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1 U/Pb dating of geodic calcite: new insights on Western
2 Europe major tectonic events and associated diagenetic fluids

3 Céline Pisapia ^{1,2,*}, Pierre Deschamps ¹, Anne Battani ^{2,b}, Stéphane Buschaert ^{2,c}, Abel
4 Guihou ¹, Bruno Hamelin ¹ & Jacques Brulhet ²

5 ¹ CEREGE, Aix-Marseille Université-CNRS-IRD, Europôle Méditerranéen de l'Arbois,
6 13545 Aix-en-Provence, France

7 ² Andra, 1-7 rue Jean Monnet, 92290 Châtenay Malabry, France

8

9 ^{*}^a Corresponding author/Present adress:

10 Institut de Physique du Globe de Paris, 1 rue Jussieu, 75238 Paris Cedex 05, France

11 Tel : +33 (0)1 83 95 75 95 – Fax : +33 (0)1 83 95 77 05

12 e-mail: celine.pisapia@gmail.com

13 ^b Present address: IFPEN, 1-4 Av. de Bois-Préau, 92852 Rueil-Malmaison Cedex, France

14 ^c Present address: BRGM, 151 Bd Stalingrad, 69626 Villeurbanne, France

15

16

17 **Abbreviated title:** U-Pb dating of diagenetic events

18

19 **Abstract**

20 This study presents the first application of the U/Pb dating method to highly Pb-depleted
21 diagenetic geodic calcites of the Jurassic formations of the Paris basin that leads to a
22 reappraisal of the palaeohydrogeology history of this region. Composite U/Pb ages from
23 multiple geodes, combined with $\delta^{18}\text{O}$ analyses, reveal two main phases of diagenetic fluid
24 circulations linked with major regional tectonic events. Dogger formations recorded a first
25 diagenetic fluid episode at 147.8 ± 3.8 Ma, i.e. at the very beginning of the emersion of the
26 basin during the Tithonian period and 30Ma earlier than previously assumed. $\delta^{18}\text{O}$ results
27 confirmed that most of the calcitic cement phases that closed the porosity of these formations

28 precipitated at the beginning of the Cretaceous period. Oxfordian formations recorded
29 another major meteoric fluid circulation at 33.5 ± 2.8 Ma, which can be related to the initial
30 stage of the European Cenozoic Rift System (ECRIS), implying that the porosity of the
31 Mesozoic formations was closed sooner than previously thought, before the main ECRIS
32 rifting phase of Oligocene age. This study shows that U/Pb dating of secondary geodic calcite
33 offers a new powerful way for reconstructing the coupled palaeohydrological and diagenetic
34 history of sedimentary basins.

35

36 **Keywords**

37 U/Pb dating, geodic calcites, diagenetic phases, palaeohydrology, Paris Basin, ECRIS

38

39

40 Determining the relative and absolute timing of fluid flow events is of critical
41 importance for understanding the past history of sedimentary basins and their geological
42 reservoirs, but also their role on the modification of the petrophysical properties of rocks, on
43 the formation and migration of hydrocarbons, or their stability for potential deep geological
44 disposal of radioactive wastes. During fluid flow events, secondary carbonates commonly
45 precipitate to fill the porosity or voids, therefore occurring as infilling cements or spar
46 calcites in geodic form. These secondary carbonates are thus relics of main fluid circulations
47 during sedimentary basin evolution and/or tectonic events. Fluid history in sedimentary
48 basins is generally reconstructed by combining petrographical and geochemical approaches
49 (fluid inclusions thermometry, stable isotopes...) allowing identification between different
50 diagenetic phases (e.g. Evans & Zalasiewicz 1996; Neymark *et al.* 2002; Worden *et al.*
51 1999). However, in most cases such approaches provide only a relative chronology of the
52 past fluid events due to the lack of appropriate absolute dating methods. One drastic point is
53 thus to have access to a reliable way of dating these diagenetic events to reconstruct the
54 paleohydrogeological and tectonic history of the basins.

55 Although lead-lead and uranium-lead methods have been extensively used for dating
56 silicates and accessory minerals for decades, direct dating of carbonates is less developed
57 (Rasbury & Cole 2009). Following the first study of Moorbath *et al.* (1987), Pb/Pb dating
58 were performed on uranium and lead-enriched (>1ppm) limestones and marbles (e.g.
59 Babinski *et al.* 1999; Jahn & Simonson 1995). The first U/Pb dating of carbonates with lower
60 uranium contents (100-500 ppb) was then reported by Smith *et al.* (1991) followed by studies
61 on quaternary corals (Getty *et al.* 2001) or speleothems (Cliff *et al.* 2010; de Ruiter *et al.*
62 2009; Pickering *et al.* 2010; Richards *et al.* 1998; Woodhead *et al.* 2006). A first study on
63 diagenetic calcite concretions was reported by Israelson *et al.* (1996) on U and Pb-rich
64 calcites with one of the highest μ ratio ($\mu = {}^{238}\text{U}/{}^{204}\text{Pb}$) ever registered on carbonate samples

65 ($\mu = 288\ 000$). Further studies showed the potential of the U/Pb method for directly
66 calibrating the geological timescale or constraining the diagenetic history of sedimentary
67 formations (Becker *et al.* 2002; Li *et al.* 2014; Luczaj & Goldstein 2000; Neymark *et al.*
68 2002; Rasbury *et al.* 1997). Recent advances in LA-ICP-MS have allowed investigating U/Pb
69 dating of secondary carbonates in calcite-mineralized faults characterized by low Pb content
70 (Coogan *et al.* 2016; Roberts & Walker 2016) but as a matter of fact, only few studies that
71 report U /Pb dating of Pb-depleted secondary carbonates.

72 The Paris Basin is an intracratonic basin formed during the Permian rifting that
73 affected the Cadomian-Variscan basement of Western Europe (Guillocheau *et al.* 2000). Its
74 tectonic and sedimentary history began with a major transgressive phase, induced by the
75 Pangaea fragmentation, and marked by Permian lacustrine to Jurassic carbonated platforms
76 sedimentation at the northern part of the Tethys platform. It was followed by a main
77 regressive phase with three major continentalization phases. First, at the upper Jurassic/lower
78 Cretaceous, the opening of the Bay of Biscay induced a fragmentation of the Jurassic
79 platform and the uplift of its northern Variscan border associated with continental
80 sedimentation. This regressive trend was marked by the Late Cimmerian unconformity
81 (LCU) at the Jurassic/Cretaceous limit (Guillocheau *et al.* 2000). Then, the upper Cretaceous
82 compressional tectonics (Africa-European convergence) induced an enhanced
83 continentalization with an evolution from marine distal formations to continental depositional
84 environments. It was accompanied by erosion processes, and increased uplift of the Variscan
85 borders. The continentalization is then definitive at the upper Oligocene. Cenozoic
86 formations were thus mainly influenced by the N-S compression of the Pyrenean phase of
87 late Eocene age (40Ma) followed by E-W extension during the European Cenozoic Rift
88 System event (ECRIS) (Dèzes *et al.* 2004; Guillocheau *et al.* 2000). The ECRIS event
89 developed as passive rifting in the foreland of the Alps and the Pyrénées. It induced the

90 formation of the main grabens in Western Europe (e.g. Upper and Lower Rhine, Limagne,
91 Bresse and Eger grabens) from the North Sea to the Mediterranean sea over more than 1000
92 km and is strongly recorded in the eastern part of the Paris Basin (Dèzes *et al.* 2004). All
93 these extensional events induced a major fracturation network of the Mesozoic formations
94 allowing meteoric fluids to percolate, and the precipitation of secondary carbonated phases.
95 ECRIS is commonly described to begin at the late Eocene, by reactivation of Variscan,
96 Permo-carboniferous and Mesozoic faults, with a main extensional episode during the
97 Oligocene period (Dèzes *et al.* 2004; Schumacher 2002). The exact chronology of this
98 extensional tectonics is not precisely known but it is generally described to be younger than
99 the Priabonian P16 zone (35.2-34 Ma) (Berggren *et al.* 1985; Guillocheau *et al.* 2000).
100 Nevertheless, evidences of shallow depressions in the Upper Rhine or Bresse grabens with
101 fluvio-lacustrine sediments might be attributed to an initial rifting phase at the middle Eocene
102 period (Dèzes *et al.* 2004; Sissingh 1998) and the debate is still open as no absolute dating
103 constraints exist.

