Origin and distribution of calcite cements in a folded fluvial succession: The Puig-reig anticline (south-eastern Pyrenees)

XIAOLONG SUN*,†, ENRIQUE GOMEZ-RIVAS†, DAVID CRUSET‡, JUAN ALCALDE‡, DANIEL MUÑOZ-LÓPEZ‡, IRENE CANTARERO†, JUAN DIEGO MARTÍN-MARTÍN†, CÉDRIC M. JOHN§ and ANNA TRAVE†

*School of Geosciences, China University of Petroleum (East China), 66 West Changjiang Road, Qingdao, 266580, China (E-mail: sun.xiaolong@upc.edu.cn)
†Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), c/Martí i Franquès s/n, Barcelona, 08028, Spain
‡Geosciences Barcelona (GEO3BCN-CSIC), Lluís Solé i Sabaris s/n, Barcelona, 08028, Spain
§Department of Earth Science and Engineering, Imperial College London, Prince Consort Road, London, SW7 2AZ, UK

ABSTRACT

As one of the predominant diagenetic products in clastic rocks, calcite cements are typical fingerprints of cement-forming fluids and are key controls on reservoir quality. The Puig-reig anticline, in the south-eastern Pyrenees (Spain), exposes excellent outcrops of conglomerates, sandstones and claystones, which were deposited from a proximal to medial fluvial system and underwent folding, fracturing and cementation. This anticline constitutes an appropriate case study to investigate the origin and distribution of calcite cements during folding evolution and how they affect reservoir quality. Based on structural, petrographic and geochemical analyses (carbon, oxygen, strontium and clumped isotopes and elemental composition), five generations of calcite cements (‘Cc0’ to ‘Cc4’) have been identified, filling intergranular porosity of host rocks, faults and four fracture sets (F1 to F4). Calcite cement Cc0 precipitated in intergranular porosity from meteoric fluids in the phreatic zone during the early diagenetic stage. During the most intense phase of thrusting and folding, Cc1 precipitated in intergranular porosity, faults and F1 to F4 fracture sets from hydrothermal fluids that migrated from deeper areas of the Pyrenean chain. During the late stage of fold growth, Cc2 precipitated in faults and their associated fractures in the anticline crest from hydrothermal fluids but at shallower burial depths than that of Cc1. Calcite cement Cc3 mainly precipitated in fractures with the same strike as F1 and F4 fracture sets in the north-western part of the anticline, from formation fluids that probably migrated through the frontal thrust of the south-eastern Pyrenees. During the continuous fold denudation, Cc4 precipitated from meteoric fluids in F1 to F4 fracture sets across the anticline. Results indicate that at foreland basin margins, external fluids coeval with compressional deformation and/or alteration of detrital carbonates contribute to intensive calcite cementation. This can result in an overall occlusion of porosity and significantly damaged reservoir quality.

Keywords Anticline, calcite cementation, fluid regime, fluvial reservoir, Pyrenees.
INTRODUCTION

Calcite in the form of cement is one of the predominant authigenic minerals in clastic rocks (Morad, 1998; Walderhaug & Bjørkum, 1998). The presence and distribution of calcite cement can exert significant effects on reservoir quality and heterogeneity (Dutton et al., 2002; Davis et al., 2006; Van den Bril et al., 2007; Xiong et al., 2016; Cui et al., 2017; Wang et al., 2017). In clastic rock successions, different phases of calcite cements can successively precipitate from local or external fluids during the evolution of sedimentary basins and orogens. On the macro scale, calcite cement distribution within clastic rocks is mainly controlled by the depositional environments and the stacking patterns of sequence stratigraphy (Morad, 1998; Taylor et al., 2000; El-ghali et al., 2006; Morad et al., 2010), and has been widely studied in shallow marine (Bjørkum & Walderhaug, 1990b; Walderhaug & Bjørkum, 1998; Taylor et al., 2000; Nyman et al., 2014), deep-water turbidite (Carvalho et al., 1995; Dos Anjos et al., 2000; Dutton, 2008; Mansurberg et al., 2009; Yang et al., 2018) and alluvial–fluvial settings (Hall et al., 2004; Wanas, 2008; Taylor & Machent, 2011; Cruset et al., 2016; Olanipekun & Azmy, 2022).

Another factor that controls cement distribution in rocks is the development of faults and fractures of multiple scales, which typically control fluid migration across different hydrostratigraphic units (Evans & Fischer, 2012; Evans et al., 2012). On the small scale, cement distribution is controlled by lithofacies and reservoir porosity and permeability, in a way that cementation tends to affect the initially more permeable deposits (Dutton et al., 2002; Hall et al., 2004; Van den Bril & Swennen, 2009). Thus, calcite cement is typically heterogeneously distributed and can exert key effects on reservoir quality, and eventually partially or totally reduce permeability (Dutton et al., 2002).

Fracture networks tend to form in fold-and-thrust belts and their adjacent foreland basin margins due to intensive progressive deformation. The analysis of calcite cements of the resulting veins and their host rocks can be used to unravel the history and timing of fluid migration events (Hansman et al., 2018), the evolution of fluid regimes, the degree of fluid–rock interaction, and the deformation history of related structures (Bons et al., 2012; Beaudoin et al., 2014). The interplay between rock deformation, fluid flow and diagenesis in compressive settings has been analyzed in many case studies, including examples from the Apennines (Smeragli et al., 2018; Beaudoin et al., 2020), the Bighorn Basin in the Sevier fold-and-thrust belt (Beaudoin et al., 2011, 2013, 2014), the Oman Mountains (Breesch et al., 2009; Gomez-Rivas et al., 2014; Balsamo et al., 2016), the Sicilian fold-and-thrust belt (Dewever et al., 2010, 2013), and the Zagros fold-and-thrust belt (Ceriani et al., 2011; Shariatinejad et al., 2013), among many others. Many studies mainly focus on unravelling the relationships between fluid flow, deformation and fluid–rock interaction in fold-and-thrust belts, whereas their adjacent foreland basins are significantly less well-documented. For example, in the South Pyrenees, an ideal natural laboratory due to its well-preserved and well-exposed outcrops, most studies focused on the cover thrust sheets (Travé et al., 1997; Lacroix et al., 2011, 2014, 2018; Beaudoin et al., 2015; Crognier et al., 2018; Cruset et al., 2018, 2020a,b; Nardini et al., 2019; Muñoz-López et al., 2020a,b), whereas only a few studies involved the Ebro Foreland Basin (Travé et al., 2000, 2007; Cruset et al., 2016). On the other hand, compressional settings have high potential for carbon capture and storage (CCS) (Sun et al., 2020). The Ebro Foreland Basin has been assessed as one of the priority regions for CCS development in Spain (Sun et al., 2021a). However, there is significant uncertainty on the suitability assessment of storage sites in this hydrocarbon-limited basin due to the very limited geological and geophysical exploration data available. Thus, well-exposed structures of this area can be used as analogues to explore cement distribution, fluid evolution and their effects on reservoir quality of such reservoir structures at depth.

At the north-eastern margin of the Ebro Foreland Basin, the Puig-reig anticline exposes excellent outcrops of proximal to medial fluvial deposits, which mainly belong to the Camps de Vall-Llonga and Solsana formations. The sedimentary and petrographic characteristics of these folded deposits have been studied recently by Sun et al. (2021b). In addition, Cruset et al. (2016) carried out a study of the geochemistry of calcite cements restricted to fracture networks only at the anticline crest and formed exclusively during fold growth. These authors described two cementation phases and unravelled the composition of the fluids from which these two cements precipitated, and related the first of them to the early fold growth and the...
second one to the fold crest collapse. Building on previous studies, the goal of this paper is to identify the complete sequence of calcite cementation filling both intergranular porosity and fractures in the whole anticline and during the complete fold evolution, including pre-folding, syn-folding and post-folding stages. This paper also aims to unravel the conditions under which these cements precipitated and relate them to the sedimentological and structural evolution of the Puig-reig anticline. Contrary to previous studies, special emphasis is put on understanding the distribution of calcite cement across different lithofacies and structural positions of the anticline. Based on the comprehensive analysis of cement distribution in the Puig-reig anticline, the results are compared with those reported from other areas worldwide in order to discuss universal rules for the distribution of calcite cement and the effects on reservoir quality in different settings. For these purposes, a multidisciplinary approach that integrates structural, petrographic and geochemical analyses is used to study fracture-filling and intergranular porosity-filling calcite cements of the Puig-reig anticline rocks. Detailed petrographic observations and geochemical analyses of several cementation phases, as well as their interpretation, distribution and impact on reservoir quality, have been presented. In addition, the lithofacies classification and the data of rock composition, intergranular porosity and cement content outlined in Sun et al. (2021b) as well as the geochemical data of the cementation phases identified by Cruset et al. (2016) have been integrated into this study.

