Stylolites and stylolite networks as primary controls on the geometry and distribution of carbonate diagenetic alterations

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Highlights

- A systematic analysis of the influence of individual stylolites and stylolite networks on other diagenetic reactions (cementation, dissolution, mineral replacement) is presented
- Bedding-parallel stylolites acted as baffles for burial dolomitization, resulting in a stratabound dolostone geometry in which stylolites bound the reaction front
- Anastomosing stylolites acted as a collective baffle for dolomitization fluids, in a way that the reaction front weaves up and down following consecutive stylolites
- The proposed analysis considers the influence on permeability of the morphology and distribution of stylolites in different sedimentary facies, from mud- to grain-dominated
- The same stylolites served later as baffles and/or conduits for different types of diagenetic fluids when the burial, stress and fluid pressure conditions changed

Abstract

There is an ongoing debate on whether stylolites act as barriers or conduits for fluids, or even play no role in terms of fluid transport. This problem can be tackled by examining the spatial and temporal relationships between stylolites and other diagenetic products at multiple scales. Using the well-known Lower Cretaceous Benicàssim case study (Maestrat Basin, E Spain), we provide new field and petrographic observations of how bedding-parallel stylolites can influence different diagenetic processes during the geological evolution of a basin. The results reveal that stylolites can serve as baffles or inhibitors for different carbonate diagenetic reactions, and act as fronts for dolomitization, dolomite recrystallization and calcitization processes. Anastomosing stylolites, which pre-date burial dolomitization, likely acted as a collective baffle for dolomitization fluids in the study area, resulting in stratabound replacement geometries at the metre-to-kilometre scale. The dolomitization front weaves up and down following consecutive anastomosing stylolites, which are typical of mud-dominated facies that characterize limestone-dolostone transition zones. Contrarily, dolostone bodies tend to correspond to grain-dominated facies characterized by parallel (non-anastomosing) stylolites. The same stylolites subsequently acted as fluid flow conduits and barriers again when the burial and stress conditions changed. Stylolites within dolostones close to faults are found corroded and filled with saddle dolomite riming the stylolite pore, and high-temperature blocky calcite cements filling the remaining porosity. The fluids responsible for these reactions were likely released from below at high pressure, causing hydraulic brecciation, and were channelised through stylolites, which acted as fluid conduits. Stylolites are also found acting as baffles for subsequent calcitization reactions and occasionally appear filled with iron oxides released by calcitization. This example demonstrates how the same type of stylolites can act as barriers/inhibitors and/or conduits for different types of diagenetic reactions through time, and how important it is to consider their collective role when they form networks.

Keywords: stylolite; dolomitization; fluid flow; barrier; waffle; conduit; diagenesis.

1. Introduction

Despite their simple mineralogy, carbonate sedimentary rocks typically undergo heterogeneous post-depositional diagenesis that can significantly alter their original textures and associated petrophysical and mechanical properties. Diagenetic processes like dissolution, cementation or mineral replacement are intimately linked to the diagenetic fluids that circulate through the rock's porosity, and are therefore controlled by the available flow pathways and volume of fluid delivered to the reaction zone. The resulting diagenetic products, in turn, impact the permeability and further reactivity of the evolving rock, creating highly complex feedback relationships that are very challenging to decipher and predict. Understanding the factors that determine the distribution of diagenetic products is key for the study of the evolution of sedimentary basins and orogens, and also for predicting permeability anisotropy and reservoir quality. A wide range of studies have focused on the identification of the main controls on fluid flow in carbonate rocks and how they determine the distribution of diagenetic products (*e.g.*, Agar and Hampson, 2014, and references therein). These include: (i) the characteristics of the pore space associated with the rock's depositional textures and diagenetic history, (ii) the distribution and properties of fracture networks, (iii) the type of pore fluids (marine, meteoric, metamorphic, etc.), their properties (temperature, pressure, salinity, etc.) and the forces that drive them (*e.g.*, Whitaker et al., 2004). However, less attention has been paid to stylolites as structures capable of partitioning fluid flow and creating permeability anisotropy that ultimately determines where, how, and when diagenetic alterations take place.

Stylolites are usually rough dissolution surfaces that form owing to intergranular pressure-solution (*e.g.*, Merino, 1992; Koehn et al., 2007; Toussaint et al., 2018). Bedding-parallel stylolites, also called diagenetic or sedimentary stylolites, form during burial and compaction as a response to layer-normal compression associated with the weight of the overburden sediments. Stylolites are ubiquitous in most carbonate formations, present variable distributions depending on the host rocks (Ehrenberg et al., 2016) and often form complex anastomosing networks (Ben-Itzhak et al., 2014; Humphrey et al., 2020). These structures have historically been considered barriers to fluid flow because they can collect insoluble material (*e.g.*, clays, mica, oxides, sulphides, organic matter) while they grow (*e.g.*, Nelson, 1981; Finkel and Wilkinson, 1990; Alsharhan and Sadd, 2000). Moreover, their growth can lead to a significant reduction of the overall porosity and permeability of the host rock because the dissolved mineral can re-precipitate nearby in the form of cement thus controlling flow pathways for fluids that can induce further diagenetic reactions (Fabricius and Borre, 2007; Vandeginste and John, 2013). However, other studies have shown how fluids can flow across stylolites (*e.g.*, Neilson and Oxtoby, 2008; Morad et al., 2018), especially at their flanks and tips (Carozzi and von Bergen, 1987; van Geet et al., 2001; Koehn et al., 2016; Humphrey et al., 2019). Stylolites can also be filled with cements, suggesting that fluids can be advected through them under certain conditions and precipitate minerals (Paganoni et al., 2016; Martín-Martín et al., 2018). Recently, laboratory permeability tests on core plugs have reported situations in which stylolites might not influence the overall vertical permeability of the rock in any way, because the measured permeability perpendicular to stylolites was the same as that in samples with no stylolites (Heap et al., 2014; Heap et al., 2018; Rustichelli et al., 2015). Furthermore, these authors also showed that stylolites can increase the overall rock permeability along the direction parallel to them. Therefore, the impact of stylolites on their host rock permeability is key for the flow of diagenetic and mineralising fluids, and also for petroleum migration (*e.g.*, Neilson et al., 1998; Baron and Parnell, 2007; Paganoni et al., 2016).

Koehn et al. (2016) proposed a new classification of stylolites in which their geometry and formation mechanisms determine whether they can be barriers to fluid flow or not. In this scheme four stylolite types are distinguished, and their potential for leaking fluids depends on the non-linearity of their growth, the insoluble material they collect and the pinning of layers and grains. Bruna et al. (2019) recently reviewed the knowledge on how the formation and evolution of stylolites can define their behaviour with respect to fluid transport and cementation, and concluded that further studies are required in order to fully understand the range of behaviour that these structures can present.

Within the framework of the ongoing debate on the impact of stylolites on fluid flow, it is critical that new insights are gained into the association of stylolites with other diagenetic products, in order to understand how they control the occurrence and distribution of diagenetic alterations in carbonate basins. Particularly important is to recognize to what extent stylolites and the networks they form can control the flow of diagenetic fluids, in what scenarios stylolites may impact fluid flow as well as transport of solutes, and if these structures can indeed act as diagenetic reaction inhibitors or enhancers, regardless of whether they are permeability barriers or conduits.

A key to constrain the influence of bedding-parallel stylolites on carbonate diagenesis is to carefully examine their spatial and temporal relationships with different diagenetic products at multiple scales. In this way three end-member scenarios can be proposed (Fig. 1). The first scenario considers that stylolites act as conduits for fluids and, therefore, the diagenetic reaction progresses from the connected stylolite outwards (Fig. 1a). A second situation can arise when stylolite porosity and permeability are the same as those of the host rock and, therefore, they do not control fluid flow and diagenetic reactions are not influenced by them (Fig. 1b). Finally, a third end-member case is one in which the diagenetic fluid cannot overcome stylolites in a way that the reaction is constrained to one of their sides and, therefore, they act as reaction baffles (Fig. 1c). These scenarios assume that the diagenetic fluid can transport enough solutes to the reaction site, by advection-diffusion, and that the reaction will occur if the fluid reactivity and environmental conditions are appropriate. Finally, another hitherto not considered key aspect is that stylolites in nature often appear arranged in networks rather than in isolation (*e.g.*, Ben-Itzhak et al., 2014; Humphrey et al., 2019; Humphrey et al., 2020). Therefore, one should collectively evaluate how individual stylolites may impact fluid flow, transport and reactions, and what the role of networks of stylolites is on these processes.

With the aim of tackling the above questions and improving our understanding of the controls that stylolites exert on fluid flow, transport and diagenetic reactions, we here present and discuss examples from shallow-marine Upper Aptian- lowermost Albian carbonates of the Benassal Fm in the Benicàssim area (Maestrat Basin, E Spain). We examine at multiple scales mineral replacement reactions (dolomitization and calcitization), dolomite recrystallization, corrosion, and precipitation of saddle dolomite, calcite and iron oxide cements. Building upon the extensive previous knowledge of the area (Martín-Martín et al., 2013; 2015; 2018; Gomez-Rivas et al., 2014; Humphrey et al., 2020; Yao et al., 2020) we provide new observations and analyses of outcrops and samples, paying special attention to cases in which individual stylolites act as baffles/inhibitors or enhancers of different types of diagenetic reactions, whether the same structures can exhibit different transport behaviour and, finally, to what extent large-scale (*i.e.*, metre to kilometre-scale) diagenetic alterations can be controlled by stylolite networks. The findings of this study have implications beyond the study of diagenesis in carbonate formations because the same principles of stylolite and fluid flow interactions apply to the circulation of geofluids (hydrocarbons, brines, groundwater, injected CO_2, etc.) in other rock types and settings.

