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Journal of the Geological Society

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DOI: <https://doi.org/10.1144/jgs2018-031>

Received 5 February 2018

Revised 27 April 2018

Accepted 28 April 2018

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Supplementary material at <https://doi.org/10.6084/m9.figshare.c.4087019>

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From axial-parallel to orthogonal groundwater flow during fold amplification: insights from carbonate concretion development during the growth of the Quattro Castella Anticline, Northern Apennines, Italy

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Abstract: This contribution is based on a multidisciplinary field and laboratory study of carbonate concretions developed in poorly lithified Quaternary, syn-kinematic sediments along the Quattro Castella Anticline, Northern Apennines (Italy). Studied concretions consist both of tabular (parallel to bedding) and elongate single to coalescent concretionary bodies oriented at different angles to bedding throughout the exposed stratigraphic succession. Concretion dimensions range from a few centimetres for single elongate concretions, up to several metres for tabular to coalescent ones. Field observations and petrophysical data indicate that concretions developed preferentially in sediments characterized by 90-290 μm mean grain sizes and permeability spanning from 7×10^2 to 7×10^4 mD. Carbon and oxygen stable isotope analysis in conjunction with petrographic investigations indicate that the precipitation of concretionary calcite occurred in a meteoric vadose realm during early eogenesis, and subsequently in a meteoric phreatic environment. Diagenetic data and concretion patterns in syn-tectonic sediments suggest they formed during lateral propagation of the anticline that, in turn, promoted a change in the local topographic-hydraulic gradient from fold axial-parallel to fold-orthogonal. Accordingly, the integrated analysis of carbonate

concretions can provide a useful tool to unravel palaeo-fluid flow history and, then, to predict fluid circulation patterns in folded siliciclastic rocks.

Supplementary material: Complete isotopic data from both hand samples and thin sections, together with statistical analysis and SEM cement images are available at <https://doi.org/10.6084/m9.figshare.c.4087019>.

Grain size distributions with performed standard operative procedure tests and detail permeability measurements are available at <https://doi.org/10.6084/m9.figshare.c.4087019>.

Unravelling fluid flow pathways within exposed rocks and sediments helps to better understand the processes affecting oil and gas reservoir quality and to facilitate hydrocarbon exploitation and preservation of groundwater reserves (Taylor *et al.* 2000; Dutton *et al.* 2002; Hall *et al.* 2004). For this purpose, diagenetic concretions and mineral masses can provide a useful tool to reconstruct palaeo-fluid flow patterns within transforming porous media involved in deformation (e.g. Johnson 1989; McBride *et al.* 1994; Mozley & Davis 1996; McBride & Parea 2001; Balsamo *et al.* 2012; Balsamo *et al.* 2013). Moreover, selective cementation plays a key role in modifying the petrophysical properties of sediments, such as porosity and permeability (Houseknecht 1987; Davis *et al.* 2006; Boutt *et al.* 2014). Pervasive cementation can eventually lead to the formation of laterally extensive, bedding-parallel low-permeability layers, that can compartmentalize reservoirs (Morad *et al.* 2000; Dutton *et al.* 2002; Hall *et al.* 2004). Diagenetic concretions within siliciclastic sediments are characterized by different shapes and sizes (e.g. Sellés-Martínez 1996; Seilacher 2001), depending on fluid flow patterns and the spatial distribution of sediments (McBride *et al.* 1994; Davis 1999; McBride & Parea 2001; Cavazza *et al.* 2009; Balsamo *et al.* 2012).

Concretion arrangement has been used as marker of fluid flow and to recognize diagenetic setting in which precipitation occurred (Pirrie 1987; McBride *et al.* 1994; Mozley & Davis 1996; Davis 1999; South & Talbot 2000). Different growth modes have been identified according to concretion types (Mozley 1996; Abdel-Wahab & McBride 2001; Mozley & Davis

2005). Recently, a significant amount of research has been done on the relationship between diagenetic concretions and fault zones within siliciclastic sediments with different degrees of lithification (Mozley & Goodwin 1995; Hendry & Poulson 2006; Balsamo *et al.* 2012; Balsamo *et al.* 2013; Philit *et al.* 2015; Williams *et al.* 2016). However, comparable information is lacking on the presence and patterns of carbonate concretions hosted in syn-kinematic sediments deformed in growing folds where fluid flow pattern may change during fold amplification.

In this paper, we present the results of a multidisciplinary study on diagenetic concretions developed within poorly lithified Quaternary syn-kinematic sediments exposed in the Quattro Castella Anticline, at the mountain front of the Northern Apennines. Petrophysical and sedimentological properties of sediments hosting the concretions were studied by laboratory analyses (grain size distribution, 2D porosity) and *in situ* measurements (permeability). Furthermore, we inferred the diagenetic environment and nature of fluids responsible for concretion formation using stable isotope analysis combined with petrographic observations on carbonate cements. Integration of field and laboratory data allowed us to constrain the control of lateral propagation and growth of the anticline on the palaeo-fluid flow pathways.

Geological framework

The Apennines fold-and-thrust belt developed since early Oligocene times as a consequence of the subduction of the Adria plate below the European plate (Boccaletti *et al.* 1971; Doglioni 1991). Subduction was responsible for the emplacement of oceanic crust remnants and related sedimentary cover of the Ligurian-Piedmont ocean (Ligurian Units) onto the inverted Adria passive margin successions (Doglioni 1991). The Epiligurian wedge-top basin successions (Eocene to Late Miocene) formed on top of the Ligurian thrust sheets during their north-eastward migration (Zattin *et al.* 2002; Remitti *et al.* 2011; Piazza *et al.* 2016).

