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An emerging thermochronometer for carbonate-bearing rocks: Δ_{47}/(U-Pb)

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ABSTRACT

Assessing the thermal evolution of sedimentary basins is critical for understanding the origin of natural resources (including ores, geothermal fluids, or hydrocarbons) and for deciphering larger-scale tectonic and geodynamic evolutions. Modern reconstructions of past subsurface temperatures mostly rely on thermochronometers that are not applicable to carbonate rocks [e.g., fission-track and (U-Th)/He analyses]. Here, by coupling carbonate clumped isotope (Δ_{47}) thermometry and laser ablation U-Pb geochronology on a complete paragenetic sequence, we demonstrate the applicability of an emerging thermochronometer for carbonate bearing-rocks. Paired Δ_{47} and U-Pb data were obtained for calcite and dolomite phases precipitated in a Middle Jurassic carbonate hydrocarbon reservoir of the Paris Basin depocenter (France). The absolute thermochronological data allow the precise reconstruction of the thermal history of these rocks: from shallow burial temperatures (~40 °C), occurring in the Late Jurassic, toward a progressive burial and heating stage (up to 87 °C) during the Cretaceous, followed by a cooling stage (down to 69 °C) during the Tertiary uplift of the basin. The inferred time-temperature path based on Δ_{47}/(U-Pb) data is mostly consistent with the thermal scenario independently deduced from organic maturity indicators from the underlying Lower Jurassic shales. The Δ_{47}/(U-Pb) thermochronological data also highlight a thermal anomaly during Aptian–Albian time that requires revisiting the accepted timing for hydrocarbon migration in the Middle Jurassic reservoir carbonates.

INTRODUCTION

Deciphering the thermal evolution of sedimentary basins over time traditionally requires obtaining data for past thermal conditions by means of organic or mineral-based maturity indicators, such as vitrinite reflectance, conodont alteration index, fluid inclusions, or fission-track analyses (Harris and Peters, 2012). Decoding this record from carbonate successions is commonly hampered by the lack of methods to reconstruct both the timing and temperature of carbonate mineral crystallization. However, the toolkit of thermochronology proxies for carbonates has recently grown to include clumped isotope thermometry on carbonate powders (Δ_{47}; see Huntington and Lechler [2015] for a review, and Bonifacie et al. [2017] for universal Δ_{47}-temperature calibration) and “in situ” U-Pb radioisotopic dating via laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS; Li et al., 2014; Roberts and Walker, 2016; Nuriel et al., 2017). These methods are suited to any carbonates formed in the full spectrum of geological settings, and offer tremendous potential to capture a snapshot of the temperature conditions prevailing at the specific time that a carbonate mineral precipitated or recrystallized. Supported by careful petrographic investigations, Δ_{47} and U-Pb dating is opening a new field of thermochronological applications. This combination of methods has been recently applied to discover hyperthermal events in middle Eocene pedogenic carbonates (Methner et al., 2016), to reconstruct paleoenvironments in spring carbonates of the Andes (Quade et al., 2017), for diagenetic history reconstruction of a carbonate unit using high-temperature kinetic behavior of Δ_{47} (Lawson et al., 2017), and for paleohydrological reconstructions based on calcite veins and breccias of the eastern Paris Basin (France; Pagel et al., 2018). Here, we apply for the first time the Δ_{47}/(U-Pb) thermochronometer on a complete paragenetic sequence that includes multiple carbonate phases precipitated throughout the depositional, burial, and uplift history of a subsurface Middle Jurassic carbonate reservoir series of the Paris Basin.

The intracratonic Paris Basin is presently filled by 3000 m of sediments in its depocenter (Fig. 1), which includes two main hydrocarbon reservoir units: Upper Triassic fluvial sandstones and the Middle Jurassic marine carbonates. The latter have been studied for both academic and exploration purposes, resulting in extensive petrographic, thermometric, and geochemical data sets (see Mangenot et al. [2018] for a review). Three features make the Middle Jurassic carbonates attractive for applying the carbonate Δ_{47}/(U-Pb) thermochronometer. First, they experienced almost continuous burial and heating up to 85 °C during the Mesozoic, followed by significant cooling during the Tertiary uplift of the basin (Uriarte, 1997; Gonçalvès et al., 2010). Second, multiple carbonate phases have been petrographically and geochemically characterized (Mangenot et al., 2018, and references therein). Third, the possibility that the carbonate Δ_{47} compositions were affected by thermal reordering of ^{13}C-^{18}O bonds during burial (Passey and Henkes, 2012) has been ruled out, notably based on the excellent agreement observed with fluid inclusion homogenization temperatures of calcite and dolomite cements collected in the studied area (Mangenot et al., 2017).