GEOLOGICAL SETTING

The Pyrenees constitute an asymmetrical and doubly verging orogenic belt that was formed during the collision between the Iberian and Eurasian plates from the Late Cretaceous to the Miocene (Muñoz, 1992; Vergés et al., 2002). This orogen comprises an antiformal stack of basement-involved thrusts (the Axial Zone), southward sided to the South Pyrenean fold-and-thrust belt and finally propagated to the Ebro Foreland Basin (Choukroune, 1989; Roure et al., 1989; Muñoz, 1992). The Vallfogona thrust acts as the major frontal thrust between the South Pyrenean fold-and-thrust belt and the eastern Ebro Foreland Basin (Fig. 1A, B and C). Vergés (1993) interpreted the Puig-reig anticline as a growth anticline at the footwall of the Vallfogona thrust due to a duplex stack at depth, which can be observed in the seismic profiles across this anticline (Fig. 1C). In the deeper part, the Banyoles and Igualada formations are composed of marine marls and deltaic sandstones deposited during the Middle and Late Eocene. These marine deposits were duplicated by thrusting and detached above the Lutetian Beuda gypsums and the late Priabonian Cardona salts (Vergés et al., 1992; Serra-Kiel et al., 2003a,b). In the upper and outcropping part of the Puig-reig anticline, the Berga Group and the Solsona Formation were deposited from alluvial to fluvial systems from the Late Eocene to the Oligocene, after the transition from marine to continental depositional environments (Costa et al., 2010). The Puig-reig anticline trends ESE/WNW and is slightly oblique to the main Pyrenean structures (Vergés, 1993). This gentle anticline has a wavelength of more than 10 km.

At the proximal area of the footwall of the Vallfogona thrust ramp, the Berga Group consists of coarse alluvial and proximal fluvial deposits and presents growth strata geometries (Ford et al., 1997; Suppe et al., 1997), which are dated between around 34 Ma and 31 Ma (Carri gan et al., 2016). These coarse deposits become progressively finer-grained and thinner bedded towards the Ebro Foreland Basin and wedge out into the fluvial Solsona Formation (Williams et al., 1998; Barrier et al., 2010). Focusing on the outcrops of the Camps de Vall-Llonga (a sub-unit of the Berga Group) and Solsona formations in the Puig-reig anticline (Fig. 1D), Sun et al. (2021b) interpreted these formations as deposited from a proximal to medial fluvial system. This anticline can be divided into five structural positions from north to south, i.e. north limb, crest–north limb transition zone (NTZ), crest, crest–south limb transition zone (STZ) and south limb (Fig. 1E). The proximal fluvial deposits, which concentrate in the north limb of the anticline and especially in the northwestern part, are characterized by sheet-like conglomerates with minor sandstone interlayers (Fig. 2A and B). These deposits represent sedimentary environments of unconfined flash floods or wide-shallow channel streams. The proximal–medial fluvial deposits, covering the NTZ, crest and STZ zones of the anticline, consist of channelized conglomerates (Fig. 2C) and interbedded sandstones and claystones (Fig. 2C and D). The medial–distal fluvial deposits dominate the south limb of the anticline and consist
Fig. 1. (A) Geographical location and (B) main structural units of the South Pyrenean fold-and-thrust belt and the Ebro Foreland Basin (Vergés, 1993). (C) Geological cross-section of the frontal part of the south-eastern Pyrenean fold-and-thrust belt and the Ebro Foreland Basin (Vergés, 1993). The seismic profile is from the Spanish Geophysical Information System. (D) Distribution of the Berga Group and the Solsona Formation and location of the studied outcrops. The strata distribution is based on the regional geological map of Catalonia (Institut Cartogràfic i Geològic de Catalunya, 2006). The subdivision of the Berga Group follows the scheme of Williams et al. (1998). (E) Geological cross-section of the north-eastern margin of the Ebro Foreland Basin, modified from Williams et al. (1998) and Barrier et al. (2010).
of interbedded beds of sandstones and clays-
stones (Fig. 2E and F). These medial fluvial
deposits represent sedimentary environments
of channel streams and overbanks. Detailed
descriptions of lithofacies, lithofacies associa-
tions and sedimentary environments can be
found in Sun et al. (2021b). The distal fluvial
deposits are located southward of our study
area, and are composed of terminal lobes repre-
senting low lake-level stages and fluvial-
dominated deltas and interdistributary bays
representing high lake-level stages (Sáez et al.,
2007).

Based on a previous study on fracture net-
works (Sun et al., 2021c), the anticline crest fea-
tures abundant fractures (Fig. 3A) and a system
of faults, including strike–slip and normal faults
characterized by displacements lower than 20 m. Other scarce small-scale low-angle reverse
faults with displacements lower than 2 m are
also present, which were previously observed in
other studies (Cruset et al., 2016). Other struc-
tural positions are characterized by abundant
fractures and a few strike–slip faults. Based on
the fracture orientations and their relationships
with the fold hinge, Sun et al. (2021c) identified
four fracture sets (not including faults) in the
Puig-reig anticline with the following strikes: F1
(NNW–SSE); F2 (ENE–WSW); F3 (WNW–ESE);
and F4 (NNE–SSW) (Fig. 3B). During the intense
phase of thrusting and folding, variable fracture
sets (F1 to F4) perpendicular or sub-
perpendicular to bedding surfaces, as well as
reverse and most strike–slip faults, formed due
to regional compression. During the late stage of
anticline growth, minor normal faults striking
NNW–SSE and their concomitant fractures with
the same strike as the F1 fracture set formed at
the anticline crest by a change of the regional
stress field. A gentle anticline geometry and the
lack of systematic extensional fractures indicate
that this anticline probably did not experience
intensive out-arc extension (Frehner, 2011). Dur-
ing continuous denudation, previous fracture
sets (F1 to F4) could have been reactivated
because these reopened fractures are generally
sub-perpendicular to bedding surfaces and host
previous calcite cements. All of these results
indicate that fracture networks mainly origi-
nated from regional compression during the
intensive fold deformation stage of the Puig-reig
anticline. However, identifying the terminations
and relative cross-cutting relationships between
the different fracture sets is difficult due to the
lack of outcrops parallel to bedding planes.
Thus, systematically establishing the chronology
of the different fracture sets and explaining their
variation across the different structural positions

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are challenging tasks. The study by Sun et al. (2021c) shows that fracture intensity is controlled by the structural position and the host rock depositional characteristics. The anticline crest and its adjacent areas feature higher fracture intensity than that of the anticline limbs. Besides, thick conglomerate bodies feature lower fracture intensities but larger fracture lengths and apertures than thin sandstone layers.

METHODS

Outcrops and samples

The Puig-reig anticline exposes excellent outcrops that mainly consist of deposits of the Camps de Vall-Llonga and Solsona formations. These outcrops are distributed in the cross-sections along roads that cut through the structure in a roughly north–south direction (i.e. almost perpendicular to the fold trace), between the towns of Sant Llorenç de Morunys in the north and Solsona in the south (Fig. 1B and D). In this study, fractures hosting calcite veins were plotted in equal-area lower-hemisphere stereograms. Samples of host rocks and fracture-filling veins, representing different structural positions of the anticline and different lithofacies, were selected for petrographic and geochemical analyses.

Petrography

A total of 108 polished thin sections of host rocks and fracture-filling calcite veins were made for petrographic observations. These were analyzed to determine host rock compositions and to distinguish different generations of calcite cements using a Zeiss Axiophot optical microscope (Zeiss Microscopy, Jena, Germany) and a Technosyn Cold Cathodoluminescence microscope, model 8200 Mk-1 operating 16 to 17 kV and 270 to 290 μA gun current [Cambridge Image Technology Limited (CITL), Hatfield, UK]. Among these, 30 sandstone thin sections were selected to determine rock compositions using the point-counting method. These results can represent the original rock compositions because host rocks of this anticline only underwent weak pressure solution rather than intensive dissolution. In addition, 60 thin sections from different lithofacies were selected to determine porosity and cement content of host rocks using NIS Elements and ImageJ software (Schneider et al., 2012). Based on the colour differences between different components, porosity was determined using microphotographs in parallel nicols, while cement content was determined using microphotographs in cathodoluminescence.

