Controls on dolomitization by means of reactive transport models applied to the Benicàssim case study (Maestrat basin, E Spain)

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ABSTRACT: Partially dolomitized carbonate rocks of the Middle East and North America host large hydrocarbon reserves. The origin of some of the dolomites has been attributed to a hydrothermal mechanism. The Benicàssim area (Maestrat basin, E Spain) constitutes an excellent field analogue for fault-controlled stratabound hydrothermal dolomitization: dolostone geobodies are well exposed and extend over several kilometers away from seismic-scale faults. This work investigates the main controls on the formation of stratabound vs. massive dolomitization in carbonate sequences by means of 2D reactive transport models applied to the Benicàssim case study. Simulation results suggest that the dolomitization capacity of fluids is maximum at temperatures around 100ºC and minimum at 25ºC. It takes on the order of hundreds of thousands to millions of years to completely dolomitize kilometer-long limestone sections with solutions flowing laterally through strata at velocities of meters per year. Permeability differences of two orders of magnitude between layers are required to form stratabound dolomitization. The kilometer-long stratabound dolostone geobodies of Benicàssim must have formed under a regime of lateral flux higher than meters per year during about a million years. As long-term dolomitization tends to produce massive dolostone bodies not seen at Benicàssim, the dolomitizing process there must have been limited by the availability of fluid volume or the flow driving mechanism. Reactive transport simulations have proven a useful tool to quantify aspects of the Benicàssim genetic model of hydrothermal dolomitization.

KEYWORDS: *Hydrothermal dolomitization, dolomite distribution, reactive transport models, Maestrat basin*

DOLOMITE IN HYDROCARBON RESERVOIRS

Dolomitization is a significant process for the hydrocarbon industry, as it affects some 50% of the Earth's carbonate rocks and can significantly alter their porosity and permeability (e.g., Zenger *et al.* 1980; Land 1985; Budd 1997; Hardie 1987; Warren 2000; Machel 2004). Large reserves exist in partially dolomitized carbonate rocks in producing areas like the Middle East or North America. However, there still is insufficient understanding on controls of porosity and permeability distribution in dolomitized reservoirs as well as on the geometry and connectivity of dolomitized geobodies. Dolostone can be a reservoir rock but can also act as a barrier to flow depending on the original properties of the host limestone, the reservoir geometry and the specific type of dolomitization (e.g. Ehrenberg 2004).

The vast majority of dolomite ($CaMg[CO_3]_2$) is of secondary origin and has formed by replacement of calcite ($CaCO_3$) under burial conditions in different tectonic and geochemical settings (Machel 2004; Warren 2000). Dolomite forms because of the interaction of an original limestone with fluids that trigger the dolomitizing reaction (for reviews see Warren 2000; Machel & Lonnee 2002; Machel 2004; Whitaker *et al.* 2004; Roure *et al.* 2005; Davies & Smith 2006). The occurrence and distribution of burial dolostones have major impacts on reservoir producibility and are mainly controlled by (a) diagenetic/hydrothermal processes that cause dissolution/precipitation reactions and enhance/reduce porosity, and (b) fault network properties and limestone permeability that determine dolomitizing fluid flow pathways.

Hydrothermal dolomite (HTD) is a type of burial dolomite that forms when the temperature of the dolomitizing fluid is higher than that of the host rock (by definition 5º C or more, according to White 1957). In most cases the formation of HTD is structurally controlled (e.g. Davies & Smith 2006). Such dolostone typically forms at shallow depths by saline and hot fluids and it is often found spatially associated with sedimentary-exhalative and Mississippi Valley–type (MVT) lead-zinc ore bodies. These hydrothermal anomalies are commonly encountered in extensional or strike-slip fault systems (e.g. Davies & Smith 2006; Wilson *et al.* 2007). Hydrothermal dolomitization can result in a variety of alteration geometries, from patches around feeding faults to fully stratabound geobodies extending away from faults (e.g., Davies & Smith 2006).

There are still many open questions regarding to the controls on the transition from massive to stratabound geometries of fault-associated dolomites. Hydrothermal dolomite may form as a direct replacement of limestone, as a secondary phase replacing pre-existing early diagenetic dolomite, or as cement filling primary and/or secondary porosity (e.g. Warren 2000; Davies & Smith, 2006). In either case, HTD produces significant changes on the rock porosity and permeability.