104 The main objective of this study was thus to bring for the first time absolute age
105 constraints on major tectonic events that affected Western Europe through U/Pb dating of
106 secondary diagenetic geodic calcites. A precise dating of major fluid circulation episodes
107 induced by the first emersion phase of the Paris Basin border and by the activation of the
108 European Cenozoic RIft System event (ECRIS) was thus achieved and gave new insights on
109 these major geological events that affected the European plate.

110

111 **Geological Setting**

112 The Eastern part of the Paris Basin (France) is characterized by Carboniferous to Cenozoic
113 sedimentary formations with a monocline structure slightly dipping westwards due to the
114 subsidence of the center part of the basin (Guillocheau *et al.* 2000). Oxfordian and Dogger

115 limestones embed the Callovo-Oxfordian clayrock unit (COx) that was recognized by the
116 French National Radioactive Waste Management Agency (Andra) as a favorable host rock
117 formation for radioactive waste disposal for High-Level and Intermediate-Level Long-Lived
118 Radioactive Wastes (HLW-LL and ILW-LL) (Delay *et al.* 2007). This area experienced
119 various tectonic phases from the end of the Mesozoic till the Oligocene extension tectonics
120 and the Rhine graben formation but presents limited impact of deformation (low seismicity,
121 little deformation and vertical displacement). These formations are affected by a fracturation
122 network, which is responsible for the compartments segmentation of the basin. Several
123 grabens are present at the south of the Andra Underground Research Laboratory (URL)
124 (Joinville, Gondrecourt and Neufchateau graben) as witnesses of the Oligocene extensional
125 tectonics (Fig. 1). The sedimentary sequence was investigated by a deep borehole drilling
126 program (Delay *et al.* 2007) and presents continuous deposits from Lower Cretaceous to
127 infra-Jurassic formations.

128 The COx formation (150-160Ma) is a low-porosity detrital claystone cemented by 25-30
129 wt% of microcrystalline calcite. Its diagenetic history occurred quite early in a marine
130 environment since no major modification was noticed after. Furthermore, the calcite cements
131 of this formation present $\delta^{18}\text{O}$ values typical of unmodified marine calcite indicating that the
132 COx has not been affected by further fluid circulations (Buschaert *et al.* 2004).

133 The diagenetic history of the embedding Oxfordian and Dogger limestones is more complex.
134 These formations are affected by several generations of stratiform stylolites and dissolution
135 veins, filled with detrital clay minerals and secondary minerals such as pyrite or dolomite
136 (Andre *et al.* 2010). Thorough examination of U-series disequilibrium within these
137 stylolitized zones has shown systematic ($^{234}\text{U}/^{238}\text{U}$) activity ratio disequilibria (Deschamps *et*
138 *al.*, 2004) indicating uranium remobilization and active transfer related to these
139 pressure/dissolution structures. Nevertheless, this uranium remobilization is limited to a few

140 centimeters range apart from the stylolites and the whole carbonates present a ($^{234}\text{U}/^{238}\text{U}$)
141 activity ratio at equilibrium. These embedding limestones have very low porosity (2-5%) and
142 permeability (10^{-9} to 10^{-10} m.s $^{-1}$) (Battani *et al.* 2011). By contrast with the CO $_x$ formation,
143 they rarely show the preservation of typical structures of early marine cements (micro-
144 crystalline cement and small euhedral crystals of micro-spar). The primary and secondary
145 porosities, as well as macro-cavities and micro-fractures, are mainly infilled by secondary
146 sparry calcites. The remaining inter-particle porosity is infilled by large crystals of sparite
147 isotopically similar to those observed in macro-cavities and in fractures inherited from the
148 Eocene-Oligocene extension (Buschaert *et al.* 2004). Successive generations of blocky
149 calcites (Cal1, Cal2, Cal3 and Cal4) were identified by microscopic observations (Carpentier
150 *et al.* 2014). Based on oxygen and carbon isotopic analyses, they were interpreted as
151 precipitated from meteoric fluids with carbon of local origin (Brigaud *et al.* 2009; Buschaert
152 *et al.* 2004; Carpentier *et al.* 2014; Vincent *et al.* 2007). This excludes an early diagenetic
153 cementation phase by marine fluids and marks later diagenetic events. Cal1 (former BC1
154 from Brigaud *et al.* 2009) were then assumed to precipitate at the early Cretaceous (during
155 LCU) following the uplift of the London-Brabant massif, Cal2 (former BC2 from Brigaud *et*
156 *al.* 2009) during the Late Aptian Unconformity (LAU) that was associated with erosion and
157 karstification of the Paris Basin borders and Cal3 to the Pyrenean compression. Finally, Cal4
158 (former BC3 from Brigaud *et al.* 2009) was related to the Oligocene extension tectonics with
159 the formation of main regional grabens and associated terrestrial sedimentation (Brigaud *et*
160 *al.* 2009; Carpentier *et al.* 2014). Nevertheless, no absolute geochronological constraints are
161 available for these blocky calcites and the question is still subject to debate (Andre *et al.*
162 2010; Brigaud *et al.* 2009; Buschaert *et al.* 2004; Vincent *et al.* 2007). The main purpose of
163 this study was thus to date precisely these phases of fluid circulation thanks to secondary

164 geodic calcites U/Pb dating in order to refine the geological history of the Paris Basin and to
165 give new insights on the major tectonic events that affected Western Europe.

166

167 **Material and Methods**

168 *Geodic calcite samples*

169 Geodic calcites were sampled from 3 Andra boreholes (HTM102, EST205 and EST433
170 boreholes, Fig. 2). HTM102 core was drilled 3 km SE from the URL through upper
171 Oxfordian to upper Bathonian formations; EST205 borehole was drilled at the URL through
172 Kimmeridgian to Oxfordian formations and EST433 borehole was drilled 8km NNW from
173 the URL through Kimmeridgian to Bundstandstein formations. Oxfordian calcites were
174 sampled from HTM102 and EST205 cores and Dogger calcites from EST433 core (Table 1).
175 Six geodes were investigated in the Oxfordian sediments from 256 m to 331 m for HTM102
176 (5 geodes) and at 375 m for EST205 (1 geode). 13 sub-samples were analyzed from these 6
177 geodes. Three geodes were investigated in the Dogger formation from 799 m to 890 m for
178 EST433 and 9 sub-samples were analyzed. Geodic calcites were carefully sampled using
179 clean diamond drills only devoted to this study and cleaned by successive ultrasonic baths
180 with mQ H₂O.

181 Geodic samples were automorphic millimetric to centrimetric semi-translucent calcite
182 minerals with no oxidation traces. The selected geodes were not connected to stylolites to
183 avoid any recent uranium remobilization (Deschamps *et al.* 2004).

184

185 *Chemical preparation*

186 Prior to sample dissolution, a ²⁰⁵Pb-²³⁶U-²³³U-²²⁹Th spike was added to each sample. The
187 spike solution was primarily calibrated by analyzing the spike solution alone, with various
188 amounts of a mixed solution of NBS-981 Pb and NBS-960 U standards, and in reference to

189 the nominal value of 137.88 for $^{238}\text{U}/^{235}\text{U}$ of natural uranium and to the concentrations of
190 NBS standards. Values of 0.95883 ± 0.00059 and $5.4677 \pm 0.0034 \text{ pmol.g}^{-1}$ were determined
191 for $^{205}\text{Pb}/^{233}\text{U}$ ratio and Pb concentration of the spike solution, respectively.

192 The chemical separation and purification of lead and uranium isotopes procedure were
193 adapted from Babinski *et al.* (1995) and Horwitz *et al.* (1992), respectively. Calcites samples
194 ranging from 140 mg to 400 mg were dissolved with a slight stoichiometric excess of 0.6N
195 HBr. Samples were directly loaded on previously cleaned AG1X8 resin (100-200 mesh, 200
196 μL) converted into HBr form with 0.6N HBr. Both sample loading and rinsing steps were
197 recovered and kept for uranium purification. Pb fraction was eluted by 6N HCl and was
198 evaporated to dryness at 120°C . Two successive purification steps of Pb samples were
199 performed after loading on AG1X8 (50 μL) and elution with 6N HCl. Taking into account
200 the very low lead concentrations of the samples, the recovery yield of this protocol was
201 carefully optimized to obtain nearly 100 %.

202 Uranium fractions were recovered after co-precipitation with iron hydroxide, dissolution with
203 4N HNO_3 and loading on previously cleaned UTEVA resin converted into nitric form with
204 4N HNO_3 . Uranium samples were eluted with mQ H_2O and evaporated to dryness (120°C). A
205 purification step was performed on UTEVA resin following the same protocol.