The study site is located at the mountain front of the Northern Apennines (Fig. 1a) and is characterized by Ligurian and Epiligurian rocks which were overthrust upon Miocene siliciclastic foredeep turbiditic sediments during Middle Pliocene times (Oppo *et al.* 2013; Gunderson *et al.* 2014; Oppo *et al.* 2015). The Quattro Castella Anticline formed in the hangingwall of a blind thrust ramp cutting through the foredeep strata that were previously overthrust by a Ligurian thrust sheet and the associated Epiligurian sediments (Fig. 1b). Such a blind thrust has been active since Late Miocene times and is still active today (Ponza *et al.* 2010; Boccaletti *et al.* 2011; Gunderson *et al.* 2014). The investigated stratigraphic succession lays in the forelimb of the WNW-ESE striking Quattro Castella Anticline, a regional-scale fold that deforms the Ligurian and Epiligurian rocks and part of the Po plain autochthonous succession (Fig. 1a, b). In particular, remarkable and continuous exposure is provided by the erosional incision of the Enza River (Fig. 2a). The outcrop consists of Pleistocene and Holocene sediments belonging to the Po plain succession that were deposited in the western periclinal termination during the late stage of fold growth. The outcrop may have recorded different fluid flow pattern induced by the anticline lateral amplification. From the base, it is composed of the silty clay Argille Azzurre Formation (Fm) deposited in a shallow prodelta environment. It is followed by the fluvio-deltaic sand of the Sabbie di Imola Fm. overlain by the lower Emilia-Romagna synthem characterized mainly by fluvio-continental deposits (Gunderson *et al.* 2014).

Analytical methods

A total of 620 structural data were collected to construct the geological cross-section through the outcrop in Figure 2. Approximately 300 m-thick of stratigraphic succession were logged, excluding the uppermost 70-80 m-thick fluvial conglomerates. A 30 m-thick stratigraphic log was measured in greater detail to investigate the typology and arrangement of carbonate concretions. Within this interval, petrophysical properties of the sediments hosting concretions were measured. In particular, 40 grain size samples were analysed using a

Mastersizer 3000 laser diffraction particle size analyser (Malvern Instruments), with an operative range spanning from 0.1 to 3500 μm , equipped with a Hydro EV wet dispersion unit using de-ionized water as dispersant fluid. Detailed information about the adopted standard operative procedures (SOP) are provided in on-line supplementary material. In correspondence to the 40 grain size sampling sites, sediment permeability was measured, using a New England Research Tiny Perm II air permeameter. The instrument has a rubber nozzle with a central hole of 0.5 cm diameter and data were calibrated according to the method used by Balsamo *et al.* (2012). Throughout the 30 m-thick detailed log we performed 900 *in situ* permeability measurements. A set of 780 permeability data was also measured upon the outer surface of concretionary bodies (see on-line supplementary material).

A total of 12 concretions of different size and shape were sampled in different stratigraphic positions along the section. 11 of them come from the sandy strata of the Sabbie di Imola Fm. while only one was sampled within the Argille Azzurre Fm., in the same interval studied by Oppo *et al.* (2015) and was used for comparative purpose. Concretion hand specimens were cut to obtain 14 thin sections impregnated with a blue-dyed resin to calculate the two-dimensional porosity and intergranular volume (IGV) from scanned high-resolution images using ImageJ image analysis software. To identify cement mineralogy (dolomite versus calcite) polished rock slabs and thin sections were stained using Alizarin Red S and potassium ferricyanide (Dickson 1966). Cold cathodoluminescence (CL) (CITL cathodoluminescence Mk5-2 with operative setting 250 μA and 10-12 kV) was used to better describe texture and spatial distribution of cement. A JEOL JSM 6400 scanning electron microscope (SEM) (operative settings of 240 μA and 20 kV) was used to acquire detail photomicrographs of cement. Bulk rock carbon and oxygen stable isotopes were analysed from powder samples extracted from fresh section cuts with a dental drill along two orthogonal transects with different sample spacing (1 cm for the horizontal trace and 0.5 cm for the vertical one). A total amount of 184 samples were collected. Concretion cements were also sampled in 45 different spots identified from thin sections, using a New Wave Research micromill with a 300 μm drill bit diameter. Micromill sampling was performed at the

Department of Earth and Environmental Sciences, K.U. Leuven (Belgium). All samples were analysed with a Thermo Finnigan DELTA plus XP mass-spectrometer, coupled with a Thermo Finnigan GasBench II. All isotopic analyses were carried out at the Department of Chemistry, Life Sciences and Environmental Sustainability of the University of Parma (Italy). Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are referred to the international standard V-PDB (Pee Dee Belemnite). The analytical precision upon carbon isotopes determination is 0.10‰ V-PDB, while on oxygen isotopes is 0.15‰, whereas the prediction uncertainty is about 0.15‰ on carbon and about 0.20‰ on oxygen isotopes.

Stratigraphic and structural description

Outcrop features

The stratigraphic interval recorded in the 300 m-long exposure spans a time period from 1.65 Ma at the base to Holocene deposits at the top (Gunderson *et al.* 2014). From base to top, two different synthem can be identified: (1) the Marine Quaternary synthem, and (2) the Lower Emilia-Romagna synthem (see Gunderson *et al.* 2014). From a lithostratigraphic point of view, the Marine Quaternary synthem is composed of two formations, i.e. the Argille Azzurre Fm. and the Sabbie di Imola Fm.