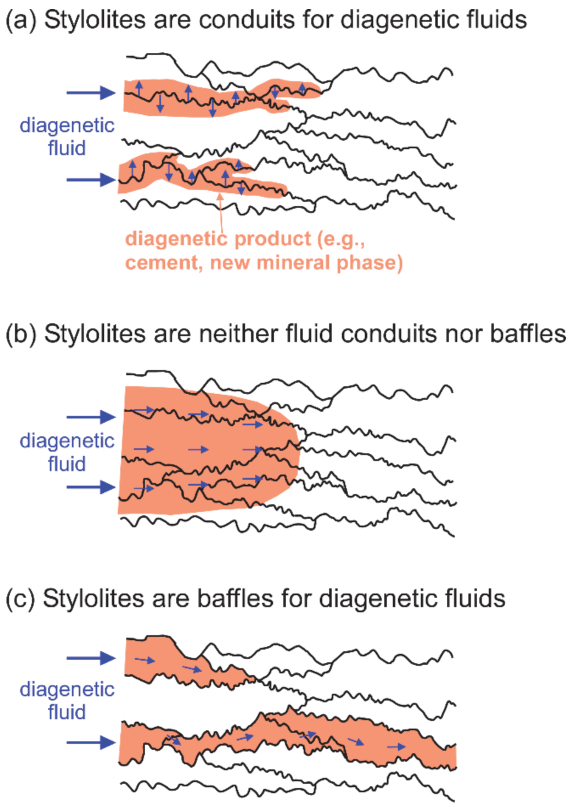

Figure 1. Sketches illustrating end-member scenarios of the potential control of stylolites on diagenetic fluid flow and reaction patterns. (a) Stylolites are more permeable than the host rocks and act as conduits for diagenetic fluids. In such cases the reaction progresses from the stylolites outwards, and the diagenetic product initially forms a halo. (b) Stylolites have the same transport properties as those of the host rock and therefore do not control flow and reactions. In such a situation the reaction front is not influenced by them. (c) Stylolites act as barriers for the diagenetic fluid and reaction, and therefore constrain the diagenetic product to one of their sides. The capacity of the fluid to overcome or not an individual stylolite may depend on the stylolite morphology and its sealing properties.

2. Geological setting

The Early Cretaceous Benicàssim carbonate platform (Maestrat Basin, E Spain) (Fig. 2a,b) constitutes a world-class example of syn-rift shallow-marine carbonate deposition and fault-controlled hydrothermal dolomitization (Yao et al., 2020). In this area, a >1,600 m-thick succession of syn-rift shallow-marine Upper Aptian- lowermost Albian limestones of the Benassal Fm were partially dolomitized as a result of the flow of warm brines that were advected from the underlying sedimentary and basement rocks along large-scale faults, which acted as feeding points for dolomitizing and subsequent mineralizing fluids (Fig. 2c; Martín-Martín et al., 2013; Gomez-Rivas et al., 2014; Martín-Martín et al., 2015; Martín-Martín et al., 2018; Yao et al., 2020). The host rock succession, which is stacked in three transgressive-regressive sequences, underwent a complex diagenetic history (Fig. 2c; Fig. 3), including mechanical compaction, early calcite and dolomite cementation, chemical compaction, two phases of replacive dolomitization, burial dissolution, local brecciation (in the vicinity of faults), calcite cementation, sulphide mineralization and, finally, calcitization of dolomite as well as late meteoric calcite cementation (see Martín-Martín et al., 2015 for a complete description of the paragenesis). The first dolomitization phase (RD1) mimicked the original limestone texture while the second dolomite phase (RD2) formed by recrystallization of RD1.

Field and petrographic observations show that bedding-parallel stylolites formed during the early stages of diagenesis in close association with the Early Cretaceous rifting. In this regard, chemical compaction (*i.e.*, stylolitization) predated dolomite cementation and replacive dolomitization stages (Martín-Martín et al., 2015; Martín-Martín et al., 2018) (Fig. 2b). Humphrey et al. (2020) investigated the prevalence of the different stylolite types in the most representative carbonate depositional facies of the Benassal Fm, using the classification of Koehn et al. (2016). Suture-and-sharp peak and wave-like stylolites are ubiquitous in all the facies analyzed, with grainstones also featuring rectangular layer-type stylolites (Fig. 4). Facies with relatively homogeneous components, such as bioclastic and ooidal/peloidal grainstones, tend to present parallel (*i.e.*, non anastomosing) stylolites with large spacings and low amplitudes (Fig. 4a,b). Stylolites in mud-supported facies, with heterogeneous grain compositions, poor sorting and meter-scale bedding typically have high amplitudes, are normally closely spaced and tend to form anastomosing networks (Fig. 4c,d). Some examples of these facies are spicule wackestone, bioclastic wackestones/packstones and rudists floatstones.

Burial curves indicate that dolomitization took place at depths less than 1 km during the Late Cretaceous post-rift period (Fig. 2c). The dolomitizing fluid was a seawater-derived brine that interacted and exchanged with the underlying Permian-Triassic and Paleozoic basement rocks (Gomez-Rivas et al., 2014). Post-replacement cements include burial calcite cement filling intercrystalline porosity, and hydrothermal saddle dolomite and blocky calcite cements found in the vicinity of faults (Martín-Martín et al., 2018). Dolomite calcitization released Fe from the dolostones and was caused by the circulation of meteoric fluids, more intensively in areas close to major faults (Martín-Martín et al., 2015). The Benicàssim and equivalent rocks in the Maestrat Basin host Mississippi Valley Type metal sulphide deposits, which were dated by U-Pb at 62.6±0.7 Ma by Grandia et al. (2000). Moreover, two events of Alpine deformation can be identified from fracture and vein networks in the area, with a first strike-slip event with WSW-ENE-oriented horizontal compression and a second oblique-slip event with SW-NE-oriented principal compressive stress (Gomez-Rivas et al., 2012).

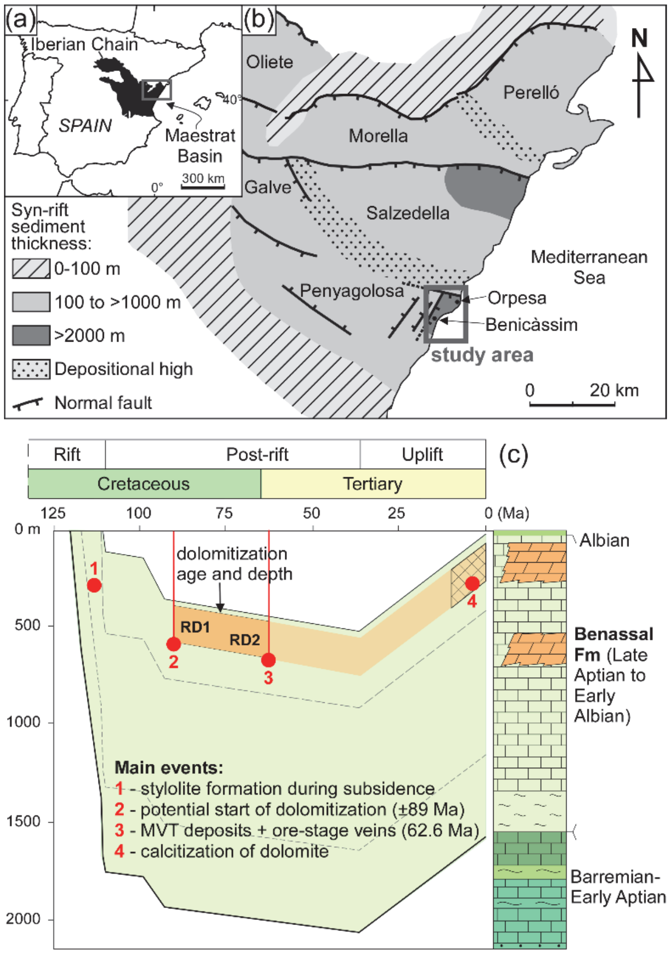

Figure 2. (a) Map of the Iberian Peninsula showing the location of the Iberian Chain and Maestrat Basin. (b) Simplified paleogeographic map of the Maestrat Basin during the Late Jurassic - Early Cretaceous rift cycle, with the location of the main faults, basin depocenters and sedimentary highs, and showing the thickness of syn-rift deposits. The name and location of sub-basins is also indicated. The location of the study area (Benicàssim half graben) is indicated with a grey rectangle, in the eastern part of the Penyagolosa sub-basin. (c) Decompacted subsidence curves displaying the burial history of the Benassal Fm limestones and dolomitized intervals. Numbered red dots indicate the main events discussed in this article. RD1 and RD2 account for replacive dolomite 1 and replacive dolomite 2 (see Fig. 3 for a summary of the paragenesis). Figures based on Martín-Martín et al. (2015).

Dolostones in the Benicàssim area crop out as seismic-scale geobodies, with geometries ranging from massive patches around large-scale faults (which were interpreted to have acted as entry points of dolomitizing fluids) to very well-defined stratabound geobodies that extend for long distances away from them. Fault zone areas are mostly covered with Quaternary deposits, and therefore are difficult to sample. However, the outcrop quality away from the large-scale faults is excellent and reaction fronts can be observed in detail. The dolomitized stratabound units in the studied outcrops have a thickness of up to 150 m (Fig. 5a) and replace limestones that were deposited mostly during the regressive cycles of the two uppermost transgressive-regressive sequences of the Benassal Fm (see Yao et al. 2020 for a detailed study of the relationships between sequence stratigraphy and dolomitization).

