U-Pb dating of calcite cement and diagenetic history in microporous carbonate reservoirs: Case of the Urgonian Limestone, France

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ABSTRACT

Microporous carbonates can constitute excellent hydrocarbon reservoirs if their micro-pore and/or nanopore structure is sufficiently developed and continuous. In such deposits, assessing the exact timing of reservoir property stabilization is critical to better understand the postdepositional processes favorable to the creation or preservation of porosity. However, placing reliable and accurate chronological constraints on the formation of microporosity in these reservoirs is a major challenge. In this study we performed absolute U-Pb dating of calcite cements occurring in the Urgonian microporous limestone (northern Tethys margin) of southeastern France. U-Pb ages ranging between 96.7 ± 4.9 Ma and 90.5 ± 1.6 Ma were obtained on the major calcitic phase responsible for the cementation, and therefore the stabilization of microporosity, indicating that this diagenetic process occurred synchronously at the regional scale following an extended subaerial exposure. Our results show that (1) the mineralogical stabilization process responsible for the formation of an excellent pervasive microporous network took place relatively early, and (2) the so-acquired reservoir quality was preserved for more than 90 m.y. These observations emphasize the importance of long exposure periods and associated meteoric influx for the formation and preservation of good microporous reservoirs.

INTRODUCTION

Establishing the relative chronology of diagenetic transformation (paragenesis) from thin section petrography is of outmost importance but it is not sufficient to link the evolution of petrophysical properties in reservoirs with basin-scale structural and burial events in a proper temporal framework. Prior studies have shown the importance of absolute dating of diagenetic cements, which may lead to major reinterpretation of the thermal history and the potential timing of oil generation, migration, and accumulation (Mark et al., 2010). More specifically, the determination of absolute ages of diagenetic events such as micrite stabilization or massive low-Mg calcite cementation in relation to burial history and sea-level fluctuations would greatly improve our ability to constrain the overall reservoir evolution and the key processes preserving or enhancing reservoir quality in microporous carbonates. Although most of these processes are thought to occur during early diagenesis, recent studies have shown that they could also take place later.

U-Pb radiometric dating is the only absolute geochronometer applicable to diagenetic carbonates. However, the most robust and accurate technique based on acid dissolution followed by isotope dilution remains inapplicable in many cases because of either low uranium or high common lead content, or because of the impossibility of microsampling a single (monogeneration) diagenetic cement of interest. Recent development of U-Pb dating of carbonates by laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) applied directly on thin sections or slabs opened a wealth of possibilities with which to date calcite-cemented fossils (Li et al., 2014), calcite-filled veins (Coogan et al., 2016; Roberts and Walker, 2016; Nuriel et al., 2017) or paleosols (Methner et al., 2016). In situ microanalysis is a very efficient approach, compared to isotope dilution, because it offers the possibility to capture a more extended range of U/Pb variability (thereby providing a greater spread of U/Pb ratios to generate isochrons), as well as rapid data acquisition and large sample throughput. However, this very promising method is currently hindered by the lack of appropriately calibrated carbonate standards and international reference material for data correction (interelement and isotopic fractionation). Li et al. (2014) proposed cross-checking the two methods in order to assess the true accuracy and precision of the U-Pb ages measured by LA-ICP-MS. In our study we combined the advantages of the two approaches, the rapid identification of appropriate samples by use of the laser ablation technique and the accuracy of isotope dilution to obtain robust absolute ages on the formation of microporosity in a typical micritic carbonate formation.

The studied samples belong to the Urgonian Limestone (UL) formation of Barremian–Aptian (lower Cenomanian) stage of southeastern France (Fig. 1), considered to be a good analog of major microporous carbonate reservoirs in the Middle East (Borgomano et al., 2013). The giant oil resources discovered in such microporous reservoirs motivated significant efforts to understand their genesis and evolution (Volery et al., 2010; Deville de Periere et al., 2011), highlighting the importance of unraveling the origin and timing of microporosity formation and stabilization.