The Argille Azzurre Fm. is made of grey-cyan colour, silt to silty clay, organized in m-thick strata with weakly defined stratification. The age covered by the formation ranges from 1.65 to 1.1 Ma (Gunderson *et al.* 2014) with a total thickness of 121 m and can be further subdivided in two distinct units. The lower one is a 70 m-thick unit composed of relatively uniform silty-clay with thin very fine-grained sand layers containing sparse marine fossils and fossilized methane expulsion vents. The upper unit of the Argille Azzurre Fm. has a total thickness of 51 m, and includes three distinct fine sand units, each of them composed of 8 to 10 m-thick, fine-grained laminated sand in which asymmetrical to symmetrical ripples are present, separated by thick silty-clay bodies (Fig. 2b). The uppermost part of the second unit shows a progressive increase in sand fraction. Consequently, the Argille Azzurre Fm. is

characterized by a general coarsening upward and the upper coarse grained interval marks the transition to the overlying Sabbie di Imola Fm. The latter is located almost in the middle part of the investigated succession (Fig. 2b). It consists of yellow-orange colour, medium to fine laminated sand with a total thickness of 28 m. The age spans from 1.1 to 0.8 Ma (Gunderson *et al.* 2014). This formation is composed of two distinct sand units separated by a 2 m-thick, grey-blue fossil-rich clay. The basal sand body is made of medium-fine-grained sand, organized in amalgamated strata with hummocky cross stratification. The total thickness of this unit is 13 m. The second depositional unit of the Sabbie di Imola Fm. shows an increase in grain size and is mainly composed of an alternation of medium-grained sand and pebble-cobble orthoconglomerates, for a total thickness of 12 m (Fig. 2b). The Lower Emilia-Romagna synthem unconformably overlays the Sabbie di Imola Fm. with an age between 0.8 and 0.4 Ma (Gunderson *et al.* 2014). At the base, it shows a 11 m-thick green to grey clay with faint stratification characterized by abundant plant roots and extensive orange-red colour mottling. These deposits are overlain, with a sharp erosive surface, by a pebble to cobble conglomerate, followed by a 4 m-thick conglomeratic mudstone. The uppermost portion of this synthem is formed by a sandy unit with a thickness of almost 15 m. The Lower Emilia-Romagna synthem passes upward, through a well-defined erosional unconformity, into the 70-80 m-thick conglomerates body of the Upper Emilia-Romagna synthem (Fig. 2b). Consequently, the stratigraphic succession is characterized by a coarsening and shoaling upward facies sequence that recorded a transition from an offshore marine environment (Argille Azzurre Fm.) to an alluvial environment (Lower and Upper Emilia Romagna synthem) (Gunderson *et al.* 2014).

Sedimentary wedging

The entire outcrop displays a wedge-shaped geometry with strata pinching towards the South and opening basin-ward to the North. The investigated succession was deposited along the forelimb of the growing anticline, thus showing a progressive decrease in bedding

dip angle from the base to the top of the outcrop. In the very first metres of the succession, within the Argille Azzurre Fm., bedding dip has a maximum value of 55° and going up section through the basal unit of this formation (i.e. within the first 70 m of the measured stratigraphic log), it decreases to 36° (Fig. 2a, b). This decrement occurs progressively and no sharp unconformities are visible in the field. Within the second unit of the Argille Azzurre Fm. bedding dip values continue to decrease from 36° to 25° at the top of the transition between the Argille Azzurre and Sabbie di Imola Fms. In this interval bedding dip variation is no longer gradual, but occurs along the erosive surfaces at the base of the three fining up sedimentary cycles. The base of the Sabbie di Imola Fm. has an average dip value of 25° , which decreases to 23° within the 2 m-thick clay layer separating the two sand units (Fig. 2b). Throughout the second sandy unit bedding dip remains almost constant at $22-23^\circ$. The Lower Emilia-Romagna synthem shows bedding dip decreasing from 18° in the continental clay to almost horizontal values at the top of the sedimentary succession (Fig. 2b). Strata dip direction remains almost constant throughout the entire section, with values spanning from N 2° to N 25° .

Carbonate concretions

Concretion types and patterns

The stratigraphic interval where diagenetic concretions are densely concentrated includes the transition between the Argille Azzurre and the Sabbie di Imola Fms. and the first sand body of the latter formation (Fig. 2b). Based on their shape, size and spatial distribution concretions can be classified into four categories as follows:

- (1) Single elongate, “cigar to blade-shaped” concretions occur within the medium-fine sand strata of the first body of the Sabbie di Imola Fm. (Fig. 3a). In some sand layers, these concretions are clustered and closely spaced, without merging together.
- (2) Elongate coalescent concretions, that make up metre-scale wide bodies can be found within the basal sand strata of the transition from the Argille Azzurre to the Sabbie di Imola

Fms. and at the top of the first sand unit of the latter formation. These concretions are massive and emerge by their strong positive relief with respect to the hosting sand due to differential weathering. Concretionary bodies are formed by joining of several single elongate bodies (Fig. 3b).

(3) Tabular concretions are frequently distributed within the first sand body of the Sabbie di Imola Fm. They appear as laterally extensive layers, oriented parallel to sand strata bedding, showing a variable thickness from 2 to 20 cm (Fig. 3c). The cementation degree is high, even if a few tabular bodies are friable in hand. The majority of these concretionary bodies display a clear elongation direction and they seem to be formed by several single, small-sized elongate concretions merged together. The merging aspect is clearly visible upon the basal and upper surfaces of the tabular concretions, but it is not distinguishable in cross-section.

(4) Nodular concretions display almost spherical shapes with diameters spanning from 4 to 15 cm. They are densely clustered in three different layers near the middle of the first sand unit of the Sabbie di Imola Fm. Inside each nodule the cementation degree varies, with small sand volumes strongly cemented and other almost non-cemented (Fig. 3d).

