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## Reactivity of Dolomitizing Fluids and Evaluation of Mg Sources in the Benicassim Area (Maestrat Basin, E Spain)

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### SUMMARY

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Hydrothermal dolomitization is one of the most important processes in enhancing or degrading carbonate porosity and permeability. This type of dolomite forms due to the circulation and/or mixing of different types of solutions, mainly seawater-derived or deep brines. The Lower Cretaceous Benicassim dolomitized ramp is an excellent example to study and evaluate the impact of hydrothermal dolomitization on reservoir quality distribution. In this contribution, the possible magnesium sources for the Benicassim case study are evaluated, as well as the reactivity of different dolomitizing fluids at variable temperatures. The results show that dolomitization at Benicassim occurred due to the circulation of a high temperature ( $> 80^{\circ}\text{C}$ ) fluid that had its origin from evolved seawater that interacted with K-rich rocks, probably from the Paleozoic basement. Reactivity evaluation of four possible dolomitizing fluids, by means of geochemical modelling, reveals that evolved seawater can be considerably more reactive than high-salinity brines. Fluid mixing between seawater and saline brines at  $100^{\circ}\text{C}$  does not seem to affect the volume of fluid required to dolomitize the whole rock, but it considerably alters the saturation index of calcite. The variation of saturation index is a strongly non-linear process when two fluids are mixed.

## Introduction

Dolomitization is one of the most important processes capable of enhancing porosity and permeability in carbonate rocks, and thus it has a direct impact on the distribution of reservoir and non-reservoir rocks and on reservoir connectivity. Understanding the origin and products of dolomitization is crucial for improving hydrocarbon recovery.

Hydrothermal or high-temperature dolomites (HTD) are formed in different tectonic settings due to the circulation of hot fluids with sufficient solutes to cause the dolomitizing reaction. To this date, there is still a great controversy over the origin, chemistry and source of such fluids, as well as forces driving their flow. This study evaluates the magnesium sources of a dolomitized Cretaceous ramp in the Benicassim area (Maestrat Basin, E Spain), as well as the reactivity of potential dolomitizing fluids at different temperatures. The effects of chemical mixing on the dolomitizing capacity of the fluids are also analyzed.

## Geologic and geochemical constraints

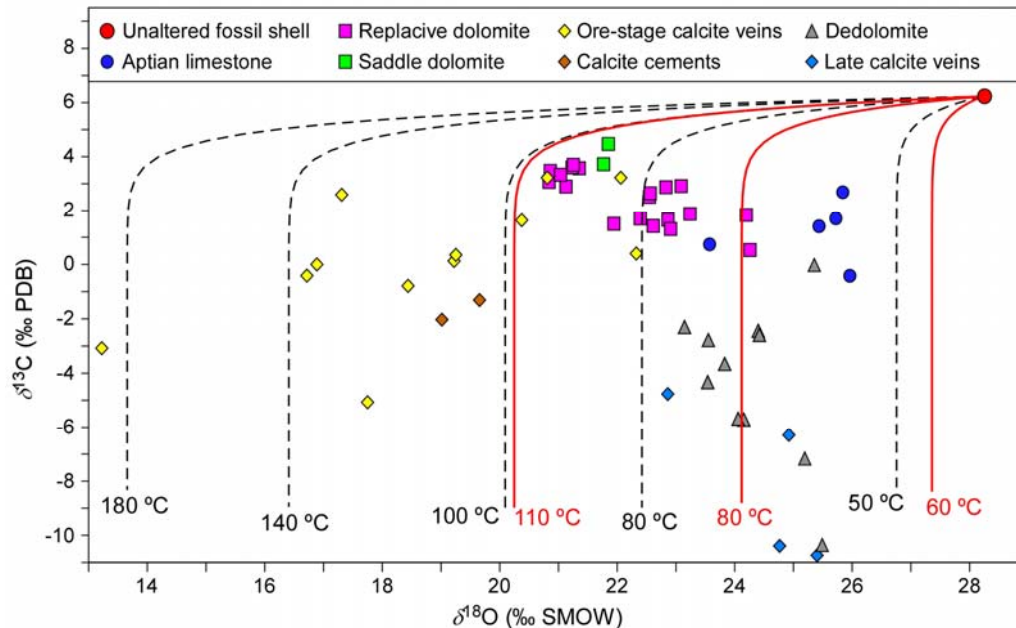
The Benicassim ramp is part of the Maestrat Basin, which was formed during the Late Jurassic - Early Cretaceous rifting cycle (Salas *et al.*, 2001). The basin was subsequently uplifted during the Alpine orogeny into the Iberian Chain. In the Benicassim area, thick sequences (~ 1.500 – 2.000 m) of shallow marine carbonates, mainly Aptian in age, overlie ~ 600 m of Permo-Triassic rocks (mainly siliciclastic) and basement shales and slates of Carboniferous age. These rocks are affected by several seismic-scale normal faults as well as dense sub-seismic scale extensional fracture networks. Some of the syn-rift Aptian carbonate layers appear partially dolomitized over several kilometres, with a wavy stratiform geometry. Field, geochemical and petrographic data (Martín-Martín *et al.*, 2009) indicate that the dolomitizing fluids circulated upwards along large-scale normal faults and laterally through the most permeable layers in the upper part of the Aptian sequence. Mississippi Valley type (MVT) ore deposits of Early Paleocene age (Grandia, 2002) outcrop in the area close to fault zones and are hosted by hydrothermal dolomites.

