiditic conglomerates and marls (Puigdefabregas and Souquet, 1986). During the climax of convergence (Middle to Late Eocene), the entire Pyrenean chain emerged and supplied large volumes of detrital sediments to the southern Aquitaine basin (Jammes et al., 2009; Masini et al., 2014).

## 3 Material and methods

### 3.1 Sampling

The core samples from the Upper Lacq carbonate reservoir were collected from the well LA-37 (latitude: 43.411004° and longitude: -0.634984°, Fig 1 and 2). Given its location in the center of a square delimited by four oil-producing wells, LA-37 constitutes a suitable control well to study reservoir properties. It reached the water table at 723 m and crosscut the Coniacian to Campanian reservoirs. The sampling strategy focused on coarse cement phases, fractures, veins, stylolites and cross-cutting relationships observable at the

190 macroscopic scale. Initially, 358 thin sections, belonging to wells LA: 52-53-57-58-62-63-  
191 69-80-84-1-10-101-36-4-37-104-102, were provided from TOTAL's archives. Public data  
192 on these wells can be found at the French national geological survey website (BRGM:  
193 infoterre.brgm.fr). After a preliminary evaluation on the thin sections, four wells were  
194 selected (LA: 37-101-104 – Fig. 2), from which 88 new core samples were collected. The  
195 samples most suitable for petrographic and chemical analyses were most retrieved from  
196 the Jouansalles formation (Fig. 3).

## 197 3.2 Staining

198 Staining is a rapid technique to distinguish calcite, ferroan calcite, dolomite and ferroan  
199 dolomite in thin sections. Preparation of the solution was performed following Dickson  
200 (1965). The solution is composed of 3/5 of alizarin red solution and 2/5 of potassium  
201 ferricyanide solution. Half of thin sections were soaked for nearly 1 minute then rinsed  
202 with distilled water and left to dry.

## 203 3.3 Petrography

204 16 facies were recognized using optical, cathodoluminescent and fluorescent  
205 microscopes. Cold Cathodoluminescence (CCL) analysis was performed by using a  
206 Cathodyne OPEA cold cathode instrument (400 mA and 13-15 kV gun current) in the  
207 GeoRessources Laboratory (Nancy, France). Limestone descriptions were carried out by  
208 using the classifications of Folk (1962) and Dunham (1962). Porosity description was  
209 based on the classification of Choquette and Pray (1970). Calcite textures and growth  
210 habits were based on the scheme of Flügel (2004) whereas dolomite textures were  
211 described according to Sibley and Gregg (1987).

## 212 3.4 Isotope Geochemistry

### 213 3.4.1 Carbon, Oxygen and clumped isotope analysis ( $\delta^{18}\text{O}$ , $\delta^{13}\text{C}$ and $\Delta_{47}$ )

214 Conventional  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  analysis were performed on 36 powder samples collected  
215 with a DREMEL micro-drill on samples not impregnated by resin. Special care was taken

216 to avoid risks of mixing several generations of cement. A Thermo Scientific MAT253  
217 isotope ratio mass spectrometer at the CRPG laboratory (Nancy France) was used to  
218 perform  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  analyses. Measurements were calibrated using international  
219 standards IAEA CO-1, IAEA CO-8 and NBS 19. Reproducibility was checked by replicate  
220 analysis of laboratory standards and was  $\pm 0.07\text{‰}$  (1SD,  $n=14$ ) for oxygen isotopes and  
221  $\pm 0.02\text{‰}$  (1SD,  $n=14$ ) for carbon isotopes. A subset of 8 samples was later selected for  
222 clumped isotope thermometry investigation.  $\Delta_{47}$  measurements have been performed at  
223 California Institute of Technology (USA) with an automated acid digestion and gas  
224 purification device coupled to a dual inlet Thermo MAT253 as described in Passey et al.  
225 (2010). Samples weighed into silver capsules ( $\sim 8$  mg) were reacted in a common  
226 phosphoric acid bath ( $\sim 103\%$ ) for 20 minutes at  $90^\circ\text{C}$  under static vacuum (evacuated to  
227  $<0.5$  Torr at the beginning of the reaction). The evolved  $\text{CO}_2$  was passed through an  
228 ethanol/dry ice U-trap ( $\sim -80^\circ\text{C}$ ) before being collected on a liquid nitrogen temperature ( $-$   
229  $196^\circ\text{C}$ ) U-trap. Following the 20 minutes reaction period, the  $\text{CO}_2$  was carried through a  
230 Porapak Q 120/80 mesh gas column held at  $-20^\circ\text{C}$  using He as the carrier gas. The  
231 purified  $\text{CO}_2$  was analyzed using a Thermo Scientific MAT 253 Mass Spectrometer  
232 configured to collect masses 44–49. Mass 48 was monitored to detect any hydrocarbon  
233 contamination. Measurements of each gas were done at 16 V of mass 44 and consisted  
234 of 8 acquisitions, each of which involved 7 cycles of sample-standard comparison with an  
235 ion integration time of 26 s per cycle (i.e., total integration time of 1456 seconds for each  
236  $\text{CO}_2$  sample).

237  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  data were also acquired as part of each  $\Delta_{47}$  analysis and were calculated  
238 using the “Brand” parameters reported in Brand et al. (2010). In order to account for the  
239 temperature dependence of oxygen isotope fractionation between  $\text{CO}_2$  gas and carbonate  
240 resulting from the reaction with phosphoric acid at  $90^\circ\text{C}$ , fractionation factors of 1.00811  
241 and 1.009218 were used for calcite and dolomite respectively following Rosenbaum and  
242 Sheppard, (1986) and Swart et al. (1991). The  $\Delta_{47}$  raw data were corrected for instrument

243 nonlinearity and scale compression (Huntington et al., 2009; Passey et al., 2010). Several  
244 heated (at 1000°C) and equilibrated gases (at 25°C) of various bulk isotopic compositions  
245 were run during each session. These gases were used to convert measurements into the  
246 interlaboratory absolute reference frame (Dennis et al., 2011).  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values are  
247 expressed in per mil with respect to the VPDB standard. To guarantee accuracy of the  $\Delta_{47}$   
248 data, we routinely analyzed two carbonate reference materials (Carrara marble and TV04,  
249 also reported by Dennis et al., 2011 and many other studies). One of these two carbonate  
250 standards was analyzed typically every five analyses and distributed along the diagenetic  
251 cement samples in order to check for analytical stability/accuracy of the whole procedure,  
252 as well as long-term external reproducibility of our measurements. The  $\Delta_{47}$  values  
253 obtained are:  $\Delta_{47\text{-CDES25}} = 0.409 \pm 0.019\text{‰}$  (1SD,  $n = 19$ ) for Carrara;  $\Delta_{47\text{-CDES25}} = 0.670 \pm$   
254  $0.014\text{‰}$  (1SD,  $n = 16$ ) for TV04.

255 Finally, the corrected  $\Delta_{47}$  values were converted into temperatures using the composite  
256  $\Delta_{47}\text{-T}$  calibration determined for all carbonate minerals for the 0–300°C temperature range  
257 (i.e. Bonifacie et al. (2017);  $\Delta_{47\text{-CDES90}} = 0.0422 \times 10^6 / T^2 + 0.1262$ ). The oxygen isotopic  
258 compositions of the water ( $\delta^{18}\text{O}_{\text{water}}$ ) from which the carbonates precipitated were  
259 calculated for each estimated  $T\Delta_{47}$  using the  $\delta^{18}\text{O}_{\text{carb}}$  values measured for the carbonate  
260 as well as the oxygen isotope fractionation between the carbonate and water from O'Neil  
261 et al. (1969) for calcite and Horita (2014) for dolomite.

### 262 3.4.2 Multiple Sulfur isotopes analysis

263 Multiple sulfur isotopes analysis ( $\delta^{34}\text{S}$ ,  $\delta^{33}\text{S}$ ,  $\delta^{36}\text{S}$ ) was performed on carbonate-associated  
264 sulphate (CAS) on anhydrite-rich samples from the LA-37 well. The extraction technique of  
265 Sansjofre et al. (2016) was used to analyze CAS isotopic signature. This technique  
266 involves leaching the soluble sulfates fraction with saline water several times before  
267 dissolving the carbonates in 4N HCl solution over 12 hours. Then, a solution of  $\text{BaCl}_2$  was  
268 added to the acidified sample to precipitate sulfates as barium sulfates.

269 The recovered barium sulfates were reacted with the Strongly Reducing Hydriodic  
270 Hypophosphorous acid solution (STRIP) (Kitayama et al., 2017) to produce  $\text{Ag}_2\text{S}$  upon  
271 reacting with  $\text{AgNO}_3$  solution. This  $\text{Ag}_2\text{S}$  is then reacted with  $\text{F}_2$  during a whole night in  
272 nickel containers at  $350^\circ\text{C}$  to produce  $\text{SF}_6$ . After cryogenic and gas chromatography  
273 separation steps, the resulting  $\text{SF}_6$  was analyzed in a ThermoFinnigan MAT 253 dual-inlet  
274 gas-source mass spectrometer. All the different steps of the multiple sulfur isotopes  
275 analysis were carried out at the Institut de Physique du Globe de Paris (IPGP, France).  
276 Values are given with respect to Vienna Cañon Diablo Troilite (V-CDT) related to the  
277 classical delta notation.

### 278 3.5 LA-ICPMS

279 Laser Ablation-Inductively Coupled Mass Spectrometry (LA-ICPMS) was used to study  
280 Rare Earth Elements (REE) in dolomite and calcite cements and to check if these samples  
281 match the prerequisite U and Pb content needed for absolute age dating. The analyses  
282 were carried out at the GeoRessources laboratory in Nancy. Laser sampling was  
283 performed with a 193 nm GeoLas Pro ArF Excimer laser (Microlas®, Göttingen, Germany)  
284 equipped with beam homogenization optics. Ablation was performed by focusing the beam  
285 at the sample surface with a constant fluency of  $10 \text{ J/cm}^2$  and constant repetition rate of 5  
286 Hz. Helium was used as a carrier gas to transport the laser generated aerosols from the  
287 ablation cell to the ICP-MS. Ablated material was analyzed by an Agilent 7500c  
288 Quadrupole ICP-MS (Agilent®, Santa Clara, California) equipped with an Octopole  
289 Reaction System with enhanced sensitivity optional lenses (Cs type, Agilent). The certified  
290 glass standards NIST610, NIST612 and NIST614 SRM were used as reference materials.  
291 Detection limits range from a few ppm for Ce to 0.5 ppm for heavy rare earth elements.  
292 For consistent representation, the REE concentrations obtained were normalized to the  
293 Post-Archean Australian Shale (PAAS).

### 294 3.6 Fluid Inclusion Microthermometry

Microthermometric measurements were performed on a Linkam THMS600 heating-cooling stage connected to an Olympus BX51 microscope (GeoRessources, Nancy, France). The stage was calibrated using synthetic H<sub>2</sub>O pure fluid inclusion standard and a natural aqueous fluid inclusion standard (Ta 33.2) with the following phase transitions: ice melting ( $T_m$  ice) at 0.0°C, homogenization temperatures ( $T_h$ ) at 164.0°C and eutectic point of H<sub>2</sub>O-NaCl at -21.2°C. The acquired temperatures of phase transition (i.e. homogenization into the liquid phase) have an accuracy of about  $\pm 0.2^\circ\text{C}$ , and the obtained data were calibrated accordingly. In the case of fluid inclusions trapped in dolomites, the glass cover of the stage was removed to allow clearer observations of the very small inclusions. Without the glass cover, the error range increased to  $+1.6^\circ\text{C}$ .

### 3.7 Raman Spectroscopy

Raman spectroscopy was used to determine the composition of gas phases in aqueous fluid inclusions following the procedure outlined in Caumon et al. (2015). Analyses were performed with a LabRAM HR spectrometer (Horiba Jobin Yvon) equipped with a 600 g.mm<sup>-1</sup> grating and an Edge filter. The confocal hole aperture was 500  $\mu\text{m}$  and the slit aperture was of 200  $\mu\text{m}$ . The excitation beam was provided by a Stabilite 2017 Arp laser at 457.9 nm or 514.5 nm and a power of 200 mW, implying a power of 20 mW on the sample. The acquisition time was 10 s and the number of accumulations was 10 in order to optimize the signal-to-noise ratio.

### 3.8 Fourier Transform – Infrared Spectroscopy (FT-IR)

FT-IR was used to identify possible compositional differences between the different types of oil inclusions. Infrared spectra were recorded with a Bruker Fourier Transform Infrared (FTIR) spectrometer Equinox 55, coupled with a Bruker A590 microscope. The microscope is equipped with a narrow-band mercury-cadmium-telluride (MCT) detector with a 100  $\mu\text{m}$  diameter window, cooled to 77 K. The spectra were obtained in transmission mode in the mid infrared range (4000-400 cm<sup>-1</sup>) with a 4 cm<sup>-1</sup> spectral resolution. A series of circular diaphragms allowed the diameter of the analyzed section to vary from 100 to 20  $\mu\text{m}$  with



322 the objective magnification of X15.  $\mu$ FTIR spectra were obtained in less than 2 minutes by  
323 the accumulation of 200 scans.