The geometrical relationship between the orientation of the concretions, marked by their longest axis, and hosting sediment bedding varies along the investigated stratigraphic succession (Fig. 4b, c). In particular, at the transition between the Argille Azzurre and Sabbie di Imola Fms. the measured elongation direction, both on single and coalescent concretions, shows a mean trend pointing towards the West. Concretion plunge is not parallel to the bedding dip direction (which is towards NNE) and is approximately oriented along the strike direction of the strata. Plunge values vary from 1° to 19° . Moving up section to the base of the first sand unit of the Sabbie di Imola Fm. mean elongation direction displays a NNW orientation (Fig. 4c). Even in this interval, concretion plunge is not parallel to the bedding dip direction, but it describes a narrower angle with it compared to the underlying concretions. Plunge values are similar to the strata dip angle (23°). Near the middle of the first sand unit, elongate concretions show a mean direction pointing almost to the North (Fig. 4c).

Concretion plunge is very constant and almost parallel to the strata dip direction. Eventually, at the top of the basal sand unit, elongate concretions plunge towards the NNE, i.e. parallel to the bedding dip direction (21°). From the base to the top of the detailed log (Fig. 4b) (almost 25 m in stratigraphic height), elongate concretion direction describes a 110° clockwise rotation (Fig. 4c).

In order to recognize changes in bedding and concretion orientation during sedimentation, unfolding of tilted strata was performed considering the dip domains illustrated in the geological cross-section (Fig. 2b). During the deposition of the strata composing the transition between the Argille Azzurre and the Sabbie di Imola Fms. bedding was almost subhorizontal with a slight dip towards the West (Fig. 5). With the ongoing sedimentation, bedding dip direction recorded a progressive clockwise rotation from the West to NE. The same rotation is also displayed by the sand strata of the Sabbie di Imola Fm. (Fig. 5). Unfolding of the mean direction of elongate concretions indicates that diagenetic bodies were affected only by a coaxial rotation during the tilting of the strata. This is testified by the increase of dip values and by the almost constant strike direction characterizing the longest axis of the concretions during deposition and tilting of the hosting strata.

Petrophysical properties

Within the transition from the Argille Azzurre and the Sabbie di Imola Fm., sand strata hosting concretions have a mean grain size varying between 145 μm and 290 μm with moderate sorting. Mean permeability of these strata spans from $1.6 \times 10^4 \pm 3.4 \times 10^3$ mD to $4.2 \times 10^4 \pm 5.6 \times 10^3$ mD. In contrast, within the Sabbie di Imola Fm. grain size and permeability show a reduced variability range. Sediments hosting concretions have a narrow grain size range varying between 103 μm and 188 μm with high sorting, while permeability spans from $1.2 \times 10^3 \pm 2.3 \times 10^2$ mD to $2.3 \times 10^4 \pm 3.1 \times 10^3$ mD (Fig. 4d). Below a grain size of 90 μm and a permeability of 600-700 mD concretions did not develop.

Porosity is almost completely interparticle showing patchy distribution, with rare intraparticle and partial moldic porosity characterizing only fossil shells affected by partial dissolution. Two-dimensional concretion porosity, ranges between 1.7% and 4.2% (table 1). Only one elongate concretionary body displays an anomalously higher porosity of 16.9% which lies outside the range identified by other concretions (table 1). Intergranular volume (IGV), varies in the sampled concretions from 44.9% to 54.8% (table 1).

Concretion petrography

Sampled concretions are composed of abundant quartz, k-feldspar and plagioclase grains, and minor amounts of opaque iron oxides, a few biotite and muscovite micas, rare lithic fragments and pyrite (Fig. 6a, c, e, g). Apart from calcite cement, carbonate phases are mostly represented by several species of foraminifera, mollusc and gastropod shell fragments as well as crinoids, peloids and a few detrital calcite grains.

Carbonate cement inside concretions is made of non-ferroan calcite (pink staining colour) (Fig. 6a, c, e, g). The majority of cement is pore-filling, with a lesser amount being grain-lining and coating one; hence the cement reduces interparticle porosity.

Based on petrography analysis, 4 main cement types can be distinguished:

(Cr) circumgranular-isopachous rims of small-sized equant calcite (crystals size < 10-20 μm) around bioclasts and fossil shells. This cement has dark CL response (Fig. 6b, f) and does not contain fluid inclusions;

(Cm) pore-lining and pore-filling fine sparitic calcite (crystals size < 25 μm) with mosaic texture, located around quartz and feldspar grains forming meniscus cement. It is dominantly non luminescent, but in a few areas a bright orange luminescence occurs (Fig. 6d). No fluid inclusions are present inside this cement;

(C1) coarse-blocky sparite with drusy texture (the size of cement crystals increases towards the centre of the pore) together with syntaxial overgrowths around crinoid fragments, biogenic and detrital calcite (Fig. 6f). This cement is characterized by crystal sizes up to 200-

300 μm , and the majority of them show zoned CL pattern consisting of alternating non-luminescent and bright sub-zones (Fig. 6b, h). Sub-zone number and width vary according to concretion type. Tabular concretions display the highest number of sub-zones with smaller width, while elongate single ones have just a few, thick and less defined sub-zones. Other crystals, belonging to the same cement pattern, do not display any zonation and are non-luminescent. Syntaxial overgrowths may develop crystals with size up to 400 μm . They are characterized by less bright sub-zones when compared to the blocky calcite, and usually the crystal cores are non-luminescent (Fig. 6f). Within this cement type, a few small (5 – 7 μm) mono-phase, all liquid fluid inclusions are present;

(C2) fine pore-filling equant sparitic calcite (crystals size < 50 μm), with constant very bright orange-yellow CL response (Fig. 6d, h). No fluid inclusions have been found inside this cement type.

SEM images revealed the presence of clustered spherical bodies (1-2 μm in diameter) located around Cm and Cr cements which could represent bacteria. Detail of cement morphology and timing by SEM photomicrographs can be found inside the on-line supplementary material.