No evidence for low-temperature, shallow or early diagenetic dolomitization has been found in the Benicassim area. On the contrary, microthermometric and stable isotope analysis of carbonates reveal that high-temperature fluids circulated through the carbonates of the Maestrat basin. Fluid inclusions in calcite veins and cements reveal homogenization temperatures ( $T_h$ ) up to 180 °C, while melting ice temperatures suggest salinities up to 23 wt % NaCl eq. These data are consistent with previous studies elsewhere in the Maestrat Basin (Grandia, 2002; Nadal, 2001), where homogenization temperatures of 80 to 120 °C with salinities of 18 to 24 wt % NaCl eq. in ore-bearing calcites and salinities of 3 to 20 wt % NaCl eq. in replacement and saddle dolomites, were obtained.

In a  $\delta^{13}\text{C}$  vs  $\delta^{18}\text{O}$  plot, a correlation between both values for dolomites, calcite cements and veins (Fig. 1) can be seen. Dolomite C and O isotope data are explained from an interaction between a hot fluid (at temperatures between 80 and 110°C) and the regional limestone, at different fluid to rock ratios (red curves in Fig. 1). Similarly, C and O isotope composition of calcite veins and cements is constrained by model curves between 80 and 140°C. The similar  $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$  values of dedolomites and late-stage calcites can be explained after the precipitation from a fluid that isotopically exchanged with the Aptian limestones at low temperatures.

Available crush-leach data of inclusion fluids from nearby dolomite beds in the Maestrat Basin (Grandia, 2002) of the same type and age suggest that the dolomitizing fluid was evolved seawater enriched in K, either because of its interaction with K-rich lithologies or because of mixing with K-rich brines.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of dolomites reported in Grandia (2002) and Martín-Martín *et al.* (2009) also suggests that seawater-derived brines interacted with basement rocks. High Fe content in the Benicassim dolomites also supports the idea that the dolomitizing fluids circulated through underlying Permo-Triassic red clays and sandstones (Martín-Martín *et al.*, 2009).

According to the calculations of [Caja \*et al.\* \(2009\)](#), the geothermal gradient during the Early Cretaceous was 30 to 35°C/km. From the subsidence curves for Benicassim, we can infer that the dolomitized beds were buried at depths of only between 200 and 1100 m during the dolomitization stage. Therefore, the dolomitizing fluids in this area, which attained temperatures higher than 60°C, were clearly hotter than the surrounding rocks and must have circulated at depths higher than 2km.



**Figure 1**  $\delta^{13}\text{C}$  vs  $\delta^{18}\text{O}$  plot of limestones, dolomites, calcite veins and cements from the Benicassim outcrops. C-O isotope model curves have been calculated in terms of fluid-rock interaction for dolomite (red solid lines) and calcite (dashed black lines) at different temperatures and fluid/rock ratios according to the method of [Zheng and Hoefs \(1993\)](#).

### Potential magnesium sources for dolomitization

Assuming mole-by-mole replacement and taking into account the full succession, including the eroded layers, we have estimated that replacive dolomitization of the Aptian limestones in the Benicassim area would require about  $5 \cdot 10^{13}$  moles of Mg. In principle, the magnesium could be derived from many different fluid sources: (a) seawater, either pristine, modified by interaction with other sources or evolved, (b) fluids with Mg from dedolomitization of Triassic and Jurassic dolomites, (c) brines that dissolved underlying evaporite rocks, (d) fluids with Mg derived from illitization of clay minerals, (e) dewatering of marls and other carbonates due to compaction and (f) brines of unknown origin that circulated through the Palaeozoic basement.