SAMPLE SELECTION AND ANALYTICAL METHODS

Carbonate samples were collected from the same stratigraphic interval (upper Bathonian–lower Callovian; 1894–1564 m depth) of four well cores located in the Paris Basin depocenter, each having experienced comparable burial and thermal histories (Figs. 1A and 1C; Table DR1 in the GSA Data Repository[1]). A previous study based on 45 samples established mineral paragenesis, petrographical, and geochemical characterizations (Mangenot et al., 2018) that guided the selection of ten carbonate samples for U-Pb analyses (Fig. 2; Fig. DR1). The selected samples belong to six different carbonate phases from which crystallization temperatures are clustered within precise intervals: (1) biogenic calcite from a brachiopod shell at 31 ± 6 °C ($n = 1$); (2) the surrounding micrite matrixes ($n = 2$) with temperatures of 49 ± 5 °C and 43 ± 6 °C; (3) blocky calcite cements with temperatures of 59 ± 10 °C, 61 ± 8 °C, and 66 ± 5 °C (designated Cal1; $n = 3$); (4) a saddle dolomite cement at 88 ± 7 °C (Dol1; $n = 1$), which bears liquid hydrocarbon fluid inclusions; (5) blocky calcite cements (Cal2 ; $n = 2$) with temperatures of 76 ± 9 °C and 78 ± 7 °C; and (6) a saddle dolomite cement at 70 ± 7 °C (Dol2 ; $n = 1$). Each carbonate phase displays a specific cathodoluminescence response (Fig. 2A) and stable isotope composition ($\delta^{13}C$, $\delta^{18}O$, Δ_{47}; Table DR1), supporting different crystallization conditions and parent fluid origins (Mangenot et al., 2018).

RESULTS

The already acquired Δ_{47} data (Mangenot et al., 2018) are complimented with new radioisotopic U-Pb dates from LA-ICP-MS analyses (see Data Repository Item DR1 for

LA-ICP-MS analytical procedures). The measured U and Pb isotopic ratios display Tera-Wasserburg linear regressions (isochrons) with a common initial $^{207}Pb/^{206}Pb$ composition of 0.844 ± 0.014 and MSWD (mean standard weighted deviation) values between 0.8 and 2.3 (Fig. 2B; Table DR1). The calculated U-Pb dates range between 154 ± 5.1 and 37.2 ± 5.3 Ma, and are systematically younger than the rock deposition age (even when 2σ uncertainties are considered) estimated at 166 ± 2 Ma from biostratigraphy (upper Bathonian–lower Callovian, *Clydoniceras discus* Zone; Gaumet et al., 1996). When individual carbonate phases are considered separately, the U-Pb dates cluster at: (1) 154.2 ± 5.1 Ma for the brachiopod shell, (2) 150 ± 16 and 151.5 ± 6.2 Ma for the two micrites, (3) 120.7 ± 2.2, 117.5 ± 5.0, and 118.5 ± 3.6 Ma for the three Cal1 samples, (4) 107 ± 13 Ma for the Dol1 sample, (5) 61.1 ± 2.5 and 68.5 ± 7.7 Ma for the two Cal2 samples, and (6) 37.2 ± 5.3 Ma for the Dol2 sample. This succession of absolute U-Pb dates agrees with the relative paragenesis previously established (Mangenot et al., 2018, Fig. 2A). Noticeably, petrographically equivalent carbonate phases analyzed from different cores display overlapping U-Pb ages and Δ_{47} temperatures, supporting their common origin. Interestingly, syn-sedimentary carbonates (brachiopod shell and micrite) exhibit U-Pb ages, $\delta^{18}O$ composition, and Δ_{47} temperatures that are slightly offset with respect to those of Middle Jurassic marine carbonates (Lécuyer et al., 2003), indicating recrystallization under shallow burial conditions (see the Data Repository for further discussion). By contrast, numerous petrographic evidences (Mangenot et al., 2018) indicate that all the other carbonate phases (Cal1, Dol1, Cal2, Dol2) were precipitated as pore-filling cements.