DIAGENETIC HISTORY OF THE MICROPOROUS UL, SOUTHEAST FRANCE

Diagenetic patterns observed in the UL were described in detail in Lénio et al. (2014), establishing a diagenetic sequence showing a number of well-characterized calcite dissolution and cementation phases. Two main generations of calcite cement, S1 and S2, have been documented in the formation, based on petrographic and textural evidence showing a continuum from the S1 microsparite to the S2 blocky calcite. Note that the S1 phase is too small and inclusion rich to be subsampled for U-Pb dating purposes. The UL is marked by several short-term syn-Urgonian exposures as well as a major regional post-Urgonian subaerial exposure (ca. 3 Ma) related to the Durancian phase (upper Albian–lower Cenomanian) (Masse and Philip, 1976). The geographical extension of the Durancian phase, evidenced by a characteristic erosion surface, is closely correlated to the spatial distribution of microporous UL and has been proposed.
as being the main factor responsible for the diagenetic evolution of this formation (Masse and Philip, 1976; Léonide et al., 2014). In Léonide et al. (2014) it was hypothesized that during the exposure, inflow of meteoric water would have induced dissolution of aragonitic and high-Mg calcite bioclasts, and the development of an epikarst below the surface of exposure. The dissolution of metastable minerals, mainly composed of rudist aragonitic shells and small-sized micrite particles, provided solutes to allow the development of low-Mg calcite overgrowth around more stable, large-size, calcite particles, according to a process called micrite stabilization (Volery et al., 2010).

This process is critical in microporosity preservation, not only because it improves connectivity between micro pores, eventually increasing permeability, but also because it enhances resistance to compaction during burial. The blocky low-Mg calcite precipitation event, referred to as S2, occluding intergranular and intragranular moldic and vuggy porosity (Léonide et al., 2014) is assumed to be coeval or to have occurred shortly after the low-Mg calcite overgrowth, and therefore to record the termination of the micrite stabilization process. The resulting porosity, mainly composed of intragranular secondary microporosity, can exceed 35% in the UL, giving the formation good reservoir properties (Fournier et al., 2011; Léonide et al., 2014). Such cementation and stabilization processes are commonly invoked in formation of microporous reservoirs (Volery et al., 2010; Deville de Periere et al., 2011; Léonide et al., 2014; Ehrenberg and Walderhaug, 2015). Coarse crystalline blocky calcite interpreted as S2 occurs within the U2 stratigraphic unit (Fig. 1B) across the entire UL (over tens of kilometers). Stable oxygen and carbon isotopic compositions of the S2 calcite range between +2.4‰ and −0.7‰ (δ18O Peedee belemnite, PDB) and −4.4‰ to −10.0‰ (δ13C PDB), respectively, reflecting a marine source of carbon and the involvement of meteoric water at low and moderate temperature (<65 °C) in a shallow burial environment (Lamarche et al., 2012; Léonide et al., 2014). Several samples of the low-Mg calcite S2 representative of this particular diagenetic phase along the platform were investigated for U-Pb dating. The S2 calcite is therefore the best candidate to constrain the timing and duration of micrite stabilization responsible for the preservation and excellent reservoir quality of the studied formation.

SAMPLES AND METHODS
Calcite S2 from the UL was sampled at five outcrop locations along a west-east transect (La Nesque, Font Jouvale, Col de la Ligne, and Rustrel, and Simiane, 5 km to the northeast of Rustrel; Fig. 1B), following the transect studied by Léonide et al. (2014). All samples were collected in a rudist-rich unit (U2) within the main reservoir facies. Seven samples of well-developed sparry crystals of vug-filling calcite were selected for U-Pb dating. Because of the large sample size required, only samples from Rustrel (7 aliquots) and La Nesque (3 aliquots) were analyzed by isotopic dilution (ID)–multicollector (MC) ICP-MS. Samples from the five locations were analyzed by LA-ICP-MS on fragments of the calcite samples mounted in epoxy resin (see Item DR1 in the GSA Data Repository 1 for analytical procedures). The U-Pb ages for Rustrel data are shown in Figure 2, as Tera-Wasserburg diagrams (207Pb/206Pb, 208Pb/206Pb) for LA-ICP-MS data, and total Pb/U isochron plots for the ID-MC-ICP-MS data. Rustrel, La Nesque, and Simiane samples were also analyzed for their δ18O and δ13C values (see the Data Repository for analytical details).