Carbon and oxygen isotopes

A total of 27 samples of fracture-filling veins and intergranular porosity-filling cements were selected for carbon-isotope and oxygen-isotope analysis for different generations of calcite cements. Using a 500 μm diameter dental drill, 50 to 70 μg of calcite powders were reacted with 100% phosphoric acid for five minutes at 70°C. The resultant CO₂ was analyzed using an automated Kiel Carbonate Device coupled to an isotope ratio mass spectrometer Thermo Finnigan MAT-252 (Thermo Fisher Scientific, Waltham, MA, USA) following a modified McCrea’s method (1950). The results were calibrated with secondary standards (RC-1 and CECC), traceable to NBS-18 and NBS-19 international standards. The standard deviation is ±0.01‰ for δ¹³C and ±0.03‰ for δ¹⁸O with respect to the VPDB standard (Vienna Pee Dee Belemnite).
Clumped isotope thermometry

Clumped isotope thermometry was applied to four samples of calcite cements to calculate the temperatures and $\delta^{18}O$ values of the fluids from which these calcite cements precipitated. Measurements were carried out in the Qatar Stable Isotope Laboratory at Imperial College London using a fully automated system, Imperial Batch Extraction (IBEX), and following the method of Adlan et al. (2020). Around 4 mg aliquots of calcite powders for each sample were individually dropped into 105% phosphoric acid at 90°C and reacted for 10 min on an automated IBEX device. The resultant CO$_2$ was separated with a Porapak-Q trap and transferred into the bellows of a Thermo MAT 253 isotope ratio mass spectrometer (Thermo Instruments, Bremen, Germany). The characterization of a replicate consisted of eight acquisitions in dual inlet mode with seven cycles per acquisition. The post-acquisition processing was completed using the free software Easotope (John & Bowen, 2016). The new Intercarb (I-CDES) approach was used to correct our clumped isotope samples (Bernasconi et al., 2021) which relies on normalization using four carbonate standards: ETH1 (0.205 $\pm$ 0.0016%), ETH2 (0.209 $\pm$ 0.0015%), ETH3 (0.613 $\pm$ 0.0014%) and ETH4 (0.451 $\pm$ 0.0018%). Values in the I-CDES are reported without acid correction factor at 90°C. The raw $\Delta_{47}$ data were corrected for non-linearity using the pressure baseline correction (Bernasconi et al., 2013). Samples were measured three times (three replicate) and the average results were converted to temperatures using the inter-laboratory calibration of Anderson et al. (2021). The calibration includes data from the Qatar Stable Isotope Laboratory, extends from 0 to 350°C, and is measured using the new I-CDES scale: it is thus an ideal calibration for our study. Carbonate $\delta^{18}O$ values were corrected with the acid fractionation factors of Kim et al. (2015). The $\delta^{18}O_{\text{fluid}}$ was calculated using the equation of Kim et al. (2007) with the clumped isotope temperatures and the carbonate $\delta^{18}O$ values, and are expressed in $\%_o$ with respect to the Vienna Standard Mean Ocean Water (VSMOW).

Strontium isotopes

Strontium isotopes ($^{87}Sr/^{86}Sr$) were measured for four samples of calcite cements. For each sample, 10 to 20 mg of calcite powders were rinsed in ultrasonic MilliQ water to remove detrital contaminants. Each sample was treated individually to ensure that sufficient rinsing steps were applied. Cleaned fragments were dissolved in dilute nitric acid, the resulting solution was centrifuged at medium speed for 20 min, and the supernatant was transferred to clean PFA beakers. Strontium was separated from matrix and Rb using an extraction resin type Eichrom Sr-Spec in the ultra-clean laboratory LIRA (UB). Strontium isotope ratios were determined by multicollector inductively coupled mass spectrometry on a Nu Instruments (Wrexham, UK) Plasma 3 MC-ICPMS at the University of Barcelona (CCiT-UB). The $^{87}Sr/^{86}Sr$ ratios were normalized for instrumental mass bias with respect to the reference value of $^{86}Sr/^{88}Sr = 0.1194$. Instrumental drift was corrected by sample-standard bracketing (SSB) using NBS987 as the primary standard with matching standard and sample Sr concentrations. External analytical reproducibility during the session is $^{87}Sr/^{86}Sr = 0.710339 \pm 0.000012 (2\sigma, n = 14)$.

Elemental composition

Nine carbon-coated polished thin sections were selected to analyse major, minor and trace element concentrations on a CAMECA SX-50 electron microprobe (Camere, Paris, France). The microprobe was operated using 20 kV of excitation potential, 6 nA of current intensity and a beam diameter of 10 μm. In total, more than 400 probe points were selected, covering all generations of calcite cements recognized by petrographic observations. Detection limits are 107 ppm for Ca, 112 ppm for Mg, 119 ppm for Mn, 254 ppm for Sr, 77 ppm for Fe and 139 ppm for Na. Precision on major element analyses average 1.03% standard error at 3σ confidence levels.

RESULTS

Petrology of host rocks

Based on Folk’s (1980) sandstone classification, all fluvial sandstone samples retrieved in the studied area plot within the litharenite field (Fig. 4A). Framework grains are mainly composed of lithic fragments (60 to 90%) with minor quartz (5 to 30%) and very limited feldspar. Based on Zuffa’s (1980) classification of hybrid arenites, these samples mainly plot in...
the carbonate extrarenite field with a minor number in the non-carbonate extrarenite field (Fig. 4B). The contents of carbonate extrabasinal grains range from 40 to 70%, mainly sourced from the Mesozoic–Cenozoic successions of the South Pyrenean cover thrust sheets and the Pyrenean Axial Zone (Devonian carbonates). The contents of non-carbonate extrabasinal grains, including non-carbonate lithic, quartz and feldspar grains, range from 30 to 60%, mainly sourced from the Pyrenean Axial Zone (Riba, 1976; Williams et al., 1998; Barrier et al., 2010).

The proximal fluvial fan has a slightly higher content in carbonate extrabasinal grains, compared to the medial fluvial fan. As shown in Fig. 4C, most samples present very low porosity, mainly ranging from 0 to 3%, with an average value of 1.2%. All samples have high contents of intergranular porosity-filling calcite cements, mainly ranging from 5 to 15%, with an average value of 11.6%. Most porosity has been destroyed by compaction and occluded by cementation.

### Petrology of calcite cements

Field and microscope observations allow distinguishing the distribution and petrographic characteristics of fracture-filling and intergranular porosity-filling calcite cements (Fig. 5). Five calcite cement generations (Cc0 to Cc4) have been recognized in the Puig-reig anticline. Among these, Cc1 and Cc2 correspond to the two cementation phases identified by Cruzet et al. (2016).

Cc0 calcite cement precipitated in intergranular pores but not in fractures (Fig. 5A1). Although Cc0 only filled a small fraction of intergranular porosity, it can be found in different structural positions across the anticline and in different lithofacies from sandstones to conglomerates. Cc0 generally precipitated along clast edges, which is more frequently observed in conglomerate and coarse sandstone lithofacies due to their larger size of intergranular pores. Cc0 consists of subhedral to euhedral blocky...
to slightly bladed crystals, with crystal sizes smaller than 0.5 mm (Fig. 5A2). Mechanical twins are rarely observed in this cement generation. Under cathodoluminescence, Cc0 crystals are non-luminescent with bright orange zonation. Occasionally, this cement shows a subtle zonation under cathodoluminescence (Fig. 5D4). Intergranular porosity was cemented by Cc1 in all samples hosting Cc3 veins (Fig. 5D3 and D4), indicating that Cc3 developed after Cc1. However, there is no direct cross-cutting relationship between Cc3 and Cc2 veins, thus the relative timing between these two generations is unclear.

Cc4 calcite cement precipitated in F1 to F4 fracture sets (Fig. 5E1), and can be identified in all the structural positions of the anticline. Cc4 is commonly found in fracture coatings as small as 1 mm thick, but occasionally occurs as up to 10 mm thick veins (Fig. 5E2). This cement is mainly characterized by anhedral to subhedral blocky crystals and a palisade structure of anhedral to subhedral bladed crystals (Fig. 5E2 to E4). Crystal sizes of Cc4 are up to 1 mm, but generally vary between 0.1 mm and 0.5 mm. This cement is generally non-luminescent under cathodoluminescence. Cc4 mainly precipitated in some re-opened fractures filled by previous cements (Fig. 5E3 and E4), and does not present crystals with clear mechanical twins (Fig. 5E2), indicating that Cc4 probably precipitated in relatively recent times after intensive compression.