### 324 3.9 Confocal Scanning Laser Microscopy (CSLM)

325 For pressure-temperature modeling, it is necessary to consider the volume percentage of  
326 the gas phase with respect to the oil volume and the temperature. This was obtained using  
327 a CSLM fitted with a Biorad Rainbow system adapted to a Nikon inverted microscope at  
328 the GeoRessources Lab (Nancy, France). The emission source was an Argon laser at 488  
329 nm and a diode laser at 405 nm. The objective had an oil immersion 60x lens. This method  
330 allows the gas volume percentage of the petroleum inclusion to be determined with an  
331 accuracy greater than 95 %. The x–y resolution is 0.2  $\mu$ m and the resolution along the z-  
332 axis is approximately 0.5  $\mu$ m. The studied chips were glued onto a glass plate using  
333 paraffin to avoid any movement during acquisition. For better accuracy, the radii of the gas  
334 phases in oil inclusions were measured prior to CSLM measurements using optical light  
335 microscopes.

### 336 3.10 Image processing

337 To perform volumetric calculations, the slices of the 3D image obtained through CSLM  
338 were processed to remove any polluting fluorescence from nearby objects. This was done  
339 through ImageJ software. First, the greyscale histogram of the images was plotted with MS  
340 Excel and its 6<sup>th</sup> degree best-fit polynomial equation ( $R = 0.95 - 0.99$ ) was obtained. Using  
341 MatLab, the second derivative was then obtained and the solution for  $f''(x) = 0$  was used as  
342 the maximum threshold limit in ImageJ. This procedure objectively and systematically  
343 cleared the noisy fluorescence to calculate the gas volume, following the steps outlined in  
344 Pironon et al., (1998).

### 345 3.11 Basin modeling

346 The Petromod 1D software was used to model the evolution of lithostatic and hydrostatic  
347 P-T conditions over time. Stratigraphic and thermal maturity data were inserted into the

348 software to better constrain the basin model. True vertical depths (TVD) from well logs  
349 were used as stratigraphic thicknesses of the drilled formations. Ages were determined  
350 following the stratigraphic chart of Biteau et al. (2006), while the duration of unconformities  
351 was deduced from Le Marrec et al. (1995), Bilotte et al. (2001) and Huyghe et al. (2012).  
352 The total subsidence evolution was obtained by using the backstripping method. The  
353 amount of eroded material associated with unconformities was estimated on the basis of  
354 the best-fit scenario between the measured and simulated vitrinite maturities.

355 Drilling reports during the operations of wells LA-101-104-37-36 provided data about  
356 porosity, permeability and density, which were added as calibrations to Petromod 1D.  
357 Also, organic geochemistry data involving RockEval results (TOC, S1, S2, S3 and Tmax)  
358 were collected from unpublished internal TOTAL reports and added as thermal  
359 calibrations. Source-rock typing by Connan and Lacrampe-Couloume (1993) provide  
360 suitable biomarker data (sterane isomerization:  $29\alpha\alpha\text{S}/29\alpha\alpha\text{R}$ ) to calibrate source rock  
361 maturity.

## 362 4 Results

### 363 4.1 Petrography of diagenetic phases

#### 364 4.1.1 Host Rock

365 Host rocks in Upper Lacq consists of intramicrite to biomicrite facies (Folk, 1962) with a  
366 wackestone to packestone texture (Dunham, 1962) (Fig. 4a). Skeletal fragments of  
367 foraminifera, echinoderms, and gastropods are abundant and can reach up to 700  $\mu\text{m}$  in  
368 length. The red color after staining indicates a non-ferroan composition of the matrix. CCL  
369 microscopy reveals a brown to dull-orange luminescence of the matrix.

#### 370 4.1.2 Glauconite

371 Pellets of glauconite have simple, rounded morphologies, with generally smooth surfaces  
372 (Fig. 4a). Sizes range between 20  $\mu\text{m}$  up to 200  $\mu\text{m}$ . Rarely, some pellets are

373 amalgamated into larger aggregates. Local concentrations of glauconite are observed  
374 associated with stylolite residues.

#### 375 4.1.3 Micrite rims

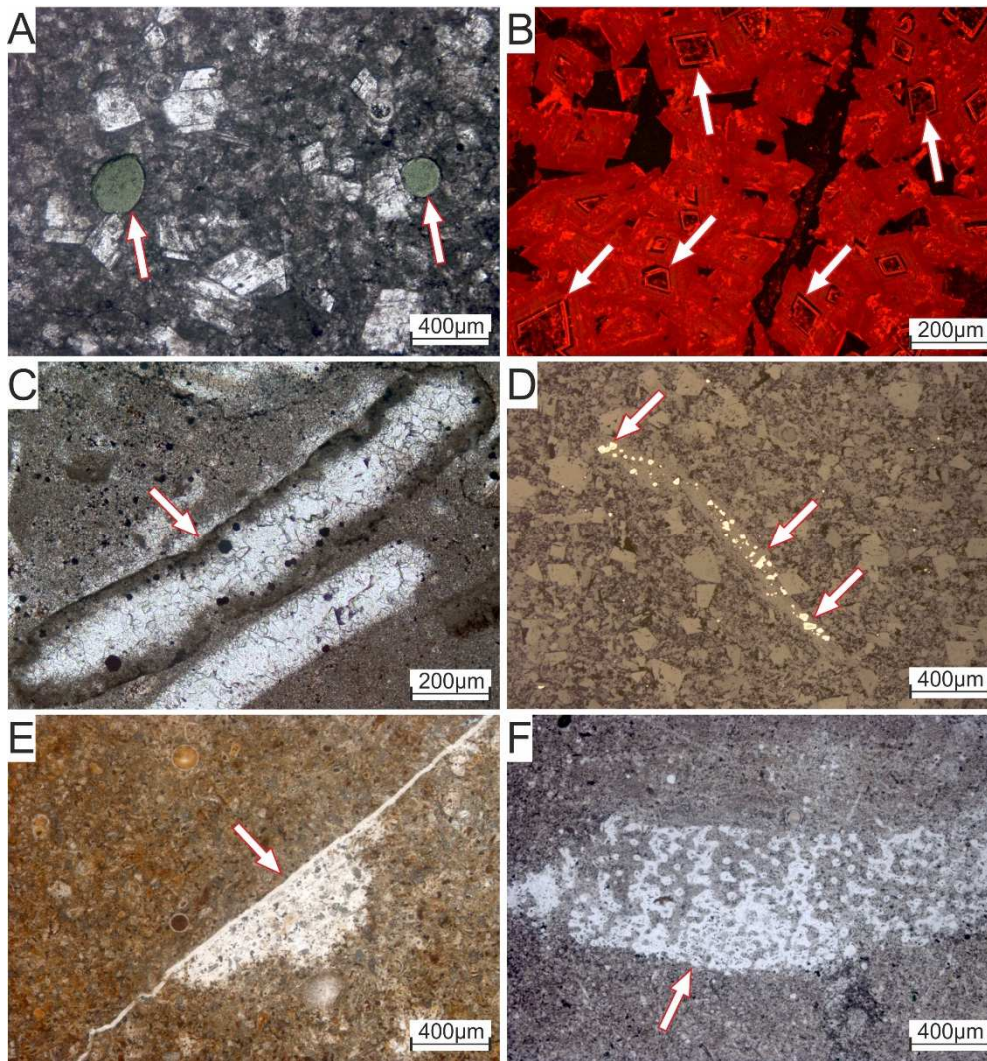
376 A few  $\mu\text{m}$ -thick rims of micrite penetrating some skeletal fragments were observed (Fig.  
377 4c). These have a dark grey color in plane polarized light (PPL) and a bright yellow  
378 luminescence under CCL.

#### 379 4.1.4 Framboidal pyrites

380 This phase of pyrite occurs as framboidal aggregates adjacent to shells and skeletal  
381 fragments. Under reflected light, pyrites appear as golden to bright yellow (Fig. 4d). Crystal  
382 sizes can reach up to 55  $\mu\text{m}$  with rounded to sub-rounded geometries.

#### 383 4.1.5 Chert Nodules

384 This scarce phase was observed only in a few samples. Individual nodules can reach up to  
385 4 cm in length with circular to oblate morphologies. In thin sections, a few silica  
386 microfractures, with thicknesses of 2-4  $\mu\text{m}$  can be seen cross-cutting or terminating at the  
387 chert nodules (Fig. 4e). Silica crystals have a white to yellowish grey color with sweeping  
388 extinction under cross-polarized light.



389

390 Figure 4. A: Limestone matrix with micrite and dolomite in PPL. Arrows point to the  
 391 rounded greenish detrital glauconite pellets. B: CCL photomicrograph showing the dark  
 392 zoned core of the D1 dolomite (arrows). The red-luminescent overgrowth corresponds to  
 393 the D2 dolomite. C: Micrite rim (arrow) penetrating a shell fragment in PPL. D: Aggregates  
 394 of bright yellow framboidal pyrite (arrows) inside in a bivalve shell in PPL. E: Microfracture  
 395 (arrow) filled by silica in contact with a displaced chert nodule (in PPL). F: Clast of  
 396 siliceous sponge (in PPL).

#### 397 4.1.6 Dolomite D1

398 This phase consists of euhedral dolomite rhombs. They constitute the cores of dolomite  
 399 crystals present in the matrix (Fig. 4b). Rhombs have average sizes between 30 and  
 400 200µm. Under PPL, D1 appears as turbid and rich in impurities. Fluid inclusions are too  
 401 small to allow measurements. Under CCL, D1 is mostly non-luminescent with a single  
 402 brightly luminescent rim. This phase is colorless after staining indicating a non-ferroan  
 403 composition.

#### 404 4.1.7 Pyrite 2

405 The second phase of pyrites appear as cubes larger than the early framboidal aggregates.  
406 Individual crystal sizes can reach up to 2.5 mm in length (Fig. 5a). In some cases, relics of  
407 dolomite rhombs were observed inside the engulfing pyrite crystals. No cross-cutting  
408 relationships with the later dolomite/calcite phases were observed and thus its timing  
409 cannot be robustly determined.

#### 410 4.1.8 Fracture (breccia)

411 Brecciated fragments of D1 were observed under PPL. Under CCL, edges of brecciated  
412 crystals show an irregular non-planar shape and a bright yellow external rim probably due  
413 to a dissolution event (Figs. 5b and 5c).

#### 414 4.1.9 Saddle Dolomite D2

415 This phase has two morphologies. The first engulfs D1 cores and appears as creamy  
416 white overgrowth cement under PPL and labeled D2. When viewed under CCL, a uniform  
417 bright red luminescence was observed (Figs. 4b and 5b). Overgrowths can reach up to  
418 150  $\mu\text{m}$  in thickness and contain some aqueous fluid inclusions that were investigated in  
419 this study. The non-ferroan composition of D2 is attested by its white color after staining. In  
420 fractures (Fig. 5b) or in mm-scale vuggy porosity, coarse dolomite crystals were observed.  
421 The latter morphology is that of the saddle dolomite crystals. Under cross-polarized light,  
422 crystals show typical sweep extinction. CCL observations revealed a uniform bright red  
423 luminescence. Crystal sizes can reach up to 2 mm in length. Similarly, colorless results  
424 after staining indicate a non-ferroan composition. This dolomite phase was not affected by  
425 brecciation (Fig. 5b), but was impacted by stylolites (Fig. 5c).

#### 426 4.1.10 Stylolites

427 Stylolites affect the brecciated D1 and the saddle dolomites (Fig. 5c). The oblique direction  
428 of stylolite peaks in vertical wells indicates that they are tectonic in origin and formed  
429 during Pyrenean shortening. Concentrations of glauconite along stylolites have also locally  
430 been observed. In a few thin sections, the amplitude of stylolites can reach few mm.

#### 431 4.1.11 Fracture and dissolution

432 Fractures with open pore spaces cross-cut the host rocks. The width of open fractures can  
433 reach 4-6 mm. Blocky calcites are often observed on the edges of fractures (Fig. 5e and f).  
434 Dissolution is mostly expressed through the partial dissolution of stylolites (Fig. 5d) and the  
435 partially eroded walls of the calcite-infilled fractures (Fig. 5e and f).