Source (b) is ruled out because Triassic and Jurassic rocks appear only slightly dedolomitized; source (c) is not plausible because Triassic evaporites were mostly eroded before the deposition of Aptian carbonates in the area. As only Triassic kaolinite was illitized in this area, option (d) seems also unreasonable. Although dewatering of marls and other carbonates by compaction (source e) could have contributed, it could not provide all the Mg needed. According to the available geochemical and geological data, our mass balance calculations suggest that the most likely source of Mg could be evolved seawater (a) and/or basement brines (f), or a mixture of both.

### Reactivity and mass-balance of dolomitizing fluids

The minimum volume of fluid that would be required to completely dolomitize a rock volume whose porosity is filled with the fluid ([Table 1](#)) has been estimated on the basis of the method described by [Land \(1985\)](#). One pore volume is defined as the volume of the saturated porosity (we assumed  $\phi=0.3$ ; [Fig. 2](#)). The volume of calcite that dissolves and dolomite that precipitates is calculated when porosity is filled by a certain solution, at a given temperature, until it reaches equilibrium with rock host

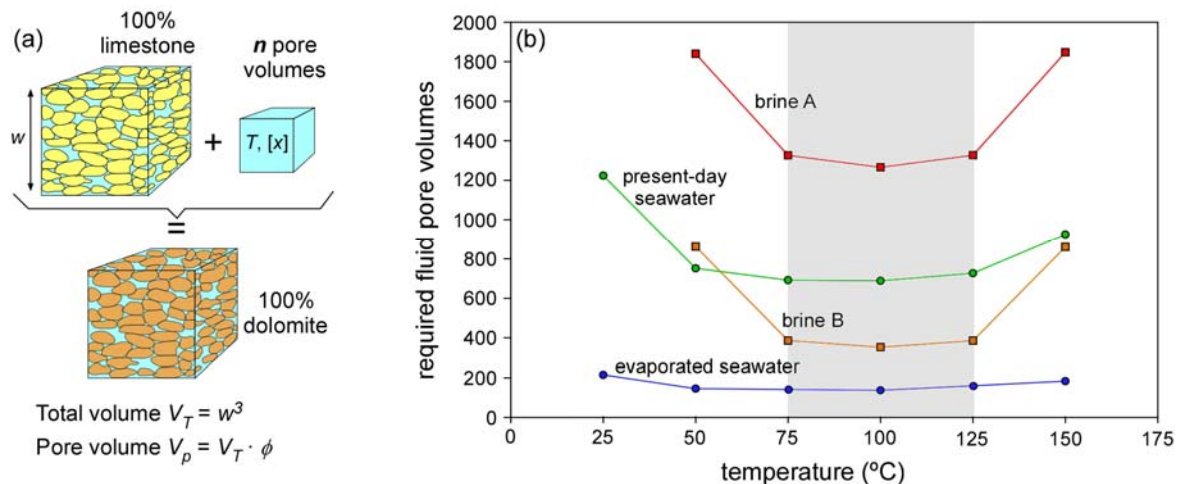
minerals. The number of pore volumes necessary to completely dolomitize the rock and the minimum volume of fluid required can be estimated. The calculations were performed using the code Phreeqc (Parkhurst and Appello, 1999) with the Phreeqc kinetic databases for different temperatures.

**Table 1** Chemical composition of the solutions used in the numerical simulations. Concentration units are mol/kg water.

	(1) Present-day seawater	(2) 5 x concentrated seawater (80%)	(3) Brine A	(4) Brine B
Ca	0.0103	0.0516	0.1285	1.1627
Mg	0.0531	0.2654	0.0314	0.1255
Na	0.4680	2.3390	4.0279	2.6838
Cl	0.5460	2.7290	4.4010	5.5849
% wt eq NaCl	3.5	17.5	25	32

References: (1) Stumm and Morgan (1981); (3) Shanks and Bischoff (1997) and (4) Kharaka and Thordsen (1992). All these fluids were equilibrated with calcite prior to calculations.