Geochemistry of calcite cements

Carbon and oxygen isotopes

Due to the small size of intergranular porosity-filling Cc0, it was difficult to sample this cement and thus it was left out of various isotope analyses, including carbon, oxygen, strontium and clumped isotopes. The carbon and oxygen isotopic composition of conglomerate carbonate clasts and Cc1 to Cc4 generations of calcite cements is summarized in Table 1 and presented in Fig. 6A. The data of carbonate clasts are from Cruset et al. (2016). The carbonate clasts present a wide range of carbon and oxygen isotopic composition with δ13C values ranging from −3.2 to +3.1‰ VPDB and δ18O values from −8.9 to −3.1‰ VPDB. Cc1 shows δ13C values between −3.3‰ and +0.8‰ VPDB and δ18O values between −8.0‰ and −4.9‰ VPDB. Cc2 shows δ13C values between −1.6‰ and +0.1‰ VPDB and δ18O values between −10.2‰ and −8.4‰ VPDB. Cc3 presents δ13C values
Ce0 in intergranular porosity

Ce1 in intergranular porosity and F1 to F4 fracture sets

Ce2 in fractures with the same strike as F1 set

Ce3 in fractures with the same strike as F1 and F4 sets

Ce4 in F1 to F4 fracture sets
Fig. 5. Lower hemisphere Schmidt stereoplots of fractures hosting calcite veins, as well as hand specimens and paired optical and cathodoluminescence (CL) microphotographs for different generations of calcite cements. ‘n’ represents the number of samples. (A1) to (A4) Cc0 calcite cement filled the intergranular porosity of host rocks and presents CL zonation characteristic. (B1) to (B4) Cc1 filled F1 to F4 fracture sets and intergranular porosity and presents homogeneous bright orange luminescence. (C1) to (C4) Cc2 veins developed in fractures with the same strike as the F1 fracture set and present duller luminescence than Cc1 filling intergranular porosity; and (C5) and (C6) limited Cc2 cement filled residual pores after Cc0 and Cc1. (D1) to (D4) Cc3 veins precipitated in fractures with the same strike as the F1 and F4 fracture sets and present duller luminescence than Cc1 filling intergranular porosity. (E1) to (E4) Cc4 veins precipitated in F1 to F4 fracture sets and present non-luminescent characteristic.

Clumped isotope thermometry
The $\Delta_{47}$ and estimated temperatures in °C and $\delta^{18}O_{\text{fluid}}$ in ‰ VSMOW of Cc1 to Cc4 calcite cements are listed in Table 1 and presented in Fig. 6B. The data of Cc1 and Cc2 are from Cruset et al. (2016). The $\Delta_{47}$ values of Cc1 and Cc2 are modified from Cruset et al. (2016) by removing the acid correction factor (0.069 ‰ at 90°C) to be able to compare to the values of Cc3 and Cc4 in the I-CDES that is expressed without correction factor at 90°C. For Cc1, $\Delta_{47}$ values are 0.479 ± 0.009‰ and 0.425 ± 0.010‰, which translate to temperatures of 92 ± 5°C and 129 ± 8°C and $\delta^{18}O_{\text{fluid}}$ values of +4.7 ± 0.6‰ and +9.2 ± 0.7‰ VSMOW. For Cc2, $\Delta_{47}$ values are 0.505 ± 0.010‰ and 0.482 ± 0.004‰, which indicate temperatures of 77 ± 5°C and 90 ± 3°C and $\delta^{18}O_{\text{fluid}}$ values of −1.7 ± 0.9‰ and −0.7 ± 0.3‰ VSMOW. For Cc3, $\Delta_{47}$ values are 0.527 ± 0.001‰ and 0.501 ± 0.007‰, which are converted to temperatures of 49 to 50°C and 59 to 65°C and $\delta^{18}O_{\text{fluid}}$ values of 3.9 to 4.3‰ VSMOW and 5.2 to 6.4‰ VSMOW. For Cc4, $\Delta_{47}$ values are 0.619 ± 0.014‰ and 0.609 ± 0.012‰, which indicate temperatures of 12 to 21°C and 16 to 23°C and $\delta^{18}O_{\text{fluid}}$ values of −5.7 to −3.6‰ VSMOW and −5 to −3.4‰ VSMOW.

Strontium isotopes
The strontium isotopic ratios of host rocks and Cc1 to Cc4 calcite cements are listed in Table 1 and presented in Fig. 7. The data corresponding to host rocks, Cc1 and Cc2 are from Cruset et al. (2016). Host rocks have $^{87}$Sr/$^{86}$Sr ratios of 0.708865 and 0.708967 for mudstone and marly limestone, respectively. Cc1 shows higher $^{87}$Sr/$^{86}$Sr ratios of 0.709138 and 0.709246. Cc2 has $^{87}$Sr/$^{86}$Sr ratios of 0.708947 and 0.709002. Cc3 shows lower $^{87}$Sr/$^{86}$Sr ratios of 0.708747 and 0.708813. Cc4 presents variable $^{87}$Sr/$^{86}$Sr ratios ranging from 0.708757 to 0.710208.

