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

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

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

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

*^a Corresponding author/Present adress:

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

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

e-mail: celine.pisapia@gmail.com

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

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

Abbreviated title: U-Pb dating of diagenetic events

Abstract

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

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

Keywords

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

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

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

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

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

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

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

Geological Setting

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

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

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

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

centimeters range apart from the stylolites and the whole carbonates present a ($^{234}\text{U}/^{238}\text{U}$) activity ratio at equilibrium. These embedding limestones have very low porosity (2-5%) and permeability (10^{-9} to 10^{-10} m.s $^{-1}$) (Battani *et al.* 2011). By contrast with the CO $_2$ formation, they rarely show the preservation of typical structures of early marine cements (micro-crystalline cement and small euhedral crystals of micro-spar). The primary and secondary porosities, as well as macro-cavities and micro-fractures, are mainly infilled by secondary sparry calcites. The remaining inter-particle porosity is infilled by large crystals of sparite isotopically similar to those observed in macro-cavities and in fractures inherited from the Eocene-Oligocene extension (Buschaert *et al.* 2004). Successive generations of blocky calcites (Cal1, Cal2, Cal3 and Cal4) were identified by microscopic observations (Carpentier *et al.* 2014). Based on oxygen and carbon isotopic analyses, they were interpreted as precipitated from meteoric fluids with carbon of local origin (Brigaud *et al.* 2009; Buschaert *et al.* 2004; Carpentier *et al.* 2014; Vincent *et al.* 2007). This excludes an early diagenetic cementation phase by marine fluids and marks later diagenetic events. Cal1 (former BC1 from Brigaud *et al.* 2009) were then assumed to precipitate at the early Cretaceous (during LCU) following the uplift of the London-Brabant massif, Cal2 (former BC2 from Brigaud *et al.* 2009) during the Late Aptian Unconformity (LAU) that was associated with erosion and karstification of the Paris Basin borders and Cal3 to the Pyrenean compression. Finally, Cal4 (former BC3 from Brigaud *et al.* 2009) was related to the Oligocene extension tectonics with the formation of main regional grabens and associated terrestrial sedimentation (Brigaud *et al.* 2009; Carpentier *et al.* 2014). Nevertheless, no absolute geochronological constraints are available for these blocky calcites and the question is still subject to debate (Andre *et al.* 2010; Brigaud *et al.* 2009; Buschaert *et al.* 2004; Vincent *et al.* 2007). The main purpose of this study was thus to date precisely these phases of fluid circulation thanks to secondary

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

Material and Methods

Geodic calcite samples

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

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

Chemical preparation

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

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

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

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

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

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

U and Pb isotopic analyses

Uranium and lead isotopic compositions were determined by Thermal Ionization Mass Spectrometry (VG sector-54). Lead samples (from 0.7 to 9.2 ng) were prepared with 2.8 μL 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 ± 0.012) and of 2.9 ‰ on ²⁰⁴Pb/²⁰⁶Pb
 222 ratio (0.059292 ± 0.00018). Replicates of NBS SRM-960 standard gave an external
 223 reproducibility of 1.5 ‰ on ²³⁵U/²³⁴U ratio (136.8892 ± 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 ± 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 ± 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

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

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

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

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

Results

U and Pb isotopic compositions of geodic calcites

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).

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

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

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

Discussion

U/Pb dating of Pb-depleted geodic calcites

To our knowledge, this is the first time that U-Pb dating was made directly on highly Pb-depleted diagenetic geodic calcite samples for paleohydrogeology reconstructions in a 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

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

Paleofluids circulations and major related tectonic events.

Fluids composition and origin

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

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

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

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

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

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

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

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

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

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

Conclusion

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

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

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

Acknowledgements and fundings

This project was supported by Andra (French National Radioactive Waste Management Agency) and by CNRS INSU. The authors want to thank Jean David and the GEOTOP geochronology team (Montreal, Canada) for providing ^{205}Pb spike, Laurence Vidal and Corinne Sonzogni from CEREGE (Aix-Marseille Université, France) for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ analyses, M. Cathelineau and T. Blaise from G2R UMR 7566 (Nancy Université, France) for samples, A. Trouiller (Andra), J. Delmas and P. Houel (IFPEN) for precious comments on the manuscript.