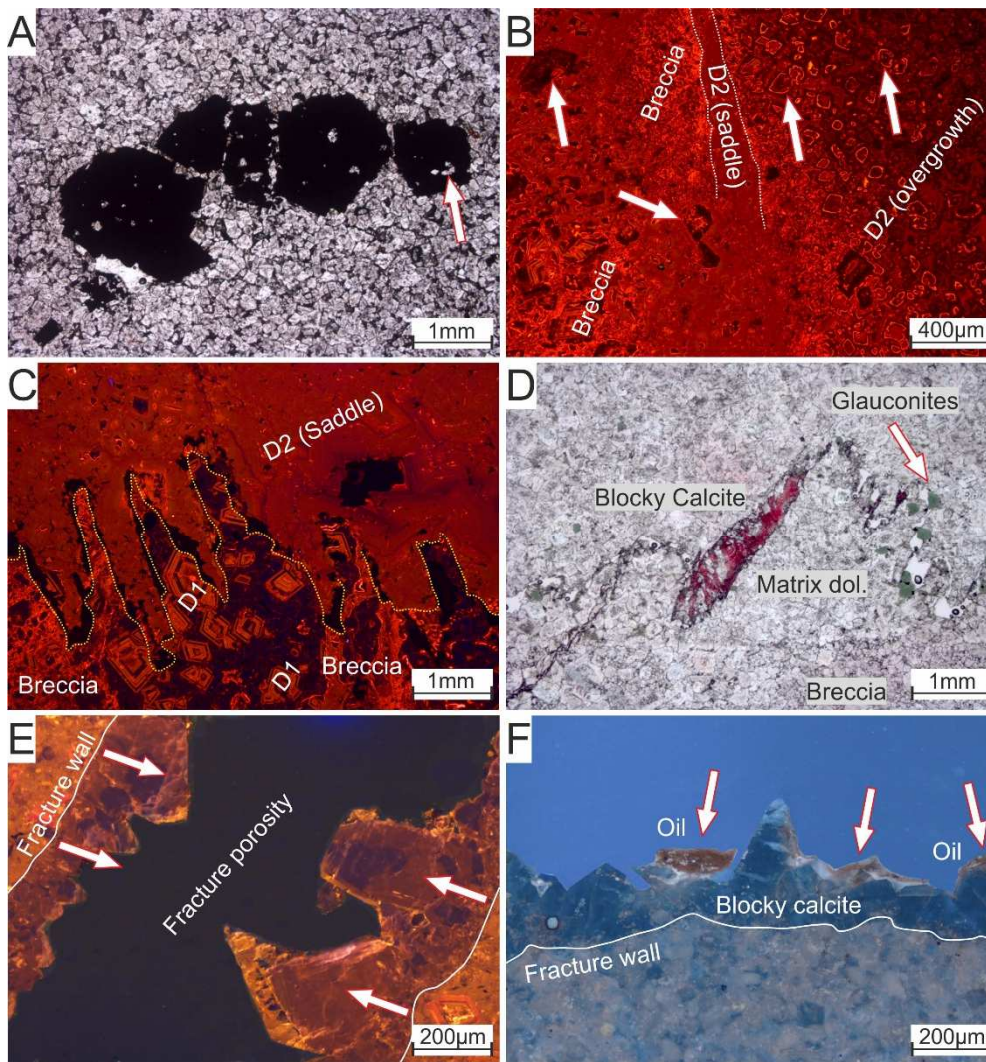
#### 436 4.1.12 Blocky Calcites

437 This cement phase is creamy white to transparent in PPL with typical cleavage planes at  
438 74° and 55°. Growth habits include equant to blocky forms with larger crystal sizes  
439 towards the center of pores and fractures (Fig. 5e). Individual crystal sizes can reach up to  
440 3 mm. CCL microscopy revealed a dark brown to dull orange luminescence (Fig. 5e).  
441 These calcites are the main pore-reducing cements and occlude most of the inter-dolomite  
442 and fracture porosity. The pink color after staining indicates a non-ferroan composition  
443 (Fig. 5d).

#### 444 4.1.13 Oil emplacement

445 Oil inclusions exist inside the blocky calcite and oil coatings occur on calcite and dolomite  
446 crystals. Oil inclusions have a brown to orange color under ultraviolet (UV) light, while the  
447 coatings on calcites show a darker brown color (Fig. 5f).





448

449 Figure 5. A: Pyrite 2 crystals engulfing some relics of dolomites (arrow; in PPL). B: CCL  
 450 Cross-cutting relationships between fractures (between dashed line), partially dissolved  
 451 and brecciated D1 rhombs (arrows) engulfed by the D2 overgrowths. C: CCL image of a  
 452 stylolite (yellow line) impacting both brecciated D1 dolomites and saddle dolomites D2. D:  
 453 Partially dissolved stylolite, in dolomite matrix, filled with pink-stained, blocky calcite (in  
 454 PPL). Glauconites (arrow) are also displaced and concentrated along the stylolite surface.  
 455 E: CCL image of fracture walls lined with dull orange to brown blocky calcites. The crystal  
 456 size increases towards the center of the fracture as indicated by the arrows. F: Same  
 457 fracture under UV light with oil coatings (arrows) on top of the blocky calcites.

#### 458 4.1.14 Anhydrite

459 A few creamy white to colorless tabular crystals of anhydrite constitute the last diagenetic  
 460 phase in the sequence. They are identified by their bright 2<sup>nd</sup> order birefringence colors  
 461 under crossed-polars (Fig. 6a). Cleavage plans are parallel to the main growth axis. These  
 462 anhydrites post-date calcite cements and contain no aqueous or oil inclusions.

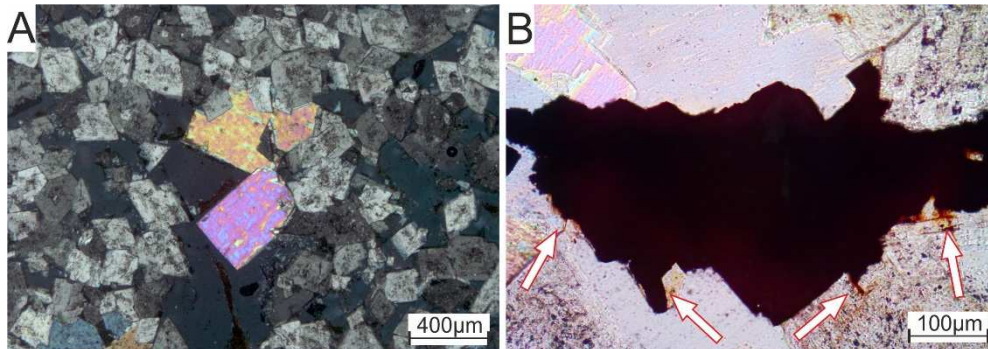
#### 463 4.1.15 Groundwater



464 Present-day operators of the Lacq field report the existence of the watertable at a depth of  
465 nearly 723 m. Ground water is thus added to the paragenesis as a separate phase.

#### 466 4.1.16 Iron Oxides

467 This scarce phase is represented by brown to orange coatings surrounding a few pyrite  
468 crystals (Fig. 6b). Under reflected light, the coatings appear dark brown to black. The  
469 pyrites engulfed by the iron oxides show non-planar and altered crystal edges.

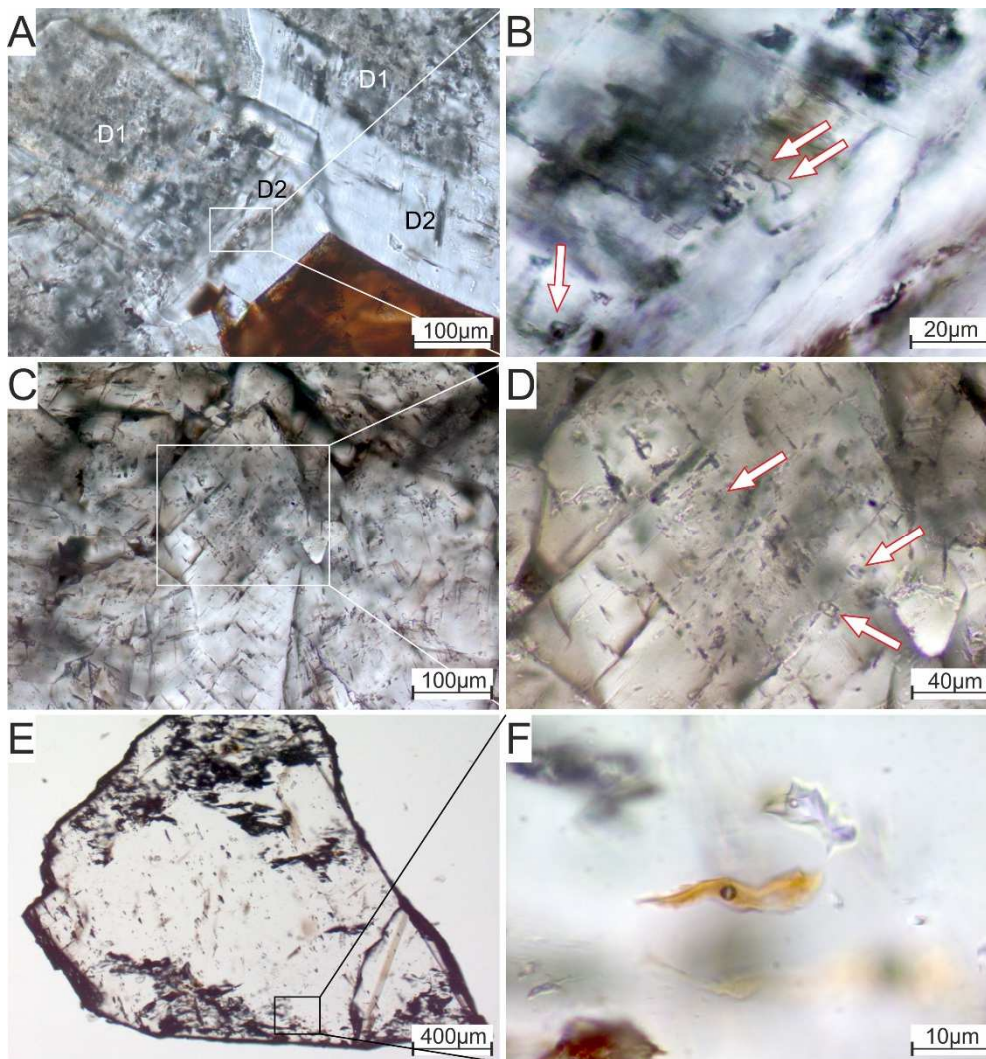


470  
471 Figure 6. A: Tabular anhydrite crystals under cross-polarized light showing typical 2<sup>nd</sup>  
472 order birefringence colors. B: Iron oxides (arrows) on the edges of a pyrite crystal. The  
473 colored crystal on the left corner is a tabular anhydrite.

#### 474 4.2 Fluid Inclusion Studies

##### 475 4.2.1 Petrography

476 Phases of interest with abundant aqueous inclusions are the D2 overgrowths, saddle  
477 dolomites and blocky calcites (Fig. 7). Fluid inclusions in the D2 dolomites (Fig. 7a) have  
478 two phases (liquid and gas) with rectangular to oval shapes and average sizes around 5-8  
479 μm (Fig. 7b). Similarly, in the saddle dolomites, two phases of aqueous inclusions were  
480 identified in growth zones (Fig. 7c) and have rectangular to elongated shapes with sizes  
481 between 5 and 10 μm (Fig. 7d). The two-phase aqueous inclusions in blocky calcites (Fig.  
482 7e) are larger, reaching up to 20 μm in size and with shapes ranging from geometric  
483 (rectangular, cubic and triangular) to lozenge and oblate (Fig. 7f).



484

485 Figure 7. A: D2 overgrowth around D1 cores. B: Zoom of the image A showing two-phase  
 486 aqueous inclusions (arrows) in D2. C: Large crystals of saddle dolomite with their typically  
 487 curved edges. D: Zoom of the image C with rectangular two-phase aqueous inclusions  
 488 (arrows). E: Crystal of blocky calcite containing patches of oil and aqueous inclusions. F:  
 489 Zoom of the image E showing two-phase oil (orange) and aqueous (clear) inclusions.

490 Two types of oil inclusions occur in the blocky calcite of Upper Lacq. Under UV, the first  
 491 type has a brown fluorescence, while the second type shows a strong white fluorescence.  
 492 Both types of oil inclusions were observed very close to aqueous inclusions in the blocky  
 493 calcite (Fig. 7f) and are absent from the D2 or saddle dolomite phases. This co-genetic  
 494 association of oil and aqueous inclusions, and their absence in older diagenetic cements  
 495 indicate that oil inclusions are primary.

496 4.2.2 Fourier Transform – Infrared Spectroscopy (FT-IR).

Hydrocarbons with a brown fluorescence are characterized by a spectrum suggesting the occurrence of water and aromatics, which are absent in the inclusions with strong white fluorescence. Both types of hydrocarbons have very low CH<sub>4</sub> content.

#### 4.2.3 Microthermometry

Microthermometry data were obtained from fluid inclusions (FIs) in D2 overgrowths, saddle dolomites (Fig. 8a) and calcite phases (Fig. 8b). Because D2 and saddle dolomites are considered as different morphologies of the same phase, their FI data are joined together. All FIs in all the studied phases homogenized into the liquid phase, i.e. disappearance of the gas phase at  $T_h$ . FIs in D2 and saddle dolomites homogenized at a  $T_h$  mode ranging between 77 and 80°C. (Fig. 8a).  $T_h$  values for blocky calcites show a more restricted mode around 76 and 80°C (Fig. 8b). Oil inclusions with brown fluorescence in blocky calcites have  $T_h$  values between 56°C and 68°C with a  $T_h$  mode around 66-68°C. Oil inclusions with white fluorescence are rare and homogenize at around 70°C (Fig. 8b).