Elemental composition
The elemental composition, including Ca, Mg, Mn, Sr and Fe of Cc0 to Cc4 calcite cements, is summarized in Table 2 and presented in Fig. 8. The elemental composition data of Cc1 and Cc2 calcite cements from Cruset et al. (2016) were integrated into these results. Cc0 has elemental composition values ranging from 546 to 2950 ppm in Mg and ranging from below the detection limits to 1024, 221 and 178 ppm in Sr, Fe and Mn, respectively. Cc1 shows values ranging from 248 to 4500 ppm in Mg and from 158 to 4199 ppm in Mn, while values range from below the detection limits to 3100 and 1221 ppm in Fe and Sr, respectively. Cc2 has values ranging from 458 to 2846 ppm in Mg and from 202 to 2300 ppm in Mn, while values range from below the detection limits to 3200 and 3000 ppm in Fe and Sr, respectively. For Cc3, the Fe, Mg and Mn contents range from 483 to 2827 ppm, from 148 to 1062 ppm and from 545 to 1050 ppm, respectively, while the Sr content ranges from below the detection limit to 312 ppm. For Cc4, the Mg content ranges from 319 to 22 340 ppm, while the Sr, Mn and Fe contents range from below the detection limits to 1601, 604 and 459 ppm, respectively. Besides, Cc4 has a Ca content ranging from 368 470 to 398 507 ppm, which is lower than...
Table 1. $\delta^{18}$O and $\delta^{13}$C values of conglomerate carbonate clasts and Cc1 to Cc4 generations of calcite cements. $\Delta_47$, temperatures and $\delta^{18}$Ofluid obtained from clumped isotope thermometry for Cc1 to Cc4. $^{87}$Sr/$^{86}$Sr ratios of host rocks and Cc1 to Cc4. $\delta^{18}$O and $\delta^{13}$C values of carbonate clasts, clumped isotope data of Cc1 and Cc2, and $^{87}$Sr/$^{86}$Sr ratios of host rocks, Cc1 and Cc2 are from Cruset et al. (2016). $\Delta_47$ values of Cc1 and Cc2 are modified from Cruset et al. (2016) by removing the acid correction factor (0.069 at 90°C) to be able to compare to the values of Cc3 and Cc4 in the I-CDES that is expressed without correction factor at 90°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cement/host rock</th>
<th>$\delta^{13}$C (‰ VPDB)</th>
<th>$\delta^{18}$O (‰ VPDB)</th>
<th>$\Delta_47$</th>
<th>T (°C)</th>
<th>$\delta^{18}$Ofluid (‰ VSMOW)</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF2-10</td>
<td>Cc1</td>
<td>+0.8</td>
<td>-7.4</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>AF2-11</td>
<td>Cc1</td>
<td>0</td>
<td>-8.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AF2-8</td>
<td>Cc1</td>
<td>-2.8</td>
<td>-7.7</td>
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<tr>
<td>AF-3</td>
<td>Cc1</td>
<td>+0.7</td>
<td>-7.9</td>
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<tr>
<td>AF-6</td>
<td>Cc1</td>
<td>-0.7</td>
<td>-7.9</td>
<td></td>
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</tr>
<tr>
<td>B-1</td>
<td>Cc1</td>
<td>-1.5</td>
<td>-8.0</td>
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<tr>
<td>BM-1</td>
<td>Cc1</td>
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<td>-6.8</td>
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<td>BM-3</td>
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<td>CF-4</td>
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<tr>
<td>DS-2</td>
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<tr>
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<td>-7.4</td>
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<tr>
<td>309B1</td>
<td>Cc1</td>
<td></td>
<td></td>
<td>0.479 ± 0.009</td>
<td>92 ± 5</td>
<td>+4.7 ± 0.6</td>
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<tr>
<td>317</td>
<td>Cc1</td>
<td></td>
<td></td>
<td>0.425 ± 0.010</td>
<td>129 ± 8</td>
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<td>309A</td>
<td>Cc1</td>
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<td></td>
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<td>0.709246</td>
</tr>
<tr>
<td>314C</td>
<td>Cc1</td>
<td></td>
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<td></td>
<td></td>
<td>0.709138</td>
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<td>+0.6</td>
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<tr>
<td>C3-2</td>
<td>Intergranular</td>
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<td></td>
<td>+0.3</td>
<td>-4.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H5-1</td>
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<tr>
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<td>Cc2</td>
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<td>-8.6</td>
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<td></td>
</tr>
<tr>
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<tr>
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<td>Cc2</td>
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<td>-10.2</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>311A</td>
<td>Cc2</td>
<td></td>
<td></td>
<td>0.505 ± 0.010</td>
<td>77 ± 5</td>
<td>-1.7 ± 0.7</td>
<td>0.708947</td>
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<tr>
<td>311D</td>
<td>Cc2</td>
<td></td>
<td></td>
<td>0.482 ± 0.004</td>
<td>90 ± 3</td>
<td>-0.7 ± 0.3</td>
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<tr>
<td>C3-3</td>
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<tr>
<td>CF2-4</td>
<td>Cc3</td>
<td>+0.8</td>
<td>-3.4</td>
<td>0.527 ± 0.001</td>
<td>50 (49 to 50)</td>
<td>+4.2 (+3.9 to +4.3)</td>
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<tr>
<td>CF-3</td>
<td>Cc3</td>
<td>-0.1</td>
<td>-3.8</td>
<td>0.501 ± 0.007</td>
<td>62 (59 to 65)</td>
<td>+5.8 (+5.2 to +6.4)</td>
<td>0.708813</td>
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<tr>
<td>B-3</td>
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<td>BD-2</td>
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<td>-5.8</td>
<td>0.619 ± 0.014</td>
<td>16 (12 to 21)</td>
<td>-4.8 (-5.7 to -3.6)</td>
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<td>-5.1</td>
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<td>H-4</td>
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<td>-5.5</td>
<td>0.609 ± 0.012</td>
<td>19 (16 to 23)</td>
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<tr>
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<td>-3.1</td>
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<td>311F</td>
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<td>-7.2</td>
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<tr>
<td>311G</td>
<td>Carbonate clast</td>
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<td>-8.9</td>
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<tr>
<td>312A</td>
<td>Carbonate clast</td>
<td>+0.6</td>
<td>-3.4</td>
<td></td>
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<tr>
<td>GP-R4</td>
<td>Mudstone host rock</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>0.708865</td>
</tr>
<tr>
<td>IP-R</td>
<td>Host-marly limestone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.708967</td>
</tr>
</tbody>
</table>

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of Cc1 to Cc3 ranging from 381 100 to 399 540 ppm.

DISCUSSION

Fluid origin of calcite cements

The petrographic and geochemical characteristics of host rocks and calcite cements can be used to unravel the origin of the fluids from which Cc0 to Cc4 precipitated in the Puig-reig anticline. Despite the lack of isotope data for Cc0, its petrological characteristics and elemental composition can be utilized to unravel the fluid source. The concentric zonation of Cc0, varying from non-luminescent to bright luminescent zones (Fig. 5A3 and A4), indicates fluctuations of the redox conditions probably in the meteoric phreatic environment (Muchez et al., 1998; Machel, 2000; Vandeginste et al., 2012). The major non-luminescent zones represent oxidizing conditions during precipitation, whereas the minor bright luminescent zones are characteristic of more reducing conditions (Grover & Read, 1983; Parcerisa et al., 2006). Cc0 has significantly lower Mn and Fe contents than the other cements (Fig. 8), generally below the detection limits, which also supports the meteoric fluid origin. As the earliest cement, Cc0 precipitated in intergranular pores along the edges of the proximal to medial fluvial clasts (Fig. 5A2 to A4). From the available data, it is inferred that Cc0 precipitated from meteoric fluids at the early diagenetic stage.

Cc1 was previously interpreted as precipitated from hydrothermal fluids from the Palaeozoic basement (Cruset et al., 2016). The clumped isotope data reveal that Cc1 precipitated at temperatures between 92°C and 129°C (Fig. 6B). Previous studies involving cross-sections (Vergés, 1993) and vitrinite reflectance data (Clavell, 1992; Vergés et al., 1998), indicate a maximum burial depth of 1.7 km for the Berga Group and the Solsona Formation in the Puig-reig anticline. Assuming the current mean geothermal gradient of 26.7°C/km in the Ebro Foreland Basin (Fernández et al., 1998) and a general surface temperature of 20°C, the maximum temperatures reached by these formations should be much lower (around 65°C) than the temperatures at which Cc1 precipitated. This suggests an external hydrothermal fluid source from a depth of around 4 km, or even deeper if one considers that ascending fluids cool down quickly when they are released upward. The δ18Ofluid of Cc1 ranges from +4.7‰ to +9.2‰ VSMOW (Fig. 6B), located within the range of

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formation, metamorphic and magmatic fluids (Taylor, 1987). Magmatic fluids are excluded because magmatism did not develop during the Pyrenean orogeny. The high \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios of Cc1, ranging from 0.709138 to 0.709246 (Fig. 7), indicate that hydrothermal fluids interacted with highly radiogenic sources, such as the Palaeozoic basement at depth and/or the silicic clasts of the Berga and Solsona fluvial deposits sourced from the Pyrenean Axial Zone (Riba, 1976; Williams et al., 1998; Barrier et al., 2010). Thus, the clumped isotope and strontium isotope data together reveal that fluids released from the Palaeozoic basement could have been the high-temperature fluids responsible for the Cc1 precipitation (Cruset et al., 2016). Hydrothermal fluids were not significantly influenced by brines potentially derived from evaporite units, because this anticline is not detached along or connected to thick evaporite units (Cruset et al., 2018). Cc2 was previously interpreted as precipitated from mixed fluids by Cruset et al. (2016). Clumped isotope data presented by these authors indicate that Cc2 precipitated at temperatures ranging between 77°C and 90°C (Fig. 6B). These precipitation temperatures are lower than those of the Cc1 precipitation but still higher than the maximum burial temperatures reached by the Berga Group and the Solsona Formation. Cc2 presents lighter \(^{\delta^{18}}\text{O}\) values than Cc1 and host rocks (Fig. 6A). Cc2 has lower \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios than Cc1 (Fig. 7), indicating that the cement-forming fluids interacted with less radiogenic sources or mixed with fluids with lower \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios. The \(^{\delta^{18}}\text{O}_{\text{fluid}}\) composition of Cc2 ranges from −1.7 to −0.7‰ VSMOW (Fig. 6B), which is lower than that of Cc1 cement but higher than −6.4 to −4.6‰ VSMOW of modern rainwater (Travé & Calvet, 2001). Based on the available data, Cruset et al. (2016) interpreted that Cc2 precipitated in fractures from the mixing of meteoric waters with the hydrothermal fluids from which Cc1 precipitated. In addition,

### Table 2

Elemental composition of Cc0 to Cc4 generations of calcite cements. ‘n’ represents the number of probe points. ‘L.D.’ represents detection limit. Elemental composition data of Cc1 and Cc2 calcite cements from Cruset et al. (2016) were integrated into these results.