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

References

- Andre, G., Hibschi, C. *et al.* 2010. Chronology of fracture sealing under a meteoric fluid environment: Microtectonic and isotopic evidence of major Cainozoic events in the eastern Paris Basin (France). *Tectonophysics*, **490**, 214–228.
doi:10.1016/j.tecto.2010.05.016
- Babinski, M., Chemale, F. & Van Schmus, E.R. 1995. The Pb/Pb age of the Minas Supergroup carbonate rocks, Quadrilátero Ferrífero, Brazil. *Precambrian Res.*, **72**, 235–245. doi:http://dx.doi.org/10.1016/0301-9268(94)00091-5
- Babinski, M., Van Schmus, W.R. & Chemale, F. 1999. Pb-Pb dating and Pb isotope geochemistry of Neoproterozoic carbonate rocks from the Sao Francisco basin, Brazil: Implications for the mobility of Pb isotopes during tectonism and metamorphism. *Chem. Geol.*, **160**, 175–199. doi:10.1016/S0009-2541(99)00067-4
- Battani, A., Smith, T. *et al.* 2011. Contribution of logging tools to understanding helium porewater data across the Mesozoic sequence of the East of the Paris Basin. *Geochim. Cosmochim. Acta*, **75**, 7566–7584. doi:10.1016/j.gca.2011.09.032
- Beccaleto, L., Hanot, F., Serrano, O. & Marc, S. 2011. Overview of the subsurface structural pattern of the Paris Basin (France): Insights from the reprocessing and interpretation of regional seismic lines. *Mar. Pet. Geol.*, **28**, 861–879,
doi:10.1016/j.marpetgeo.2010.11.006
- Becker, M.L., Rasbury, E.T., Meyers, W.J. & Hanson, G.N. 2002. U–Pb calcite age of the Late Permian Castile Formation, Delaware Basin: a constraint on the age of the Permian–Triassic boundary (?). *Earth Planet. Sci. Lett.*, **203**, 681–689.
doi:10.1016/S0012-821X(02)00877-4
- Berggren, W.A., Kent, D. V, Swisher, C.C. & Aubry, M. 1985. A revised Cenozoic geochronology and chronostratigraphy. *SEPM*, **54**, 129–212.
- Brigaud, B., Durlot, C. *et al.* 2009. The origin and timing of multiphase cementation in carbonates: Impact of regional scale geodynamic events on the Middle Jurassic Limestones diagenesis (Paris Basin, France). *Sediment. Geol.*, **222**, 161–180.
doi:10.1016/j.sedgeo.2009.09.002
- Buschaert, S., Fourcade, S. *et al.* 2004. Widespread cementation induced by inflow of continental water in the eastern part of the Paris basin: O and C isotopic study of carbonate cements. *Appl. Geochemistry*, **19**, 1201–1215.
doi:10.1016/j.apgeochem.2003.01.001
- Carpentier, C., Brigaud, B. *et al.* 2014. Impact of basin burial and exhumation on Jurassic carbonates diagenesis on both sides of a thick clay barrier (Paris Basin , NE France). *Mar. Pet. Geol.*, **53**, 44–70. doi:10.1016/j.marpetgeo.2014.01.011
- Cheng, H., Edwards, R.L. *et al.* 2000. The half-lives of uranium-234 and thorium-230. *Chem. Geol.*, **169**, 17–33. doi:10.1016/S0009-2541(99)00157-6
- Cliff, R.A., Spötl, C. & Mangini, A. 2010. U-Pb dating of speleothems from Spannagel Cave, Austrian Alps: A high resolution comparison with U-series ages. *Quat. Geochronol.*, **5**, 452–458. doi:10.1016/j.quageo.2009.12.002
- Cole, J.M., Rasbury, E.T. *et al.* 2005. Using U-Pb ages of Miocene tufa for correlation in a terrestrial succession, Barstow Formation, California. *Geol. Soc. Am. Bull.*, **117**, 276.
doi:10.1130/B25553.1
- Coogan, L.A., Parrish, R.R. & Roberts, N.M.W. 2016. Early hydrothermal carbon uptake by the upper oceanic crust: Insight from in situ U-Pb dating. *Geology*, **44**, 147–150.
doi:10.1130/G37212.1
- Cros, A., Gautheron, C. *et al.* 2014. 4He behavior in calcite filling viewed by (U-Th)/He dating, 4He diffusion and crystallographic studies. *Geochim. Cosmochim. Acta*, **125**,