Most of the published dolomitization case studies are based on the characterization of dolostones with stratigraphic, petrographic and geochemical approaches (for reviews on the topic see Warren 2000; Machel 2004). Dolomitization models must also be hydrologic models (Machel 2004; Whitaker *et al.* 2004), as they need to account for a realistic fluid-flow mechanism for the transport of solutes to and from the reaction zone for the specific case study. Nowadays, the existing numerical techniques that couple fluid and heat flow with solute transport and chemical reactions (reactive transport simulations) constitute valuable tools to quantify conceptual models, evaluate possible scenarios and compare the influence of different factors in geological processes that are not easily reproduced in laboratories. Several authors have analyzed dolomitization in early-diagenetic low-temperature conditions using reactive transport numerical simulations (e.g. Jones *et al.* 2002; 2003; 2009; Jones & Xiao 2005, Xiao & Jones 2006; 2007; Whitaker & Xiao 2010). However, fewer studies have focused on the controls of hydrothermal dolomitization by means of reactive transport simulations (Ayora *et al.* 1998; Corbella *et al.* 2006; Sttaford *et al.* 2009; Jones *et al.* 2011).

The Benicàssim area (Maestrat basin, E Spain) constitutes an excellent field example of fault-controlled stratabound dolomitization (Martín-Martín *et al.* 2013). In this area, shallow-marine limestones of Early Cretaceous age have been partially replaced by hydrothermal dolostones. Dolostone layers extend over several kilometers away from seismic-scale faults, which acted as feeding points of hot dolomitizing fluids. The present work contributes to the understanding of the genesis of hydrothermal dolostones by means of 2D reactive transport models applied to the Benicàssim case study. Specifically, the goal of the paper is to constrain some of the parameters of the dolomitization process of carbonate rocks by testing the sensitivity of models to porosity distribution, fluid composition and fluid velocity.

THE BENICÀSSIM CASE STUDY

The Maestrat Basin is a Late Jurassic-Early Cretaceous intraplate rift basin located in the East of the Iberian Peninsula (Salas & Casas, 1993; Salas *et al.* 2001) (Fig. 1). Extensional faults are dominantly NW-trending and produce offsets of hundreds to few thousands of meters, creating tilted blocks that accommodate up to 4500 m-thick Lower Cretaceous syn-rift deposits (Salas *et al.* 2001). A second set of NE-trending basement faults occur in the Benicàssim area (Penyagolosa sub-basin, Fig. 1). There, the NW-trending (Campello) and the NE-trending (Benicàssim) fault systems intersect each other forming a semi-graben structure that contains a 2100-m-thick Lower Cretaceous succession (Martín-Martín *et al.* 2013). This semi-graben, as the rest of the Maestrat Basin, was inverted during the Paleogene (Alpine) compression, forming the eastern margin of the Iberian Chain fold-and-thrust belt (Fig. 1). The Alpine compressional structure was subsequently overprinted by the Neogene extension, resulting in the present-day western Mediterranean basin (València Trough; Roca & Guimerà 1992).

The relevance of the Lower Cretaceous succession of the Benicàssim area is twofold (Martín-Martín *et al.* 2013): (a) it registers one of the thickest Aptian-to-Albian carbonate successions reported from the northern Tethyan margin; and (b) the limestones of the Benassal Formation are partially replaced by dolostones, providing a new case study of stratabound fault-controlled hydrothermal dolomitization.

The Benassal Fm is a 1500-m-thick succession formed almost entirely by shallow marine carbonates (Martín-Martín *et al.* 2010; Tomás *et al.* 2008: Salas *et al.* 2001; Fig. 2). Based on orbitolinids and ammonites specimens, a Late Aptian to Early Albian age was inferred (Martín-Martín *et al.* 2013; Moreno-Bedmar *et al.* 2009). The carbonate succession represents the evolution of a ramp-type system dominated by orbitolinid foraminifera, corals and rudist bivalves (Martín-Martín *et al.* 2010; Tomás *et al.* 2008). The succession is stacked into three transgressive-regressive (T-R) sequences (Martín-Martín *et al.* 2013; Fig. 2). Transgressive lithofacies are typically constituted by basinal marls, spicule mudstones to wackestones, and orbitolinid wackestones. Regressive lithofacies varies from coral limestones, bioclastic and peloidal packestones, ooidal grainstones and rudist floatstones to rudstones. This lithofacies commonly form the top of the T-R sequences.