206 Final uranium and lead samples were evaporated to dryness with one H_3PO_4 drop.

207 Similar procedures without calcite samples were conducted for lead and uranium blanks
208 determination (concentration and isotopic composition).

209

210 ***U and Pb isotopic analyses***

211 Uranium and lead isotopic compositions were determined by Thermal Ionization Mass
212 Spectrometry (VG sector-54). Lead samples (from 0.7 to 9.2 ng) were prepared with 2.8 μL
213 of silica gel and loaded on pre-degassed rhenium monofilaments. Uranium samples (from 6.5

214 to 307.2 ng) were dissolved with 1 μ L HNO₃ 0.05N and were loaded on individual pre-
215 degassed rhenium monofilaments between two graphite lays.

216 Uranium isotopes signals (²³³U, ²³⁴U, ²³⁵U, ²³⁶U, ²³⁸U) and lead isotopes signals (²⁰⁴Pb, ²⁰⁵Pb,
217 ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb) were measured on a Daly ion counter with a 20 ns and 22 ns dead-time
218 value, respectively. Data considered in this study formed a linear array in both ²⁰⁷Pb/²⁰⁶Pb vs.
219 ²⁰⁴Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb vs. ²⁰⁴Pb/²⁰⁶Pb diagrams and were aligned for both Oxfordian and
220 Dogger samples (Fig. S1). Replicates of NBS SRM-981 standard gave an external
221 reproducibility of 0.5 ‰ for ²⁰⁸Pb/²⁰⁶Pb ratio (2.1636 \pm 0.012) and of 2.9 ‰ on ²⁰⁴Pb/²⁰⁶Pb
222 ratio (0.059292 \pm 0.00018). Replicates of NBS SRM-960 standard gave an external
223 reproducibility of 1.5 ‰ on ²³⁵U/²³⁴U ratio (136.8892 \pm 0.1993). The uranium (²³⁴U/²³⁸U)
224 activity ratio was calculated using the decay constants $\lambda^{234}\text{U} = 2.8263 \cdot 10^{-6}$ (Cheng *et al.*
225 2000) and $\lambda^{238}\text{U} = 1.5513 \cdot 10^{-10}$ (Jaffey *et al.* 1971) and was checked to be at equilibrium for
226 the samples considered in this study.

227 Uranium and lead blank concentrations and isotopic compositions were determined for each
228 analytical series. Uranium blanks were very good around 10 pg (10 \pm 3 pg, n = 4) for all
229 analytical sessions except for the first session (187 pg). These values were similar and in the
230 lower range of published data in similar conditions (Getty & de Paolo 1995; Grandia *et al.*
231 2000; Israelson *et al.* 1996; Pickering *et al.* 2010; Smith *et al.* 1991). Lead blanks obtained all
232 along analytical sessions (117 \pm 37 pg, n = 5) were in the range of published data on similar
233 size (100 to 400 mg) calcite samples (Becker *et al.* 2002; Cliff *et al.* 2010; Getty & de Paolo
234 1995; Israelson *et al.* 1996; Pickering *et al.* 2010; Polyak *et al.* 2008; Richards *et al.* 1998;
235 Smith *et al.* 1991). Nevertheless, the analyzed Pb amounts (from 0.8 ng to 8.1 ng for
236 Oxfordian samples and from 1.2 ng to 5.1 ng for Dogger samples) were in the lower range of
237 published data on continental carbonates (Cliff *et al.* 2010; de Ruiter *et al.* 2009; Getty *et al.*
238 2001; Pickering *et al.* 2010; Richards *et al.* 1998). Consequently, Pb blanks from chemical

239 procedures were not negligible and corresponded to $4 \pm 3\%$ in average of the sample Pb
240 content and up to 15 % for samples with the lowest Pb content, which can significantly
241 contribute to total final error of data. Isotopic raw data were then treated according to the
242 data-reduction technique proposed by Schmitz & Schoene (2007). Each sample was corrected
243 from the isotopic composition and concentration of the associated blank sample prepared and
244 analyzed during the same analytical session, and with an additional error corresponding to the
245 standard error of all the Pb blank concentrations. The accuracy of this correction and
246 influence on age calculation were checked by comparing results obtained from data before
247 and after blank corrections (Fig. S2 and Table S1).

248 U/Pb isochrons were constructed using Isoplot software 3.0. from Ludwig (2003).
249 Considering that analyzed calcites came from different samples precipitated from fluids with
250 possible different initial lead isotopic composition, model 2 and 3 solutions from Isoplot
251 software were used to calculate ages.

252

253 *$\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ analyses*

254 Stable isotopic analyses ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) were conducted on crushed geodic calcite samples
255 using a mass spectrometer (Finnigan Delta Advantage) equipped with a carbonate device.
256 Measured isotopic values were normalized against international standard NBS-19. Mean
257 external reproducibility was better than 0.03 ‰ for $\delta^{13}\text{C}$ and 0.05 ‰ for $\delta^{18}\text{O}$. Each geode
258 was analyzed with 3 aliquots of 60 μg weight each.

259

260 **Results**

261

262 *U and Pb isotopic compositions of geodic calcites*

263 Results obtained on calcites from geodes are summarized Table 1.

264 All geodic calcites considered for this study presented very low concentration of Pb, ranging
265 from 3.4 to 21.7 ppb and from 4.2 to 17.5 ppb for Oxfordian and Dogger samples,
266 respectively. They also presented relatively low radiogenic ^{206}Pb signals with $^{206}\text{Pb}/^{204}\text{Pb}$
267 ratio from 23.1 ± 0.3 to 95.6 ± 18.8 for Oxfordian geodes and from 26.0 ± 0.3 to 110.8 ± 4.1
268 for Dogger geodes.

269 Samples presented more variable concentrations of U (from 43.8 to 782.4 ppb and from 22.2
270 to 331.8 ppb for Oxfordian and Dogger geodes, respectively) with μ ratios ($^{238}\text{U}/^{204}\text{Pb}$) from
271 256.3 ± 4.2 to 13258.6 ± 2849.6 and from 243.5 ± 1.8 to 3916.4 ± 155.6 for Oxfordian and
272 Dogger geodes, respectively (Table 1).

273 Oxfordian and Dogger samples were then used for isochron reconstructions with Isoplot 3.0
274 software (Ludwig 2003). In both cases, absolute dating was achieved from composite
275 isochrons obtained from several sub-samples from different geodes sampled at different
276 depths and from several drill cores. The calculated ages are then likely to represent regional
277 fluid flow episodes. Two distinct patterns were observed for Oxfordian and Dogger samples.

278 Data were plotted on Tera-Wasserburg diagrams (Fig. 3) and gave an age of 33.5 ± 2.8 Ma
279 for the Oxfordian samples (MSWD = 23, model 2 solution, 95% confidence) and of $147.8 \pm$
280 3.8 Ma (MSWD = 41, model 2 solution, 95% confidence) for the Dogger samples.

281 Considering the limited size of each geode, sub-sampling was not sufficient to achieve a
282 complete dating of each geode. It was only possible to determine an isochron age for a single
283 geode (G10) from the Dogger formation. The 6 sub-samples of this geode exhibited an age of
284 144.6 ± 9.2 Ma (MSWD = 27, model 2 solution, 95% confidence) on a Tera-Wasserburg
285 diagram and of 145.2 ± 8.9 Ma (MSWD = 32, model 3 solution, 95% confidence) on a ^{238}U -
286 ^{206}Pb plot (Fig. 4). These results were consistent with the calculated ages from the global
287 composite isochrons obtained for Dogger samples (Figs. 3b and S3b,d).

288 The initial lead isotopic compositions were calculated to be 20.7 ± 2.2 for $^{206}\text{Pb}/^{204}\text{Pb}$ and
289 15.8 ± 0.2 for $^{207}\text{Pb}/^{204}\text{Pb}$ for the Oxfordian geodes and of 20.4 ± 1.2 for $^{206}\text{Pb}/^{204}\text{Pb}$ and 15.8
290 ± 0.1 for $^{207}\text{Pb}/^{204}\text{Pb}$ for the Dogger geodes, thus indistinguishable from each other.