- 414–432. doi:10.1016/j.gca.2013.09.038
- de Ruiter, D.J., Pickering, R. *et al.* 2009. New Australopithecus robustus fossils and associated U-Pb dates from Cooper's Cave (Gauteng, South Africa). *J. Hum. Evol.*, **56**, 497–513. doi:10.1016/j.jhevol.2009.01.009
- Delay, J., Rebours, H., Vinsot, A. & Robin, P. 2007. Scientific investigation in deep wells for nuclear waste disposal studies at the Meuse/Haute Marne underground research laboratory, Northeastern France. *Phys. Chem. Earth*, **32**, 42–57. doi:10.1016/j.pce.2005.11.004
- Deschamps, P., Hillaire-Marcel, C. *et al.* 2004. $^{234}\text{U}/^{238}\text{U}$ Disequilibrium along stylolitic discontinuities in deep Mesozoic limestone formations of the Eastern Paris basin: evidence for discrete uranium mobility over the last 1–2 million years. *Hydrol. Earth Syst. Sci.*, **8**, 35–46. doi:10.5194/hess-8-35-2004
- Dèzes, P., Schmid, S.M. & Ziegler, P.A. 2004. Evolution of the European Cenozoic Rift System: interaction of the Alpine and Pyrenean orogens with their foreland lithosphere. *Tectonophysics*, **389**, 1–33. doi:10.1016/j.tecto.2004.06.011
- Evans, J. & Zalasiewicz, J. 1996. U-Pb, Pb-Pb and Sm-Nd dating of authigenic monazite: implications for the diagenetic evolution of the Welsh Basin 144.
- Getty, S.R., Asmerom, Y., Quinn, T.M. & Budd, A.F. 2001. Accelerated Pleistocene coral extinctions in the Caribbean Basin shown by uranium-lead (U-Pb) dating. *Geology*, **29**, 639–642. doi:10.1130/0091-7613(2001)029<0639:APCEIT>2.0.CO;2
- Getty, S.R. & de Paolo, D.J. 1995. Quaternary geochronology using the U-Th-Pb method. *Geochim. Cosmochim. Acta*, **59**, 3267–3272. doi:10.1016/0016-7037(95)00197-8
- Grandia, F., Asmerom, Y. *et al.* 2000. U-Pb dating of MVT ore-stage calcite: implications for fluid flow in a Mesozoic extensional basin from Iberian Peninsula. *J. Geochemical Explor.*, **69–70**, 377–380. doi:http://dx.doi.org/10.1016/S0375-6742(00)00030-3
- Guillocheau, F., Robin, C. *et al.* 2000. Meso-Cenozoic geodynamic evolution of the Paris Basin: 3D stratigraphic constraints. *Geodin. Acta*, **13**, 189–245. doi:10.1016/S0985-3111(00)00118-2
- Horwitz, E.P., Dietz, M.L. *et al.* 1992. Separation and preconcentration of uranium from acidic media by extraction chromatography. *Anal. Chim. Acta*, **266**, 25–37. doi:10.1016/0003-2670(92)85276-C
- Israelson, C., Halliday, A.N. & Buchardt, B. 1996. U-Pb dating of calcite concretions from Cambrian black shales and the Phanerozoic time scale. *Earth Planet. Sci. Lett.*, **141**, 153–159. doi:darobfit
- Jaffey, A.H., Flynn, K.F. *et al.* 1971. Precision measurement of half-lives and specific activities of ^{235}U and ^{238}U . *Phys. Rev. C*, **4**, 1889–1906.
- Jahn, B. & Simonson, B.M. 1995. Carbonate Pb-Pb ages of the Wittenoom Formation and Carawine Dolomite, Hamersley Basin, Western Australia (with implications for their correlation with the Transvaal Dolomite of South Africa). *Precambrian Res.*, **72**, 247–261.
- Li, Q., Parrish, R.R., Horstwood, M.S.A. & McArthur, J.M. 2014. U-Pb dating of cements in Mesozoic ammonites. *Chem. Geol.*, **376**, 76–83. doi:10.1016/j.chemgeo.2014.03.020
- Luczaj, J.A. & Goldstein, R.H. 2000. Diagenesis of the Lower Permian Krider Member, Southwest Kansas, U.S.A.: Fluid-Inclusion, U-Pb, and Fission-Track Evidence for Reflux Dolomitization During Latest Permian Time. *J. Sediment. Res.*, **70**, 762–773. doi:10.1306/2DC40936-0E47-11D7-8643000102C1865D
- Ludwig, K.R. 2003. ISOPLOT a plotting and regression program for radiogenic isotope data, Version Ex/3.00.
- Moorbath, S., Taylor, P.N. *et al.* 1987. First direct radiometric dating of Archean stromatolitic limestone. *Nature*, **326**, 865–867.