Dolostone distribution

The Benassal Fm was partially dolomitized in close association with seismic-scale basement faults (fault-controlled dolostones; Martín-Martín *et al.* 2013). Dolostones, which appear mostly in hanging wall fault blocks, form seismic-scale stratabound geobodies up to 150-m-thick (Fig. 3). They extend up to 7 km away from the fault zones and crop out for several thousands of square meters over the study area. Field and petrological data indicate that grain-dominated facies were preferentially replaced (Martín-Martín *et al.* 2013). According to these authors, non-replaced, tight micrite-dominated facies and/or early-cemented grain-dominated facies appear intercalated between the dolostone geobodies. These low-porosity facies probably enhanced lateral flow causing the stratabound geometry of the dolostones away from the feeding points (i.e. seismic-scale faults) (Martín-Martín *et al.* 2013). This suggests that, together with the primary control of the fault system as conduits for dolomitization and mineralization, the depositional facies and the early diagenetic alterations partially controlled the replacement of the host limestones out of fault zones.

Quantitative subsidence analysis based on field observations and regional geology indicate that the dolomitization of the Benassal Fm carbonates occurred during the Late Cretaceous post-rift stage of the Maestrat Basin at burial depths <1000 m (Martín-Martín *et al.* 2010).

Dolostone petrography and geochemistry

The Benicàssim dolostone exhibits the typical burial paragenesis including host limestone replacement, dolomite cementation and MVT sulfide mineralization (Martín-Martín *et al.* 2010; 2013). The replacement stage is pre-dated by calcite and dolomite cementation, which controls the subsequent dolomitzacion of the host rock. Dolomite cement is abundant in packestone and grainstone facies, and is interpreted as the initial stage of replacement (Martín-Martín *et al.* 2010; Fig. 4). According to this study, the bulk of the dolomite is a replacive dolomite with a characteristic fabric-retentive texture and very low porosity (Fig. 3). Neomorphic recrystallization of the replacive dolomite, which occurred in relation to high-permeability rocks, was associated with an increase in crystal-size and intercrystalline porosity. The reported replacement sequence is associated with a decrease in the oxygen isotopic composition of dolomite, which has been interpreted to result from progressively higher temperatures (Martín-Martín *et al.* 2010; Gomez-Rivas *et al.* 2010a; Fig. 4). Following Gregg & Sibley (1984), nonplanar textures in replacive dolomites indicate replacement temperatures exceeding 60ºC (Martín-Martín *et al.* 2010).

After the replacement stage, porosity considerably increased in dolostones by dissolution associated with acidic fluids derived from the MVT mineralization (Martín-Martín *et al.* 2010). Saddle dolomite and ore-stage calcite cement filled most of the newly created porosity. Taking into account the presence of saddle dolomite and the burial depth reported above, the origin of the Benicàssim dolostones and sulfide ore deposits have been interpreted to be hydrothermal (Gomez-Rivas *et al.* 2010a; Martín-Martín *et al.* 2010; 2013). This also agrees with microthermometry data from neighbor ore-stage calcite (Grandia, 2001; Grandia *et al.* 2003; Gomez-Rivas *et al.* 2010a).

Following the MVT mineralization, precipitation of calcite cements resulted from the circulation of meteoric-derived fluids during the Alpine uplift and the Neogene extension (Martín-Martín *et al.* 2010). Dolomite porosity measured in outcrop samples range from 1 to 7.4 %, whereas permeability values range from 0.01 to 0.18 mD (Martín-Martín *et al.* 2010). According to this study, the relatively poor reservoir quality of the Benassal dolostones is mainly due to burial carbonate cementation (calcite and dolomite) after the replacement stage, and especially to calcite cementation associated with uplift and subaerial exposure.