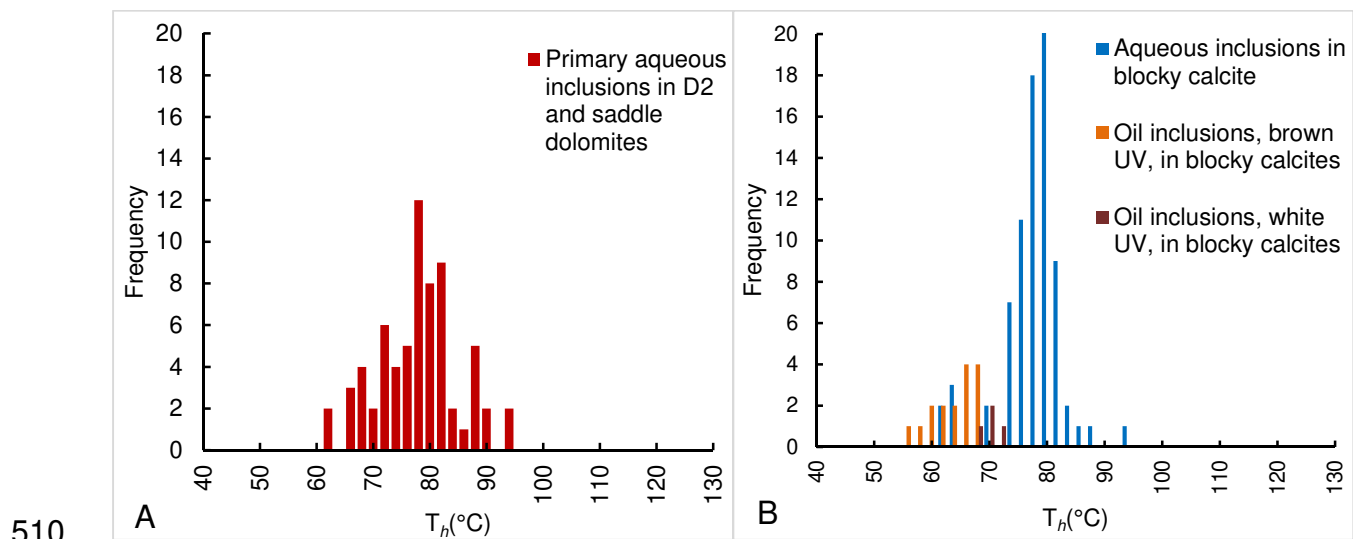
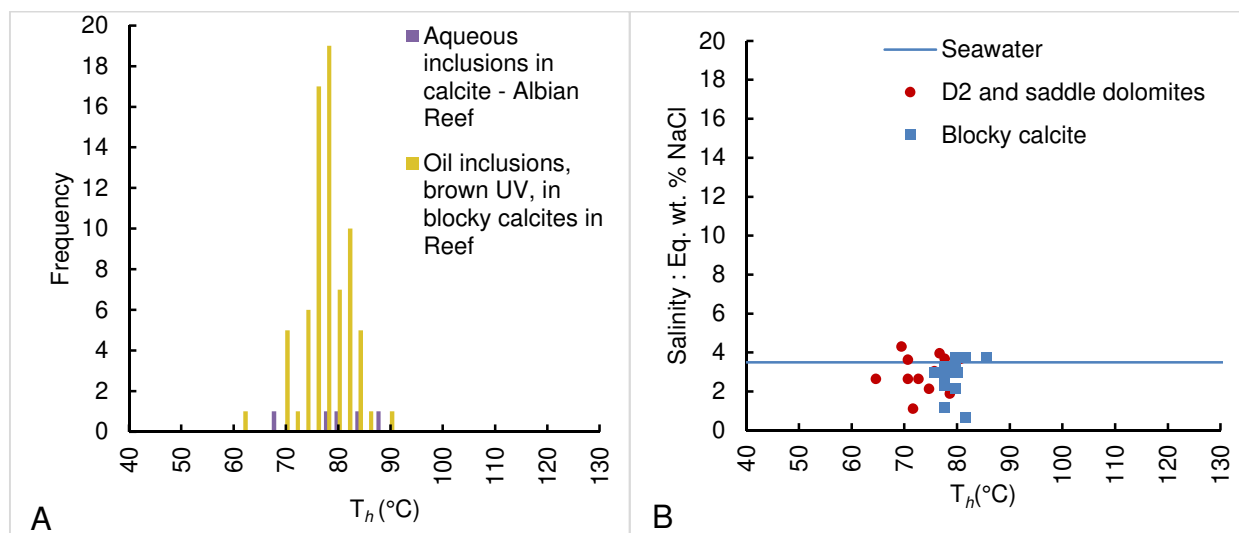


Figure 8: Frequency histograms of the homogenization temperatures of aqueous and oil inclusions in (A) dolomite and (B) calcite phases.

In the Albian reefs (Fig. 3) at depths of 1400-1403 m, the main inclusion type trapped in the blocky calcite phase is a brown-fluorescent oil homogenizing at around 76-80°C (Fig. 9a). Aqueous inclusions are very rare but homogenize in the same temperature range as the oil inclusions. After freezing down to -100°C, phase changes were observed, and final ice melting temperatures were recorded. Eutectic ( $T_e$ ) or first-melting temperatures were

518 difficult to record in most FIs, but in a few inclusions, first melting of ice with coexistence of  
 519 solid (ice), liquid, and gas phases occurred between  $T_e$  of -21 to -22°C. Final ice melting  
 520 temperatures were measured between -4 and -0.2°C. These values correspond to very  
 521 low salinities, equal or lower than values of seawater (Fig. 9b).



522

523 Figure 9: (A) Frequency histogram of homogenization temperatures of aqueous and  
 524 inclusions in the blocky calcite of the Albian Reef Formation (Fig. 3). B:  $T_h$  vs. salinity  
 525 cross-plot of the studied phases.

#### 526 4.2.4 Raman Spectroscopy

527 The very low salinities measured with microthermometry were confirmed by Raman  
 528 spectroscopy. Analysis of the liquid phase in fluid inclusions of the blocky calcite reveal  
 529 salinities ranging between 1.2-2.4 % eq. wt. NaCl. These values are in the same range  
 530 that those obtained through microthermometry. Raman measurements made on the gas  
 531 phases showed no  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{S}$  or any other gas component except  $\text{H}_2\text{O}$  vapor.  
 532 Unfortunately, high fluorescence in dolomites prevented the acquisition of reliable data.

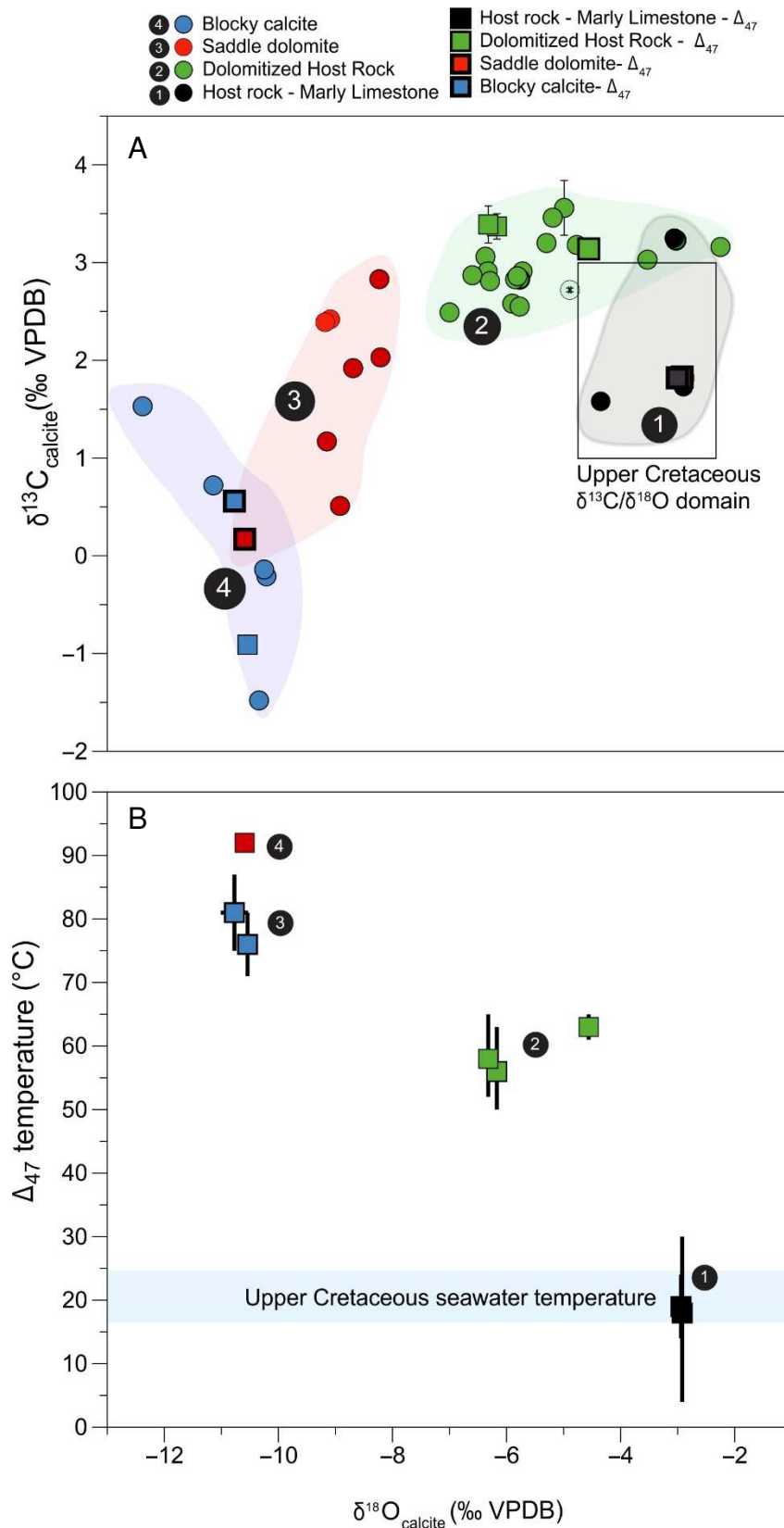
#### 533 4.3 Isotope Geochemistry

534  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  composition were measured in four different carbonate phases : (1) the  
 535 host rocks ( $n=3$ ), (2) the dolomitized matrix constituted by a mixture of D1 and D2  
 536 dolomites ( $n=28$ ), (3) saddle dolomites ( $n=6$ ) and (4) the final blocky calcite ( $n=6$  ; Fig. 10).  
 537 A few sub-samples from each carbonate phase were further investigated by carbonate  
 538 clumped isotope thermometry ( $\Delta_{47}$ ). Figure 10 and Table 1 report the average  $\delta^{18}\text{O}_{\text{carb}}$ ,

539  $\delta^{13}\text{C}_{\text{carb}}$ ,  $\Delta_{47}$ ,  $T(\Delta_{47})$  and  $\delta^{18}\text{O}_{\text{water}}$  results. The investigated carbonate rock has a “bulk”  
 540  $\delta^{13}\text{C}$  values ranging from -1.48‰ to 3.56‰ (VPDB) and  $\delta^{18}\text{O}$  ranging from -2.25‰ to -  
 541 12.38‰ (VPDB). However, the genetically distinct phases show more homogeneous and  
 542 clustered  $\delta^{18}\text{O}/\delta^{13}\text{C}$  values, with respective  $\delta^{18}\text{O}$  composition of  $-3.44 \pm 0.79\text{‰}$  for the host  
 543 rock,  $-5.34 \pm 1.23\text{‰}$  for the dolomitized matrix,  $-8.72 \pm 0.42\text{‰}$  for the saddle dolomite and -  
 544  $10.58 \pm 1.08\text{‰}$  for the last blocky calcite. Average  $\delta^{13}\text{C}$  values are of  $2.19 \pm 0.92\text{‰}$  for the  
 545 host rock,  $2.96 \pm 0.29\text{‰}$  for the dolomitized matrix,  $2.02 \pm 0.80\text{‰}$  for the saddle dolomite,  
 546 and  $0.27 \pm 1.10\text{‰}$  for the blocky calcite. The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  composition of the host rock  
 547 fall within the range of expected values for biogenic calcites precipitated in equilibrium with  
 548 Late Cretaceous seawater (Steuber, 1999). In contrast, the younger carbonate phases  
 549 show a gradual depletion in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ .

550 Similarly, each carbonate phase displayed distinctive  $\Delta_{47}$  compositions convertible into  
 551 precipitation temperature estimations. Values obtained are of (1)  $19 \pm 5^\circ\text{C}$  and  $18 \pm 15^\circ\text{C}$   
 552 for the host rock, (2)  $58 \pm 7^\circ\text{C}$ ,  $63 \pm 2^\circ\text{C}$  and  $56 \pm 7^\circ\text{C}$  for the dolomitized matrix samples,  
 553 (3)  $92^\circ\text{C}$  (error unknown as only one measurement) for the saddle dolomite and (4)  $76 \pm$   
 554  $5^\circ\text{C}$ ,  $81 \pm 6^\circ\text{C}$  for the blocky calcite. As illustrated in figure 10b, the decrease in  $\delta^{18}\text{O}$   
 555 values is correlated with an increase in  $\Delta_{47}$  temperatures. The calculated oxygen isotopic  
 556 compositions of the parent fluids ( $\delta^{18}\text{O}_{\text{water}}$ ) are of -1.9 to -1.7‰ SMOW for the host-rock, -  
 557 1.6 to +1.2‰ SMOW for the dolomitized matrix, -0.6‰ SMOW for the saddle dolomite and  
 558 +0.4 to +0.8‰ for the blocky calcite.





559

560 Figure 10. A:  $\delta^{18}\text{O}/\delta^{13}\text{C}$  cross plot. Symbol colors refer to specific carbonate phases  
 561 numbered from '1' to '4'. The colored areas highlight the dispersion of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$   
 562 values recorded for each carbonate phase. Square symbol represents the sample selected  
 563 for clumped isotope measurements. When not shown, uncertainties are included in the  
 564 symbol size. The black rectangle represents the expected  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of marine  
 565 carbonate precipitated in equilibrium with Upper Cretaceous seawater (Steuber, 1999). B:  
 566 Cross-plot of  $\delta^{18}\text{O}$  versus  $T(\Delta_{47})$ . Uncertainties are reported as 1SD of the mean out of  
 567 one to three replicates. Expected Upper Cretaceous seawater temperature  
 568 is reported in the blue shaded area (Steuber, 1999).