291

292 *Geodic calcites $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ composition*

293 Results from stable isotopes are summarized Table 2 and Fig. 5 for all geodes. They were
294 reproducible from one aliquot to another for each geode and between different analytical
295 sessions. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data (Fig. 5) were in agreement and within the range of previous
296 published data on spar cements, vugs or fracture infillings of Mesozoic carbonated
297 formations of the Eastern part of the Paris Basin (Andre *et al.* 2010; Brigaud *et al.* 2009;
298 Buschaert *et al.* 2004; Carpentier *et al.* 2014; Vincent *et al.* 2007). Similarly to U/Pb dating,
299 two patterns were observed between Oxfordian and Dogger samples. All geodes from
300 Oxfordian sediments (G1 to G6) presented the same $\delta^{18}\text{O}$ range values between -10.24 ‰_{PDB}
301 and -8.95 ‰_{PDB} (mean $\delta^{18}\text{O}_{\text{PDB}} = -9.28 \pm 0.46$ ‰) and $\delta^{13}\text{C}$ values between $+2.22$ ‰_{PDB} and
302 $+2.70$ ‰_{PDB} (mean $\delta^{13}\text{C}_{\text{PDB}} = +2.5 \pm 0.2$ ‰). These data fell into the range of the previously
303 described Cal4 blocky calcite (Fig. 5). Similarly, all geodes from Dogger samples (G8 to
304 G10) had the same $\delta^{18}\text{O}$ range values between -6.72 ‰_{PDB} and -6.42 ‰_{PDB} (mean $\delta^{18}\text{O}_{\text{PDB}} =$
305 -6.54 ± 0.15 ‰) and $\delta^{13}\text{C}$ values between $+1.92$ ‰_{PDB} and $+2.49$ ‰_{PDB} (mean $\delta^{13}\text{C}_{\text{PDB}} =$
306 $+2.2 \pm 0.3$ ‰) corresponding to the Cal2 blocky calcite range (Fig. 5).

307

308 **Discussion**

309 *U/Pb dating of Pb-depleted geodic calcites*

310 To our knowledge, this is the first time that U-Pb dating was made directly on highly Pb-
311 depleted diagenetic geodic calcite samples for paleohydrogeology reconstructions in a
312 sedimentary basin. As mentioned by Rasbury and Cole (2009), U-Pb dating of carbonate

313 samples require a particular attention during the analytical steps (choice of sample, chemical
314 procedure and blanks contribution, isotopic analyses). The main bias when dating Pb-
315 depleted carbonates samples resides in the chemical procedure and blanks correction. As
316 explained before, our data were then carefully corrected from Pb blanks using the data-
317 reduction technique from Schmitz & Schoene (2007).

318 Isochron reconstructions gave MSWD higher than 1 in all cases (Fig. 3). We have thus to
319 consider our results as errochrons, which is commonly observed for carbonate samples (e.g.
320 de Ruiter *et al.* 2009; Getty *et al.* 2001; Pickering *et al.* 2010; Rasbury & Cole 2009). Part of
321 this high MSWD might be explained by analytical errors. Notably internal errors on our data
322 were very low, inducing small error ellipses and artificially increasing MSWD values as
323 previously evoked by Cole *et al.* (2005). This point was confirmed by the small MSWD
324 obtained on ^{235}U - ^{207}Pb plots (0.15 and 0.56 for Oxfordian and Dogger samples, respectively,
325 Fig. S3) with larger analytical errors and error ellipses. Similarly, it is confirmed by the
326 strong influence of Pb blank correction and error propagations on MSWD values (Table S1).

327 We observed a great decrease of MSWD values after age calculations from data corrected
328 from Pb blanks relative to calculations from data not corrected from Pb blanks, whereas no
329 influence was observed on calculated ages. But, the high MSWD obtained from the Terra-
330 Wasserburg plots might not be totally explained by analytical errors. This high scatter of the
331 isochron data may be induced by (i) variation in the initial disequilibrium (mainly $^{234}\text{U}/^{238}\text{U}$)
332 between the intermediate daughters of uranium series, (ii) open-system conditions with gain
333 or loss of intermediate compounds or (iii) heterogeneity of initial Pb isotopic composition
334 (Cole *et al.* 2005). This last point was also evoked by Rasbury & Cole (2009) who have
335 shown that slight variations of the initial lead isotopic compositions may induce non-
336 negligible MSWD variations. In this study, the great concordance of the calculated ages for
337 ^{238}U and ^{235}U decay series and Tera-Wasserburg Concordia (34.6 ± 3.1 Ma, 29.7 ± 9.2 Ma

338 and 33.5 ± 2.8 Ma, respectively for Oxfordian samples and 147.1 ± 3.5 Ma, 152.8 ± 7.7 Ma
339 and 147.8 ± 3.8 Ma, respectively for Dogger samples, Figs. 3 and S1) advocates for a
340 minimal influence of $^{234}\text{U}/^{238}\text{U}$ disequilibria and allows to rule out any secondary opening of
341 the system (Cole *et al.* 2005). At the contrary, age calculations were done from composite
342 isochrons using geodic calcites sampled at different depths and from different cores a few
343 kilometers away in the basin (Figs. 1 and 2). They are representative of fluid flow events at a
344 regional scale. Geodes used for these calculations may then have been precipitated from
345 fluids with slight fluctuations of the initial lead isotopic composition. These latter, inherent to
346 natural carbonated environments, were similarly often assumed to be responsible for quite
347 large MSWD of calculated isochrons (de Ruiter *et al.* 2009; Getty *et al.* 2001; Pickering *et al.*
348 2010). Moreover, we cannot also rule out that part of the scatter around the isochron lines
349 reflected in high MSWD is tied to the duration of the precipitation of calcite in vugs. Inherent
350 to the use of U/Pb isochrons is that formation of the analyzed phase is instantaneous. This
351 assumption is very likely no longer valid when the method is applied to geodic calcites that
352 witness to processes such as fluid circulations and porosity sealing which might have
353 occurred during time-laps of a few million years. Consequently, in this study, high MSWD
354 might then reflect geological processes such as heterogeneity of natural fluids or duration of
355 diagenetic events as well as low data internal errors. For these reasons, we can reasonably
356 consider that the calculated ages reflect major geological events occurring at a regional scale
357 in the investigated area.

358

359 ***Paleofluids circulations and major related tectonic events.***

360 *Fluids composition and origin*

361 The stable isotopic composition in oxygen and carbon of the analyzed geodes
362 indicated two patterns in agreement with previous published data (Andre *et al.* 2010; Brigaud

363 *et al.* 2009; Buschaert *et al.* 2004; Carpentier *et al.* 2014; Vincent *et al.* 2007). Indeed, except
364 Vincent *et al.* (2007) who obtained a -9 ‰ $\delta^{18}\text{O}_{\text{PDB}}$ value for all spar cements, Brigaud *et al.*
365 (2009), Buschaert *et al.* (2004) and Carpentier *et al.* (2014) reported a wider range for $\delta^{18}\text{O}$
366 values of spar cements and vugs in both Oxfordian and Dogger formations. The different
367 identified blocky calcites presented distinct $\delta^{18}\text{O}_{\text{PDB}}$ values while their $\delta^{13}\text{C}_{\text{PDB}}$ were similar
368 (see Fig. 5). All geodes from Oxfordian formations presented the same range of $\delta^{18}\text{O}$ and
369 $\delta^{13}\text{C}$ values than Cal4 blocky calcites. Similarly, all geodes from Dogger samples presented
370 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data related to Cal2 blocky calcites.

371 As previously mentioned by Buschaert *et al.* (2004), the $\delta^{13}\text{C}$ values of the blocky
372 calcites directly reflect and vary with the ones of the host limestones indicating a local origin
373 of the carbon. Similarly, the $\delta^{13}\text{C}$ values of geodic calcites obtained in this study (Fig. 5)
374 were similar for both Oxfordian and Dogger samples, and consistent with those of the
375 limestones (from 2.04 ‰ to 3.39 ‰) implying a similar local source of the carbon. Based on
376 $\delta^{18}\text{O}$ data and microthermometry calculations from primary fluid inclusions analyses,
377 Brigaud *et al.* (2009), Buschaert *et al.* (2004), Carpentier *et al.* (2014) and Vincent *et al.*
378 (2007) also demonstrated that the blocky calcites, jointly with calcites from vugs and macro-
379 cavities, were precipitated from the input of fresh meteoric waters. These fluids may have
380 circulated thanks to the direct connection of the limestone aquifers with surface water or to
381 the circulation of water through regional fault system (Buschaert *et al.* 2004). Similarly, $\delta^{18}\text{O}$
382 values of geodic calcites were consistent with those of blocky calcites. It highly suggested
383 that geodes might also have been precipitated from meteoric water without any seawater
384 mixing. This tends to confirm that the fluids that precipitated all geodes were of local
385 meteoric origin.