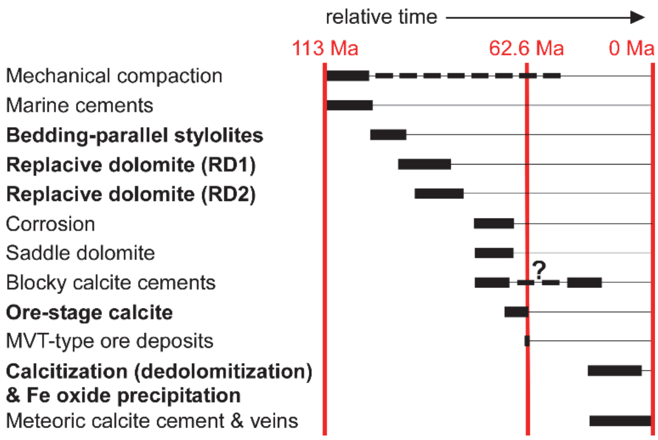

Figure 3. Simplified paragenetic sequence of the Benassal Fm showing the main diagenetic events and products. Those events marked in bold are discussed in this study. 113 Ma is the estimated age of the end of the Benassal Fm deposition. 62.6 Ma is the age of MVT deposits in the Maestrat Basin (Grandia et al., 2000). For a complete description of the paragenesis see Martín-Martín et al. (2015) and Martín-Martín et al. (2018).

3. Methods

Expanding upon extensive research at the Benicàssim area, we have carefully mapped and examined diagenetic replacement fronts at variable scales, ranging from the km- to the μm-scale, away from large-scale faults and within the stratigraphic and structural context. We have re-examined more than 300 thin sections analyzed in previous studies (*e.g.*, Martín-Martín et al., 2013; 2015; 2018; Gomez-Rivas et al., 2014; Humphrey et al., 2020, Yao et al., 2020). Moreover, 20 additional samples of selected reaction fronts were collected for a detailed characterization of such surfaces. Samples were collected with a portable drill, to acquire cylinders with a diameter of 1”. Double-polished thin sections were made from those samples. Details of stylolites and diagenetic reaction fronts have systematically been studied with standard petrographic and cathodoluminescence microscopy, the latter with a Technosyn Cold Cathode Luminescence model 8200 MkII equipment, with operating conditions of 15-18 kV and gun current of 300-350 A. Thin sections of existing and new samples were carbon-coated for their study using an ISI ABT-55 Scanning Electron Microscope (SEM) at 15 kV at the University of Aberdeen.

Stylolites were classified according to Koehn et al. (2016). It is worth noting that in the present contribution the term wave-like stylolites also includes the so-called wispy seams and pressure-solution seams (with peak amplitude < 1 cm) of Alsharhan and Sadd (2000). Depositional textures are defined using the scheme of Dunham (1962), including the additional terms of Embry and Klovan (1971).

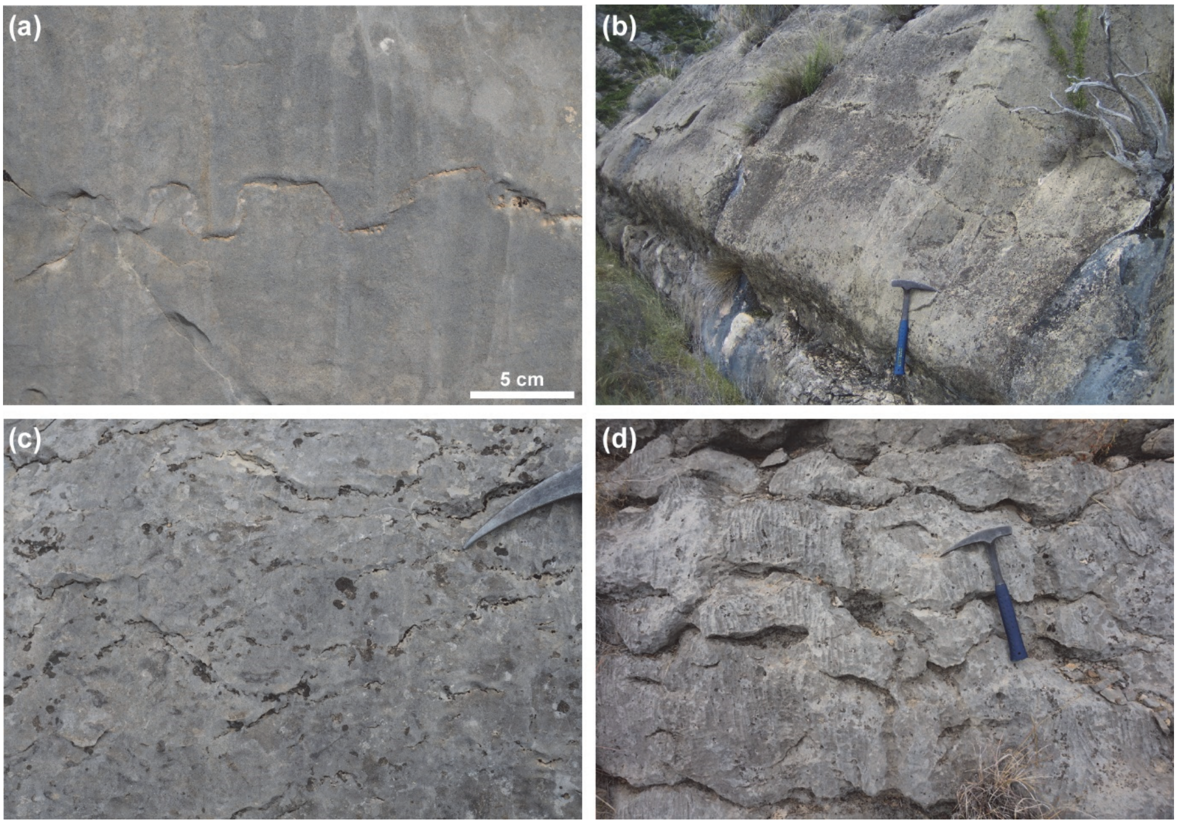

Figure 4. Main stylolite types at the Benicàssim area. (a) Rectangular layer type stylolites in oolitic grainstones. (b) Stylolites are long, parallel and relatively widely spaced in grainy facies, such as bioclastic and peloidal grainstones. (c) Suture and sharp peak type stylolites forming anastomosing networks in muddy facies with heterogeneous grain size, such as rudist and *chondrodonta* floatstone. (d) Anastomosing networks of simple wave-like type stylolites in coralline facies.

4. Results

The analysis of diagenetic reaction fronts cropping out in the Benicàssim area where dolostone geobodies are stratabound reveals that bedding-parallel stylolites commonly form dolomitization fronts, and thus define the contact between dolostones and host limestones (Figs. 5, 6). Less frequently, stylolites appear separating the two dolomite textures RD1 and RD2 (Fig. 6) or form contact surfaces separating dolomite and calcitized dolomite (Fig. 7). Additionally, stylolites are also found open, corroded, and filled with saddle dolomite and calcite cements, and in some other cases with iron oxides (Fig. 8). In this section we describe the characteristics of the relations between stylolites and five types of diagenetic reactions: dolomitization, dolomite recrystallization, corrosion, cementation and dolomite calcitization.

A close look at the outcrops away from faults reveals that dolomitization fronts are always extremely sharp at the centimetre to metre scale, parallel to bedding and very frequently coincide with suture-and-sharp peak and wave-like stylolites (following the classification of Koehn et al., 2016) (Fig. 5b-d). The statistical analysis of Humphrey et al. (2020) reveals that dolomitized units tend to have stylolite distributions like those of relatively homogeneous grainy facies (*e.g.*, bioclastic and ooidal/peloidal grainstones). However, we have observed that limestones with anastomosing networks of stylolites frequently bound dolostones, where stylolites from dolomitization fronts (Fig. 5b-d). Accordingly, this type of limestones typically corresponds to mud-rich facies with a relatively heterogeneous distribution of component size.

Field observations in the areas where dolostones are stratabound indicate that the dolomitization fronts weave up and down following consecutive stylolites (Fig. 5b-c), and this is especially evident in facies in which stylolites form anastomosing networks and abut on each other. Stylolite networks in such situations typically show the same geometry and distribution on both sides of the dolomitization front, so that these fronts do not necessarily coincide with bed surfaces or boundaries between different types of facies (Fig. 5b). On the contrary, fronts are embedded within the same facies.

The analysis of dolomitization fronts at the microscale reveals that suture-and-sharp and wave-like stylolites and reaction fronts associated with them are not strictly sharp at the small scale, but have a width of up to a few tens of microns (Fig. 6). Fig. 6a-c shows an illustrative example of a reaction front bounded by a series of stylolites. In the central part of this micrograph, the dolomitization front is limited by an up to 100 μm wide single pressure-solution zone (Fig. 6d). However, laterally two other stylolites bound the front resulting in a partial dolomitization of the rock volume between the two consecutive stylolites (Fig. 6b-c). Pressure-solution zones corresponding to stylolites that are clearly visible at the outcrop and thin section scale are not discrete surfaces at the microscale, but have a certain width. These zones present a relatively high concentration of iron oxides (Fig. 6d) with some scarce clay minerals, mostly illite. However, a massive and continuous fraction of non-carbonate material at the pressure solution zone cannot be observed in the Benicàssim stylolites. The lack of a high and laterally continuous content of insoluble material is a common characteristic of many stylolites in different settings (Toussaint et al., 2018). The absence of a systematic and continuous stylolite residue and is consistent with the lack of clastic components of the >1,600 m of Benassal Fm sediments (Yao et al., 2020). The amount of insoluble material collected by a stylolite depends on whether it can dissolve and offset layers and also on the host rock composition (see Koehn et al., 2016 for a discussion on this issue).