<table>
<thead>
<tr>
<th>Cement</th>
<th>Mg (ppm)</th>
<th>Mn (ppm)</th>
<th>Fe (ppm)</th>
<th>Sr (ppm)</th>
<th>Ca (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cc0</td>
<td>47</td>
<td>2950</td>
<td>546</td>
<td>1716</td>
<td>178</td>
</tr>
<tr>
<td>Cc1</td>
<td>242</td>
<td>4500</td>
<td>248</td>
<td>1797</td>
<td>4199</td>
</tr>
<tr>
<td>Cc2</td>
<td>137</td>
<td>2846</td>
<td>485</td>
<td>1650</td>
<td>2300</td>
</tr>
<tr>
<td>Cc3</td>
<td>22</td>
<td>1062</td>
<td>148</td>
<td>539</td>
<td>1050</td>
</tr>
<tr>
<td>Cc4</td>
<td>48</td>
<td>22340</td>
<td>319</td>
<td>7449</td>
<td>604</td>
</tr>
</tbody>
</table>
the Fe and Sr contents of Cc2 are slightly higher than those of Cc1 (Fig. 8), which was interpreted as the expulsion of formation fluids relatively rich in Fe and Sr from shale layers due to progressive compaction during burial (Hanshaw & Coplen, 1973; Travé et al., 1997; Cruset et al., 2016). In this study, an alternative model has been proposed, in which Cc2 could have precipitated from similar hydrothermal fluids as Cc1 but sourced from shallower burial depths at lower temperatures compared to the parent fluids of Cc1. The interaction between the hydrothermal fluids and the shallower basement must have been relatively weak and allowed retaining the signatures of meteoric fluids to some extent (Bons & Gomez-Rivas, 2020), which resulted in relatively lower precipitation temperatures, $\delta^{18}O_{\text{fluid}}$, $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ ratios of the Cc2 cement. A more detailed discussion of the fluid flow and precipitation processes is provided in the next section.

Cc3 was only identified in the north-western part of the study area (section C in Fig. 1D). This area is dominated by proximal fluvial deposits, which have higher contents of carbonate clasts than medial and distal fluvial deposits (Sun et al., 2021b). These clasts were mainly sourced from the marine carbonates of the Mesozoic–Cenozoic series of the South Pyrenean cover thrust sheets (Riba, 1976; Williams et al., 1998; Barrier et al., 2010) and the Pyrenean Axial Zone. Compared to the other cements, Cc3 has heavier $\delta^{18}O$ and $\delta^{13}C$ values (Fig. 6A), which are closer to the isotopic compositional

---

**Fig. 8.** Mg, Mn, Fe and Sr composition of Cc0 to Cc4 generations of calcite cements. Elemental composition data of Cc1 and Cc2 calcite cements from Cruset et al. (2016) were integrated into these results.
range of marine carbonates (Veizer et al., 1999). This probably suggests interaction between the cement-forming fluids and marine carbonate clasts. Based on the LOWESS curve (McArthur et al., 2012), the $^{87}$Sr/$^{86}$Sr ratios of Cc3 between 0.708813 and 0.708747 are higher than those of seawater when the Mesozoic marine carbonates were deposited, but slightly lower than those of the host rocks of the Berga Group and Solsona Formation (Fig. 7). This would suggest fluid–rock interaction between the cement-forming fluids and the radiogenic silicic clasts of the host rocks sourced from the Palaeozoic basement in the Axial Zone. Muñoz-López et al. (2020a) studied the influence of basement rocks on fluid chemistry in other outcrops elsewhere in the Pyrenees, and concluded that calcite cements precipitated from fluids that strongly interacted with basement rocks could have resulted in a significantly higher $^{87}$Sr/$^{86}$Sr ratio (>0.710) in nearby areas. The $^{87}$Sr/$^{86}$Sr ratios of Cc3 in our study area are lower than this value, probably because carbonate clasts dominate over silicic clasts in the zone where Cc3 precipitated. The $\delta^{18}$O$_{\text{fluid}}$ of Cc3 ranges from +4.1 to +5.8‰ VSMOW (Fig. 6B), which corresponds to the range of formation fluids (Taylor, 1987). Compared to Cc1 and Cc2, Cc3 precipitated at significantly lower temperatures, ranging between 50°C and 62°C (Fig. 6B). According to the current mean geothermal gradient of 26.7°C/km in the Ebro Foreland Basin (Fernández et al., 1998), and assuming a general surface temperature of 20°C, strata with burial depths around 1.5 km can reach the temperatures at which Cc3 precipitated. However, the depth could be slightly higher if it is considered that fluids cool down quickly while ascending. Compared to other generations of calcite cements, Cc3 presents high Fe and low Mg and Sr concentrations (Fig. 8). The high Fe concentration could result from the interaction between the cement-forming fluids and host rocks or be sourced from external fluids. Based on the available data, it is inferred that Cc3 precipitated from formation fluids that strongly interacted with the host rocks.

Cc4 is found coating fracture planes or as palisade structures of bladed crystals (Fig. 5E3 and E4). This cement is non-luminescent and has low Mn and Fe concentrations (Fig. 8). Based on clumped isotope data, Cc4 precipitated from a fluid with temperatures ranging between 16°C and 19°C and with $\delta^{18}$O$_{\text{fluid}}$ ranging from −4.8 to −4.3‰ VSMOW (Fig. 6B), which is very close to the $\delta^{18}$O$_{\text{fluid}}$ range of modern rainwater (−6.4 to −4.6‰ VSMOW) (Travé & Calvet, 2001). All of these characteristics indicate a low-temperature meteoric fluid. In addition, Cc4 is characterized by highly depleted values of $\delta^{13}$C with respect to host rocks, ranging from −10.2 to −4.2‰ VPDB (Fig. 6A), indicating a strong influence of organic-derived carbon (Irwin et al., 1977; Cerling, 1984; Vilasi et al., 2006). In the Puig-reig anticline, the exposed fine sediments, deposited from fluvial overbanks, have experienced intensive pedogenesis and can provide soil-derived carbon for calcite cement (Cerling & Quade, 1993). Other studies documented that similar calcite cements with palisade structures and depleted $\delta^{13}$C precipitated from meteoric fluids with a strong influence of soil-derived carbon related to pedogenic processes (Travé & Calvet, 2001; Cantarero et al., 2010, 2014a). The significantly variable $^{87}$Sr/$^{86}$Sr ratios of Cc4, with a low value of 0.708757 and a very high value of 0.710208 (Fig. 7), could be related to variable interactions between fluids and the different compositions of host rocks. The high $^{87}$Sr/$^{86}$Sr ratio probably indicates strong interaction between the fluid and the highly radiogenic silicic clasts in host rocks sourced from the Palaeozoic basement of the Axial Zone. Besides, this high ratio could also be affected by the clayey or siliceous impurities existing between the multi-layer palisades of Cc4 (Fig. 5E3 and E4). During the stages of no calcite cementation, clayey or siliceous impurities resulted from pedogenic processes could be transported by meteoric fluids. The presence of small percentages of clay minerals can significantly increase the measured $^{87}$Sr/$^{86}$Sr ratios due to the decay of $^{87}$Rb to $^{87}$Sr (Banner, 1995).

Changes in fluid flow regime during fold evolution

This section discusses the changes in fluid regimes during the complete fold evolution, combining the fluid origin of calcite cement and the tectonic evolution of the Puig-reig anticline. As a thrust-related anticline at a foreland basin margin, the Puig-reig anticline developed as a growth anticline due to a duplex stack at depth (Vergès, 1993). This anticline experienced layer-parallel shortening and growth during an intensive phase of thrusting and folding due to regional compression. This anticline probably did not experience intensive out-arc extension because the resulting fold is not tight (Sun et al.,

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After fold growth, the anticline crest could locally have developed normal faults by a change of the regional stress field, while the north limb was likely to have been affected by the deformation of the Vallfogona thrust ramp after fold growth (Vergés, 1993). Finally, this anticline underwent continuous denudation.

As the earliest cement, Cc0 developed in all structural positions and lithofacies, indicating that the meteoric fluids from which Cc0 precipitated affected the whole anticline (Fig. 9A). This cement only precipitated in intergranular pores along clast edges and before the predominant Cc1 cement (Fig. 5A2 to A4). Therefore, it is interpreted that Cc0 precipitated during early diagenetic stages before systematic fracturing and significant burial. At this stage, deposits had not undergone intensive compaction and still had high intergranular porosity. Meteoric fluids in the phreatic zone filled the intergranular pores of these unconsolidated sediments deposited in the proximal to medial fluvial system and dominated the fluid regime from which Cc0 precipitated. Other studies documented similar calcite cements precipitated from meteoric fluids in a phreatic environment during early diagenetic stages (e.g. Emery & Dickson, 1989; Parcerisa et al., 2005; Cantarero et al., 2014b; Li et al., 2017).