386

387 *Paleohydrological history of the eastern part of the Paris Basin*

388 Two major events were clearly identified from both U/Pb and stable isotopic data of
389 geodic calcites. Considering that analyzed geodes for both Oxfordian and Dogger formations
390 came from different cores and at different depth, we may consider that these two events were
391 related to major phases of fluid circulations and then to regional tectonic events. We can then
392 replace these two events into the tectonic and diagenetic history of the sedimentary basin.

393 The first phase of fluid circulation occurred at 147.8 ± 3.8 Ma and deeply affected the
394 Dogger formations, as determined thanks to global composite isochron (Fig. 3) and to
395 individual geode age calculation (Fig. 4). These geodes from Dogger formations clearly
396 presented the same $\delta^{18}\text{O}_{\text{PDB}}$ range (-6.5 ± 0.2 ‰) than blocky calcites Cal2. We then assume
397 that both analyzed geodes and Cal2 were synchronous in Dogger formations. As the blocky
398 calcites (Cal1 to Cal4) were supposed to be witnesses of major phases of fluid circulations,
399 Brigaud *et al.* (2009) and Carpentier *et al.* (2014) correlated these diagenetic phases to major
400 regional tectonic events and emersion phases. They assumed that Cal1 precipitated during the
401 Late Cimmerian Unconformity (LCU) during early Cretaceous, which is commonly
402 associated to a widespread erosional event in western Europe and to the uplift of the London-
403 Brabant massif and of the Paris Basin borders (Guillocheau *et al.* 2000). They also postulated
404 that Cal2 precipitated later during the Late Aptian Unconformity (LAU) at the Albian/Aptian
405 transition (≈ 113 Ma) that induced a major erosion episode with karstification and ferricrete
406 soil formation. However according to our absolute U/Pb dating of geodes from the Dogger
407 formations at 147.8 ± 3.8 Ma, all the secondary mineral precipitations from Cal1 to Cal2
408 occurred during the Tithonian period, which means ~ 30 Ma sooner than initially proposed by
409 Brigaud *et al.* (2009) and Carpentier *et al.* (2014). This also means that most of the porosity
410 of the Dogger formations was closed at the beginning of the Cretaceous period considering
411 that Cal1 and Cal2 may represent up to 90% of total volume cement in Middle Jurassic
412 limestones (Brigaud *et al.* 2009; Carpentier *et al.* 2014). It is usually postulated that the

413 emerged islands at the end of the Jurassic period were not sufficient to induce large meteoric
414 fluid percolations into Mesozoic formations. Nevertheless, several massifs at the northern and
415 southern borders of the Paris Basin (i.e. Rhenish, Bohemian and London Brabant massifs to
416 the north and Morvan to the south) were shown to uplift as soon as the upper Jurassic linked
417 to the Late-Cimmerian phase tectonics and to the rifting and oceanic accretion of the Bay of
418 Biscay (Beccaletto *et al.* 2011; Schumacher 2002; Thiry *et al.* 2006; Vercoeur & Van den
419 Houtte 1993). This induced an erosion of their Paleozoic to early Mesozoic sedimentary cover
420 between the end of the Jurassic and the late Cretaceous (Thiry *et al.* 2006; Vercoeur & Van
421 den Houtte 1993). This erosion was recorded through karstifications, paleosoils and
422 paleosurfaces that were representative of a residual infra-Cretaceous relief (Quesnel 2003)
423 and were dated from 120 to 140 Ma and up to 160 Ma (Théveniaut *et al.* 2007; Thiry *et al.*
424 2006). Consequently the uplift of these massifs may have favored the emergence of Mesozoic
425 formations and then percolation of meteoric fluids. Nevertheless, if the emergence of the
426 Tithonian formations at the end of the Jurassic period was established, there is no evidence
427 for the emergence of Dogger at that time. It is mainly due to the Late Aptian Unconformity
428 that had truncated LCU and Jurassic formations (Guillocheau *et al.* 2000), but it does not
429 preclude a possible emergence of Dogger formations associated with meteoric fluid
430 percolation at that time. Our U/Pb absolute dating seems to corroborate this hypothesis, and
431 gives new information about the initiation of the infra-Cretaceous unconformity at the
432 Tithonian period. It may imply marked concomitant uplift and erosion processes at that time,
433 bringing Dogger formations at the surface. These data may then indicate that a major phase
434 of meteoric fluid circulation and diagenetic precipitation could have occurred as soon as the
435 Tithonian period inducing the formation of main geodes and all blocky sparites from Cal1 to
436 Cal2 into Dogger formations, and of Cal1 and Cal2 cements in Oxfordian formations. It is
437 also consistent with the microscopic observations that both Cal1 and Cal2 infill F1 fractures

438 assumed to be of Kimmeridgian/Tithonian age and that mainly affected Middle Jurassic
439 formations (Carpentier *et al.* 2014).

440 The second main phase of fluid circulation at 33.5 ± 2.8 Ma was solely recorded in
441 geodic calcites from the Oxfordian formations. It was clearly related to BC3/Cal4 calcites
442 evoked by Brigaud *et al.* (2009), Buschaert *et al.* (2004) and Carpentier *et al.* (2014) with
443 similar mean $\delta^{18}\text{O}_{\text{PDB}}$ values ($\delta^{18}\text{O}_{\text{PDB}} = -9.3 \pm 0.5$ ‰, Fig. 5). Previous studies attributed
444 BC3/Cal4 precipitation to the Eocene/Oligocene extension tectonics, during the ECRIS,
445 considering that BC3/Cal4 $\delta^{18}\text{O}$ values were similar to the ones of the infilling calcites of
446 Eocene/Oligocene fractures. The absolute U/Pb dating of geodic calcites at 33.5 ± 2.8 Ma is
447 consistent with this conclusion. It is also in agreement with the U/Th-He dating attempts of
448 fracture-infilling calcites from the ECRIS-induced fractures at the Gondrecourt graben (Cros
449 *et al.* 2014). Due to He diffusion, U/Th-He dating gave highly variable ages (from 0.2Ma to
450 204Ma) that were not reproducible among 63 samples except for one sample at 29-36Ma.
451 U/Pb dating of geodic calcites shows then accurately the existence of a main phase of
452 meteoric fluid circulation induced by the fracturation of the carbonate formations of the
453 eastern part of the Paris Basin during the ECRIS tectonics. This tectonic event that affected
454 western and central Europe was activated during the late Eocene and was followed by a main
455 rifting phase at the Oligocene. During the Late Eocene, the Alpine foreland was subjected to
456 intra-plate compressional stresses induced by Alpine and Pyrenean collision zones (Dèzes *et*
457 *al.* 2004; Ziegler 1992). These stresses reactivated late Variscan, Permo-Carboniferous and
458 Mesozoic fracture systems that controlled the localization of the main individual grabens
459 such as the Rhine graben in the eastern part of the Paris Basin (Schumacher 2002; Ziegler
460 1992). This area was marked by a widespread Bartonian phase of progressive regional uplift
461 of the graben shoulders accompanied by meteoric fluid circulations and erosion (Sissingh,
462 1998). Our results indicate that large regional meteoric fluid circulations and subsequent

463 precipitation of secondary calcites occurred as soon as late Eocene during the initial phases of
464 rifting. It affected all the Oxfordian formations and finally closed the porosity of the
465 limestones. We cannot exclude that this main phase of fluid circulation could also have
466 affected Dogger formations but to a lesser extent considering that only a few BC3/Cal4
467 samples were identified in Dogger rocks (Brigaud *et al.* 2009; Buschaert *et al.* 2004;
468 Carpentier *et al.* 2014). We can also assume that the porosity of the Dogger formations was
469 already largely closed following the late Jurassic/early Cretaceous diagenetic event. This is
470 the first time that a reliable absolute age is given for ECRIS event. It tends to confirm that
471 this major tectonic phase that affect all Western Europe may have begun from the Late
472 Eocene as soon as 34Ma.

473 These results do not preclude the existence of phases of fluids circulations between
474 148Ma and 34Ma (*i.e.* during the LAU). But we can assume that these potential events, if
475 they occurred, should have been limited by the closure of the porosity of the formations at
476 148Ma and might not have induced major dissolution/reprecipitation of secondary geodic
477 calcites in the carbonated formations of the Eastern part of the Paris Basin.