Cement types Cm, C1 and C2 are pore-filling and often prevent the contact between quartz and feldspar clasts, giving rise to a floating fabric, explaining the high IGV. Tabular, elongate single, coalescent, and nodular concretions show different amounts of the above mentioned calcite cements. In particular, in elongate single and coalescent concretions, pores are filled by almost equal proportions of C1 and C2 cements, while in tabular bodies C1 becomes prevalent. Cr and Cm are rare and subordinated to C1 and C2 in all concretion types. Eventually, cement within nodular concretions is almost completely composed of C2 occurring in a very scattered pattern. Zoned C1 cement is subordinated and it occurs as small-sized crystals when compared to those found in tabular and coalescent concretions.

Stable carbon and oxygen isotopes

Bulk isotopic analyses ($n = 184$) on concretions from the Sabbie di Imola Fm. show $\delta^{13}\text{C}$ spanning from -10.7‰ to -2.5‰ , while $\delta^{18}\text{O}$ covers a narrower interval from -7.6‰ to -5.5‰ V-PDB (Fig. 7a). In a cross-plot, the isotopic data show a near-vertical alignment (Fig. 7b). Nodular and small elongate single concretions have the least depleted $\delta^{13}\text{C}$ values (-2.5‰), while tabular and elongate coalescent bodies usually show the most depleted isotopic response (-10.7‰). Data from a “chimney-shaped” concretion collected within the Argille Azzurre Fm. for comparative purposes, displays extremely depleted $\delta^{13}\text{C}$ (-41.2‰ to -21.8‰) and slightly enriched $\delta^{18}\text{O}$ values ($+2.8\text{‰}$ to $+5.1\text{‰}$ V-PDB) (Fig. 7a). Isotopic data obtained with the micromill ($n = 45$) allow a more precise evaluation of the isotopic signature of the main cement types (Fig. 7c, d, e). In single elongate concretions, C2 cement has an isotopic signature similar to C1: $\delta^{13}\text{C}$ ranges from -7.2‰ to -4.4‰ while $\delta^{18}\text{O}$ spans from -8.5‰ to -5.9‰ V-PDB (Fig. 7c). Conversely, in tabular and coalescent concretions, C2 cement has less depleted $\delta^{13}\text{C}$ (-6.4‰ to -4.5‰) than the C1 cement (-8.8‰ to -5.5‰), while the $\delta^{18}\text{O}$ spans from -8.8‰ to -6.0‰ V-PDB (Fig. 7d, e). Statistical analysis to assess the difference in isotopic signature of C1 and C2 cements can be found in on-line supplementary material. No sample from Cr and Cm could be isolated due to their sizes which were below the sampling resolution of the micromill device.

Along the isotopic sampling lines, single elongate concretions show slightly less depleted $\delta^{13}\text{C}$ values near the centre along the horizontal transects, while $\delta^{18}\text{O}$ remains almost constant. On vertical transects both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are almost constant (Fig. 8a). Coalescent concretions display the less depleted $\delta^{13}\text{C}$ and more depleted $\delta^{18}\text{O}$ values around the centre. Approaching the outer margin, $\delta^{13}\text{C}$ shifts towards the more depleted values, while $\delta^{18}\text{O}$ displays slightly less depleted signatures (Fig. 8b). Tabular concretions record oscillating $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values along the horizontal transects. On vertical transects, moving away from the centre, $\delta^{13}\text{C}$ becomes more depleted, while $\delta^{18}\text{O}$ shows less depleted values (Fig. 8c). Nodular concretions are characterized by an alternation of less depleted and more depleted $\delta^{13}\text{C}$ values and stable $\delta^{18}\text{O}$ around -6.0‰ V-PDB along the horizontal transect. On the vertical sampling lines $\delta^{13}\text{C}$ shows the less depleted values in the central part,

decreasing towards the outer margin. The $\delta^{18}\text{O}$ value shows only small oscillations around -6.5‰ V-PDB (Fig. 8d).

Discussion

Carbonate concretion diagenetic history

According to petrographic observations and stable isotope data, four cementation stages are proposed (Fig. 9a):

- (1) The first cement is Cr (Fig. 9b). The isopachous texture and dark CL-pattern possibly suggest an oxidizing (high $p\text{O}_2$) meteoric phreatic environment (Moore 1989; Budd & Land 1990; Hiatt & Pufhal 2014).
- (2) The second cement to precipitate is Cm (Fig. 9b). The dominant dark CL response likely testifies to an environment with stable oxidizing geochemical conditions. The mosaic texture and the presence of meniscus cement around quartz and feldspar clasts supports cementation in a meteoric vadose zone above the water table (Moore 1989) (Fig. 9a).
- (3) The third, more pervasive cementation stage consists of C1 (Fig. 9b). The zonations are induced by changes in water geochemistry (Habermann *et al.* 1996; Habermann *et al.* 1998; Hiatt & Pufhal 2014), possibly caused by Eh and pH oscillations. It testifies to shifts from fully oxidizing to partially reducing-suboxic conditions and vice versa (Barnaby & Rimstidt 1989). This feature is common in meteoric phreatic environments with increasing reducing conditions moving away from the water table with depth (Li *et al.* 2017). The presence of zoned crystals could be related to cementation occurring within the meteoric phreatic zone in a deeper vertical position with respect to Cr and Cm cements (Fig. 9a, b). The depleted $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of this cement support a meteoric origin of fluid with contribution from soil-derived CO_2 (Hudson 1977). The mono-phase fluid inclusions also support the hypothesis that C1 precipitated in a temperature range $< 40\text{--}50^\circ\text{C}$ (Goldstein & Reynolds 1994).
- (4) The fourth cementing stage consists of C2 (Fig. 9b). The homogeneous bright orange CL response could be related to an environment with stable reducing conditions (low $p\text{O}_2$)

(Barnaby & Rimstidt 1989; Hiatt & Pufhal 2014). The $\delta^{13}\text{C}$ is less depleted compared to C1, likely due to a less contribution of soil-derived CO_2 caused by deeper conditions (Fig. 9a).