CONCEPTUAL MODEL

The geological and geochemical data summarized above indicate that the Benicàssim dolostones generated by the circulation of hydrothermal fluids. Mass-balance calculations of the required versus available Mg and fluid for the replacement reaction constrained the dolomitization conditions at Benicàssim (Gomez-Rivas *et al.* 2010a; 2010b), and helped in delineating the conceptual model.

Mg sources

The amount of Mg required to dolomitize the Aptian limestones at Benicàssim is on the order of ~10^{13} moles of Mg, taking into account the volumes of rock that have been eroded (Gomez-Rivas *et al.* 2010a). Such a quantity could only be delivered by seawater, modified or pristine, or/and basement brines (Gomez-Rivas *et al.* 2010a). Local sources that can be ruled out include: brines originated from underlying Permian-Triassic evaporites, as they had been mostly eroded during the Late Cretaceous times (Roca *et al.* 1994); Triassic and Jurassic dolostones, as they appear only slightly dedolomitized, and Permian-Triassic red beds, which contain small amounts of Mg-rich clays (Martín-Martín *et al.* 2005).

Fluid flow

Fluid and heat flow simulations of the dolomitizing fluids applied to the Benicàssim case study were presented by Gomez-Rivas *et al.* (2010b) considering two end-member scenarios: (a) dolomitization during the a syn-rift Early Cretaceous cycle, where overpressured fluids sealed below impermeable layers would have been rapidly released along faults, opened by episodic movements, similar to the seismic pumping mechanism (Sibson *et al.* 1975); (b) dolomitization related to fluid circulation during the tectonically quiescent Late Cretaceous post-rift setting, driven by differences in pressure (head differences) or temperature (anomalous gradient) within the basin, which would have been maintained over long periods of time. Syn-rift advection, case (a), could have provided enough volume of dolomitizing fluids to the reacting Aptian limestones with repeated pulses of fluid. However, the calculations indicated that these fluids would have cooled down rapidly when flowing upwards along the faults, so that warm temperatures at the carbonate beds could not have been kept for more than a hundred years (Gomez-Rivas *et al.* 2010b). The results of long-lived fluid convection simulations, case (b), indicate that lateral flow rates on the order of meters/year could have been maintained as long as the pressure or temperature gradient was strong enough. Moreover, the shallow limestones could have been heated up to 150-200 ºC due to the continuous heat flow that occurs in convective systems (Gomez-Rivas *et al.* 2010b).

Conceptual genetic model

According to 1) geological and geochemical data available (Grandia 2001; Nadal 2001; Martín-Martín *et al.* 2010; 2013; Gomez-Rivas *et al.* 2010a), 2) reactive transport modeling (Stafford *et al.* 2009), 3) Mg mass-balance calculations (Gomez-Rivas *et al.* 2010a), and 4) fluid and heat flow numerical simulations (Gomez-Rivas *et al.* 2010b), the most plausible model for the genesis of the Benicàssim dolomitization consists of an open system during the Late Cretaceous post-rift stage in which a warm brine played a major role. This brine could have originated as seawater that infiltrated downwards (Stafford *et al.* 2009), interacted with Permian-Triassic and/or Paleozoic basement rocks, where it could have mixed with other fluids, and flowed upwards along seismic-scale faults. From the faults as feeding points, it spread and flowed through high-permeability beds (Fig. 5). The fluid circulation of this warm brine during Late

Cretaceous had probably been favored by high temperature gradients in the Iberian Chain at the time. They could have been caused by either the thinning of the Earth's crust below the Iberian Peninsula during the Late Cretaceous, as a consequence of the strong Early Cretaceous rifting period, or by an abnormal heat flow as proposed by Salas *et al.* (2005). These authors summarized the existence of the abnormal heat flow during Late Cretaceous, which included measured temperatures in nearby veins (Tritlla & Cardellach 2003), low-grade metamorphism of Permian-Triassic rocks in the vicinity of Benicàssim (Martín-Martín *et al.* 2005; Martín-Martín *et al.* 2009) and Cretaceous (Albian to Santonian) bathyal submarine volcanism North of the Iberian Chain (Castañares *et al.* 2001).