478

479 **Conclusion**

480 This study presents and discusses the first U/Pb dating of diagenetic geodic calcites,
481 highly depleted in lead, of the Mesozoic formations of the eastern part of the Paris Basin. We
482 have shown that composite isochrons realized from different geodic calcites can allow
483 determining the absolute age of main regional fluid flow events. We also showed that, when
484 geodes are large enough, individual age of one geode can also be determined. In the present
485 study, the obtained results on one geode were consistent with global composite isochron age.
486 These U/Pb analyses, jointly with oxygen and carbon isotopic analyses clearly indicated two
487 main phases of fluid circulation: at 148 Ma and 34 Ma. We have correlated these two phases

488 of fluid circulation and precipitation of calcite to the blocky calcite phases previously
489 described in the literature. The absolute chronology obtained for the two major diagenetic
490 events allow us to revisit the history of the eastern part of the Paris Basin and to demonstrate
491 that the first phases of diagenetic closure of the porosity may have occurred sooner than
492 previously thought. In Dogger formations, most of the spar cements were precipitated earlier
493 than 148Ma. Nevertheless, a more recent major phase of fluid circulation occurred at 34Ma
494 linked with the major ECRIS extension tectonics of the Eocene/Oligocene period that
495 affected Western Europe. These results tend to indicate that meteoric fluid percolation
496 induced by the ECRIS tectonics were important from its first stages during late Eocene,
497 sooner than previously thought.

498 The U/Pb dating method of secondary calcites may then be a powerful tool for
499 diagenetic, paleohydrological and tectonic reconstructions. This study opens new
500 perspectives for diagenetic minerals dating and especially for future cement analyses or fault-
501 formed carbonates.

502

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511

512 **Conflict of interest statement**

513 The authors declare no conflict of interest.

514

515 **Author contribution**

516 C. Pisapia made the analyses, data treatment and interpretation, and wrote the paper. P.

517 Deschamps, A. Guihou, B. Hamelin participated to sample analyses and/or data treatment.

518 All co-authors discussed the results and co-wrote the paper.

519

520

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522

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678 **Table Captions**

679 **Table 1:** *Synthesis of U and Pb elemental and isotopic data obtained on geodic calcites*
680 *from the eastern part of the Paris Basin for Oxfordian and Dogger samples.*

681 **Table 2:** *Stable isotopic data for geodic calcites analyzed in this study. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values*
682 *are reported for the 3 aliquotes of each geode.*

683

684 **Figure Captions**

685

686 **Figure 1: Simplified geological map of the studied area** with the localization of EST 205,
687 EST 433 and HTM 102 cores (modified from Buschaert *et al.* 2004).

688 **Figure 2: Synthetic logs of EST 205, HTM 102 and EST433 cores.** The sampling positions
689 of the analyzed geodes for Oxfordian and Dogger samples are specified and optical
690 photographs of two typical analyzed geodes (G2 and G3 from HTM 102 borehole) are given.

691 **Figure 3: Tera-Wasserburg Concordia diagrams** for Oxfordian (a) and Dogger (b)
692 samples using Isoplot software 3.0 (Ludwig 2003) (model 2, 95% confidence) and calculated
693 ages obtained.

694 **Figure 4: $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{238}\text{U}/^{204}\text{Pb}$ isochron (a) and Tera-Wasserburg Concordia (b)**
695 obtained for 6 sub-samples of one geode (G10) using Isoplot software 3.0 (Ludwig 2003) and
696 calculated ages obtained.

697 **Figure 5: $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ compositions of geodic calcites** analyzed in this study. Error bars
698 are within the points. Data from Oxfordian limestones, COx claystones and Dogger
699 limestones from Buschaert *et al.* (2004) are specified ($\delta^{18}\text{O}$ data were converted from SMOW
700 to PDB thanks to the equation from Coplen *et al.* 1983: $\delta^{18}\text{O}_{\text{SMOW}} = 1.03091 * \delta^{18}\text{O}_{\text{PDB}} +$
701 30.91). Grey squares summarize Blocky Calcites mean data (Cal1, Cal2, Cal3 and Cal4) from
702 Brigaud *et al.* (2009) and Carpentier *et al.* (2014).

703

Table 1

Sample name	Weight (mg)	U (ppb)	Pb (ppb)	μ ($^{238}\text{U}/^{204}\text{Pb}$) $\pm 2\sigma$ [%]		$^{206}\text{Pb}/^{204}\text{Pb}$ $\pm 2\sigma$ [%]		$^{235}\text{U}/^{204}\text{Pb}$ $\pm 2\sigma$ [%]		$^{207}\text{Pb}/^{204}\text{Pb}$ $\pm 2\sigma$ [%]		$^{238}\text{U}/^{206}\text{Pb}$ $\pm 2\sigma$ [%]		$^{207}\text{Pb}/^{206}\text{Pb} \pm 2\sigma$ [%]	
<i>Oxfordian</i>															
G1-1	395	266.2	5.8	3935.6	4.4	39.3	3.5	28.5	4.4	16.6	4.1	100.08	1.5	0.423	3.1
G1-2	407	284.8	4.2	6947.9	7.0	56.9	6.0	50.4	7.0	17.5	6.5	122.03	1.6	0.308	5.0
G1-3	324	331.3	6.2	4769.8	3.6	44.4	2.9	34.6	3.6	16.8	3.4	107.44	1.1	0.379	2.6
G1-4	144	577.8	11.1	4910.1	6.8	48.6	5.1	35.6	5.0	17.0	4.8	100.95	1.3	0.350	3.7
G2-1	378	420.7	7.2	5379.2	4.0	47.4	3.3	39.0	4.0	17.0	3.7	113.55	1.2	0.358	2.8
G2-2	402	254.8	6.8	3050.1	3.5	35.7	2.7	22.1	3.5	16.4	3.3	85.34	1.3	0.460	2.5
G2-3	118	247.4	8.1	3516.6	5.8	43.1	4.8	25.5	5.8	16.8	5.6	81.62	1.7	0.389	4.4
G3-1	237	301.3	3.4	13258.6	21.5	95.6	19.6	96.2	21.5	19.5	19.5	138.67	2.8	0.204	14.7
G3-2	261	336.2	6.8	4512.7	4.1	46.1	3.4	32.7	4.1	16.9	3.9	97.93	1.1	0.367	3.1
G4-1	372	782.4	21.7	2856.6	1.3	35.5	0.9	20.7	1.3	16.4	1.1	80.43	0.7	0.462	0.8
G5-1	348	43.8	3.7	872.3	4.6	26.0	3.4	6.3	4.6	16.0	4.5	33.56	2.2	0.614	3.3
G5-2	251	50.9	4.4	830.5	1.9	26.3	1.4	6.0	1.9	16.0	1.9	31.62	1.0	0.608	1.3
G6-1	362	35.0	9.4	256.3	1.7	23.1	1.2	1.9	1.7	16.0	1.6	11.10	0.9	0.691	1.1
<i>Dogger</i>															
G8-1	246	39.0	11.6	243.5	0.7	26.1	0.5	1.8	0.7	16.1	0.7	9.33	0.4	0.615	0.5
G9-1	269	22.2	5.8	272.7	1.3	26.0	1.0	2.0	1.3	16.1	1.3	10.50	0.7	0.619	0.9
G9-2	295	25.8	4.2	474.8	1.9	31.6	1.5	3.4	1.9	16.4	1.8	15.02	0.8	0.518	1.3
G10-1	279	230.3	11.2	2398.8	1.1	76.1	1.0	17.4	1.1	18.6	1.0	31.53	0.2	0.244	0.8
G10-2	289	243.1	17.5	1297.9	0.6	51.4	0.5	9.4	0.6	17.4	0.5	25.26	0.3	0.339	0.4
G10-3	224	281.6	9.8	2626.1	1.2	82.3	1.1	19.0	1.2	18.9	1.1	31.90	0.2	0.230	0.9
G10-4	250	331.8	12.7	3916.4	4.0	110.8	3.7	28.4	4.0	20.3	3.6	35.34	0.5	0.183	2.7
G10-5	244	324.7	13.3	3328.3	3.5	96.3	3.2	24.1	3.5	19.5	3.2	34.56	0.6	0.202	2.5
G10-6	260	156.6	8.7	1938.0	4.0	64.0	3.5	14.1	4.0	17.9	3.8	30.27	0.9	0.280	3.0