The reconstructed diagenetic sequence reflects vertical variation of diagenetic settings, with a progressive deepening trend (Fig. 9a, b). This could be due to: (1) growth of the anticline southward of the study site, causing a steepening of the hydraulic gradient; (2) increase in rainfall related to climate changes during the diagenetic history.

Studied concretions developed in a shallow diagenetic setting, as confirmed by (1) the limited thickness of overlying strata, (2) the presence of floating grains surrounded by cement and (3) high values of IGV (table 1), which collectively indicate a maximum burial depth of ~ 100-120 m (Houseknecht 1987; Cibin *et al.* 1993). The Sabbie di Imola Fm. sand strata were deposited in a shallow marine setting, along very proximal fluvial lobes close to the shore. However, no evidence of marine cement have been found. This could mean that sediments underwent a quick change in sedimentary environment caused by: (1) a period of sea level fall, in agreement with Gunderson *et al.* (2014); (2) uplift induced by the growth of the Quattro Castella Anticline (Ponza *et al.* 2010; Gunderson *et al.* 2014; Oppo *et al.* 2015). Another hypothesis could be the onset of topography-driven meteoric flow affecting the permeable fluvial sand lobes after their deposition in a shallow marine setting (Chafetz *et al.* 1988).

Concretion growth mode

Concretion size and arrangement, depend on several factors such as: (1) spatial distribution of cementation nuclei, (2) sedimentary facies, (3) grain size-permeability structure and (4) fluid flow pattern. These factors are discussed below.

(1) Cementation nuclei are the sites where calcite precipitation started (Bjorkum & Walderhaug 1990; Abdel-Wahab & McBride 2001). Within the studied concretions, early cement generations (Cr and Cm in Fig. 6b, d) are often associated with fossil shells and detrital calcite grains, whose limited dissolution likely influenced fluid saturation condition.

(2) Several authors linked the presence of carbonate concretions to peculiar sedimentary facies (Cavazza *et al.* 2009; Van Den Bril & Swennen 2009; Arribas *et al.* 2012). Along the Enza River section, concretion occurrence seems not to be strictly constrained to specific facies. However, outcrop-scale 3D facies distribution and geometry influenced concretion development. At the lamina-scale concretions cut with different angles lamina sets of ripple and hummocky cross stratification, thus implying that the internal organization of facies did not exert a direct control on concretion development. This could be due to a low-permeability contrast between the different lamina-sets or to fast advective flow forcing fluids to neglect the internal structure of facies.

(3) Grain size and permeability distributions associated with the hosting sediments were the main drivers for concretions development (Mozley & Davis 1996; Davis *et al.* 2006). Studied concretions developed in sediments characterized by a mean grain size $> 90 \mu\text{m}$ and permeability $> 700 \text{ mD}$. Below these two threshold values, concretions did not develop, possibly due to the limited fluid flow through the sediments unable to efficiently provide the constituents needed for cementation.

(4) Single elongate concretionary bodies represent the first stage of concretion growth (Fig. 10a, d). Such elongate bodies (Fig. 3a) preferentially develop parallel to the advective fluid flow direction (McBride *et al.* 1994; McBride & Parea 2001; Balsamo *et al.* 2012). Their occurrence suggests that after the early cementation, the system was locally no longer saturated with respect to calcite and unable to promote any further broadening of the concretionary bodies (Bjorkum & Walderhaug 1990). At other sites where the system was still saturated, cementation continued and closely spaced “blade-shaped” concretions merged together by newly formed cement bridges (Fig. 10b). Eventually, persistent and laterally extensive fluid flow allowed cementation of many elongate concretions to form tabular bodies parallel to basal and upper strata surfaces (Fig. 10c). Conversely, elongate coalescent concretions originated from focused advective fluid flow caused by 3D outcrop-scale facies distribution (Fig. 10d). Single elongate bodies progressively merged together (Fig. 10e) and eventually formed metre-wide concretions (Fig. 10f). Nodular concretions with

spherical shape are likely related to a steady, diffusion-dominated fluid flow regime (Theakstone 1981; Bjorkum & Walderhaug 1990; Wanas 2008).

The proposed evolutionary pathways is consistent with the outward-propagation of the cementation front (Bjorkum & Walderhaug 1990; Bjorkum & Walderhaug 1993; Klein *et al.* 1999; Abdel-Wahab & McBride 2001; Mozley & Davis 2005), which agrees with the observed outward-depletion concentric pattern of $\delta^{13}\text{C}$ values. The along-strike oscillatory pattern of $\delta^{13}\text{C}$ values indicates the non-cylindrical, three-dimensionally complex outward propagation of cementation fronts and the possible interference among multiple growing cementation sites.