569

570 Table 1. Stable isotope results ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$  and  $\Delta_{47}$ ) of the samples set investigated.

Phase	n	$\delta^{18}\text{O}$		$\delta^{13}\text{C}$		$\Delta_{47}$	$\Delta_{47}$ errors (‰)		$T(\Delta_{47})$ error (1SD)			$\delta^{18}\text{O}$ water
		‰VPDB	±STD	‰VPDB	±STD		STD	SE	Mean <sup>(2)</sup>	Min	Max	
Blocky cal.	3	<b>-10,77</b>	0,03	<b>0,56</b>	0,24	0,463	0,011	0,006	<b>81</b>	87	75	<b>0,8</b>
Blocky cal.	3	<b>-10,54</b>	0,08	<b>-0,91</b>	0,09	0,473	0,010	0,006	<b>76</b>	81	71	<b>0,4</b>
Matrix dol.	3	<b>-6,17</b>	0,14	<b>3,37</b>	0,13	0,515	0,016	0,009	<b>56</b>	63	50	<b>-1,6</b>
Matrix dol.	3	<b>-4,56</b>	0,04	<b>3,14</b>	0,1	0,500	0,004	0,002	<b>63</b>	65	61	<b>1,2</b>
Matrix dol.	3	<b>-6,32</b>	0,07	<b>3,39</b>	0,19	0,511	0,015	0,009	<b>58</b>	65	52	<b>-1,4</b>
Saddle dol.	1	<b>-10,59</b>		<b>0,17</b>		0,442			<b>92</b>	-	-	<b>-0,6</b>
Host rock	2	<b>-2,92</b>	0,05	<b>1,83</b>	0,04	0,624	0,043	0,030	<b>18</b>	32	6	<b>-1,9</b>
Host rock	2	<b>-2,94</b>	0,22	<b>1,82</b>	0,05	0,621	0,017	0,012	<b>19</b>	24	14	<b>-1,7</b>

"Note. Errors on average  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  are given as 1S.D. Errors on samples  $\Delta_{47}$  and  $T\Delta_{47}$  are 1 SD of the mean values calculated out of replicate  $\Delta_{47}$  measurements of the same powder.  
(n) is the number of replicate measurements of the same carbonate powder  
<sup>(1)</sup>  $\Delta_{47}\text{CDES90}$  are values relative to the 'carbon dioxide equilibrium scale' CDES, without acid fractionation correction.  
<sup>(2)</sup> Paleotemperatures calculated using the composite  $\Delta_{47}$ -T calibration (Eq. 3 from Bonifacie et al. 2017)  
<sup>(3)</sup> Oxygen isotope compositions of waters are calculated using  $T\Delta_{47}$  and the equations of fractionation of oxygen isotopes between the carbonate and water of either O'Neil et al. (1969) for calcite and Horita (2014) for dolomite.

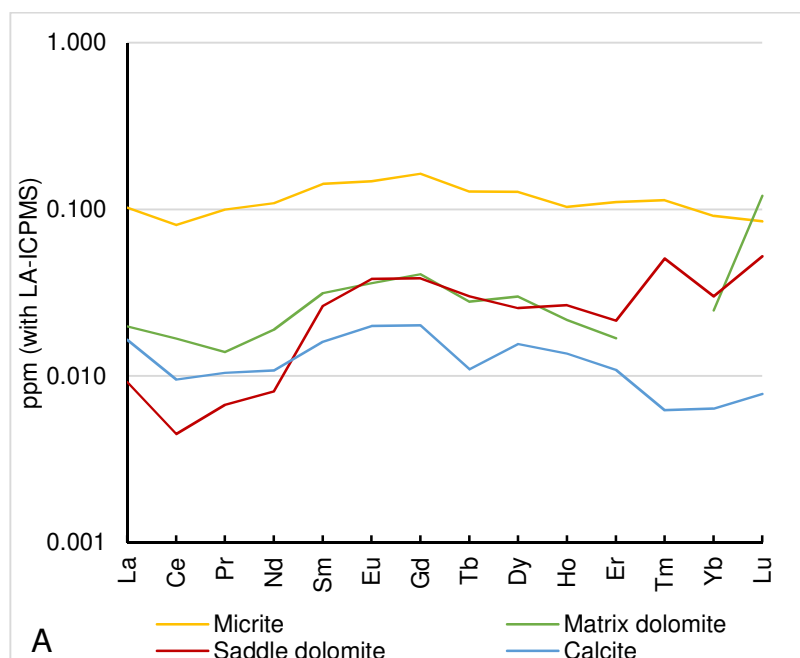
571

572 Multiple sulfur isotopes analysis on CAS resulted in  $\delta^{34}\text{S}$  of  $20.00\text{‰ V-CDT} \pm 0.013\text{‰}$ ,  $\delta^{33}\text{S}$   
573 of  $10.28\text{‰ V-CDT} \pm 0.016\text{‰}$  and  $\delta^{36}\text{S}$  of  $37.85\text{‰ V-CDT} \pm 0.091\text{‰}$ . From these values,  $\Delta^{33}\text{S}$   
574 and  $\Delta^{36}\text{S}$  were calculated and yielded values of  $-0.487\text{‰} \pm 0.016\text{‰}$  and  $-0.487\text{‰} \pm$   
575  $0.091\text{‰}$ , respectively.

## 576 4.4 REE Patterns

577 REE concentrations were obtained from micritic limestones, matrix and saddle dolomites,  
578 and the calcite cements. Figure 11 presents the PAAS-normalized REE patterns plotted on  
579 a logarithmic scale. Micrites are more enriched in REE than the dolomite and calcite  
580 phases. Also, the middle REE elements show a bulge pattern with slightly higher  
581 concentrations than the light and heavy elements. In the case of the matrix dolomites, Tm  
582 concentration was lower than the detection limit of the spectrometer and a valid  
583 measurement was therefore not possible.





584

585 Figure 11. PAAS-normalized REE pattern of the micritic host rock, matrix dolomites,  
586 saddle dolomite and calcite. Patterns of dolomite and calcite phases show a bulge (relative  
587 enrichment) in the middle REE.

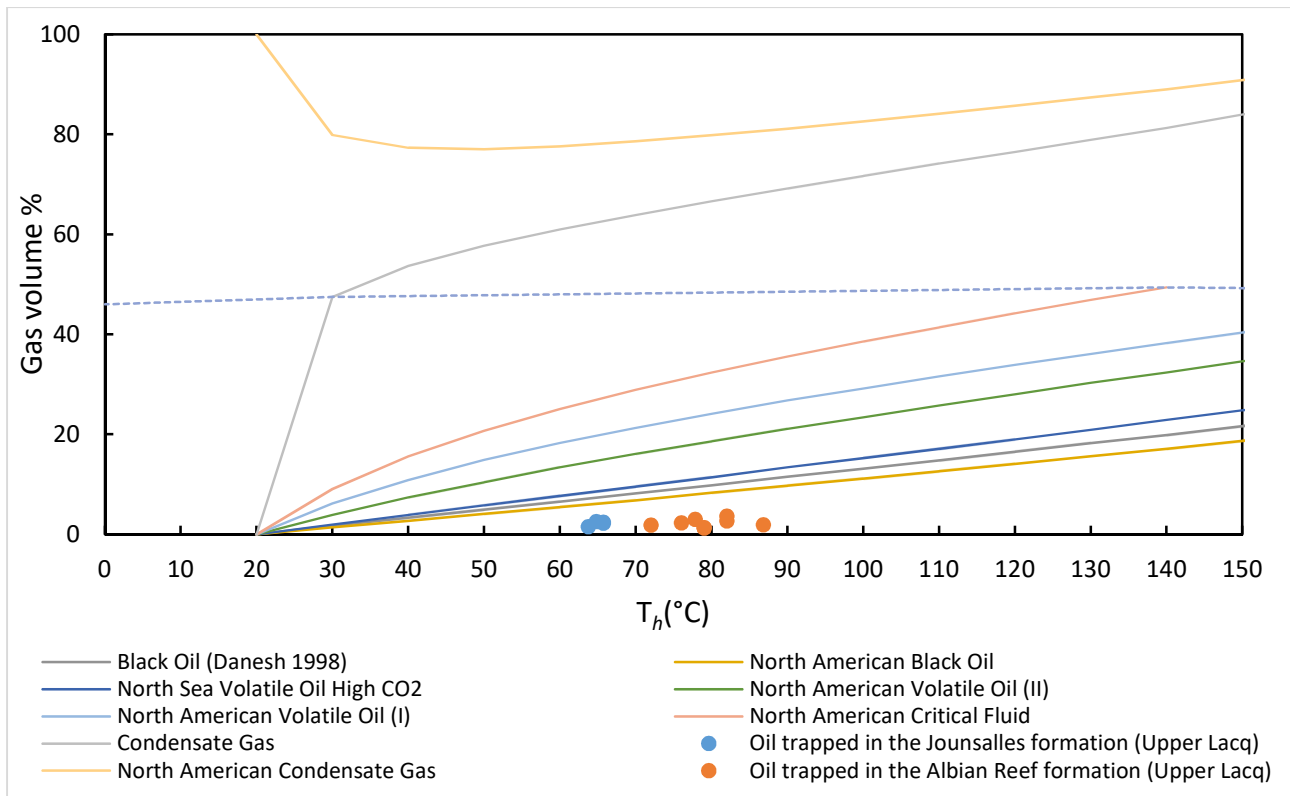
#### 588 4.5 U-Pb LA-ICPMS absolute age dating

589 In order to obtain absolute dating with the U/Pb method on calcite and dolomite phases 15  
590 measurements were performed with LA-ICPMS to estimate the U and Pb elemental  
591 concentration. Obtained concentrations are in the range of 0.001 to 0.005 ppm for U and  
592 Pb and were thus too low to meet the minimum requirement for absolute age dating.

#### 593 4.6 Fluid inclusions thermodynamics modeling

594 Petroleum inclusion thermodynamic (PIT) and aqueous inclusion thermodynamic (AIT)  
595 modeling were applied to the oil and aqueous inclusions of the blocky calcite. This step  
596 allowed the construction of isochores for the two inclusion types and allowed to estimate  
597 P-T conditions of trapping indicated by their intersection domain. The inclusions used are  
598 coeval primary inclusions selected during petrographic analysis (part 4.2). The results  
599 indicate a trapping temperature between 82 and 92°C at pressures of 136-210 bars  
600 respectively. For the Albian reef located at a depth of 1400m, the double-isochore  
601 technique was not possible due to the scarcity of aqueous inclusions and the difficulty in  
602 accurately determining their co-genetic relationships with the oil FIs.

603 By using the confocal scanning microscopy and associated image processing, the volume  
 604 of gas can be used to obtain a qualitative assessment of the type of trapped oil. Figure 12  
 605 displays the evolution of 8 different types of reference oils (Bourdet et al., 2008) with the  
 606 results for Upper Lacq and Albian reef oils. The close association of the plotted Lacq oil to  
 607 the North American Black Oil indicates that the Lacq oil is heavy.



608  
 609 Figure 12. Gas volume % vs.  $T_h$  trends for 8 different reference oils with plotted results for  
 610 Upper Lacq and Albian reef oils. L-V line separates the homogenization to the liquid  
 611 domain below from the gas domain above. Modified after Bourdet et al., (2008).

## 612 4.7 Basin modeling

### 613 4.7.1 Basal heat flow scenario

614 Modeling the syn-rift to post-rift basal heat flow requires taking into account the thermal  
 615 maturity of organic material using vitrinite reflectance data as well as the geodynamic  
 616 history of Lacq since the late Aptian. This history includes (i) the Albo-Aptian rifting,  
 617 followed by (ii) an erosion phase during the Late Albian - Early Cenomanian, (iii) a phase  
 618 of post-rift cooling during the Cenomanian - end Santonian, and (iv) the principal inversion  
 619 and shortening episode during the Eocene. These input data constrain a best-fit model

620 where the heat flow reaches a peak of about 130 mW/m<sup>2</sup> during the Aptian extension  
621 before a decrease to nearly 56 mW/m<sup>2</sup> at the onset of N-S convergence. These values  
622 were modeled to obtain an acceptable present-day geothermal gradient of 50°C/km. Such  
623 a geothermal gradient is reasonable since the foreland basin was superimposed directly  
624 on a still-hot rift with ongoing thermal subsidence that is driven by the post-rift thermal  
625 cooling (Angrand et al., 2018).

#### 626 4.7.2 Thermal history reconstruction constrained by vitrinite reflectance data

627 Vitrinite reflectance measurements are plotted according to their stratigraphic location in  
628 figure 13. Basin modeling results in an acceptable fit between the modeled thermal  
629 gradient (black line in figure 13) and the measured vitrinite reflectance values. The thermal  
630 maturity of Upper Cretaceous formations follows a normal burial trend, interrupted by a  
631 minor erosional event on the base Oligocene boundary. Our modeling assumes 200  
632 meters of eroded material at the base Cenomanian unconformity, and 400 meters during  
633 the maximum exposure at the base Oligocene unconformity. These values take into  
634 account the shape of the onlaps and toplaps of reflectors on both sides of the  
635 unconformities (Fig. 2).