- Neymark, L.A., Amelin, Y., Paces, J.B. & Peterman, Z.E. 2002. U-Pb ages of secondary silica at Yucca Mountain, Nevada: implications for the paleohydrology of the unsaturated zone. *Appl. Geochemistry*, **17**, 709–734. doi:10.1016/S0883-2927(02)00032-X
- Pickering, R., Kramers, J.D. *et al.* 2010. U–Pb dating of calcite–aragonite layers in speleothems from hominin sites in South Africa by MC-ICP-MS. *Quat. Geochronol.*, **5**, 544–558. doi:10.1016/j.quageo.2009.12.004
- Polyak, V., Hill, C. & Asmerom Y. 2008. Age and evolution of the Grand Canyon revealed by U-Pb dating of water table-type speleothems. *Science*, **319**, 1377–1380.
- Quesnel, F. 2003. Paleoweathering and paleosurfaces from northern and eastern France to Belgium and Luxembourg : geometry, dating and geodynamic implications. *Géologie la Fr. Spec. Conf. "Paleoweathering Paleosurf. Ardennes-Eifel Reg. (F. Quesnel coord.)* 1, 95–104.
- Rasbury, E.T. & Cole, J.M. 2009. Directly dating geological events: U-Pb dating of carbonates. *Review of Geophysics*, **47**, 1–27. doi:10.1029/2007RG000246.1.
- Rasbury, E.T., Hanson, G.N., Meyers, W.J. & Saller, A.H. 1997. Dating of the time of sedimentation using U-Pb ages for paleosol calcite. *Geochim. Cosmochim. Acta*, **61**, 1525–1529. doi:darobfita
- Richards, D.A., Bottrell, S.H. *et al.* 1998. U-Pb dating of a speleothem of Quaternary age. *Geochim. Cosmochim. Acta*, **62**, 3683–3688. doi:10.1016/S0016-7037(98)00256-7
- Roberts, N.M.W. & Walker, R.J. 2016. U-Pb geochronology of calcite-mineralized faults: Absolute timing of rift-related fault events on the northeast Atlantic margin. *Geology*, **44**, 531–534. doi:10.1130/G37868.1
- Schmitz, M.D. & Schoene, B. 2007. Derivation of isotope ratios, errors, and error correlations for U-Pb geochronology using 205Pb-235U-(233U)-spiked isotope dilution thermal ionization mass spectrometric data. *Geochemistry, Geophys. Geosystems*, **8**, 1–20. doi:10.1029/2006GC001492
- Schumacher, M.E. 2002. Upper Rhine Graben: Role of preexisting structures during rift evolution. *Tectonics*, **21**. doi:10.1029/2001TC900022
- Sissingh, W. 1998. Comparative tertiary stratigraphy of the Rhine Graben, Bresse Graben and Molasse Basin: Correlation of Alpine foreland events. *Tectonophysics*, **300**, 249–284. doi:10.1016/S0040-1951(98)00243-1
- Smith, P.E., Farquhar, R.M. & Hancock, R.G. 1991. Direct radiometric age determination of carbonate diagenesis using U-Pb in secondary calcite. *Earth Planet. Sci. Lett.*, **105**, 474–491.
- Théveniaut, H., Quesnel, F., Wyns, R. & Hugues, G. 2007. Palaeomagnetic dating of the “Borne de Fer” ferricrete (NE France): Lower Cretaceous continental weathering. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **253**, 271–279. doi:10.1016/j.palaeo.2007.01.010
- Thiry, M., Quesnel, F. *et al.* 2006. Continental France and Belgium during the early cretaceous: Paleoweatherings and paleolandforms. *Bull. la Soc. Geol. Fr.*, **177**, 155–175. doi:10.2113/gssgfbull.177.3.155
- Vercoutere, C. & Van den Houte, P. 1993. Post-Palaeozoic cooling and uplift of the Brabant Massif as revealed by apatite fission track analysis. *Geol. Mag.*, **130**, 639–646.
- Vincent, B., Emmanuel, L., Houel, P. & Loreau, J.-P. 2007. Geodynamic control on carbonate diagenesis: Petrographic and isotopic investigation of the Upper Jurassic formations of the Paris Basin (France). *Sediment. Geol.*, **197**, 267–289. doi:10.1016/j.sedgeo.2006.10.008
- Woodhead, J., Hellstrom, J. *et al.* 2006. U-Pb geochronology of speleothems by MC-ICPMS. *Quat. Geochronol.*, **1**, 208–221. doi:10.1016/j.quageo.2006.08.002

671 Worden, R.H., Coleman, M.L. & Matray, J.M. 1999. Basin scale evolution of formation
672 waters: a diagenetic and formation water study of the Triassic Chaunoy Formation, Paris
673 Basin. *Geochim. Cosmochim. Acta*, **63**, 2513–2528.
674 Ziegler, P.A. 1992. European Cenozoic rift system. *Tectonophysics* 208, 91–111.
675 doi:10.1016/0040-1951(92)90338-7
676
677

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

Figure Captions

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

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

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

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

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

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

[Click here to access/download](#)

Supplementary material (not datasets)
Pisapia_Supp_Material.pdf