Table 2

Core	Sample name	$\delta^{18}\text{O}$ (‰/PDB)	$\pm 2\sigma$	$\delta^{13}\text{C}$ (‰/PDB)	$\pm 2\sigma$
<i>Oxfordian</i>					
EST 205	G4 EST 07057	-8.98	0.02	2.68	0.012
		-8.90	0.04	2.70	0.03
		-8.98	0.01	2.72	0.039
HTM 102	G1 HTM 00544	-9.36	0.03	2.69	0.04
		-9.21	0.01	2.73	0.04
		-9.23	0.02	2.66	0.05
	G2 HTM 00595	-9.24	0.02	2.41	0.06
		-9.18	0.03	2.43	0.02
		-9.28	0.02	2.33	0.02
G3 HTM 80513	-8.98	0.02	2.55	0.02	
	-9.02	0.02	2.54	0.03	
	-8.99	0.04	2.60	0.04	
G5 HTM 02854	-10.26	0.02	2.35	0.06	
	-10.20	0.02	2.36	0.02	
	-10.26	0.04	2.38	0.04	
G6c HTM 331	-8.96	0.01	2.68	0.02	
	-8.95	0.02	2.70	0.02	
	-9.05	0.02	2.72	0.01	
<i>Dogger</i>					
EST 433	G8 EST 29185	-6.67	0.04	2.28	0.03
		-6.80	0.04	2.26	0.04
		-6.69	0.02	2.25	0.01
G9 EST 29192	-6.47	0.04	2.47	0.03	
	-6.33	0.02	2.51	0.03	
	-6.47	0.02	2.50	0.02	
G10 EST 30904	-6.44	0.02	1.82	0.01	
	-6.56	0.02	1.92	0.02	
	-6.42	0.03	1.91	0.02	
G11 EST 34826	-9.37	0.05	0.39	0.02	
	-9.37	0.04	0.39	0.02	
	-9.36	0.03	0.41	0.02	