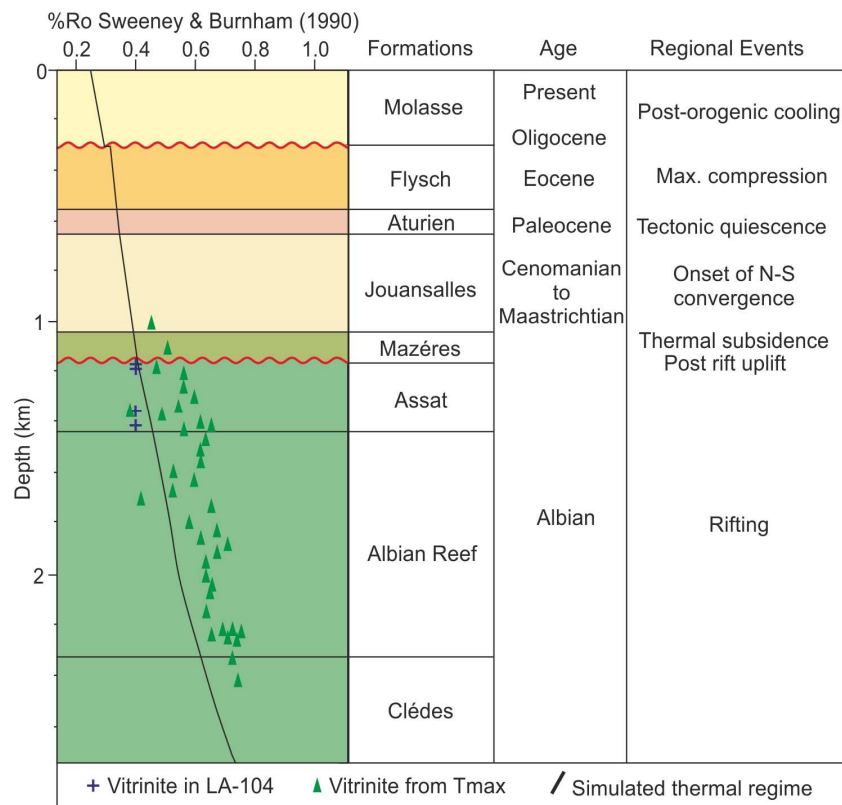
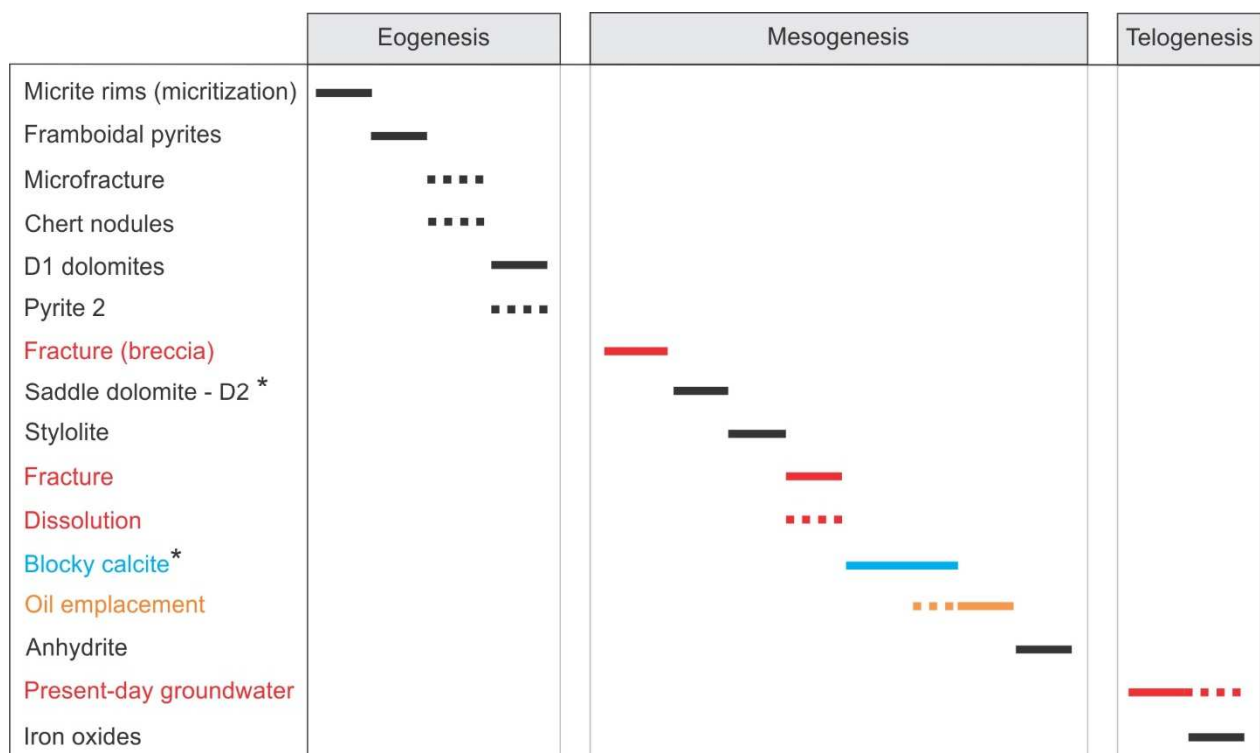


Figure 13. Simulated thermal regime in Petromod constrained by vitrinite reflectance measurements.

## 5 Discussion

### 5.1 Paragenesis and fluids involved

The chronological sequence of diagenetic phases deduced from petrographic observations is represented in figure 14.



644

645 Figure 14. Chronology of diagenetic phases and fracturing events observed in Upper Lacq  
646 from oldest at the top to youngest at the base. Dashed lines correspond to phases whose  
647 exact paragenetic timing cannot be precisely constrained. Asterisks\* indicate the phases  
648 investigated here in thermometric studies (FI and  $\Delta_{47}$ ).

649 The wackestone/packstone facies precipitating in a shallow marine depositional  
650 environment has been characterized by  $\Delta_{47}$  thermometry. Carbonate clumped isotopes  
651 show surface temperatures around 20°C and  $\delta^{18}\text{O}$  of parent fluids around -1.9 ‰SMOW  
652 (Table 1). These values (1) point towards precipitation conditions in a shallow marine  
653 depositional environment, by marine fluids with a potential meteoric water influx and (2)  
654 demonstrate the absence of significant recrystallization of the host-rock during burial.

655 During eogenesis, microborers and bacterial activity resulted in destructive micritization of  
656 carbonate clasts with the micrite envelope developing from the edges to the center of the  
657 grain (Bathurst, 2007). Framboidal pyrites precipitated as a result of bacterial sulphate  
658 reduction (BSR) of organic matter just below the surface of the sediment (Machel, 2001).  
659 Such an interpretation is supported by the distribution of framboidal pyrites that are mainly  
660 associated with skeletal grains and micritized rims. The relative timing of silicification is  
661 difficult to constrain as chert nodules were observed only in micritic, non-dolomitized  
662 samples. However, given the occurrence of siliceous sponges (Fig. 4f), the timing was

663 relatively early as diagenesis of amorphous organic silica is favored by pH variations due  
664 to the degradation of organic matter at low temperature during early burial (Hinman, 1990).  
665 Silica was provided by siliceous sponges after the death of organisms and locally  
666 reprecipitated by replacement of the micritic matrix. Early diagenesis ends with the D1  
667 dolomites. Their non-luminescence and  $\delta^{18}\text{O}$  of parent fluids of -1.6 to +1.2‰SMOW  
668 (Table 1) suggest a mixing between oxidizing meteoric fluids and trapped formation fluids,  
669 of a marine origin, that can provide Mg needed for this volumetrically-limited dolomite  
670 phase. Since the bulk powders extracted from the matrix dolomites are a mixture of D1  
671 and D2 dolomite phases, the  $\Delta_{47}$  temperature of around 60°C could reflect an average  
672 between these two end-members. Pyrite 2 post-dates D1 rhombs since relics of D1 were  
673 observed inside pyrites. Merino and Canals (2011) argue that if the dolomitizing fluids  
674 contain some metals, and if enough organic matter is present in the host carbonates,  
675 pyrites should precipitate during and after the dolomitization phase by the reduction of  
676 aqueous sulphates released from organic carbon. The non-ferroan composition of all  
677 dolomite phases in Upper Lacq, as well as contacts between some pyrite 2 and the D1  
678 dolomite are in accordance with such a mechanism. Any  $\text{Fe}^{2+}$  in the dolomitizing fluids was  
679 likely consumed by the precipitation of reduced sulfur species, and the dolomitizing fluid  
680 was then depleted in iron. The scarce distribution and limited quantity of pyrites observed  
681 suggest that initially the quantity of  $\text{Fe}^{2+}$  in the dolomitizing fluids was actually low. A  
682 similar mechanism has been demonstrated in the Neogene Monterey and Sisquoc  
683 Formations in Santa Maria Basin, California (Compton, 1988).

684 During mesogenesis, the Upper Lacq reservoir experienced its main diagenetic  
685 modifications. Here we consider that mesogenesis is the burial domain isolated from  
686 surface-related processes while telogenesis occurs only the late stage of exhumation  
687 when oxidizing surficial fluid enter in the diagenetic system. Mesogenesis started with an  
688 episode of fracturing and brecciation that generated new pathways for dolomitizing fluids.  
689 Some breccias are cross-cut and cemented by D2 and saddle dolomite, suggesting that

690 these dolomites formed during or just after fracture opening. Therefore, after the early D1  
691 phase, new dolomitizing fluids circulated along fractures and precipitated D2 as  
692 overgrowth cements in intercrystalline pores or as pore-filling saddle dolomite crystals in  
693 the open fractures. This dolomitization possibly occurred under high pressures given the  
694 occurrence of breccia and fractures in these dolomitized facies. Differences in dolomite  
695 sizes and extinction behavior can be attributed to the crystallization space available  
696 (Machel, 2004). Using  $\Delta_{47}$  temperatures, more depleted values of -0.6 ‰SMOW were  
697 obtained for D2. These isotopic signatures point toward a marine source different than the  
698 meteoric parent fluids of D1.

699 Post-dolomitization diagenesis involved fracturing, calcite cementation, and oil migration. A  
700 second fracturing phase preceded the precipitation of the blocky calcite. FIs in calcite have  
701 a  $T_h$  range of 70-90°C with highest modes at 80°C, with salinities being equal to or lower  
702 than that of seawater (Fig. 9b). The  $\delta^{18}\text{O}$  of the parent-fluids precipitating the calcite is in  
703 the range of +0.4 to +0.8‰SMOW (table 1), typical of a marine source. The opening of  
704 new fractures and circulation pathways for the parent-fluids of the blocky calcite may have  
705 connected the Upper Lacq reservoir with new reservoirs of trapped connate fluids depleted  
706 in Mg. This fluid pulse is distinct from that responsible for dolomite precipitation especially  
707 in that it is associated with oil migration.

708 Several pulses of oil migration can explain the coexistence of two types of oil inclusions in  
709 the same calcite cement. Scarce inclusions with a strong white fluorescence, and  
710 containing water, as indicated by FT-IR spectra, are probably more mature than inclusions  
711 with brown fluorescence. They are therefore associated with a second pulse of oil  
712 migration. A third pulse is assumed to be responsible for the oil coatings on top of calcite.  
713 This last pulse was important enough to allow an economically valuable infill of the Upper  
714 Lacq reservoir. PIT modeling also demonstrates that the oil trapped as inclusions in the  
715 blocky calcite phase is heavy. This is in agreement with Connan and Lacrampe-Couloume



716 (1993) who propose that the oil in Upper Lacq originally migrated as heavy oil and was not  
717 a consequence of post-migration modifications.

718 After calcite cementation and oil emplacement, anhydrites precipitated. The multiple sulfur  
719 isotopes signatures of CAS are listed in Table 2 and are compared with the Eocene  
720 marine fluids signatures (Crockford et al., 2019 and references therein). The overlap in the  
721 results indicates a marine seawater origin for the parent fluids.

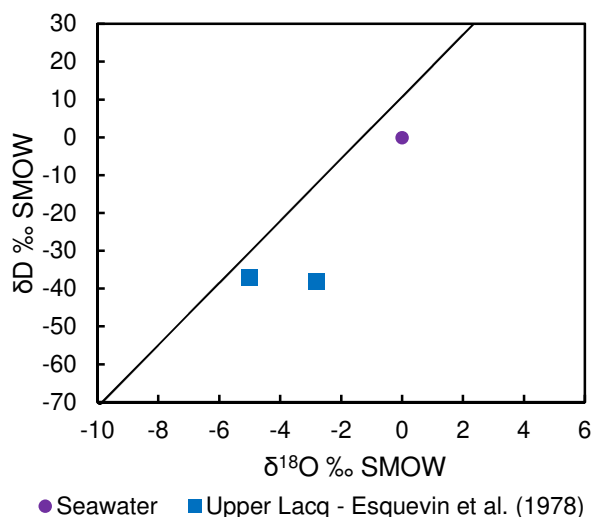
722 Table 2. Multiple sulfur isotope signature of CAS from anhydrite-rich samples (this study)  
723 and those of the reference Eocene seawater of Crockford et al. (2019) and references  
724 therein.

	This study		Eocene marine water	
	Value (‰ V-CDT)	Error (‰ V-CDT)	Value (‰ V-CDT)	Error (‰ V-CDT)
$\delta^{34}\text{S}$	20.00	$\pm 0.013$	22.87	$\pm 7.86$
$\Delta^{33}\text{S}$	0.036‰	$\pm 0.016$	-0.001	$\pm 0.042$
$\Delta^{36}\text{S}$	-0.487‰	$\pm 0.091$	0.713	$\pm 0.508$

725

726 The relative enrichment of seawater with calcium sulphates provided a source for this  
727 anhydrite phase, which can precipitate after Mg depletion, as previously documented in  
728 the dolomitized Devonian reservoirs of Alberta, Canada (Butler, 1970; Mountjoy et al.,  
729 1999; Machel, 2004).