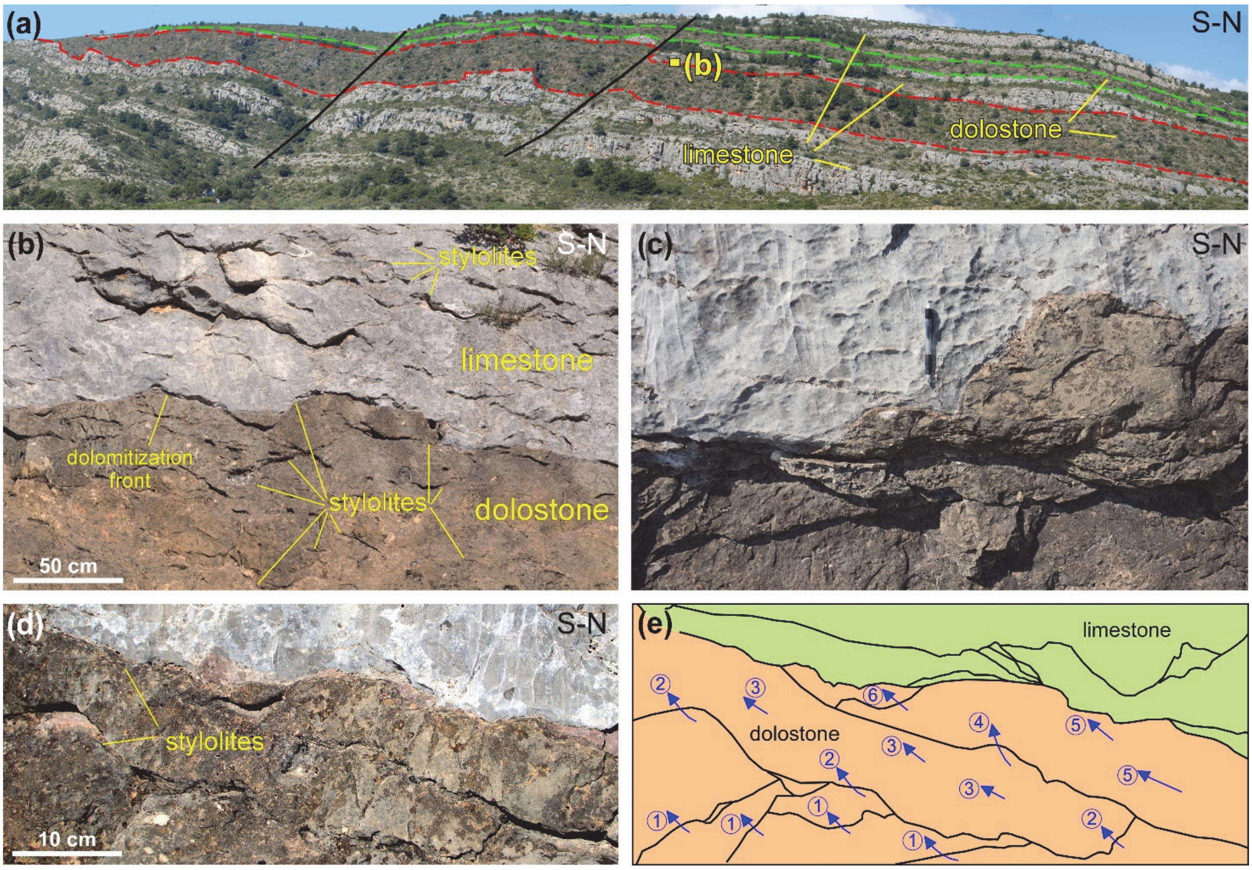

Figure 5. Outcrop images of stylolites acting as dolomitization fronts at the Benicàssim area. (a) Panoramic view of the Racó del Moro outcrop (see Yao et al., 2020), where dolostone geobodies present a stratabound geometry, and dolomitized layers extend for several km away from large-scale faults. The two main dolostone bodies are indicated. (b-d) Zooming into dolomitization fronts. A pervasive network of bedding-parallel suture-and-sharp peak and wave-like stylolites can be observed both in the limestones and dolostones. The dolomitization front waves up and down following consecutive stylolites. (e) Interpretation of image (d), where limestone is represented in green, dolostone in orange and arrows with numbers that represent the progressive flow of dolomitizing fluids. Each number (1 to 6) represents a sequential step of the reactive fluid overcoming the barrier of one stylolite and dolomitizing the rock volume constrained by the next reaction barrier (stylolite). Please note that in this outcrop the dolomitizing fluid is interpreted to have flowed from the North, as suggested by Yao et al. (2020).

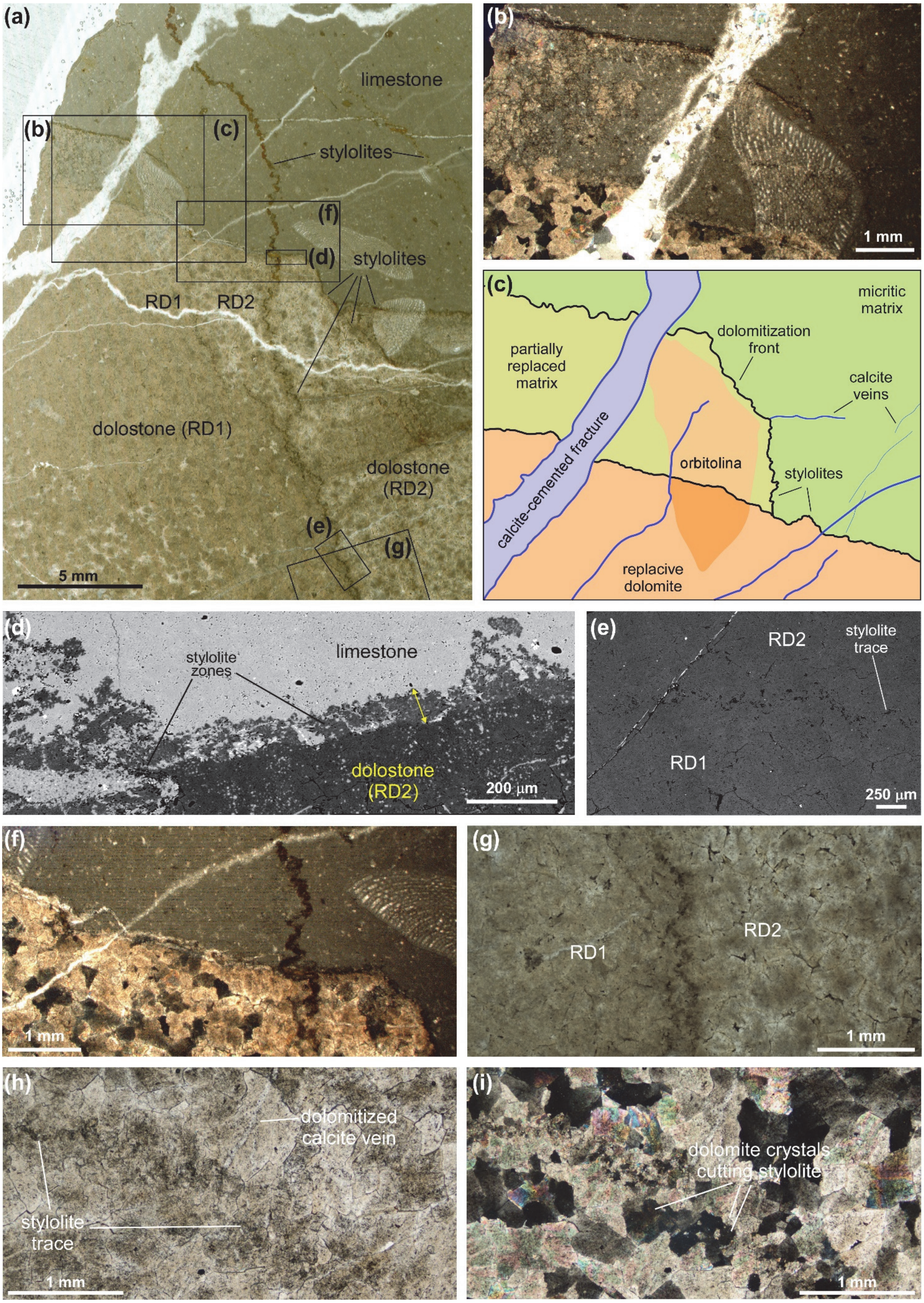
(a)
limestone
(b)
(c)
stylolites
(f)
(d)
stylolites
RD1
RD2
dolostone (RD1)
dolostone
(RD2)
(e)
(g)
5 mm
(b)
1 mm
(c)
micritic
matrix
partially
replaced
matrix
dolomitization
front
calcite
veins
calcite-cemented fracture
orbitolina
stylolites
replacive
dolomite
(d)
limestone
stylolite
zones
dolostone
(RD2)
200 μm
(e)
RD2
stylolite
trace
RD1
250 μm
(f)
1 mm
(g)
RD1
RD2
1 mm
(h)
dolomitized
calcite vein
stylolite
trace
1 mm
(i)
dolomite crystals
cutting stylolite
1 mm

Figure 6. (a) Scanned image of a thin section showing a dolomitization front. (b) Detail of dolomitization front related to two anastomosing stylolites. The whole volume of rock below the lowermost stylolite has been dolomitized, while the volume in between the two consecutive stylolites appears partially dolomitized. (c) Sketch with the interpretation of the arrangement of stylolites, dolomite, limestone and veins. (d) SEM image of the dolomitization front coinciding with a stylolite. The reaction front and pressure-solution seam have a width of a few tens of microns (see yellow arrow), dolomite has a slightly lighter colour (*i.e.*, dolomite richer in Calcium) than the completely dolomitized part (RD2), and contains iron oxides (white spots). (e) SEM image showing the trace of a stylolite after being partly erased by dolomitization. (f) Photomicrograph showing a detail of a dolomitization front defined by a single stylolite, and (g) Remain of a stylolite acting as a recrystallization reaction front separating RD1 and RD2 dolomite phases. (h) Photomicrographs in plane polarized and (i) cross polarized light of a trace stylolite that is cross-cut by dolomite crystals, thus showing how replacive dolomitization post-dates the formation of the stylolite.