RESULTS
LA-ICP-MS spots in the S2 sparry calcite exhibit extremely high radiogenic isotope composition, with 207Pb/206Pb showing pure radiogenic Pb. The results obtained by LA-ICP-MS yield statistically homogeneous ages between 91.7 ± 2.2 Ma and 94.7 ± 2.6 Ma (all systematic errors were propagated; see Item DR1) for La Nesque, Rustrel, Font Jouvale, and Col de la Ligne samples. The Simiane sample (two fragments in the same sample) displays a more complex pattern (see Item DR1), with data spread in two different sets, suggesting the existence of two distinct isochrons. The first set shows 42 laser spots nicely aligned, forming an isochron at 93.0 ± 2.3 Ma, in good agreement with the age of Rustrel, La Nesque, Font Jouvale, and Col de la Ligne samples. The second set (32 laser spots) shows a significantly younger age at 34.0 ± 0.9 Ma, and a highly radiogenic lower intercept. Several samples (11 spots) are intermediate between the two sets.

ID-MC-ICP-MS isochrons from Rustrel and La Nesque show a much less variable U/Pb ratio than LA-ICP-MS ones, probably because ID-MC-ICP-MS requires a much larger amount of material (mg range) compared with LA-ICP-MS, which inherently averages small-scale variability in the sample (see Item DR1). Ages for samples from La Nesque and Rustrel are 96.7 ± 4.9 Ma and 90.5 ± 1.6 Ma, respectively, and are within error of the ages obtained by LA-ICP-MS. Excluding Simiane, the four other sites can be considered as representative of a same calcite generation yielding a weighted mean age for 1 GSA Data Repository item 2018061, analytical procedures, stable isotope information, Figure DR1 (U-Pb methodology with isotope dilution and LA-ICP-MS and results), Figure DR2 (stable isotope methodology and results), and Figure DR3 (general model of diagenetic evolution of Urgonian Limestone), is available online at http://www.geosociety.org/datarepository/2018/ or on request from editing@geosociety.org.
This would be consistent with meteoric water percolation during the Durancian exposure period. The involvement of meteoric water in the formation of the S2 calcite is supported by their low δ18O values (~–8.3‰ PDB) versus ~–7.8‰ for δ18O; see Fig. 3; Item DR2). Considering the onset of the exposure event from the late Albian (Masse and Philip, 1976), the completion of the micrite stabilization process, which includes (1) dissolution of metastable minerals, (2) overgrowth of low-Mg calcite particle, and (3) massive cementation by S2 calcite precipitation in intergranular and intragranular porosity, lasted ~8 ± 3 m.y. Such a duration is at odds with modern diagenetic studies in similar environments showing that complete occlusion of macroporosity by low-Mg calcite in shallow phreatic environment can be very short, i.e., <1 m.y. (Budd, 1988; Whitaker and Smart, 2007). We then propose the alternate hypothesis that the Durancian phase exposure event would be younger by several million years (upper constraint tied to the late Cenomanian at 94 Ma) than previously estimated, ca. 100 Ma, i.e., Albian–early Cenomanian.

S2 of 92.4 ± 1.7 Ma (95% confidence interval) based on all ID-MC-ICP-MS and LA-ICP-MS measurements. This Turonian age is considered as representing the absolute time of the fluid circulation event responsible for S2 cementation at the regional scale.

EARLY (92 Ma) CALCITE CEMENTATION EVENT

Our results demonstrate that the extensive and first occurrence of massive cementation phase of low-Mg calcite S2 took place at 92.4 ± 1.7 Ma; this is much younger than the biostratigraphic deposition age for UL (125–120 Ma), and excludes a syndepositional origin of the cement.

The S2 calcite is composed of blotty luminescent to nonluminescent coarse crystalline blocky calcite (Léonide et al., 2014), suggesting that it may have formed from oxidizing fluids. This would be consistent with meteoric water percolation during the Durancian exposure period. The involvement of meteoric water in the formation of the S2 calcite is also supported by their low δ18O values (~–8.3‰ to ~–6.1‰ PDB; see Item DR2).