Sources of carbonate cement

Depleted $\delta^{13}\text{C}$ values and the vertical alignment in the $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ cross-plot of cement isotopic data shown by concretions within the Sabbie di Imola Fm. is consistent with a carbonate source mainly provided by infiltration of CaCO_3 -saturated meteoric fluids carrying soil-derived CO_2 (Fig. 7a, b) (Hudson 1977; Nelson & Smith 1996) facilitated by the shallow burial depth (< 120 m). A further evidence of the meteoric origin of fluid comes from the back-calculated $\delta^{18}\text{O}$ composition of the cementing fluid. Assuming a superficial temperature of 12°C , a normal geothermal gradient ($25^\circ\text{C}/\text{Km}$) and 120 m of maximum burial, Friedman & O'Neil (1977) fractionation formula for water-calcite system, gives $\delta^{18}\text{O}$ from -9.2‰ to -6.1‰ V-SMOW. These values are in accordance with the expected isotopic composition of meteoric water at the mountain front of the Northern Apennines (Giustini *et al.* 2016). Additional carbonate could be provided by the partial dissolution of detrital calcite, foraminifera and mollusc shells (Bjorkum & Walderhaug 1990; Wanas 2008; Van Den Bril & Swennen 2009). The limited presence of bacteria cells inside fossil shells and the occurrence of framboidal pyrite, suggest that bacterial activity may have influenced the distribution of nucleation sites during early cementation (Folk 1993; McBride *et al.* 1994; Abdel-Wahab & McBride 2001; McBride & Parea 2001).

Methane-rich fluids responsible for “chimney” concretions formation had no contribution to cementation of studied concretions inside the Sabbie di Imola Fm. as confirmed by the difference of the isotopic signatures (Fig. 7a).

Anticline growth and related fluid flow pathways

The growth-wedge geometry of studied succession (Fig. 2b) and the clockwise rotation of bedding dip direction indicate sedimentation during the growth of the anticline (Figs. 4, 5). In particular, during the deposition of the transition between the Argille Azzurre and the Sabbie di Imola Fms. strata were dipping towards the West. In this stratigraphic interval also carbonate concretions are aligned along the same westward direction (Fig. 4b, c). During the deposition of the Sabbie di Imola Fm. bedding dip direction shifted from NW at the base to NNE at the top, and the same trend is shown by concretions (Fig. 4b, c). Therefore, we propose that palaeo-groundwater flow recorded by concretions was controlled by changes in topographic gradients induced by the lateral propagation of the anticline (Fig. 11). This is also confirmed by the nearby streams changing flow direction from parallel to orthogonal respect to the Apennines topographic front during fold amplification (Maestrelli *et al.* 2018). In particular, during the early lateral propagation stage of the anticline, the higher topography was positioned East of the studied outcrop (Fig. 11a) thus promoting a topographic and hydraulic gradient toward the West. After the incorporation of the studied outcrop within the fold forelimb, topography increased rapidly in the crestal region of the fold (Fig. 11b), forcing groundwater fluxes towards NW (Fig. 11c), and eventually to NNE during further fold amplification (Fig. 11d). The evidence that the older concretions do not record the growth direction of the younger ones, implies that concretions geometry recorded only the first fluid flow direction within hosting sediments. This means that the first fluid flow direction imprinted the shape of the early concretions, while later groundwater flow likely increased concretion sizes without affecting the original shape and elongation direction. The outer layer of pre-

cemented bodies acted as nucleation surface (Bjorkum & Walderhaug 1990) for new calcite precipitation provided by later fluid flow.

Conclusions

Studied concretions within Pleistocene syn-kinematic sediments of the Sabbie di Imola Fm., exposed along the Enza River stratigraphic section are interpreted to record different past groundwater fluid flow patterns.

Four major conclusions can be drawn from our results.

- (1) Fossil fluid flow through weakly lithified sediments is still recognizable in the form of selective cementation of tabular, elongate and nodular carbonate concretions and flow direction can be inferred from concretion long axis.
- (2) Carbonate concretions nucleated just after sand deposition in a transitional environment between meteoric vadose and meteoric phreatic. Cementation continued in a meteoric phreatic environment with contribution of fluids percolating through soils. Concretions developed according to the “concentric” growth model, with advective flow forming elongate and tabular concretions, while nodular-spherical bodies grew under diffusion-dominated mass transfer.
- (3) Concretionary bodies are selectively hosted in sediments with permeability between 7×10^2 and 7×10^4 mD and mean grain size from 90 to 290 μm , regardless of the internal structure of sedimentary facies.
- (4) The clockwise rotation shown by elongation direction of concretions, indicates that the lateral propagation of the Quattro Castella Anticline promoted a change in topographic and hydraulic gradient along its western periclinal termination. Mean groundwater fluid flow direction locally changed from East-West (axial-parallel) to South-North (axial-orthogonal).

Acknowledgements

The reviewers R. T. Williams and G. Rawling, and the Editor V. Vandeginste are warmly acknowledged for their suggestions and criticisms, which helped in improving the final version of this paper. The authors wish to thank E. M. Selmo and A. Di Matteo (University of Parma) for stable isotope data. A. Comelli and L. Barchi (University of Parma), are thanked for thin section preparation and support during SEM observations, respectively. S. Boullion, D. Vanhove and Z. Kelemen (K.U. Leuven) are kindly acknowledged for their support during micromill sampling. M. Pizzati collected field and laboratory data, and wrote the manuscript; F. Balsamo participated to field work and to data interpretation; F. Storti conceived the research and took part to data interpretation; M. Mozafari and R. Swennen, participated to the interpretation of diagenetic data; P. Iacumin contributed to the interpretation of stable isotope data; R. Tinterri participated to facies interpretation.

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Figure captions

Fig. 1. (a) Simplified geological map of the topographic front of the Northern Apennines, with the position of the study area along the Enza River valley (modified after Oppo *et al.* 2015).

(b) Reflection seismic section with line-drawing interpretation showing the main structural features in the vicinity of the studied field site (modified after Oppo *et al.* 2015).

Fig. 2. (a) Detailed geological map of the Enza River outcrop. Stereonets (Schmidt equal area projection lower hemisphere) report the mean bedding planes with dip angles and poles to bedding measured in different sites along the outcrop. (b) Detailed geological section across the entire Enza River outcrop. Bedding dip domains are also reported and show a progressive decrease of dip from the base to the top of the succession.