730 During telogenesis, meteoric fluids were laterally re-introduced in the diagenetic system.  
731 Vertical input is unlikely given the integrity of the Paleocene seal. Late input of meteoric  
732 fluids is supported by the occurrence of present-day groundwater in the Upper Lacq  
733 reservoir at a depth of -723 m. Groundwater samples, collected from Upper Lacq, were  
734 analyzed for their  $\delta\text{D}$  and  $\delta^{18}\text{O}$  isotopes by Esquevin et al. (1987) and are plotted against  
735 the Global Meteoric Water Line (GMWL) in figure 15. The results show that the  
736 groundwater in Upper Lacq is slightly modified and enriched with  $\delta^{18}\text{O}$  relative to the  
737 GMWL. This minor enrichment could be the result of fluid-rock interactions and possible  
738 contributions of  $\delta^{18}\text{O}$ -enriched formation fluids. This minor enrichment could result from  
739 the mixing of  $\delta^{18}\text{O}$ -enriched pore fluids with more recent meteoric water recharges.



740

741 Figure 15.  $\delta D$  vs.  $\delta^{18}O$  in ‰ SMOW for the groundwater collected from Upper Lacq plotted  
 742 against the Global Meteoric Water Line (GMWL). The slight enrichment compared to the  
 743 GMWL could be the result of mixing with  $\delta^{18}O$  – enriched formation fluids or contamination  
 744 by the host rock.

745 The mixing of this groundwater with  $H_2S$ , currently present in and commercially extracted  
 746 from the Lacq reservoirs may contribute to sulfuric acid speleogenesis (SAS) that can  
 747 explain the karstic cavity at a depth of nearly 2200 m reported in the drilling reports of LA –  
 748 101. Similar cases of SAS have been recently documented in Jurassic and Cretaceous  
 749 carbonates of the north Pyrenean foothills and the southern Aquitaine foreland basin  
 750 (Laurent et al., 2019).

751 In summary, three different origins of fluids contributing to diagenesis can be documented;  
 752 these are: (1) a mixture of meteoric and marine fluids precipitating D1 dolomites, (2)  
 753 another mixture of marine and clay-released fluids for saddle dolomite, calcite and  
 754 anhydrite cements, and then a (3) modified meteoric source for the present day  
 755 groundwater in the reservoir.

756 An important criterion to consider here is the amount of magnesium required for  
 757 dolomitization and its possible sources. Several sources can be involved such as: (a)  
 758 Mg derived from the Triassic evaporites of the core of the Lacq anticline, (b) serpentization  
 759 reactions close to the exhumed mantle domain, which could have released Mg into the  
 760 fluids, (c) Mg-rich fluids released from the compaction and dewatering processes of the  
 761 Albo-Aptian Ste-Suzanne and Assat marls. Mg sourced from the salt diapir in the core of

762 the anticline is ruled out because of the very low salinities measured in the aqueous fluids  
763 inclusions of the D2 and saddle dolomite phases.

764 Serpentinization- or mantle-derived Mg from the exhumed mantle domain is plausible given  
765 the geodynamic setting and the proximity to the exhumed mantle bodies, e.g. Sarrance  
766 anticline and Arbailles Massifs (Salardon et al., 2017). However, such a deep source  
767 would provide higher values of  $\delta^{18}\text{O}$ ‰ SMOW and inclusions should contain evidence of  
768 mantle-derived  $\text{CO}_2$  or  $\text{H}_2$ . The lack of supporting evidence in the studied samples makes  
769 it difficult to support this hypothesis.

770 Clay dewatering is a very likely candidate to provide the amount of Mg required for  
771 dolomitization. The Apto-Albian Sainte Suzanne and Assat Marl formations reach  
772 considerable thicknesses of more than 5 km in the southern Lacq basin (Fig. 2; Biteau et  
773 al., 2006). Such a thickness would contain enough Mg, trapped in formational fluids that  
774 were expelled along faults and fractures and dolomitized the Upper Lacq reservoirs.  
775 Fluids generated by dewatering are characterized by low salinities because of the  
776 reduction of the total dissolved salts (TDS) through clay ultrafiltration (Tremosa et al.,  
777 2019), an increase in the  $\delta^{18}\text{O}$  signature upon clay dehydration (Minami et al., 2018), and  
778 an enrichment in Mg due to the diagenetic smectite-illite transformations (Schrijver et al.,  
779 1996).

780 As supported by the isotope geochemistry, the parent fluids of saddle dolomites and  
781 calcites were marine in origin. These marine fluids, trapped as connate waters in deep part  
782 of the basin, were expelled during the first fracturing phase that opened new circulation  
783 pathways. During their migration they were modified by mixing with low salinity Mg-rich  
784 fluids generated by clay dewatering.

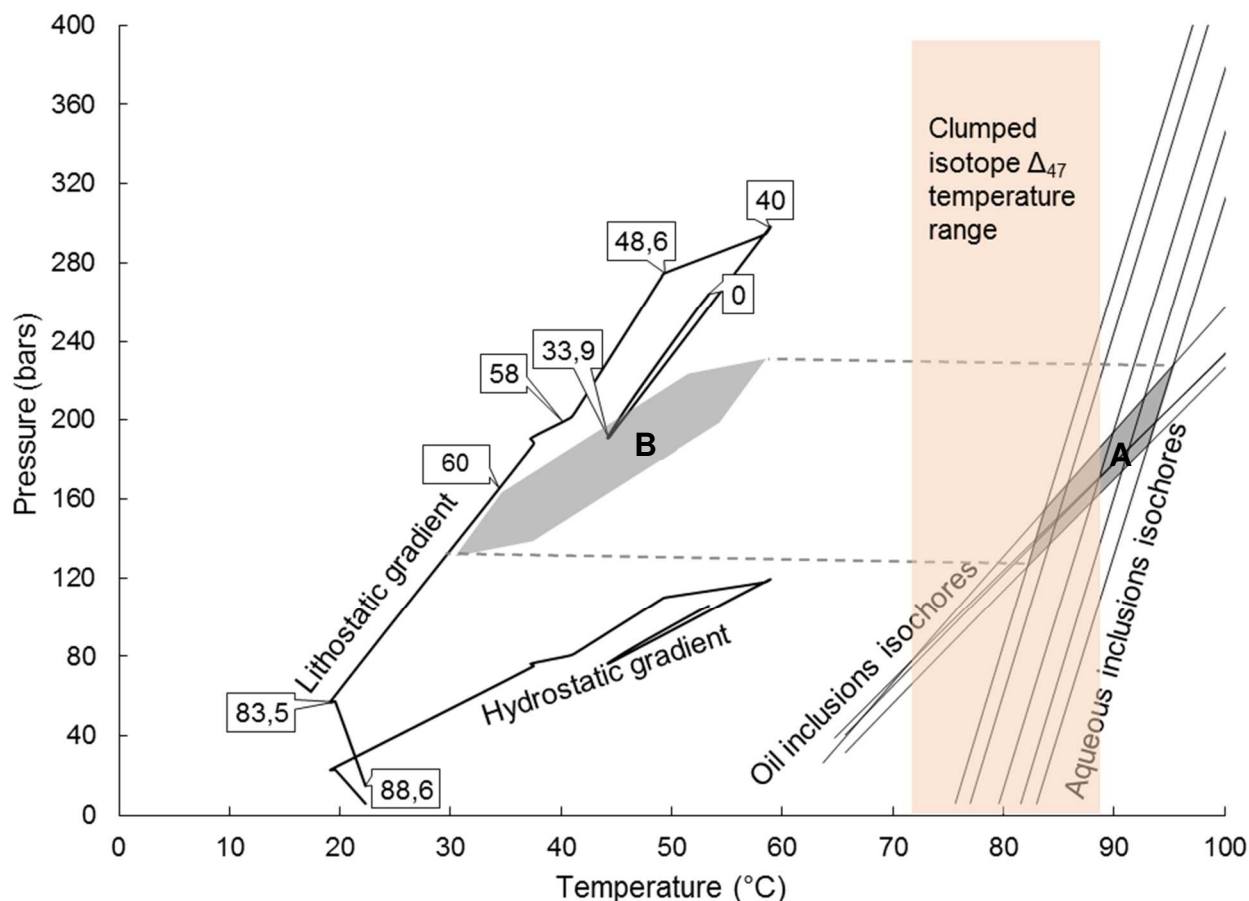
785 5.2 Redox conditions

786 The nonluminescence of D1 dolomites and the contribution of meteoric fluids, at very  
787 shallow depths suggest that the first dolomitizing fluids were oxidizing. Later fluids involved

788 in saddle dolomitization and calcite cementation were relatively enriched in middle REE  
789 (MREE). Such a REE pattern can be interpreted as the signature of fluids circulating in a  
790 reducing environment (Haley et al., 2004). Further indications of this reducing state are  
791 provided by the dull red and dull orange luminescence of the saddle dolomite and calcite  
792 respectively (Barnaby and Rimstidt, 1989). In addition, such a reducing system is also in  
793 agreement with the presence of not biodegraded and unoxidized oil inclusions in calcites.  
794 During telogenesis, oxidizing conditions were recovered with the present-day groundwater  
795 (Figs. 14 and 15) at the origin of the oxidization of the pyrite 2.

### 796 5.3 Hydrothermal activity

797 To better constrain the evolution of P-T conditions during the burial history of the Upper  
798 Lacq reservoir, fluid pressure gradients need to be estimated. Figure 16 illustrates the  
799 evolution of hydrostatic and lithostatic pressure gradients experienced by the Upper Lacq  
800 reservoirs assuming a geothermal gradient decreasing from 110°C/km during the peak  
801 Aptian rifting to 50°C/km in the present day (Angrand et al., 2018; Renard et al., 2019).  
802 Cooling between 88.6 and 83.5 Ma is a continuation of the isostatic rebound after the  
803 Aptian rifting. The loop in the gradients (between 40 and 33.9 Ma) is the caused by the  
804 base Oligocene unconformity. The grey shaded area named (A) represents the range of  
805 trapped P-T conditions obtained with PIT-AIT modeling. These conditions are not in  
806 equilibrium with the thermal evolution of the reservoir. The good match observed between  
807 temperature estimates based on two independent geothermometers (fluid inclusions with  
808 the double isochore technique and carbonate clumped isotope thermometry, figure 16)  
809 strongly support the reliability and accuracy of each thermometer (c.f. see Mangenot et al.,  
810 2017). The two techniques reveal a thermal disequilibrium between the mineralizing fluid  
811 and the host-rock. Indeed, a gap of at least 30-40°C, between the maximum burial  
812 temperatures and the minimum trapping conditions, is observed. This suggests that the  
813 parent fluids of calcites and similarly of dolomites were hotter than the burial temperatures  
814 and hence imply the involvement of hot hydrothermal fluids.

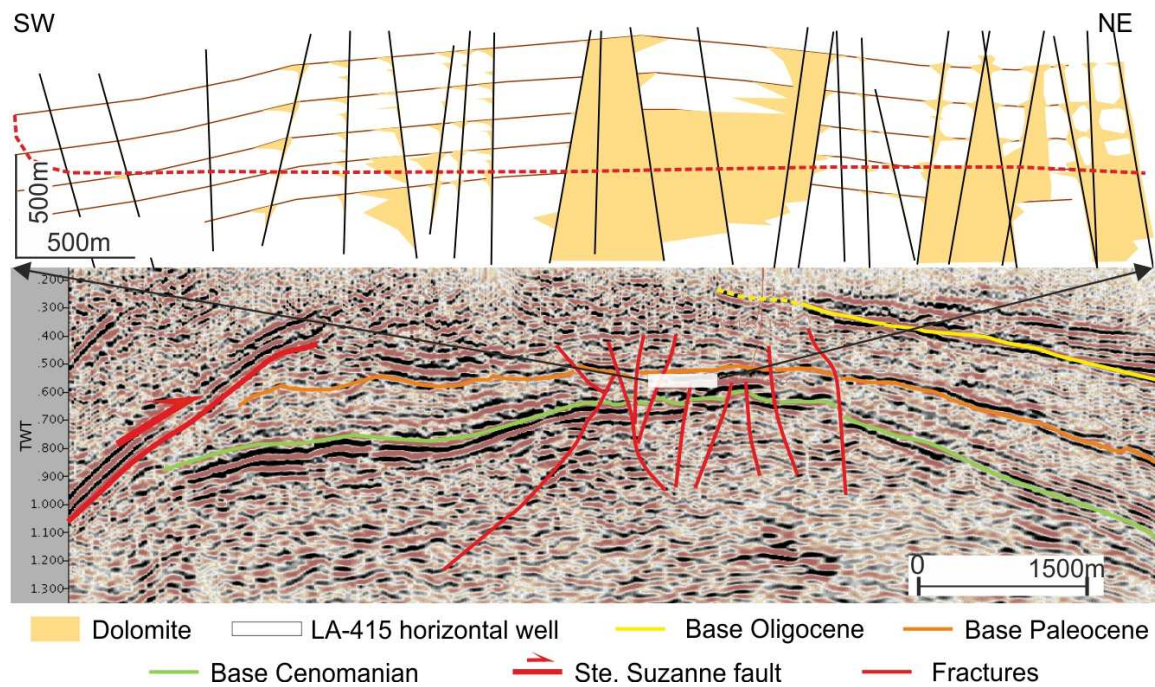


815

816 Figure 16. P-T trapping conditions and evolution of fluid pressure gradients simulated with  
 817 Petromod-1D and PIT-AIT respectively. Numbers in tags are ages in Ma. The pink area  
 818 represents the calcite temperature estimation deduced from  $\Delta_{47}$  thermometry (i.e. an  
 819 isotopic thermometer independent of any pressure effect). The grey shaded area (A) is the  
 820 intersection of both isochore types and hence indicates the trapping conditions of  
 821 inclusions in blocky calcites. The loop in the hydrostatic and lithostatic gradients represent  
 822 the base Oligocene unconformity at 40-34 Ma. The dashed lines correspond to the  
 823 extrapolation of the P-T conditions in (A) to the shaded area (B) in the domain between the  
 824 hydrostatic and lithostatic fluid pressure.