Considering the onset of the exposure event from the late Albian (Masse and Philip, 1976), the completion of the micrite stabilization process, which includes (1) dissolution of metastable minerals, (2) overgrowth of low-Mg calcite particle, and (3) massive cementation by S2 calcite precipitation in intergranular and intragranular porosity, lasted ~8 ± 3 m.y. Such a duration is at odds with modern diagenetic studies in similar environments showing that complete occlusion of macroporosity by low-Mg calcite in shallow phreatic environment can be very short, i.e., <1 m.y. (Budd, 1988; Whitaker and Smart, 2007). We then propose the alternate hypothesis that the Durancian phase exposure event would be younger by several million years (upper constraint tied to the late Cenomanian at 94 Ma) than previously estimated, ca. 100 Ma, i.e., Albian–early Cenomanian.

Overall the present-day reservoir quality observed at the outcrop was thus acquired relatively early in the geological history of the UL, but more important, it was preserved from degradation (cementation, compaction) to the present day, i.e., for ~90 m.y., despite subsequent burial.

LATE (ca. 34 Ma) CALCITE CEMENTATION EVENT

For the Simiane sample, LA-ICP-MS U-Pb results unambiguously show the intimate coexistence of 2 calcite generations dated as 93.0 ± 2.3 Ma and 34.0 ± 0.9 Ma (see Fig. DR1). The common lead composition determined from ID-MC-ICP-MS data (207Pb/206Pb = 0.87, La Nesque and Rustrel) can be used to calculate a model age for each individual spot measured by LA-ICP-MS, and therefore investigate the spatial distribution of the two different diagenetic phases in this sample. The age map shown in Figure 3 illustrates that the young calcite is preferentially located in the central part of the vug, consistent with a later precipitation. The O-C isotope determinations in the Simiane sample indicate that the late calcite exhibits somewhat lower δ13C and δ18O values than the early calcite on average (i.e., ~0.8‰ versus ~2.1‰ for δ13C and ~8.3‰ versus ~7.8‰ for δ18O; see Fig. 3; Item DR2).

The 34 Ma fluid circulation event cemented the residual macroporosity of the reservoir but did not affect the UL microporosity, or it implies that a greater porosity existed before this circulation event than currently measured at the site. Although the 34 Ma age of the late calcite must be taken with caution, it brings useful information for the understanding of fluid circulations and diagenetic evolution of the UL. In particular, this event may be related to meteoric fluid circulations caused by the extensional regime during the western European rifting (see Pisapia et al., 2017) that resulted in formation of several
grabens during Priabonian time in the Provence region (Séranne, 1999).

**IMPLICATIONS FOR THE DIAGENETIC RECONSTRUCTION OF THE URGONIAN CARBONATE RESERVOIRS**

The results of this study indicate that the extended exposure period that favored inflow of meteoric waters in the UL under humid climate is favorable for promoting micrite stabilization and porosity preservation in microporous reservoirs and constitutes a key phase in the diagenetic evolution of the microporous limestone. In the UL, the process of micrite stabilization was not syndepositional, as often proposed (e.g., Volery et al., 2010), but occurred ~30 m.y. after younger than the time of deposition. One of the successful application of U-Pb dating of carbonate outcrops in Provence (SE France): Implications for carbonate reservoir characterization: Journal of Petroleum Geology, v. 36, p. 5–41, https://doi.org/10.1111/jpg.12540. Budd, D.A., 1988, Aragonite-to-calcitization during fresh-water diagenesis of carbonates: Insights from pore-water chemistry: Geological Society of America Bulletin, v. 100, p. 1260–1270, https://doi.org/10.1130/0016-7606(1988)100<1260:ATCDTF>2.3.CO;2.

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**ACKNOWLEDGMENTS**

This study was supported by the French Investissement d’Avenir program through the Equipex ASTER-CEREGE and by the Excellence Initiative of Aix-Marseille University (A*MIDEX). Total SA provided financial support for Godeau’s doctoral research. This paper greatly benefited from constructive comments by P. Nuriel, F. Whittaker, and an anonymous reviewer. We are grateful to C. Sonzogni and L. Vidal for the stable isotope analyses, and to H. Mariot and W. Barthélémy for their technical support.

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