Thin sections of stylolites in Benicàssim show that they also appear separating different types of replacive dolomite as those (RD1 and RD2) previously reported by Martín-Martín et al. (2015) (Figs. 3 and 6a,g). RD1 pervasively replaced micrite, skeletal and non-skeletal grains as well as pre-dolomitization calcite cements, causing a mimetic replacement that did not significantly alter the original porosity and permeability of the limestone. RD2 replaced RD1 facies in the most permeable areas resulting in non-mimetic, medium to coarse planar-s to non-planar-a crystal mosaics with higher porosity and permeability than RD1 dolomite. RD2 dolomite frequently appears surrounding RD1 cloudy cores and patches of relict RD1 crystal mosaics, demonstrating that RD2 formed from RD1 by recrystallization. SEM analysis of stylolites within dolostone in the Benicàssim area reveals that stylolites pre-date dolomite crystal formation (Fig. 6e,h-i). In thin sections these stylolites are observed to occasionally coincide with recrystallization fronts of RD1 into RD2 (Fig. 6g). It is worth noting that all the stylolites of Fig. 6g belong to the same anastomosing network, and that the relative angle they form with each is a sectioning effect. Distinguishing between RD1 and RD2 at outcrops is difficult, and their differentiation is mainly based on thin section analysis. This implies that it is not possible to systematically evaluate and quantify the lateral extent and frequency of stylolites acting as recrystallization fronts.

A relatively high proportion of the Benicàssim dolostones appears calcitized (*i.e.*, dedolomitized) in the volume of rock near outcrop surfaces and in the vicinity of faults (Martín-Martín et al., 2015) (Fig. 7). This calcitization is associated with the formation of Fe oxides that give the characteristic brown/orange colour of dolostones on outcrop surfaces (Fig. 7a,b). Bedding-parallel stylolites can also be found coinciding with calcitization fronts. The Benicàssim dolostones have a variable but relatively high amount of Fe (up to 28,600 ppm), and when dolomite is calcitized this Fe is not incorporated in the structure of the newly formed calcite crystals and is released to form Fe oxides (Fig. 7c, e). Moreover, calcitization can also result in the formation of irregularly distributed vuggy porosity. Both Fe oxides and newly formed pore space can clearly be identified in hand specimen, and by optical and SEM petrography (Fig. 7e,f). Fe oxides can be found within stylolites (Fig. 8g).

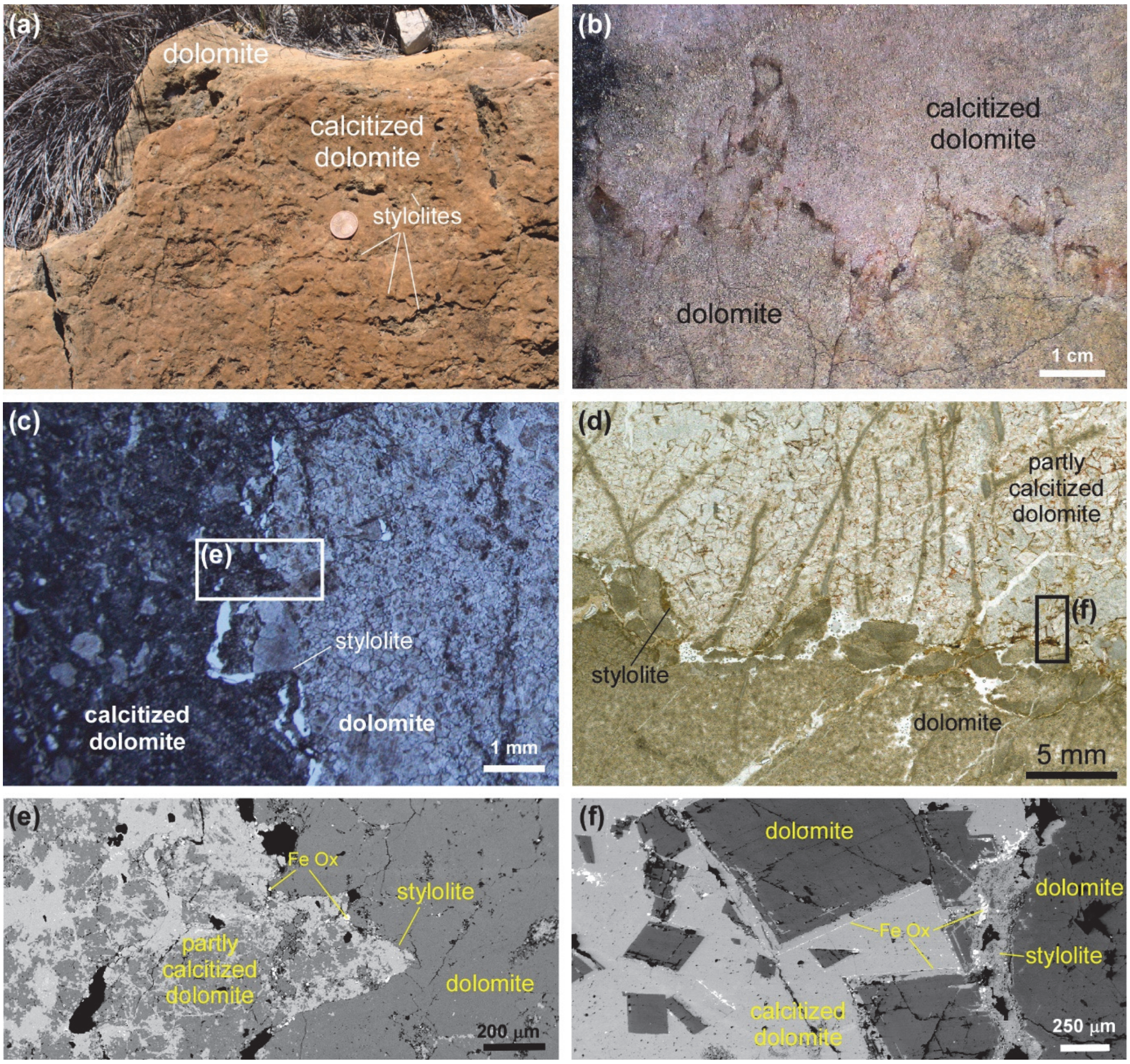

Figure 7. (a-b) Field images of calcitization (i.e., dedolomitization) fronts. (a) Note the different aspect of dolomite and calcitized dolomite. The orange tone reveals the presence of iron oxides, while less altered dolomite is brown. (b) A rectangular stylolite separating calcitized from unaltered dolomite. (c) Photomicrograph in plane polarized light and (d) scanned thin section showing calcitization fronts coinciding with stylolites and vertical dolomite relicts of microfractures. (e) SEM image of (c) showing a detail of a stylolite acting a calcitization front. (f) SEM image of (d) showing a detail of dolomite rhombs dissolution resulting in the precipitation of iron oxides (labelled as Fe Ox) around them. In (e) and (f) dolomite is dark grey while calcite is seen as light grey. The calcitization process is associated with the formation of a relatively large volume of Fe oxides (Fe Ox, in white) and the creation of porosity (in black).