IMPLICATIONS FOR BASIN THERMAL AND FLUID-FLOW HISTORY

The distinct Δ_{47} temperatures (from 31 to 87 °C) and U-Pb ages (from 154.2 to 37.2 Ma) from six petrographically and geochemically distinct carbonate phases enable the construction of a time-temperature path experienced by the host rocks (Fig. 3). Each time-temperature pair reflects a snapshot of the temperature conditions that prevailed at the time of each event of carbonate crystallization (fluid based). In the Middle Jurassic reservoirs of the Paris Basin, the reconstructed time-temperature path starts with temperatures of 31 °C (brachiopod shell) and 46 °C (micrites) during Middle and Late Jurassic times, continues with a progressive heating to 64 °C (Cal1 samples) in the Aptian–Albian and 87 °C (Dol1 sample) in the Albian–Cenomanian, and ends with cooling recorded by temperatures of 77 °C (Cal2 samples) at the Cretaceous-Tertiary boundary and 69 °C[(Dol2 sample) in the Oligocene–Eocene. Except for the temperature indicated by the Dol1 cement, this thermal scenario (solid black line in Fig. 3) agrees with the thermal evolution model previously established for the Paris Basin depocenter (black dotted line in Fig. 3; Uriarte, 1997). This previous (rock-based) thermal model used a burial history determined from stratigraphic thickness, lithology, and depositional ages of the whole sedimentary column, calibrated in temperature with organic thermal indicators such as vitrinite reflectance.

The good agreement observed between the Δ_{47}/(U-Pb) fluid-based thermal history reconstructed in this study and the previous thermal model (Uriarte, 1997) indicates that the new Δ_{47}/(U-Pb) thermochronology approach allows the capturing of the time-temperature history of carbonate-bearing geological units during both the heating and cooling stages of basin evolution. Most importantly, by contrast with more conventional paleothermometers, the Δ_{47}/(U-Pb) thermochronometer works without prerequisite hypotheses on the geodynamic, stratigraphic, or thermal evolution of the investigated units. The excellent match between fluid- and rock-based thermal history also suggests that most of the carbonate phases analyzed have precipitated from fluids in thermal equilibrium with the ambient rocks. The Dol1 sample exhibits a temperature offset of between 10 and 30 °C compared with the Uriarte (1997) model, depending on reported uncertainties on temperature and age. This offset points toward a thermal anomaly during the Early Cretaceous, which may be explained by one, or a combination, of three geological scenarios. The first scenario would imply that Middle Jurassic strata were buried more deeply than expected at the time of precipitation of the Dol1 phase (107 ± 13 Ma). Burial by an additional 300–600 m of Upper Jurassic and Lower Cretaceous sediments, coupled with a 35 °C/km geothermal gradient, could justify a precipitation temperature of 85–90 °C for the Dol1 sample. The second scenario implies a brief increase of basement heat flow during Cretaceous time that would justify higher temperatures in the Middle Jurassic carbonates. Indeed, such a short-duration heat flow increase would have remained undetectable by the vitrinite reflectance proxy used by Uriarte (1997) to calibrate his thermal model (refer to Item DR2 and Fig. DR3 in the Data Repository). The third scenario implies that the dolomitizing fluid was locally in thermal disequilibrium with the ambient rocks, suggesting that precipitation of the Dol1 phase occurred under a hydrothermal regime—a common scheme invoked for the origin of saddle dolomites (e.g., Honlet et al., 2017).