Due to progressive burial and compressional tectons, abundant fractures were formed in the Puig-reig anticline during thrusting and folding. The damage zones of the blind thrust system, responsible for the development of the Puig-reig anticline (Fig. 1C), could have provided the pathways for the hydrothermal fluids to migrate upward from the Palaeozoic basement to the Berga Group and the Solsona Formation (Cruzet et al., 2016). The connected fracture network and intergranular porosity of these alluvial-fluvial deposits would have allowed vertical and lateral migration of the hydrothermal fluids across different stratigraphic units. Cc1 filled most intergranular pores in all lithofacies of different structural positions and the authors did not find equivalent samples free from Cc1 cement. This reveals that the hydrothermal fluids from which Cc1 precipitated would have migrated along the whole anticline (Fig. 9B). Besides, Cc1 filled all fracture sets as well as reverse and strike-slip faults, indicating that such fractures and faults formed due to regional compression during the intensive fold deformation stage. Fluid flow would have been triggered by horizontal to sub-horizontal compressive principal stress (for example, when the least principal stress is vertical), rather than by fluid pressure increase associated with decompression or fluid heating (Staude et al., 2009). Moreover, Cruzet et al. (2018) identified similar hydrothermal fluids migrating along fractures of the Vallfogona thrust fault zone from the Late Eocene to the Early Oligocene. However, these fluids did not reach the El Guix anticline in the relative central area of the north-eastern Ebro Basin, which was dominated by meteoric fluids (Travé et al., 2000). These results indicate that the hydrothermal fluids affected a regional area including the South Pyrenean fold-and-thrust belt and its adjacent basin margin.

Cruzet et al. (2016) proposed that normal faults and their associated fracture networks formed in the crest of the Puig-reig anticline during crestal collapse, which could have provided connected pathways for the percolation of low-temperature meteoric fluids from the surface to the bottom of the Berga and Solsona strata. These infiltrated meteoric fluids would have then mixed with the upward flowing hydrothermal fluids from the basement, from which Cc1 precipitated (Fig. 9C1). Then the mixed fluids would have migrated upward through these connected faults due to the increasing fluid pressure related to the build-up stresses during compres- sion (Henderson & McCaig, 1996) and finally would have resulted in the precipitation of Cc2. Such hydrological models need to involve asynchronous downward flow of meteoric fluids and upward flow of hydrothermal fluids to be hydro-dynamically plausible. Simultaneous downward and upward flow, such as that invoked in other conceptual models of mixing of surface-derived and deep-derived fluids, necessitates a geologically implausible fluid sink (Bons et al., 2012). To avoid the ambiguity, an alternative model has been proposed in this study, that Cc2 could have precipitated from hydrothermal fluids from the basement but at shallower burial depths and at lower fluid temperatures compared to those that formed Cc1 (Fig. 9C2). Meteoric fluids could have migrated downward from the erosional surface of the Pyrenees to the shallower basement through thrusts of the Pyrenees driven by topography differences, but not through the faults in the Puig-reig anticline crest. The relatively low burial temperatures in such a basement level would have resulted in a low degree of fluid–rock interaction, thus preserving part of the meteoric signatures of the parent fluids of Cc2 (Bons & Gomez-Rivas, 2020). In contrast,
the Cc1 cement-forming fluids would have been sourced from deeper parts of the basement according to their geochemical signature and higher clumped isotope temperature. Such a hydrological model was proposed by Bons et al. (2014) to explain the hydrothermal ore deposits.
of the Schwarzwald district in south-west Germany. Bons & Gomez-Rivas (2020) pointed out that meteoric fluids can infiltrate down from an erosional surface to be buried and then remobilized millions of years later, partly preserving their meteoric signatures. Such signatures can be preserved for long periods of time if temperatures are relatively low. In the late stage of the Puig-reig anticline growth, the underneath thrusting could have mobilized the shallower hydrothermal fluids to the bottom of the anticline. In addition, the anticline crest could have raised and undergone partial exhumation, which could have decreased the overburden pressure of the rocks underneath, thus resulting in over-pressure of the trapped pore fluids. To maintain the original relative fluid pressure underneath, fluids would need to be expelled upward, which could have resulted in the precipitation of Cc2 in the anticline crest. Such a hydrogeological model was proposed by Staude et al. (2009) and was tested on the Schwarzwald hydrothermal ore district in south-west Germany.

After Cc1 precipitation, external formation waters also characterized the fluid system of the Puig-reig anticline, resulting in Cc3 cement with different petrographic and geochemical characteristics compared to the other cements. Cc3 concentrates in the western zone of the north limb, indicating that the formation fluids locally migrated within the Berga Group (Fig. 9D). Based on the cross-sections (Fig. 1C and E), the frontal thrusts (such as the Vallfogona thrust) could have acted as the migration pathways for the formation fluids. For example, the blind branch of the Vallfogona thrust propagated into the lower and middle Berga Group in the north limb of the Puig-reig anticline, which could have facilitated the local input of formation waters into the Berga Group. Besides, fractures hosting Cc3 veins were not previously filled by Cc1 or Cc2 veins, indicating that these fractures could have been newly formed due to the local structural deformation in the western zone of the north limb.

Owing to continuous denudation after the fold growth of the whole Puig-reig anticline, the burial depths of the Berga and Solsona strata became shallower. Besides, some of the fractures sealed by previous calcite veins could have been reactivated during exhumation while new faults and fractures formed. These reopened and newly formed faults and fractures allowed the input of meteoric fluids driven by topography from which Cc4 precipitated. Cc4 developed in different fracture sets and different structural positions of the anticline, indicating that the meteoric fluids affected the whole study area (Fig. 9E). Besides, Cc4 mainly precipitated in reopened fractures filled by previous cements (Fig. 5E3 and E4), indicating that fractures hosting Cc4 veins could have been mainly reactivated from the previous fracture sets formed during the intensive fold deformation stage.

### Distribution patterns of calcite cements in different settings

Based on the comparison between the calcite cement distribution in the Puig-reig anticline and other areas worldwide, this section discusses the distribution patterns of calcite cements in detrital reservoirs in different structural or stratigraphic settings. In the Puig-reig anticline, abundant fractures were filled by Cc1 to Cc4 calcite veins. Cc1 and Cc4 veins precipitated across the whole anticline, whereas Cc2 and Cc3 precipitated locally in the anticline crest and north limb, respectively. In addition, as described by Sun et al. (2021c), the propagation, reopening and widening of existing fractures, together with the formation of new ones, are processes that can operate at the same time in all the structural positions and affect all the lithofacies. It is difficult to form a significant number of new fractures in thick conglomerate bodies to accommodate strain. Thus, the propagation,
reopening and widening of existing fractures can accommodate strain when the stress is not high enough to form new fractures. This likely resulted in fractures with larger vein length and width but with lower intensity in conglomerate bodies compared to thin sandstone layers. The intergranular porosity of host rocks corresponding to proximal and medial fluvial deposits was cemented by Cc1 and minor Cc0 calcite cements. A more detailed discussion of the distribution of intergranular-filling calcite cements and their effects on reservoir quality is provided in the next section. As the predominant calcite cement in both intergranular porosity and fractures, Cc1 precipitated from external hydrothermal fluids. These fluids are from relatively more internal and deeper parts of the south-eastern Pyrenees, which migrated along connected thrusts and their damage zones to the Ebro Foreland Basin. Such fluids flowed coevally with the anticline growth during horizontal compression.