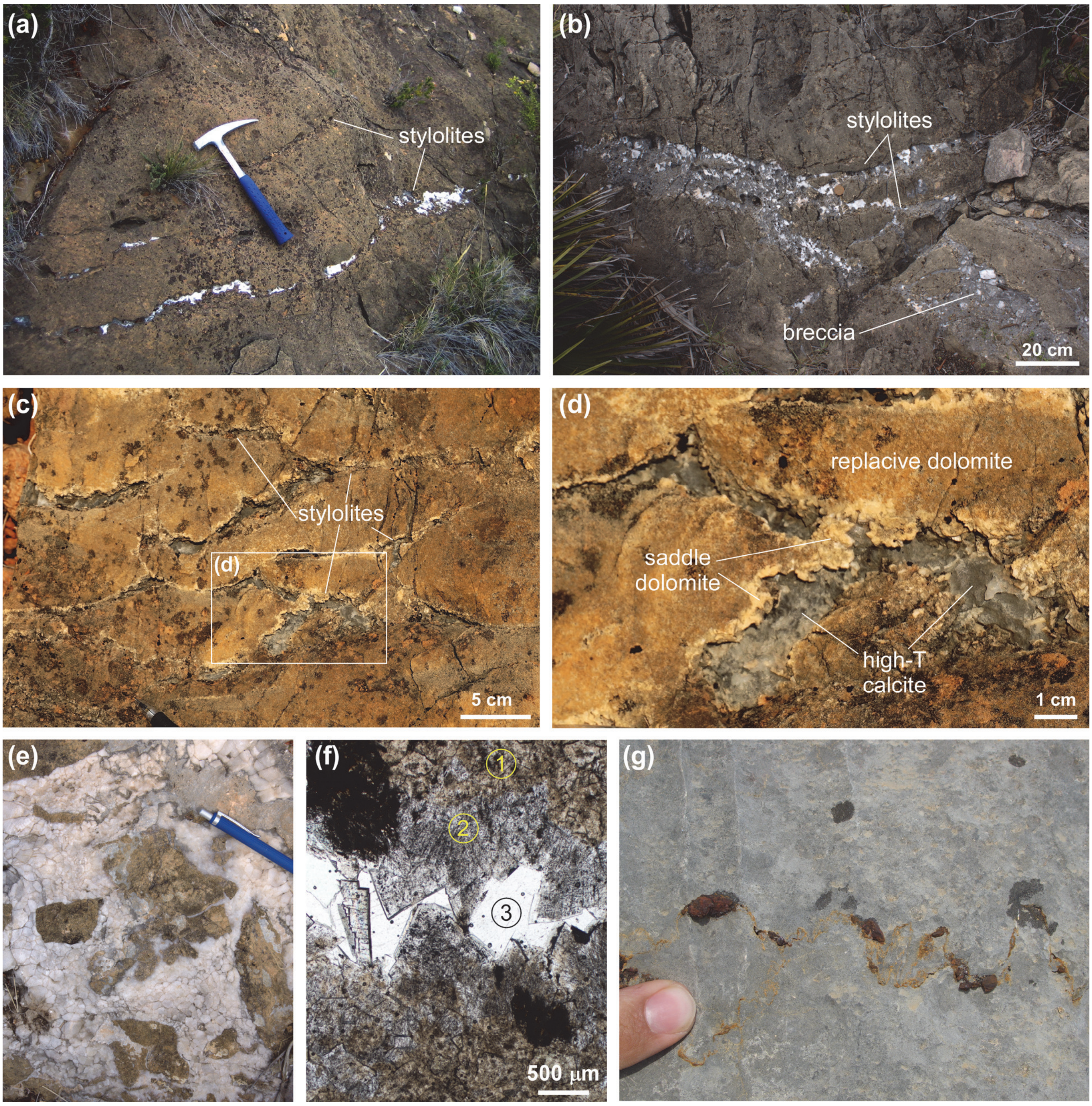

Figure 8. Examples of stylolites acting as conduits for diagenetic fluids. (a-e) Stylolites filled with saddle dolomite and high-temperature calcite. (a) Cemented wave-like stylolites. (b-c) Anastomosing stylolite networks filled with saddle dolomite and calcite cements. Note brecciation within stylolites in (b). (d) Detail of (c), where the host rock around stylolites is corroded and stylolite porosity is filled with a rim of saddle dolomite while the remaining porosity is filled with high-temperature calcite cement. (e) Close view of a hydraulic breccia of high-temperature calcite cements that engulf host rock replacive dolostone and saddle dolomite clasts. (f) Photomicrograph of a stylolite showing signs of corrosion of the replacive dolomite (1), saddle dolomite rimming the stylolite porosity (2), which is filled with white calcite crystals (3). (g) Stylolitic porosity filled with iron oxides that probably resulted from dolomite calcitization.

Contrarily to dolomitization, the processes of dolomite recrystallization and calcitization are more heterogeneously distributed and difficult to be spatially characterized. Therefore, unlike the case of dolomitization, the systematic quantification of the relationships between stylolites and stylolite networks and dolomite recrystallization and dolomite calcitization from outcrop studies would require the collection of a very large number of core plugs thus damaging the outcrops.

Bedding-parallel stylolitic porosity in the Benicàssim dolostones are also found filled with saddle dolomite and calcite cements, which were interpreted to have formed from high-temperature diagenetic fluids (Martín-Martín et al., 2018; Fig. 8a-f). The replacive dolostones appear partly corroded in the proximity of metre- to decametre-scale faults, such as those shown in Fig. 5a. It is worth noting that such corrosion does not affect limestones. Dolostones contain elongated dissolution pores, often in the form of corrosion vugs, which are aligned following stylolites (Fig. 8a-d,f). These dissolution features present a thickness of millimetres to centimetres, although in certain cases they can present lengths of up to about two metres. This type of dissolution porosity is clearly aligned parallel to bedding and concentrates along stylolites of the same types as those described as coincident with dolomitization fronts. Stylolitic porosity is generally filled with saddle dolomite cements that rim the pores formed by corrosion (Fig. 8d,f). These cements typically have a white to pale yellowish colour and millimetre crystal size, and are composed of mosaics of blade-shaped non-planar crystals. The remaining porosity left by the saddle dolomite cement rims is filled with coarse subhedral blocky calcite cement characterized by coarse and white to pale orange crystals. This cement commonly engulfs clasts of the host dolostone and saddle dolomite (Fig. 8e), and can be found in contact with etched margins of replacive dolomite and/or saddle dolomite crystals indicating that dissolution preceded its precipitation. Corroded stylolites filled with these cements, and related to brecciation, typically branch away from faults (Fig. 8b).

5. Discussion

5.1. Stylolites and stylolite networks as diagenetic reaction baffles/inhibitors

The Benicàssim case study clearly demonstrates how individual stylolites and anastomosing networks of stylolites can act as baffles for successive diagenetic reactions (Fig. 9). This section discusses several aspects of this relationship, from their timing, to the role of stylolites as baffles for dolomitization, recrystallization and calcitization reactions at multiple scales.

5.1.1. Relative timing of stylolite formation versus dolomitization

The statistical analysis of stylolite distributions presented in Humphrey et al. (2020) shows how the vast majority of stylolites in the Benicàssim area are of the suture-and-sharp peak and wave-like type. Both types of stylolites grow in a non-linear fashion, present low roughness and can potentially collect a laterally continuous amount of insoluble material (Koehn et al., 2016). Therefore, according to their morphology and formation conditions, they should have a relatively high sealing potential compared to the other stylolite types (*i.e.*, rectangular and seismogram pinning). This agrees with observations on drill core samples by Vandeginste and John (2013). Stylolite dolomitization fronts mostly occur in facies where stylolites form anastomosing networks (*i.e.*, in mud-rich beds; Fig. 4b), while most of the dolostone volume replaced grainy facies units. This is supported by the following observations: (i) dolostone units tend to feature stylolite distributions similar to those of the grainy facies with relatively homogeneous grain size (*i.e.*, bioclastic and ooidal/peloidal grainstones), and (ii) the systematic petrographic analysis of dolostones shows that such type of grainy facies is preferentially replaced (Martín-Martín et al., 2015). However, stylolites in the beds bounding dolostone fronts frequently appear in anastomosing networks (Fig. 5), revealing that limestones in these diagenetic reaction front zones present higher grain size heterogeneity and a high proportion of micrite matrix (as suggested by the statistical analysis of Humphrey et al., 2020) and therefore do not correspond to the typical (grainier) dolomitized facies. Bedding-parallel stylolite spacing is typically lower in mud-dominated facies because the quenched noise associated with grains in grainy facies triggers the pinning process favouring stylolite roughening. In this way stylolites in grainy facies accommodate dissolution by roughening, while stress in muddy facies can be preferentially accommodated by forming new seams instead of roughening the existing ones. Anastomosis is also promoted by cannibalization of pre-existing stylolites, a process that is also enhanced in lithofacies with grain size heterogeneity and poor sorting (Ben-Itzhak et al., 2014). The presence of anastomosing stylolites in dolomitization front zones compared with the non-anastomosing character of most dolostones can explain why the dolomitization reaction stopped at these levels and did not progress further to upper or lower strata (Fig. 9). The dolomitization fluid could invade the volume of host limestones corresponding to facies with non-anastomosing stylolites but would be stopped in the volumes of rock containing anastomosing stylolite networks that would have collectively acted as reaction baffles. This can be explained by the weaving of the reaction fronts up and down and by the stylolite distribution being very similar in the proximity of the observed fronts and on both of their sides (see Fig. 6). Fluid flow cannot easily bypass stylolites when anastomosing, as they abut on other stylolites thus inhibiting fluids infiltrating laterally. Dewit et al. (2014) described high-temperature dolostone bodies bounded by a unit of thick-bedded bioclastic wackestone alternating with nodular limestone beds. They interpreted that this massive limestone acted as an impermeable unit and that dolomitizing fluids could only overcome it by faults. In our case, this type of lithology also bounds dolostone geobodies, but with the stylolites playing a key role at the scale of the replacement reaction front.