The first scenario can be ruled out because an additional burial of 300–600 m of Upper Jurassic and Lower Cretaceous sediments is very unlikely, given the present-day thickness of the stratigraphic column overlying the investigated strata and the lack of significant erosional unconformities in the depocenter area (Guillocheau et al., 2000). We therefore favor the last two hypotheses because the age measured for the Dol1 sample (107 ± 13 Ma) broadly overlaps with the age reported for hydrothermal fluorite from the southeastern Paris Basin (130 ± 15 Ma; Gigoux et al., 2015) and with the ages inferred for carbonate cementation (Aptian–Albian; ca. 113 Ma) in the eastern Paris Basin (Carpentier et al., 2014). This provides independent geological evidence for the occurrence of hot temperature regimes and/or fluid-flow reactivations during Early Cretaceous times, possibly associated with extensional tectonics and the consequent opening of the Bay of Biscay (Guillocheau et al., 2000). This tectonic phase would have reactivated deep fractures and facilitated hydrothermal activity or heat transfer increase in the Paris Basin. The precise definition of the processes causing the 10–30 °C temperature offset for precipitation of the Dol1 phase (Fig. 3) requires in-depth tectonothermal modeling to be addressed, and is beyond the scope of this study.

Furthermore, U-Pb data of oil inclusion–bearing carbonate cements give important insights into the timing of the Paris Basin petroleum system. Previous studies indicate that oil generation started at 65 Ma and was almost complete at 35 Ma (Espitalié et al., 1988; Monticone et al., 2012). Conversely, petrographic analysis revealed that crystals in the Dol1 phase (117 ± 13 Ma) bear primary oil inclusions, suggesting that oil migration had already begun during the Early Cretaceous (Fig. 3). This finding suggests that the timing for hydrocarbon migration in the Middle Jurassic reservoirs should be revisited, because this potentially occurred some 40 m.y. earlier than previously thought, and perhaps in association with a hydrothermal event.

The data presented here demonstrate how the coupling of the Δ_{47} thermometer and the laser ablation U-Pb chronometer can improve our ability to precisely reconstruct sedimentary basin thermal and fluid-flow history by relying on the analysis of carbonate minerals only. Combining conventional rock-based modeling with emerging fluid-based Δ_{47}/(U-Pb) thermochronometry may offer additional powerful insight for basins having experienced hydrothermalism. Given the widespread occurrence of carbonates in a variety of crustal and sedimentary settings, such an approach opens a new realm of thermochronological applications and is likely to grow rapidly in the future.

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FIGURE CAPTIONS

Figure 1. A: Stratigraphic column of Paris Basin depocenter (France) with location of studied stratigraphic interval.

B: Geological map of Paris Basin (scale 1:1,000,000) with location (black frame) of surveyed depocenter area. C: Map of iso-T_{max} (T—temperature) from Rock Eval organic matter pyrolysis (http://www-odp.tamu.edu/publications/tnotes/tn30/tn30_11.htm) for Toarcian source rocks. Locations of the four studied well cores are shown with gray symbols; green square represents borehole used by Uriarte (1997) for rock-based thermal modeling.

D: West-east geological cross section of Paris Basin (line of section shown in C). Modified after Gély and Hanot (2014).

Figure 2. Carbonate mineral paragenesis and Tera-Wasserburg diagrams. A: Schematic carbonate mineral paragenesis. Numbers 1–6 refer to different carbonate phases analyzed (see text for description), whereas colors refer to their cathodoluminescence response. B: Tera-Wasserburg plots displaying ^{238}U/^{206}Pb versus ^{207}Pb/^{206}Pb for four of the analyzed Carbonates.

Samples are ordered from top left to bottom right from oldest to youngest, regardless of uncertainty ranges. *T*(Δ_{47})—??; MSWD—mean squared weighted deviates; *n*—number of ablation spots analyzed.

Figure 3. Thermal history of Middle Jurassic rocks in Paris Basin depocenter from deposition to present day. Black dashed line represents thermal history modeled by Uriarte (1997) using conventional rock-based approaches. Solid black line interpolates temperature-time data deduced from Δ_{47} and U-Pb analyses (this study; fluid based) on multiple carbonate phases.

[1] GSA Data Repository item 2018xxx, LA-ICP-MS analytical procedures, discussion on “syn-sedimentary” carbonates, vitrinite reflectance kinetic modeling, Figure DR1 (sample petrography), Figure DR2 (all isochrones), and Figure DR3 (computed evolution of Ro% versus time),

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