At foreland basin margins or fold-and-thrust belts, fracturing, thrusting and folding are generally accompanied by fluid flow of various external fluids. Connected fracture networks allow fluid migration across different hydrostratigraphic units (Evans & Fischer, 2012; Evans et al., 2012). The intensive deformation and inflow of external fluids result in changes of fluid conditions that circulate through host rocks and fractures, including temperature, pressure, pH, Eh, solute concentration, and thus provide the material sources and physical–chemical conditions for cementation. Thus, prevalent calcite cementation can take place in detrital rocks and their fracture networks at basin margins (Fig. 10A). This has been observed extensively in multiple formations of different basins, such as the Berga Group and the Solsona Formation at the north-eastern margin of the Ebro Basin (Cruyet et al., 2016), the Peraltilla and Sarriñena formations at the northern margin of the central

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**Fig. 10.** Schematic diagram of calcite cementation and distribution in detrital rocks in different settings. (A) Sufficient external sources migrate through connected fracture network. (B) External sources migrate through connected pore structure. (C) External sources migrate from adjacent shale layers. (D) External sources migrate from the top surface of an overpressured compartment. (E) Internal sources from host rocks: in situ dissolution–reprecipitation. (F) Internal sources from host rocks: dissolution–migration–reprecipitation.
because these reservoirs favour fluid flow from which calcite cement can precipitate (Fig. 10B) (McBride et al., 1995; Dutton et al., 2002; Hall et al., 2004; Van den Bril & Swennen, 2009). Other studies revealed that more intense calcite precipitation tends to occur along reservoir margins where sandstone reservoirs pinch out into fine deposits or are in contact with fine deposits (Fig. 10C), for example, the Lower Cretaceous Pendencia Formation in the Potiguar basin (Dos Anjos et al., 2000) and the Upper Permian Bell Canyon Formation in the Delaware Basin (Dutton, 2008). Organic acids generated during the maturation of organic matter in these fine deposits could result in the dissolution of carbonate elements, which could be transported to adjacent sandstone reservoirs and provide external fluids for calcite cement (Dos Anjos et al., 2000; Dutton, 2008). In addition, other studies documented that calcite cementation also occurs at the top of overpressured reservoirs, where periodic changes of fluid pressure and formation hydrochemical conditions resulted in calcite cement (Fig. 10D), for example, the overpressured sandstone reservoirs in the central Junggar Basin (He et al., 2009; Yang et al., 2010) and in the Dongying Depression of the Bohai Bay Basin (Han et al., 2012; Zhang et al., 2019). In settings containing internal sources for carbonate cement, such as biogenic carbonates and carbonate rock fragments (Walderhaug & Bjørkum, 1998), cement distribution tends to be controlled by the distribution of these internal sources through in situ dissolution and reprecipitation (Fig. 10E), for example, the Fensfjord Formation (Walderhaug et al., 1989) and the Rannoch Formation (Bjørkum & Walderhaug, 1990a) in the North Sea. In addition, Liu et al. (2019) concluded a different fluid–rock interaction model of dissolution, migration and re-precipitation in the Xujiahe Formation of the Sichuan Basin. Hydrocarbon-related acidic fluids tend to flow along the more permeable reservoirs, resulting in intensive dissolution in coarse reservoirs, whereas intensive re-precipitation occurs in the marginal impermeable fine reservoirs (Fig. 10F).

Effects of calcite cements on reservoir quality
Calcite cement distribution can be controlled by one of the aforementioned patterns or be affected by several patterns at the same time, depending on the specific geological conditions. Likewise, there are variable relationships between calcite cementation and reservoir quality in different
settings. Intergranular porosity-filling cements are dominated by Cc1 cement in the Puig-reig anticline. This is interpreted as a result of the flow of hydrothermal fluids from the deep basement and during the early stage of anticline growth. Intergranular porosity of the host rocks was predominantly occluded during burial rather than during the exposure of formations to the surface. Thus, although the collected samples are from outcrops, they can be utilized to understand the distribution of burial cements in the subsurface. The distribution pattern of Cc1 cement can be used to predict cement distribution in buried formations of this anticline and other areas in similar settings. Calcite cementation is widely considered an important factor controlling reservoir quality because of its ability to occlude porosity and reduce permeability (Davis et al., 2006; Dutton, 2008; Xiong et al., 2016). As an example of this control, the predominant calcite cement (Cc1) filled most intergranular pores and resulted in the overall low porosity of host rocks in the Puig-reig anticline, which is currently lower than 2% on average (Figs 4C and 11). On the other hand, calcite cement tends to precipitate in permeable rocks (McBride et al., 1995; Dutton et al., 2002; Hall et al., 2004; Van den Bril & Swennen, 2009). For example, medium to coarse sandstones from the medial fluvial fan of the Puig-reig anticline contain relatively high porosity and high calcite cement content. The amount of porosity and cement varies across different lithofacies (Fig. 11), and these two parameters do not present a clear negative correlation. Relatively high porosity, mainly ranging from 2 to 8%, concentrates in channelized or massive medium to coarse sandstones of the medial fluvial fan. However, these lithofacies also feature

Fig. 11. Distribution of porosity and calcite cement contents in different lithofacies, sedimentary facies and structural positions. ‘n’ is the number of thin sections. The detailed descriptions of different lithofacies can be found in Fig. 2 and Sun et al. (2021a). The cross-section is modified from Cruset et al. (2016).
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almost the highest cement content. These sandstone lithofacies have better grain sorting than conglomerate ones and lower contents of ductile clayey matrix than fine lithofacies. Thus, they had a more appropriate pore structure for fluid flow from which calcite cement precipitated, and had a higher number of intergranular pores for cement growth plus residual porosity. This resulted in the coexistence of relatively high cement content and porosity for these lithofacies. Similar cement and porosity distribution patterns controlled by lithofacies have been documented in other studies. For example, in the Huagang Formation in the Xihu Depression of the East China Sea Basin, coarse sandstone reservoirs have higher porosity but also relatively high content of quartz cement than other reservoirs (Sun et al., 2017).

Apart from reducing reservoir porosity and permeability, early calcite cement can affect the later evolution of reservoir quality (Hosa & Wood, 2017). For example, early cement can preserve intergranular space and improve reservoir quality by providing secondary porosity under the specific circumstance of intensive dissolution during later diagenetic stages, for example, the Lower Devonian Jauf Formation in Saudi Arabia (Al-Ramadan et al., 2004), the Biyadh Formation in the western central Masila Basin (Hakimi et al., 2012) and the Upper Jurassic Ti-3 sandstones in the Flemish Pass Basin (Xiong et al., 2016). Besides, mechanical contrasts between layers could be affected by the distribution of early calcite cement, which could have a significant effect on fracture development and thus reservoir potential, an effect observed for example in the Madison Formation in the Sheep Mountain of the Bighorn Basin (Barbier et al., 2012) and the Calcare Massiccio unit in the Umbria-Marche Apennines (Di Naccio et al., 2005). Thus, to determine the distribution of calcite cement and its real effects on reservoir potential, the specific geological backgrounds of host rocks should be fully considered.

CONCLUSIONS

The Puig-reig anticline, in the south-eastern Pyrenees (Spain), exposes excellent outcrops of detrital rocks deposited from a proximal to medial fluvial system and cemented by calcite. The integration of structural, petrological and geochemical analyses allows unravelling the calcite cementation history and the related fluid regime changes during the anticline evolution. The comparison between this study and others worldwide in different settings allows the exploration of the distribution of calcite cement and its effects on reservoir quality. The following conclusions have been reached:

1 Five generations of calcite cements (Cc0 to Cc4) and five phases of fluid regimes have been identified. Cc0 precipitated in intergranular pores from meteoric fluids. As the predominant cement, Cc1 precipitated in intergranular pores, faults and F1 to F4 fracture sets from hydrothermal fluids. Cc2 mainly developed in normal and strike-slip faults in the anticline crest from the mixing between hydrothermal and meteoric fluids or from hydrothermal fluids with more meteoric signatures than Cc1. Cc3 developed in F1 and F4 fracture sets in the western area of the north limb from formation fluids with temperatures between 50°C and 62°C. Cc4 precipitated in F1 to F4 fracture sets from meteoric fluids with temperatures between 16°C and 19°C.

2 Calcite cementation and fluid regime changes occurred as the anticline evolved. In the early diagenetic stage, before intensive deformation, the fluid regime was dominated by meteoric fluids (Cc0). During the most intense phase of thrusting and folding, hydrothermal fluids from the internal and deeper parts of the south-eastern Pyrenees migrated upward through connected thrust systems and fracture networks and dominated the fluid regime (Cc1). In the later stage of the anticline growth, the mixed fluids between hydrothermal and meteoric fluids dominated the fluid regime in the anticline crest during the crest collapse (Cc2). Alternatively, the anticline crest could be dominated by the hydrothermal fluids at shallower burial depths than that of Cc1. Besides, formation fluids migrated through the frontal thrusts and dominated the western part of the north limb (Cc3). During the continuous denudation, the anticline was dominated by meteoric fluids due to the exhumation of strata, migrated through reopened and newly formed fractures (Cc4).

3 In the Puig-reig anticline, the predominant calcite cement (Cc1) resulted from external fluids coeval with the compressional deformation of the anticline and the substantial detrital carbonates of host rocks. Calcite cement filled abundant fractures and reduced the overall intergranular porosity of host rocks. Contrarily, in other settings not featuring intensive deformation and sufficient
external fluids, calcite cement tends to show heterogeneous distributions. Carbonate cement exerts significant but variable effects on reservoir quality, which largely depend on the specific geological backgrounds.

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CONFLICT OF INTEREST

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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