Fig. 3. Concretions types hosted within the stratigraphic succession. (a) Elongate single “cigar, blade-shaped” concretions emerging from loose sand at the base of the Sabbie di Imola Fm. (b) Coalescent elongate concretion displaying elongation traces on the top surface. (c) Tabular metre-wide bedding-parallel concretions. (d) Nodular and tabular bedding-parallel concretions.

Fig. 4. Stratigraphic, structural and petrophysical properties of the investigated succession. (a) Stratigraphic log comprising the entire exposed succession. (b) 30 m-thick detailed log illustrating the transition between the Argille Azzurre and the Sabbie di Imola Fms. and the first sand unit of the latter formation. (c) Concretion structural data through the detailed log (Schmidt equal area projection lower hemisphere). (d) Grain size and permeability variation curves.

Fig. 5. Progressive tilting of strata calculated from the unfolding of the dip domains illustrated in Fig. 2b within the stratigraphic interval comprising the Argille Azzurre-Sabbie di Imola (transition AZ-SI) and the Sabbie di Imola Fm. In the same deformation steps mean direction of elongate concretions was calculated and is displayed as azimuth and dip angles (Schmidt equal area projection lower hemisphere).

Fig. 6. Photomicrographs of the cement on stained thin sections under transmitted light and under cathodoluminescence. (a-b) Circumgranular rim of equant calcite (Cr) around bioclast followed by blocky zoned calcite (C1) with several zonations inside a tabular concretion

sample. **(c-d)** Rare meniscus dully luminescent calcite (Cm) and fine equant sparitic calcite (C2) surrounding bioclast inside single elongate concretion. **(e-f)** Syntaxial overgrowth around crinoid fragments and blocky zoned calcite (C1) in tabular concretion. **(g-h)** Fine equant sparite (C2) postdating blocky-zoned calcite (C1) inside elongate coalescent concretion. Qz, quartz; K-f, feldspar; B, bioclast; P, porosity.

Fig. 7. Isotopic data collected on hand specimens **(a-b)** and on thin sections with micromill technique **(c-d-e)**. **(a)** Cumulative isotopic data characterizing concretions inside the Sabbie di Imola and the Argille Azzurre Fms. **(b)** Detailed isotopic trend shown by concretions hosted within the Sabbie di Imola Fm. Isotopic data gained from single elongate **(c)**, coalescent elongate **(d)** and tabular concretions **(e)** with micromill technique.

Fig. 8. Sampling methods and isotopic trends on representative concretion hand specimens. **(a)** Single elongate, **(b)** elongate coalescent, **(c)** tabular and **(d)** nodular concretion.

Fig. 9. **(a)** Diagenetic environments inferred from the four identified cementation stages. **(b)** Schematic cementation sequence deduced from petrographic and cathodoluminescence observations. Cement colour are referred to the different CL-response. Cr, isopachous rim of equant calcite; Cm, meniscus mosaic sparitic calcite; C1, blocky zoned calcite; C2, fine equant sparitic calcite; Qz, quartz; K-f, feldspar; B, bioclast; Crd, crinoid.

Fig. 10. Concretion development modality for tabular **(a-b-c)** and coalescent elongate concretions **(d-e-f)**. **(a)** Alignment of cementation nuclei leads to the formation of single elongate concretions in a pattern parallel to the strike of strata. **(b)** With a laterally spread fluid flow pattern (parallel to bedding surface) single elements may merge together forming tabular bodies. **(c)** Pervasive cementation eventually allows the development of widely extensive tabular concretions. **(d)** Scattered and sparse cementation nuclei arrangement is responsible for the formation of densely clustered arrays of single elongate concretions. **(e)** Focused fluid flow pattern induces the cementation of bigger elongate bodies. **(f)** Coalescent

elongate concretions increase their size until the fluid flow is able to carry solutes necessary to the cementation.

Fig. 11. 3D conceptual sketch with inferred fluid flow patterns induced by the anticline growth from carbonate concretions data. **(a)** In the first stage of fold growth the anticline was propagating near the study site hence fluid flow and sediment supply were directed parallel to fold axis from the East to the West. **(b)** With topography increase southern-ward from the Enza River, fluid flow direction started to rotate clockwise towards NW. **(c)** The westward fold axis propagation led to shallow fluxes heading to the North. **(d)** Eventually during the late stage of fold growth shallow fluid flow was mainly directed to NNE following the hydraulic and topographic gradient induced by the growing anticline.

Table 1. *Morphology, main cement types, percentage of porosity, cement and intergranular volume (IGV) of the sampled concretions*

Pizzati et al.
Figure 1

Pizzati et al.
Figure 2

Pizzati et al.
Figure 3

Pizzati et al.
Figure 5

Pizzati et al.
Figure 6

Pizzati et al.
Figure 7

Pizzati et al.
Figure 8

Pizzati et al.
Figure 9

Pizzati et al.
Figure 10

Pizzati et al.
Figure 11

Sample name	Concretion type	Cement type	Porosity (%)	Cement (%)	IGV (%)
SP1.3C	Single elongate	C2	16.9	33.5	50.4
SP1.18C	Tabular	C1, C2	4.1	46.7	50.8
SP1.24C	Tabular	C1, C2	1.7	43.2	44.9
SP1.27C	Tabular	C1, C2	3.1	43.3	46.4
SP1.28C	Single elongate	C2	2.1	45.7	47.8
SP1.29C	Single elongate	C2	2.2	44.3	46.5
SP1.31C	Tabular	C1, C2	4.1	42.9	47
SP1.33C	Nodular	C2	1.9	47.2	49.1
SP1.34C	Coalescent elongate	C1, C2	2.8	42.8	45.6
SP1.38C	Coalescent elongate	C1, C2	1.9	52.9	54.8