The dolomitizing capacity of these solutions, measured as the number of pore volumes needed to completely dolomitize a volume of rock, does not appear to be directly proportional to the Mg concentration of the fluid (Fig. 2). Besides, an 80% evaporated seawater with a salinity of 17.5 % wt eq NaCl and 5 times more Mg than the original seawater is much more reactive, in terms of dolomitization capacity, than the brines (A and B). More importantly, from Fig. 2 it is evident that the optimum temperature for dolomitization ranges from 75 to 125 °C for most of the fluids.



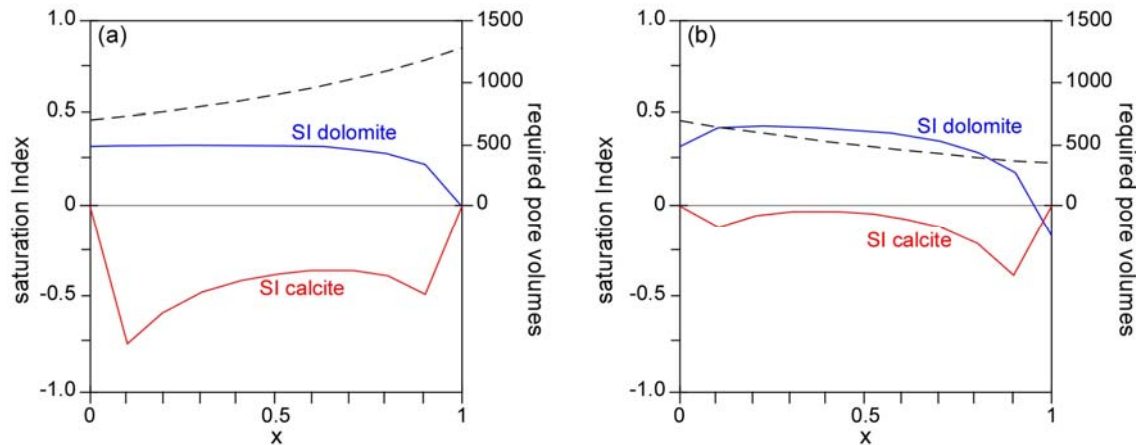
**Figure 2** (a) Sketch showing the concept of pore volume; (b) quantification of pore volumes that are required to dolomitize a cube of rock depending on their composition and temperature.

### Role of fluid mixing

The mixture of two different fluids, each initially saturated with respect to calcite, may not be in equilibrium with calcite after mixing occurs. This fact can be observed at a wide range of fluid temperatures and is caused by the intrinsic effects of chemical mixing (Corbella and Ayora, 2003). We have evaluated the reactivity of different mixtures of fluids presented in Table 1 at a temperature of 100 °C. The results show that the calcite and dolomite saturation indexes vary non-linearly when seawater is mixed with either brine A or brine B (Fig. 3); indeed, the supersaturation of the mixture with respect to calcite is maximum at intermediate values of the mixture, especially with brine B (Fig. 3b). This fact evidences the complexity of the mixtures of fluids. However, in terms of volume of solution required to cause dolomitization, fluid mixtures do not strongly modify the reactivity of end-member solutions. Nevertheless, the coincidence of maximum supersaturation with minimum pore volume amounts at a 50% seawater-50% brine B mixture and at a temperature of 100°C (Fig. 3b) suggests this could have been the most efficient dolomitizing solution in the Benicassim area.

## Conclusions

According to geologic and geochemical data, dolomitization in the Benicassim area resulted from the circulation of a seawater-derived brine and/or a basement brine at temperatures above 80 °C. An evaluation of the reactivity of these solutions shows that the modelled fluids are more reactive when their temperature range between 75° and 125 °C. Evolved seawater can be considerably more reactive than deep saline brines. When these fluids are mixed calcite saturation index becomes strongly non-linear, but it does not affect the volume of fluid required to dolomitize the whole rock.



**Figure 3** Effects of fluid mixing. Saturation index represent solid lines (positive values mean supersaturation and negative values subsaturation). Pore volumes required to completely dolomitize the rock volume for mixtures of seawater ( $x=0$ ) with brines A and B ( $x=1$ ) are shown by dashed lines.

## Acknowledgements

This work was financed and supported by the ExxonMobil Upstream Research Company and the ExxonMobil (FC)<sup>2</sup> Alliance (Fundamental Controls on Flow in Carbonates).

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