Figure 1

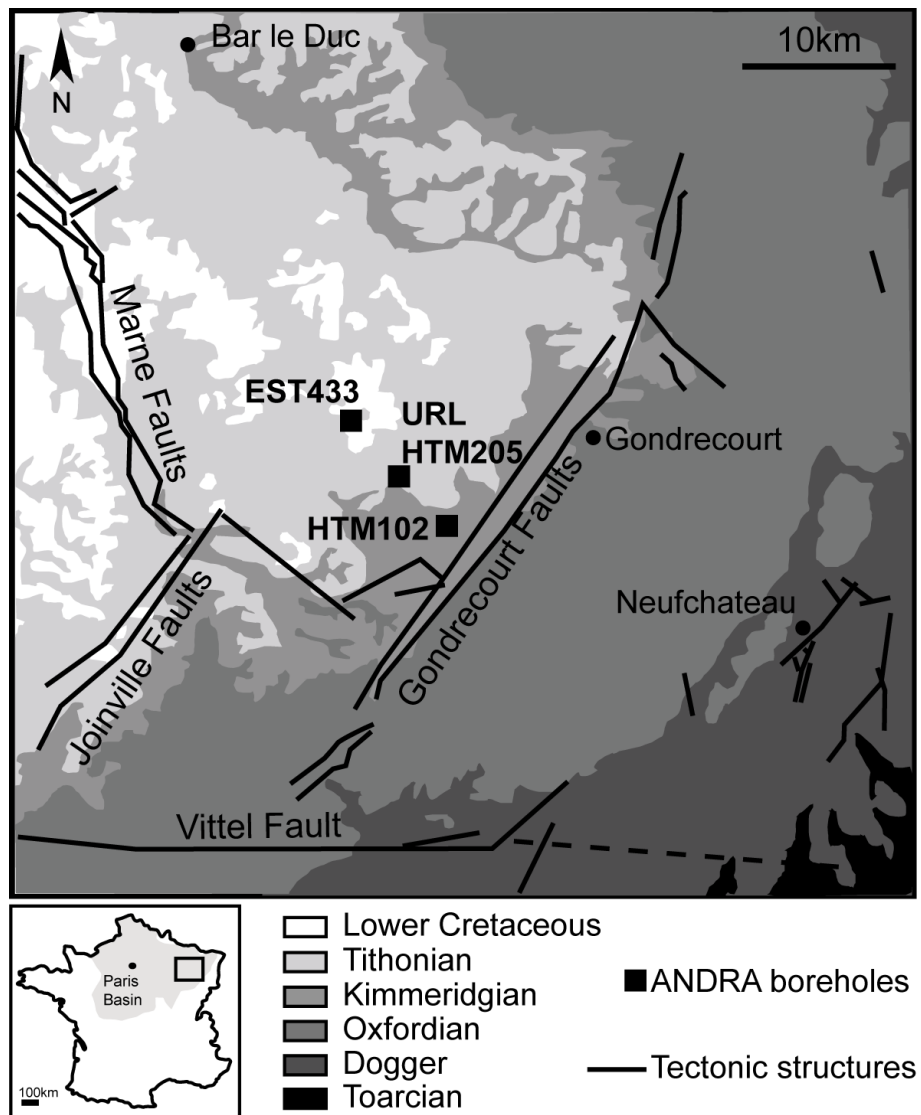


Figure 2

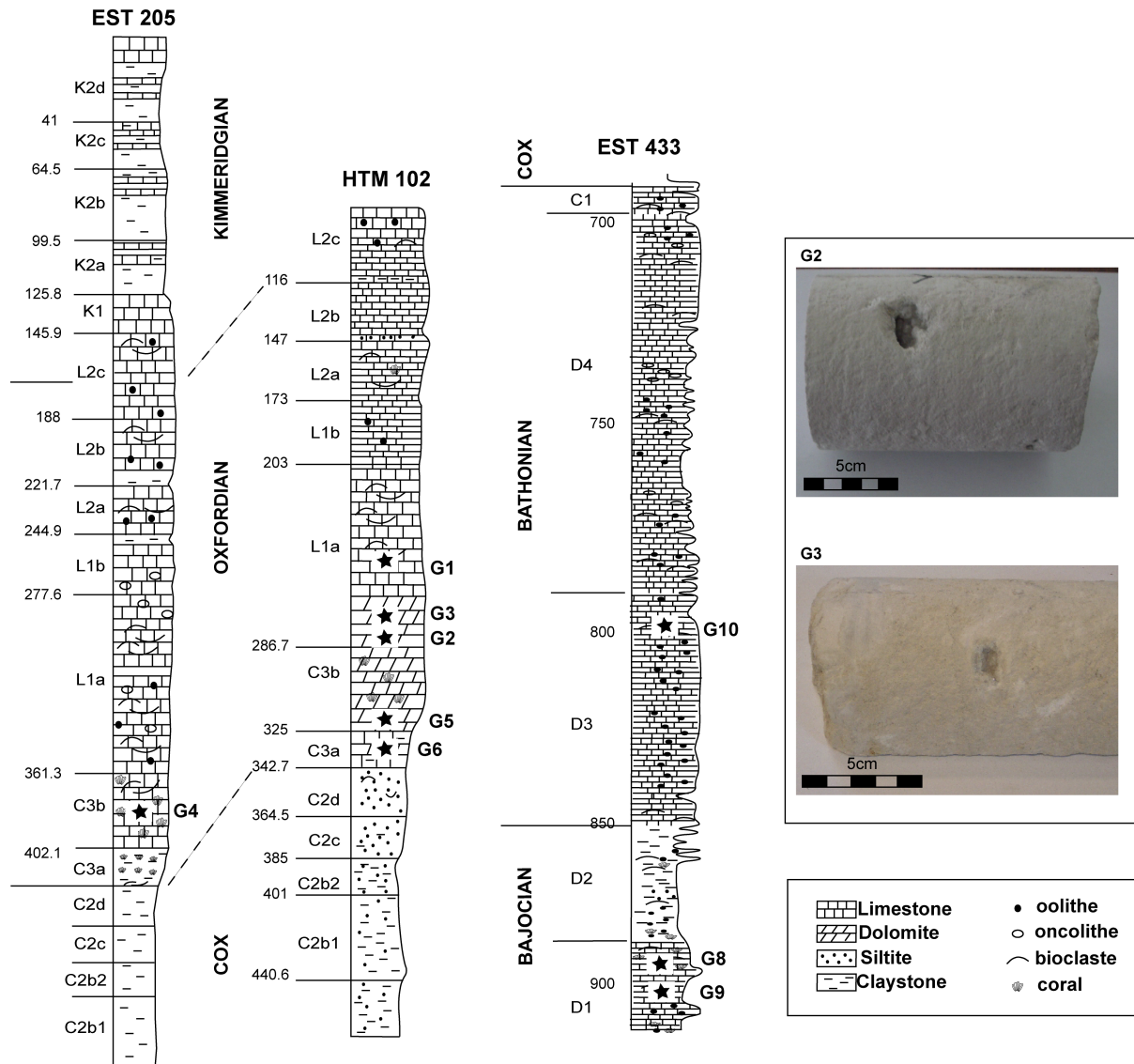


Figure 3

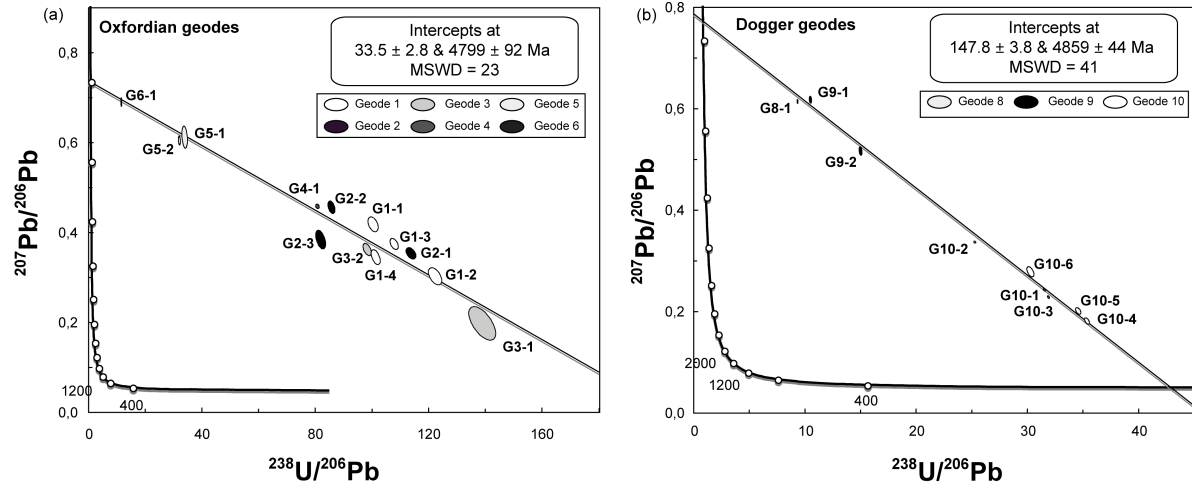


Figure 4

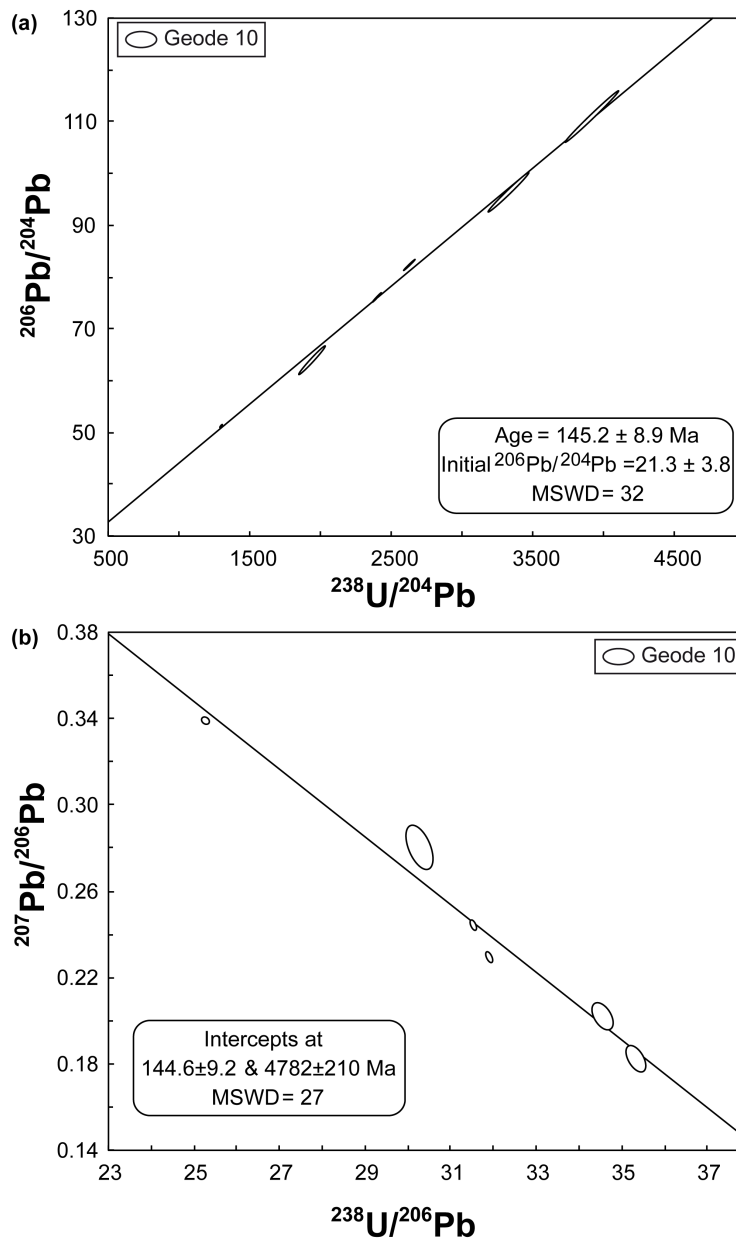
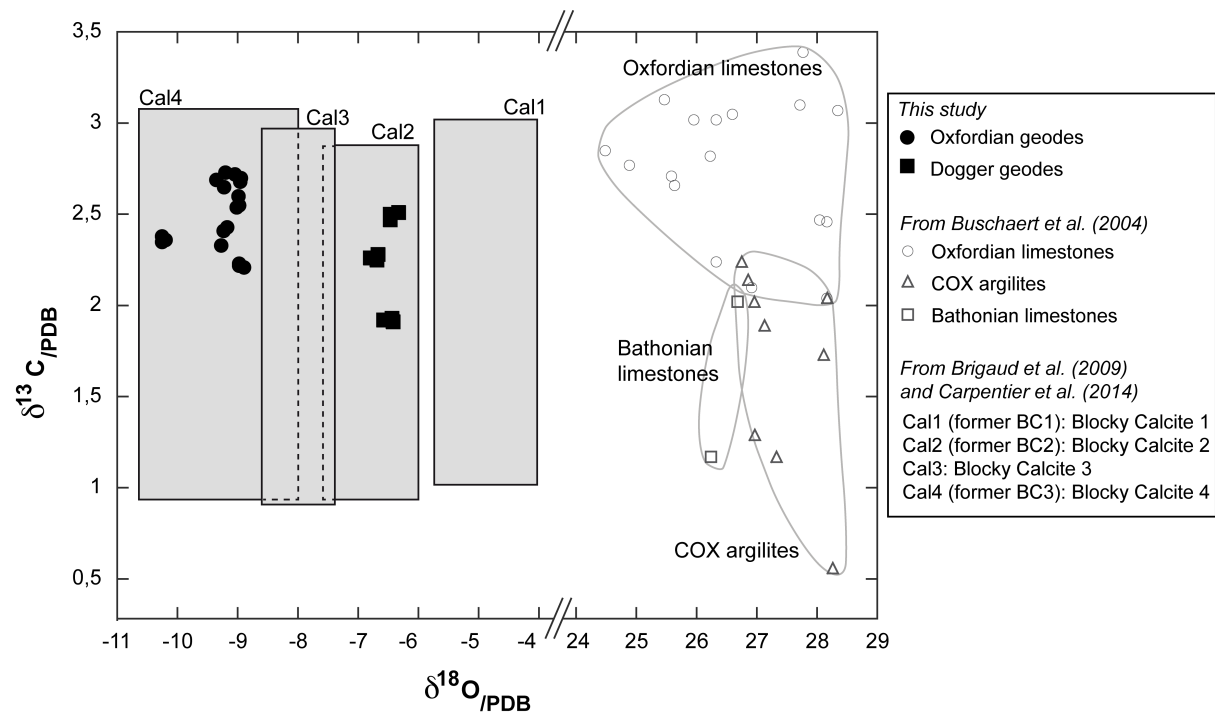


Figure 5





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Supplementary material (not datasets)

Pisapia_Supp_Material.pdf