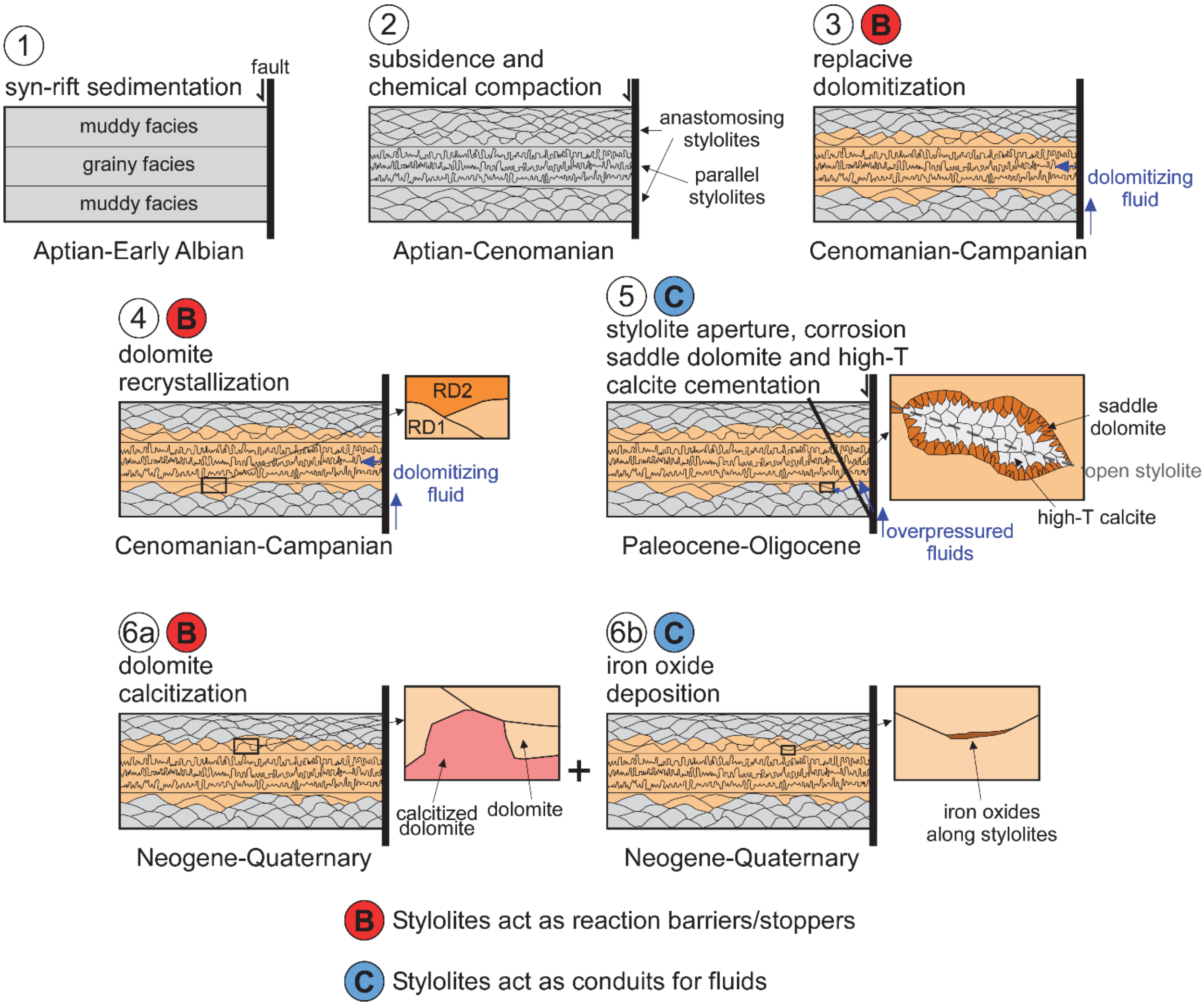

Figure 9. Synthetic sketches showing the relationships between stylolites and diagenetic processes during the geological evolution of the Benicàssim area. (1) Limestones and marls were sedimented during the Aptian-Early Albian syn-rift period. (2) Subsidence caused chemical compaction since deposition and during burial, resulting in the formation of networks of stylolites with various morphologies and distributions. In general, grainy facies feature relatively non-anastomosing bedding-parallel stylolites, while muddy facies tend to present more anastomosing stylolite networks (for the full statistical analysis see Humphrey et al., 2020). (3) Replacive dolomitization during the Late Cretaceous post-rift stage was controlled by the presence of networks of stylolites, which acted as stoppers for the replacement reaction. The dolomitization front weaves up and down following consecutive anastomosing stylolites. (4) Some stylolites acted as stoppers for dolomite recrystallization reactions at the local scale, separating two phases of replacive dolostones (RD1 and RD2) with different texture and geochemical signature. (5) At some stage between the Paleocene and the Oligocene some bedding-parallel stylolites within dolostones close to faults were opened, and overpressured fluids flowed along them causing corrosion, saddle dolomite and high-temperature calcite cementation and hydraulic brecciation. (6) The Benicàssim dolostones were partly calcitized at outcrop surfaces and fault zones by meteoric fluids from the Neogene to the Quaternary, and some stylolites also acted locally as stoppers for calcitization reactions. Stylolites are also occasionally found filled with iron oxides resulting from the calcitization reaction. (B) and (C) refer to stages in which stylolites have acted as barriers/baffles/stoppers and conduits for diagenetic fluids and reactions.

5.1.2. Stylolites and anastomosing stylolite networks as dolomitization reaction baffles

The fact that anastomosing stylolites acted as collective baffles to the dolomitization fluids reveals that it is the network of stylolites rather than individual ones that constrain the dolomitization reaction to one side of them by channelling fluid flow parallel to layering. This clearly matches the stratabound character of the replacement reaction, as observed in many case studies of hydrothermal dolomitization (*e.g.*, see Davies and Smith, 2006; Dewit et al., 2014). An individual stylolite by itself may not be able to constrain the diagenetic fluid, but the ensemble of partial fluid baffles in the form of a network of connected stylolites would constitute an efficient diagenetic reaction baffle. In such a scenario, a stylolite-bound volume of rock would be invaded by the diagenetic fluid that induces the replacement reaction. When the fluid overcomes the barrier of an individual stylolite, it will invade the whole the rock volume enclosed by the neighbouring stylolite, as indicated by the sequence of arrows in Fig. 5e. This mechanism of overcoming (or not) consecutive flow baffles explains why replacement is constrained by stylolites and why the front weaves up and down following them. Clear evidence that anastomosing stylolites constrain the reaction front is that such stylolite networks typically show a similar geometry and distribution on both sides and vicinity of the front (Fig. 5b). The strong continuity and lateral extension of networks of suture-and-sharp peak and wave-like stylolites contribute to the marked stratabound character of dolostone geobodies in the eastern side of the Benicàssim half graben, where they extend laterally for at least 7 km away from the feeding faults. A similar case of kilometre-scale continuity of stylolite networks was described by Ben-Itzhak et al. (2012) in Northern Israel.

The clear role of stylolites as dolomitization reaction baffles observed at the outcrop scale becomes more complex at the small scale. Petrographic observations from optical and electronic microscopy show how reaction fronts present a certain width. This width can range from a few tens of microns when the front is just formed by a single stylolite (Fig. 6f) or a few millimetres when it is constrained by two consecutive stylolites (Fig. 6b). However, it is worth noting that stylolites tend to be sharp when they are found either in limestone or dolostone, and only becomes a more diffuse pressure-solution zone when it coincides with the dolomitization front, forming a transition zone in which both calcite and dolomite crystals can be found (Fig. 6b,d).

Similar observations of stylolites bounding dolostones were described by Narkiewicz (1979) in a case study of hydrothermal dolomitization of Upper Devonian carbonates from Southern Poland. This author suggested that stylolites, especially horse tail ones (*i.e.*, wave like), formed a barrier to dolomitization, and that stylolite seams within limestones contain dispersed dolomite rhombohedra. Narkiewicz (1979) also describes how in certain cases the replacement front is gradual over a few centimetres, a feature that we have also observed at the petrographic scale. Miller and Folk (1994) also describe stylolite-controlled burial dolomitization of the Uppermost Triassic Portoro Limestone of Liguria (Italy). These authors interpreted that dolomitization fluids were fed by faults and then were buffered in their proximity. They also observed dolostones systematically bounded by bedding-parallel (wispy) stylolites, which clearly pre-date dolomitization, as in our case study. Miller and Folk (1994) also observed partial dolomitization in between two consecutive stylolites, in a way that one stylolite could not constrain the reaction, but the following stylolite could halt it. This represents another example in which the stylolite network rather than individual stylolites controlled the progress of the replacement reaction. The case studies of Narkiewicz (1979) and Miller and Folk (1994) share very similar characteristics with the Benicàssim outcrops, in terms of the dolomitization mechanism, type of stylolites and arrangement of dolomitization fronts with regard to stylolite networks.

The stylolites analyzed with SEM in this study do not clearly contain a continuous residue of insoluble minerals collected during their growth. They do contain some insoluble material such as Fe oxides and clays, but not in a continuous fashion. Accordingly, it is not the presence of impermeable insoluble minerals that stops the flow of the dolomitization fluid, or a lot least is not the only mechanism. Instead, there should be a different mechanism to explain why the dolomitization reaction can be constrained by stylolites. A potential explanation is that the diagenetic replacement reaction can be constrained when it reaches a surface in which the characteristics of carbonate grains are different due to factors such as local variations in mineral composition depending on the carbonate components (*e.g.*, aragonite, high-Mg calcite or low-Mg calcite), different reactive surface area when there are partially dissolved crystal facets, and the presence of small amounts of insoluble material that can contribute to hinder the replacement reaction. In such a scenario a rough surface resulting from chemical dissolution can potentially act as a baffle and do not allow the reaction front to progress, without needing to contain a continuous volume of insoluble and impermeable residue.

The progressive lateral jump of the dolomitization front up and down between neighbouring stylolites reveals that a single stylolite may not act as an insurmountable barrier to transport, but the statistical combination of multiple barriers in the form of a connected stylolite network can certainly stop a diagenetic reaction. The overall distribution of stylolites can define anisotropy of permeability at the metre to kilometre scale, and thus result in anisotropy of advective transport (Fig. 9). Additionally, the merging or cannibalization of stylolites during the formation of anastomosing networks can certainly enhance the porosity heterogeneity effect and also contribute to explain their role as dolomitization reaction baffles. Peacock et al. (2017) demonstrate by means of numerical models how the progressive addition and interaction of stylolites during the progressive formation of bedding-parallel stylolite networks can result in porosity heterogeneity, in a way that porosity can be lower close to stylolites and higher away from them.

5.1.3. Stylolites as dolomite recrystallization and calcitization reaction baffles

Examples of stylolites separating two dolomite textures have also been found in the Benicàssim area (see Fig. 6). This indicates that pressure-solution structures also acted as baffles for diagenetic fluids producing recrystallization at the small scale (Fig. 9). The fluid responsible for the formation of RD2 had an oxygen isotopic composition slightly depleted with respect to RD1, which was interpreted as a result of a higher temperature (Allan and Wiggins, 1993; Martín-Martín et al., 2015). Compared to dolomitization, the process of dolomite recrystallization is heterogeneous and its lateral and vertical extension is difficult to quantify in the field.

The role of stylolites as calcitization reaction baffles is not as systematic as that of dolomitization fluid flow barriers. This is because the process of synchronous dolomite dissolution and calcite precipitation is widespread and heterogeneous, as described extensively in the literature (*e.g.*, Schoenherr et al., 2018 and references therein). This is also the case of calcitization in the Benicàssim area, where it has been interpreted as related to the infiltration of meteoric water and therefore restricted to the rock volume at or very near the outcrop surface or around faults of various scales (Martín-Martín et al., 2015). Calcitization in the Benicàssim area is associated with dolomite dissolution because this process resulted in a clear texture change with the calcitized dolomite having a cavernous and occasionally a sandy appearance, as previously described by Ayora et al. (1998) or Nader et al. (2008). A close look at fronts at the microscale indicates that calcitization is a progressive process that can present variable intensity (Fig. 7). The presence of stylolites acting as barriers to calcitization fluids has also been reported from studies of mudstones of the Zechstein Ca2 Stassfurt carbonate of the Southern Permian Basin (NW Germany) (Koehn et al., 2016; Schoenherr et al., 2018; Humphrey et al., 2019). Although the extent and distribution of dolomite recrystallization and calcitization products are difficult to quantify, the Benicàssim case study demonstrates that stylolites can constrain these diagenetic reactions acting as barriers for the fluids that caused them. The slow character of the calcitization reaction, as suggested by geochemical and reactive transport models (Escorcia et al., 2013), makes it plausible that stylolites can play a role in controlling the permeability of the calcitizing rock and thus locally control the distribution of the reaction (Fig. 9).