NUMERICAL APPROACH

Reactive transport simulations solve the coupled equations of solute transport, mass of fluid flow, and heat flow considering the solute reactivity. As for dolomitization scenarios, reactive transport modeling offers the possibility of contrasting the dolomitizing capacity of different geological fluids, temperatures of reaction, fluid fluxes or host rock permeability, among others.

Reactive transport simulator

The code RETRASO (REactive TRAnsport of SOlutes; Saaltink *et al.* 1998) has been used to simulate dolomitization of limestones under different settings. It is a program that couples multicomponent solute transport with chemical reactions of these components and host rocks at temperatures ranging between 0 and 300º C. RETRASO incorporates aqueous complexation and adsorption as well as precipitation/dissolution of minerals, which can either be applied with thermodynamic laws considering local equilibrium or kinetic rates. This numerical code utilizes Garlekin finite element discretization in space and a fully implicit finite difference scheme in time. It uses the global implicit method to solve the initial set of non-linear equations, solving simultaneously transport and chemical equations with a Newton-Raphson procedure (Saaltink *et al.* 1998).

Only the reactions involved in the dolomitization process were considered: aqueous complexation reactions among dissolved species and dissolution/precipitation of minerals. Complexation reactions are usually very fast, so it is assumed that they occur under equilibrium conditions and are thus calculated according to the EQ3NR thermodynamic database (Wolery 1992). The activity coefficients of aqueous species were computed with the B-dot form of the extended Debye-Hückel equation (Helgeson & Kirkham 1974). Precipitation and dissolution reactions were computed with published kinetic rate laws instead of thermodynamics (equilibrium) data in case that under different flow conditions the mineral reactions were not sufficiently fast.

Mesh and boundary conditions

Two different systems were used to simulate the dolomitization features observed in Benicàssim at two different outcrop scales: a) 100 m long and 20 m high section, with either the same or different flux velocities along strata defined by contrasting permeabilities; b) 1400 m long and 200 m high, section with predominantly horizontal fluid flow through high-permeability layers and vertical flow along faults. Both models consisted on rectangular domains (2D sections; Fig. 6). Calculations of the first type were discretized into meshes with 861 nodes or grid points and 1600 triangular elements. Type (b) models were run with a mesh of 1197 nodes and 2240 triangular elements.

Lateral Darcian fluid velocities on the order of meters/year were used in all simulations. Fluid flow along faults was also considered of the same order of magnitude. Brine entered the system through the left boundary of the model (Fig. 6), with some simulations also having an inflow along faults and from the top boundary. The fluids exited through the right hand corner. No-flow conditions were imposed on the rest of the boundaries. Simulations with an open fault on the top were also tried and they did not modify the overall pattern of flow and chemical reactions.

Parameters and fluid compositions

The parameters that describe the initial physical system of Benicàssim are given in Table 1. Based on petrographic observations, the porosity of the host limestones were assumed as 0.1 and 0.3 for low and high porosity and permeability layers, respectively. The faults were given an initial porosity of 0.45. Hydraulic conductivities varied between 6 m/a and 150 m/a in the horizontal direction, and between 4 m/a and 80 m/a in the vertical direction according to the different types of limestones, in order to account for the least favorable conditions to flow, that is from beds with matrix permeability only, to those more favorable, including fracture permeability. The faults were assumed to have a higher hydraulic conductivity in the vertical direction (K_v=500 m/a) than in the horizontal direction (K_h=100 m/a). RETRASO updates porosity at each time-step but not permeability. Therefore, the results should be considered as minima. The pressure distribution in the sections was calculated from the fluid fluxes fixed with the boundary conditions.