825 However, by extrapolating the pressure range of the fluids to the domain between  
 826 hydrostatic and lithostatic gradients (dashed lines in figure 16), a timing between 60 and  
 827 40 Ma can be estimated from the shaded area (B). This age corresponds to the Selandian-  
 828 Bartonian (Paleocene to mid-Eocene), during the Pyrenean compression. In the Rousse  
 829 reservoir, 30 km southeast of Lacq (Fig. 1), Renard et al. (2019) concluded that one of the  
 830 two fluid pulses experienced by the Rousse system was due to Eocene Pyrenean tectonic  
 831 compression. By measuring the difference between the trapped FI pressure and the  
 832 hydrostatic pressure gradient, an overpressure of nearly 80 bars can be estimated. Such  
 833 an overpressure is very common in oil-producing anticlines.

834 Further evidence that supports the hydrothermal activity are data provided by the well LA-  
 835 415 (400m east of LA-37, Figs. 1 and 2). This horizontal NNE-SSW-oriented well on the  
 836 crest of the Lacq anticline penetrated the productive reservoirs of Upper Lacq and cross-  
 837 cut N100° and N60° trending vertical fractures (Fig. 17). The close association of fractures  
 838 and dolomite bodies was interpreted as evidence of fracture-controlled hydrothermal  
 839 dolomitization (Lambert et al., 2006).



840  
 841 Figure 17. Schematic model of the distribution of dolomite bodies and fractures in the  
 842 Upper Lacq reservoir based on observations in the well LA-415 (red dashed line). The  
 843 fractures drawn in the scheme are located on the larger scale NE-SW seismic cross  
 844 section (Based on Lambert et al., 2006).

#### 845 5.4 Fluid circulation schemes

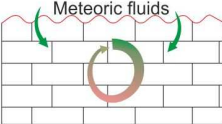
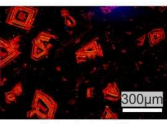
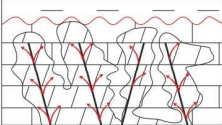
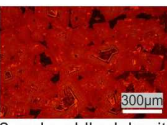
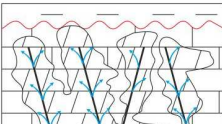
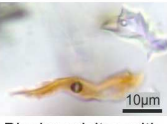
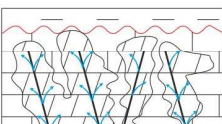
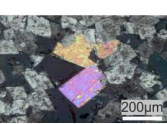
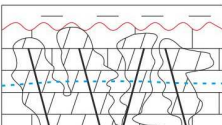
846 A synthesis diagram of all fluids involved in the diagenetic evolution of the Upper  
 847 Cretaceous Upper Lacq reservoir, their circulation pathways and resulting products are  
 848 summarized in figure 18. The early oxidizing meteoric fluids involved in the precipitation of  
 849 the D1 dolomite rhombs are relatively early since the Paleocene seal was not in place to  
 850 prevent the vertical circulation of fluids to the reservoir. Reflux and mixing zone (or dorag)  
 851 dolomitization models can explain this process in a lagoonal and shallow marine setting on  
 852 the carbonate platform behind the Albian reef barrier. The evaporated seawater  
 853 percolating downwards and the interstitial formation fluids provided the Mg required for this





854 minor dolomitization phase. When the Paleocene flysch was deposited, the vertical supply  
855 of meteoric fluids was interrupted. The clay-released fluids from the thick Albo-Aptian  
856 formations in the Southern Lacq basin (Fig. 2) became the dominant fluids involved in  
857 hydrothermal dolomitization (Fig. 18). The Sainte Suzanne Fault, activated during the  
858 Eocene compression, could have provided a pathway for the circulation of deep connate  
859 hot fluids from the Southern Lacq Basin to the relatively cooler, lower pressure area on the  
860 crest of the Lacq anticline. This fault crosscuts the clay-rich Albo-Aptian formations (i.e.  
861 Sainte Suzanne and Assat marls), which, upon fracturing and squeezing, may have  
862 released Mg-rich fluids with low salinity. Additional Mg could have been provided by the  
863 precursor D1 dolomites, which were partially dissolved upon fracturing and brecciation.

864 The early reflux to mixing zone dolomitization model agrees with previous interpretations  
865 that considered the dolomites of Upper Lacq as being early products that precipitated in a  
866 shallow marine evaporitic platform (Bouroullec et al., 1986; Le Marrec et al., 1995).  
867 However, the overpressured hydrothermal activity that formed the bulk of the dolomite  
868 bodies of Upper Lacq was not previously considered.

869



Age	Fluid types and sources	Main events	Schematic illustration (not to scale)	Main product	Supporting evidence
Upper Cretaceous ?	Meteoric and formational fluids	Mg from formation fluids and evaporated seawater Meteoric fluids contribute to oxidizing conditions Mixing zone dolomitization		 D1 dolomites	Early diagenesis, oxidizing conditions, low-temperature end-member that resulted in $\Delta_{47}$ temperature $\sim 60^\circ\text{C}$
Eocene	Hot, deeply buried marine and clay-released Mg-rich fluids	Fracturing and faulting during compression. Change in hydrological system. Orogeny-driven fluid flow. Hydrothermal dolomitization		 D2 and saddle dolomites	Reducing conditions, salinities lower than seawater, $\delta^{18}\text{O}$ of parent fluids in the marine domain, $\Delta_{47}$ temperature $\sim 90^\circ\text{C}$
Eocene	hot, deeply buried Mg-poor fluids and oil-rich fluids	Mg already expelled from the clays. Oil starts migrating from Deep Lacq. Orogeny-driven fluid-flow continues. Hydrothermal fluid circulation		 Blocky calcites with oil and aq. FLs	Reducing conditions, salinities lower than seawater, $\delta^{18}\text{O}$ of parent fluids in the marine domain, fluid trapping temperature $\sim 90^\circ\text{C}$
Eocene	hot, deeply buried marine fluids ?	Same Eocene seawater became oversaturated with respect to sulphates after calcite cementation. Oil already in Upper Lacq.		 Anhydrites	Multiple sulfur isotopes indicate an Eocene seawater origin of the parent fluid of anhydrite
Present-day	Modified groundwater	Lateral supply of groundwater.		Groundwater table at -723m	Drilling reports of present-day operators

 Limestone
  Dolomite
  Paleocene Flysch
  Paleocene unconformity
  Groundwater table

870

871 Figure 18. Summary diagram of fluid circulation schemes with their main products.

872

873 Stress variations in and around a seismically active fault system would affect local fluid

874 pressures and allow the mobilization of considerable volumes of fluids (Sibson et al.,

875 1975). This orogeny-driven style of fluid migration was involved in the dolomitization of the

876 Albian carbonates of the Asón valley in the Basque Cantabrian Basin of northern Spain

877 (López-Horgue et al., 2010), the middle Jurassic oil reservoirs of the Paris Basin (e.g.

878 Carpentier et al., 2014; Mangenot et al., 2018b) and the dolomitized carbonates in the St.

879 George Group of western Newfoundland, Canada (Conliffe et al., 2010). The new

880 fracturing event that preceded calcite cementation probably connected the Upper Lacq

881 reservoir with another reservoir of fluids. This is supported by the fact that the new fluids

882 are depleted with respect to dolomite and the associated oil migration started only with

883 calcite cementation. The new fracturing stage was probably linked to modifications in

884 regional tectonic stress that have affected the intensity of clay dewatering and

885 consequently the amount of Mg expelled. Fluid and basin modeling suggest that also  
886 during the Eocene compression, these circulating fluids were not in thermal equilibrium  
887 with the host rocks (Fig. 16). These Ca-rich fluids have possibly mixed with oil-rich fluids  
888 expelled from the Deep Lacq source rocks as new fluid pathways opened and the  
889 connection with new fluid reservoirs started during this second fracturing stage. The origin  
890 of oil in Upper Lacq is debated given complexities in the structural and thermal evolution of  
891 the petroleum system (Connan and Lacrampe-Couloume, 1993; Le Marrec et al., 1995;  
892 Serjouné, 1995; Houzay et al., 2008). However, the most probable scenario is a  
893 dysmigration from the Deep Lacq source rocks passing through the Albian reefs. This  
894 circulation scheme was documented by the correlation of sterane distribution patterns  
895 between the Deep Lacq source rocks, Albian reefs and oils of the Upper Lacq reservoir.  
896 Connan and Lacrampe (1993) concluded that oils found in Upper Lacq migrated from the  
897 Jurassic-Barremian sources rocks laterally through the reef to accumulate in Upper Lacq.  
898 The abundance in oil inclusions observed in the Albian reef samples is also in agreement  
899 with this scenario of oil migration. Therefore, lateral flow of connate (marine) fluids mixed  
900 with the migrating oil and precipitated blocky calcites rich in oil and aqueous inclusions.

901 Multiple sulfur isotopes indicate an Eocene marine origin for the parent fluids of anhydrites.  
902 Thermodynamically, the solubility of calcite is reduced in sulphate rich solutions and  
903  $\text{CaCO}_3$  would be the first mineral that precipitates (Li and Duan, 2011). Since the timing of  
904 calcite cementation is also mid-Eocene in age, we suggest that the marine parent-fluid of  
905 anhydrite was the same as the parent-fluid of calcites. Because of the precipitation of  
906 blocky calcite, the fluid became gradually depleted in  $\text{CO}_3^{2-}$  and permitted the precipitation  
907 of anhydrite (Fig. 18). The precipitation of this sulphate phase is typical for solutions  
908 originating from marine to modified marine fluids as documented in the Devonian  
909 reservoirs of Alberta, Canada (Butler, 1970; Mountjoy et al., 1999; Machel, 2004).

910 Finally, during uplift and telogenesis, differences in hydraulic heads from nearby elevated  
911 areas would provide a suitable driving mechanism for the lateral supply of the crest of the  
912 anticline with the present-day groundwater (Fig. 18).

## 913 6 Conclusion

914 A revised paragenesis for the Upper Cretaceous Upper Lacq oil reservoir is presented  
915 where the evolution of the Pyrenean domain and the Aquitaine foreland basin have played  
916 a major role in controlling the timing of carbonate reservoir diagenesis. We argue that at  
917 least three fluid sources were involved in the diagenetic modifications of the Upper Lacq  
918 reservoir.

919 After shallow-marine carbonate deposition and early bacterial diagenesis during the Late  
920 Cretaceous, a mixture of marine fluids during reflux evaporation in a lagoonal setting,  
921 together with formational fluids allowed the precipitation of the early D1 dolomite phase.  
922 Microthermometric and chemical evidence support a model with multiple fluid pulses  
923 driven by regional orogenic forces. After the deposition of the Paleocene seal and during  
924 the Major orogenic compressive phase, Mg-rich, low salinity, hot, relatively deep fluids  
925 from the Southern Lacq Basin migrated along the Saint Suzanne and Lagor thrust faults,  
926 under a state of thermal disequilibrium being at least 30-40°C hotter than the ambient host  
927 rocks. These fluids dolomitized the Upper Lacq reservoir. After the end of Mg expulsion  
928 from Albian clays of the Southern Lacq Basin, due to modifications in regional tectonic  
929 stress, hot low-saline fluids continued to be squeezed out of this basin and towards Upper  
930 Lacq. The combination of the Mg-poor, hot, low salinity fluid from the Southern Lacq Basin  
931 and the oil that migrated from the Deep Lacq source rocks precipitated blocky calcites rich  
932 in oil and aqueous inclusions. AIT-PIT and basin modeling also suggest an Eocene timing  
933 for this fluid pulse. After calcite cementation, the remaining fluids became oversaturated  
934 with respect to sulphates and a minor phase of anhydrite precipitated. The timing of  
935 anhydrite precipitation is supported by the multiple sulfur isotopes that indicate an Eocene  
936 seawater signature of the parent fluid. Finally, during telogenesis, oxidizing fluids were

937 reintroduced possibly by lateral input because the overlying Paleocene flysch seal would  
938 inhibit downward percolation of fluids.

939 In conclusion, by using a multidisciplinary petrographic, geochemical and modeling  
940 approach we provide evidence that the main diagenetic events in the southern Aquitaine  
941 basin were mainly linked to the Pyrenean convergence during the Eocene. Even if a minor  
942 early dolomitization event cannot be totally ruled out, orogeny-driven hydrothermal  
943 dolomitization is the principal mechanism that affected the Upper Cretaceous carbonate  
944 reservoirs in the Lacq area.

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