5.1.4. Stylolites and permeability

The observations made in this and other studies showing how stylolites can act as barriers to fluid flow, or at least to diagenetic reactions in certain circumstances, appear to contradict laboratory measurements of bulk permeability of stylolite-bearing rocks. For example, Heap et al. (2014) and Rustichelli et al. (2015) carried out permeability tests of stylolite-bearing samples, and found how stylolites in their samples were not barriers to fluid flow and indeed obtained higher permeability values in the direction parallel to them. Heap et al. (2014) attribute this result to the existence of zones of enhanced porosity in the proximity of stylolites, while Rustichelli et al. (2015) report the existence of open microcracks and vuggy porosity in the surroundings of stylolites, and explain how stylolite porosity could also be related to shearing and exhumation of the rock. Heap et al. (2018) described that permeability measured by water injection tests is lower than that measured with a gas permeameter, due to clay expansion. These results indicate that gas permeability measurements should be taken with care, and that there may be effects of drying and saturating samples, compared to their in-situ behaviour. Additionally, samples utilized for permeability tests have necessarily been exhumed from their "natural" place (*i.e.*, subsurface zones where stylolites form and where most diagenetic reactions take place), either by natural uplift or by recovering them while drilling. Therefore, the samples used for permeability tests have been first unconfined from the subsurface and then confined again in the laboratory, and this effect can strongly affect the transport properties of rocks containing strong discontinuities such as stylolites. Rustichelli et al. (2015) report how normally samples break along stylolite planes during preparation, highlighting the discontinuous character of stylolite-bearing samples. Heap et al. (2018) also report how zones of higher porosity, with elongated pores, surround the stylolites they studied. The findings of these studies show (i) how permeability anisotropy can arise when stylolites are present, (ii) that the permeability of stylolite-bearing rocks is strongly related to the processes that accompany stylolite formation, and (iii) how these processes vary depending on the rock considered (and its diagenetic evolution). Processes associated with stylolite formation include cementation of the dissolved material in their proximity (Toussaint et al., 2018), but also dissolution. Additionally, they can act as mechanical discontinuities for further deformation events. This complex heterogeneity can result in the individual or collective role of stylolites as diagenetic reaction baffles, as the present contribution reports. Stylolites at the Benicàssim outcrop surfaces are clearly visible not because of their colour contrast with their host rocks, as one could expect, but clearly because they weather faster than them. This is because exhumed stylolites are planes of mechanical weakness and allow penetration of rainwater. Accordingly, stylolites can be barriers for fluid flow when intact, but can also become mechanically weak and permeable surfaces as permeability tests predict.

5.2. Stylolites as diagenetic fluid flow conduits

Stylolitic porosity in the study area can be found filled with saddle dolomite and blocky calcite cements (Fig. 8), indicating that some stylolites were open at some stage and acted as conduits for the fluids that precipitated these cements (Fig. 9). It is worth noting that cemented stylolite porosity is only found within dolostones (*i.e.*, not in non-replaced limestones) and in the proximity of faults. Field observations and petrographic characteristics indicate that stylolitic porosity was enhanced by corrosion, and later cemented first by saddle dolomite, which rims the stylolitic pore space, and then by blocky calcite cement. Martín-Martín et al. (2018) analyzed the petrography and geochemistry of these cements and concluded that both resulted from the flow of high-temperature brines. Moreover, hydraulic brecciation took place synchronously with cementation, because clasts of replacive dolostone and saddle dolomite are engulfed by blocky calcite crystals (Fig. 8e). This type of brecciation (Jébrak, 1997) indicates that fluids were overpressured, in a way that the fluid pressure minus the overburden pressure exceeded the tensile strength of the rock. The processes of corrosion, saddle dolomite cementation, hydraulic brecciation and blocky calcite cementation probably took place a long time after dolomitization, either during the early Paleocene ore deposit formation event or during the Alpine compression stage (Eocene to Mid Oligocene; Salas et al., 2001). As explained in section 2, the Alpine orogeny is characterized in the study area by the presence of veins and tectonic stylolites that formed because of horizontal to subhorizontal compression during two different stages. The circulation of hot fluids could have been triggered by a reduction of the overburden pressure, while horizontal to subhorizontal compression could have contributed to the opening of stylolites next to faults in a way that hot and overpressured fluids could flow through them causing corrosion, brecciation and cementation. These stylolites belong to the same network as those bounding dolomitization fronts. Accordingly, stylolites can experience a dual behaviour, first acting as baffles and later as conduits for diagenetic fluids, depending on the burial conditions and the characteristics of the diagenetic fluids.

The role of stylolites as conduits for diagenetic fluids in very different diagenetic settings has been documented in the literature. Stacey et al. (2021) describe low-amplitude stylolites cross-cutting (and thus post-dating) four phases of hydrothermal replacive dolomite in the Middle Cambrian Cathedral Formation of the Western Canadian Sedimentary Basin, and how they are filled with a late dolomite cement. As in the case of the Benicàssim case study, these authors relate this cement to hydrobreccias related to fluid volume expansion. Barnett et al. (2015) observed stylolites acting as conduits for mesogenetic corrosive fluids, as well as for the formation of secondary microporosity offshore Mumbai (India). Chandra et al. (2014) also observed corrosion associated with transport along stylolites in a giant Paleogene reservoir. They describe how stylolites and related tension gashes were opened during tectonic uplift and served as conduits for reactive fluids that corroded the host rock and delivered sulphides, silica and aluminium. As in the Benicàssim case study, they also suggest that such fluids could have been fed by faults. Olierook et al. (2014) described a case study in which stylolites contain halos of quartz cements and are sealed in fault zones. Braithwaite (1989) proposed fluid overpressure as a key mechanism to enhance permeability along stylolites, while Paganoni et al. (2016) reported a case study in an Abu Dhabi hydrocarbon reservoir where hot brines and oil migrated along stylolites during horizontal compression. They found how such brines produced precipitation of carbonates, clays and other minerals around stylolites, changing their role from conduits during brine flow to their present-day behaviour as barriers to vertical fluid flow. The Benicàssim case of stylolites acting as conduits for high-temperature overpressured fluids shares key similarities with all these studies, showing how a change of burial, stress and fluid pressure conditions can produce a switch of their impact on permeability and thus on diagenetic reaction patterns.

The classification of Koehn et al. (2016) suggests that the sealing capacity of stylolites can be linked to their morphology and formation mechanisms. In this scheme, rectangular layer and seismogram pinning type stylolites would be more prone to leaking across their flanks compared to the suture and sharp peak and simple wave-like types. The Benicàssim case study demonstrates that these two latter stylolite types can be prone to opening, allowing fluid flow along them, and this may be due to their lower roughness related to their more uniform growth mechanism and strong lateral continuity compared to the other types.

The present study shows an integrated example of how stylolites and stylolite networks can control the distribution of diagenetic reactions from the millimetre to the metre and even kilometre scales. The successive dual behaviour of stylolites and stylolite networks at Benicàssim as baffles and conduits for fluids depending on the burial and stress conditions, as well as the host rock characteristics, is summarized in Fig. 9. Understanding this dual behaviour has key implications not only to unravel the diagenetic history of an area, but also in terms of societal challenges. Stylolites can play a role in petroleum migration and entrapment systems (Dunnington, 1954; Ehrenberg et al., 2016), ore deposit distribution (Tucker, 2015; Humphrey et al., 2019) and can also potentially control mineral reactions in geothermal reservoirs and storage sites. This contribution reveals how the presence or not of insoluble material is not the only control on the transport behaviour of stylolites, and also how studying networks of stylolites is as important as analysing individual ones. Further systematic work is required to fully understand how these structures determine fluid migration and mineral reactions.

6. Conclusions

The main conclusions of this study are:

1. Individual stylolites can act as baffles/inhibitors for different types of carbonate diagenetic reactions. We report examples of stylolites acting as fronts for dolomitization, dolomite recrystallization and calcitization reactions.

2. Networks of anastomosing bedding-parallel stylolites, rather than individual stylolites, can control the geometries and extent of large-scale (*i.e.*, metre to kilometre scale) diagenetic alterations, such as dolomitization. The replacive dolomitization reaction at Benicàssim was controlled by stylolite networks in a way that the stratabound dolomitization front weaves up and down following consecutive anastomosing stylolites depending on whether the reactive fluid could overcome or not the baffles formed by stylolites. The anastomosing network acted as a collective baffle in mud-dominated limestone facies, preventing them from undergoing replacement by dolomite. In contrast, most dolostone units present parallel and non-anastomosing stylolite networks, which correspond to limestones dominated by grainy facies.

3. Stylolites acting as diagenetic reaction barriers do not present a continuous seam of insoluble material at the microscale, and normally present a width of a few tens to hundreds of microns. Their role as reaction baffles/inhibitors must then be due to their different reactive surface area or slight variations of carbonate mineral composition compared to the reacting limestone components.

4. The same stylolites that were baffles to fluids can subsequently act as fluid conduits when the tectonic stress, burial conditions and/or fluid pressure change. At Benicàssim stylolites within dolostones close to faults are found corroded and filled with saddle dolomite riming the stylolite pore and high-temperature blocky calcite filling most of the remaining porosity. The fluids responsible for these reactions are interpreted to have been released at high pressure, also causing hydraulic brecciation. Stylolites are also found filled with iron oxides resulting from the calcitization process associated with meteoric fluids.

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