All simulations were performed assuming a constant temperature system: fluid and rock had reached or were close to thermal equilibrium, so that temperature differences within the section were considered negligible. Four fluids of different compositions were tested as dolomitizing fluids in the Benicàssim transport simulations (Table 2): (a) present-day seawater, (b) concentrated seawater, (c) brine A and (d) brine B. Seawater was used with the composition described by Stumm & Morgan (1981), whereas an evaporated seawater composition (b) was calculated by concentrating 5 times the composition of present-day seawater. Two more brines were selected from the literature: a brine A with 25 %Wt eq NaCl salinity and low Mg concentration (Shanks & Bischoff 1997) and a more saline brine B, with higher Mg and Ca content (Kharaka & Thordsen 1992). Both brines were obtained from areas with similar lithological composition to that of Benicàssim. In order to avoid the early stage effects of reactivity with the host limestone, all fluids were equilibrated with calcite prior to the starting of simulations. This simplification is reasonable given the fast dissolution kinetics of calcite, thus expecting that fluids circulating through limestones would have equilibrated with them. The initial total carbonate concentration of each fluid was restricted according to the equilibrium with calcite.

The list of solute species for reactive transport simulations included Cl^-, Na^+, Ca^{2+}, Mg^{2+}, CO_2(aq), H^+, OH^-, HCO_3^-, NaCl(aq), $CaCl^+$, $CaCl_2$(aq), $NaHCO_3$(aq), $CaHCO_3^+$, $MgHCO_3^+$, $MgCl^+$, CO_3^{-2}, $NaCO_3^-$, $CaCO_3$(aq), $CaOH^+$, $MgCO_3$(aq), $Mg_4(OH)_4^{+4}$, NaOH(aq), HCl(aq), of which the first 6 were component species. For simplicity, the only minerals allowed to precipitate or dissolve were calcite and dolomite.

REACTIVE TRANSPORT MODELS

The sensitivity of the conceptual model to different parameters was tested with two types of simulations. First, simple reactive transport simulations were performed in small sections in order to analyze the dolomitization capacity of the selected fluids as well as the fluid temperature influence on the dolomitization process. These models are in fact 1D simulations of one fluid reacting with a limestone. The permeability difference and the formation of stratabound and 'Christmas-tree' dolomitization (e.g. Davies & Smith 2006) were tested in larger 2D sections containing a central fault in order to simulate the effect of flow along faults and through permeable beds.

Dolomitizing capacity of fluids

The dolomitizing capacity or reactivity of four fluids at 100ºC (Table 2) was tested with 1D models. They consisted on 100 m long sections of limestone with an initial porosity of 30% and initial composition of 99% calcite and 1% dolomite. These initial configurations were flooded from the left hand side model boundary with the different dolomitizing fluids with a flux of 6 m/a. After 75,000 years of simulation time two of the solutions, concentrated seawater and brine B, had completely dolomitized the limestone section (Fig. 7). As expected, these are the dolomitizing fluids with the highest Mg concentration. Present-day seawater and brine A, the solutions with the lowest Mg content, only dolomitized the first dozens of meters after 75,000 years of simulation time (Fig. 7).

Temperature influence

The influence of temperature on dolomitization is shown in Fig.8, where the same sections were invaded by concentrated seawater at different temperatures. This saline solution dolomitized the original limestone at all simulated temperatures, but the more extensive dolomititzation was caused by the fluid at 100ºC. The slowest dolomitization occurred at 25ºC, whereas the same solution at 50ºC and at 150ºC produced intermediate results (Fig. 8). Similar temperature effects were also obtained with the rest of the considered fluids. Therefore, it appears that, given the same geological and geochemical conditions, warm fluids at ~100ºC can replace more effectively a limestone with dolomite than colder or hotter fluids. These results suggest that in active tectonic settings, where fluid fluxes might be short-lived, intense and/or extensive dolomitization would more easily occur by warm fluids.

Duration of the dolomitization process and mixing effects

The time it takes to dolomitize 1 km-long limestone section depends on the flow rate of the solution, the concentration of Mg in the solution and the reaction temperature. Using the most reactive fluid (five times concentrated seawater at 100ºC, similar to the fluid found in inclusions by Grandia et al. 2003) as input fluid the dolomitization front took about 2.5 Ma to reach the right boundary of the model, 1 km a part, with a flow velocity of 1 m/a. With a velocity of several meters/year the same solution employed less than a million years to completely dolomitize the section, whereas with a Darcy velocity of 0.1 m/a the fluid needed 9 Ma to cover the 1 km long section. Therefore, if a very reactive fluid is considered, and using the RTM approach and aforementioned assumptions, the dolomitization of the Benicàssim area must have occurred during a time span of some hundreds of thousands to a few million years. With less reactive fluids the dolomitization period would have been on the order of several million years.

The results of simulations in which two input fluids were inserted in the section showed the effects of fluid mixing. The slight precipitation of calcite and porosity decrease in the zone next to the fault, located in the middle of the section, reflected the pH front (Fig. 9). The supersaturation of the mixture fluid with respect to calcite, eventhough the fluids were independently in equilibrium with respect to this mineral, was caused by the mixing of fluids of different acidity (Corbella & Ayora, 2003). Therefore, with the fluids used in these simulations, no calcite dissolution was obtained as a consequence of fluid mixing. Similarly, no mixing effects were observed enhancing or preventing dolomite precipitation, as the only dolomitization observed was that related to each individual fluid (Fig. 9). These results contrast those of MVT genetic models (Corbella *et al.* 2006) where fluid mixing is necessary in order to enhance carbonate dissolution or hydrothermal karsting, which occurs simultaneously with sulfide precipitation.

Stratabound dolomitization and the dolomitization front

The stratabound dolomitization as observed in Benicàssim was originated by the preferential fluid flow through the most permeable layers. Together with the primarily control of the fracture network, the depositional facies and the carbonate cementation during early diagenesis in areas out of the fault zones controlled the carbonate permeability and therefore, the subsequent dolomitization (Martín-Martín *et al.* 2013). The simulations that reproduced the layered dolomitization where those with at least two orders of magnitude difference on fluid fluxes (Fig. 10). Therefore, the permeability contrast that leads to such flow differences must also have been, at least, of two orders of magnitude. The length of the differential dolomitization among the two beds ranged between 50 and 100 m in length with the fluid rates and total time used in these simulations.

In all simulations, dolomitization led to porosity increase (Figs. 9, 10 and 11). As there were no mixing effects on dolomitization, the porosity increase was originated by the assumption of RETRASO with the EQ3NR database that reactions occur in a mole-by-mole basis. Therefore, the replacement of calcite by dolomite prompts a molar volume gain of 13%. In the Benicàssim dolostones, a significant increase in porosity with respect to the host rock is observed in recrystallized replacive dolomite (Fig. 3C), which is the one that was simulated here. Contrarily, the initial stage of dolomitization resulted in replacive dolomites that preserved most of the original rock porosity (mimetic texture of Martín-Martín *et al.* 2010; Fig. 3B). Consequently, this first dolomitization must have been replacing an equal volume of calcite and was not the one simulated here, but it must have facilitated the second type with the first crystals acting as dolomite seeds, assisting the nucleation of the second ones so that the kinetic barrier was easier to surmount. These observations suggest that a dolomitization process similar to that modeled here will enhance porosity only when the dolomitizing flow system is active long enough to surpass the volume-by-volume replacement and arrives to the mole-by-mole dolomitization.

The contrasting dolomitizing rate of the two layers is due to a different propagation rate of the dolomitizing front. The differential dolomitization is maintained during a few hundreds of thousands of years with the flow rates used in the above simulation (Fig. 9). However, the front advances in both layers, so that in a long-lived system (i.e., with unlimited dolomitizing fluid volumes and fluid flow mechanism), both layers would end up, at some stage, completely dolomitized. In such cases, widespread saddle dolomite, zebra textures and hydraulic breccias would be expected, as reported from N Spain (López-Horgue *et al.* 2010; Shah *et al.* 2010; Nader *et al.* 2012) or Canada (see Davis & Smith; and references therein). The Benicàssim outcrops, although containing some saddle dolomite, do not present the other textures. Nevertheless, hydraulic breccias have been described in more central parts of the Maestrat basin

(Grandia *et al.* 2001). It is therefore inferred that the fluid flow mechanism or the fluid volume were limited in the Benicàssim area but not in other areas of the Maestrat basin. This may be due to the location of Benicàssim next to the southern margin of the basin, where upwards flow of warm brines was more restricted.

The replacement of calcite by dolomite was not a synchronous process. The kinetic rate law of calcite dissolution is much faster than that of dolomite precipitation, so there was a time gap between the two chemical reactions. This fact is observed in the simulations as a relatively wide front of calcite dissolution and a sharper dolomitization front (Fig. 11). The dolomitization front appeared to form short fingers in response to the strata permeability differential. Moreover, in the first few hundreds of thousands of years of simulation time, calcite dissolved preferentially in the high permeability strata whereas dolomite precipitated predominantly in the low permeability strata where the dolomitizing fluid flux was lower (Fig. 11). This result agrees with the observation of dolomite in reservoirs mostly occurring in tight rocks (Gluyas and Swarbrick 2004). Another implication of the result is that calcite dissolution does not seem to be the limiting factor for dolomitization in the case tested here of fluid flux on the order of meters/year. Nevertheless, with the fluid velocities used, most simulations presented massive dolomites that completely replaced limestones at both low- and high-permeability beds behind the dolomitization front after 60,000 to 100,000 years.

Stratabound dolomitization was also observed in an alternative simulation scenario with seawater percolation from above, similar to those of Stafford *et al.* (2009). In this case, dolomitization was pervasive in the upper beds, independently of their permeability, as well as in the high-permeability strata of the rest of the section (Fig. 11). However, the kilometric stratabound dolomitization was only observable in the intermediate stages of dolomitization, that is, prior to 0,5 million years. Consequently, as long as the flow system is active, with both driving force and volume of fluid available, dolomitization proceeds to completion and obliterates the initial limestone textures and enhances porosity (Fig. 11). Although this setting was capable of generating kilometer-long preferentially dolomitized beds, or kilometer-long stratiform dolostone geobodies, it is difficult to reconcile with the observations of a hydrothermal dolomitizing fluid at Benicàssim.

According to the presented simulations, the kilometer-scale preferential dolomitization observed at Benicàssim must have been formed in a geologic scenario where beds of contrasting permeabilities allowed strong lateral fluxes, higher than those simulated here. Moreover, the preserved stratiform dolostones of Benicàssim must have only undergone through the initial and intermediate stages of a complete dolomitization process, as some intercalated beds of undolomitized limestone have been preserved between the dolomitized bodies away from fault zones (Martín-Martín *et al.* 2012).

The fluid flow patterns through strata and along faults simulated with reactive transport models are supposed to be a small part of a larger-scale convective system in the Maestrat basin. Such convection pattern may have been facilitated by high thermal gradients and active seismic-scale faults that conform the post-rift scenario in Late Cretaceous times in the Eastern Iberian Peninsula.

CONCLUSIONS

Reactive transport simulations of limestone replacement by dolomite applied to the Benicàssim case study (Maestrat Basin, E Spain), indicate that the dolomitization capacity of fluids is maximum at temperatures around 100ºC and minimum at 25ºC. As expected, the fluids with higher Mg concentration (concentrated seawater and high-Mg brine) had a higher dolomitization capacity than the fluids with lower Mg-concentration (seawater and low-Mg brine).

It takes on the order hundreds of thousands to millions of years to completely dolomitize kilometer-long limestone sections, such as observed in Benicàssim, with solutions flowing laterally through strata at velocities of meters per year, which are normal velocities in basin aquifers. Fluid velocity differences of two orders of magnitude are required to form stratabound dolomitization. Nevertheless, the differential dolomitization along strata can be obliterated by a long-term (on the order of 100,000 years) dolomitizing fluid flow giving way to massive dolomites.

Although calcite dissolution starts in high-permeability beds, dolomitization commences in the low-permeability strata. This difference is maintained during the first few tens of thousands of years of simulation time. Effects of fluid mixing from the presented reactive transport simulations are only observed as slight calcite precipitation and porosity occlusion along the pH front formed at the mixing interface. In the Benicàssim scenario, fluid mixing appeared not to help dolomitization.

The kilometer-long stratiform dolostone geobodies at Benicàssim must have formed under a regime of lateral flux higher than meters per year. The dolomitizing process must have lasted a maximum of a few million years; otherwise, the dolomitization would have also affected the low-permeability strata and would have thus been more massive. The fluid flow pattern through strata and along faults in the Benicàssim area could be part of a larger-scale convective system that may have been active in the Maestrat basin during a Late Cretaceous post-rift episode.

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