# Diagenetic minerals and paleothermal constraints in Maestrat Basin, Iberian Range: relation to rift stage and other regional thermal events

## Minerales diagenéticos y paleotemperaturas en la Cuenca del Maestrazgo: relación con la etapa de rift y otros eventos térmicos regionales


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**Abstract:** In the Lower Cretaceous sandstones of the Maestrat Basin are present several diagenetic minerals that provide information about their temperature of precipitation. Quartz cement (homogenisation temperatures with a mode of 145ºC), fibrous illite replacing feldspars (70-130ºC), the complete transformation of kaolinite to dickite (90-130ºC), the complete albitization of detrital feldspars (>105ºC) and barite and saddle dolomite cements (associated to hydrothermal fluids). Vitrinite reflectance of the organic matter in the intercalated marls revealed burial temperatures from 119 to 134ºC. However, these temperatures are not consistent with the thermal modelling of Penyagolosa sub-basin (Maestrat Basin). In the Penyagolosa Sub-basin model, the Lower Cretaceous sediments reached a maximum burial temperature of 65ºC, based on a thermal gradient of 30ºC/km, which was estimated by subsidence analysis, vitrinite reflectance and the stretching factor and thermal conductivities during syn-rift stage 2. Thus, in the Maestrat Basin existed conditions of relative higher temperature than predicted in a typical rift basin. These thermal anomaly is consistent with the existence other high-temperature events, such as alkali basaltic volcanism, metamorphism, thermal heating associated with high thermal gradients, and Hg-Sb bearing deposits have been reported in the Basque-Cantabrian Chain, the Pyrenean Mountains and the Iberian Chain.



**Key words:** *diagenesis, diagenetic transformations, paleothermal constraints, Maestrat Basin.*



***Resumen:*** *Las areniscas del Cretácico inferior de la Cuenca del Maestrazgo presentan varios minerales diagenéticos y transformaciones que proporcionan información directa o indirecta de las condiciones de temperatura: Cemento de cuarzo (temperaturas de homogeneización con moda 145ºC), ilita fibrosa reemplazando a feldespatos (70-130ºC), transformación completa de caolinita a dickita (90-130ºC), albitización completa de los feldespatos (>105ºC) y cementos de barita y dolomita saddle (asociados con fluidos hidrotermales). La reflectancia de la vitrinita en la materia orgánica de las margas intercaladas ha revelado temperaturas de enterramiento entre 119 y 134ºC. Sin embargo, los rangos de temperaturas que indican todos estos minerales y procesos diagenéticos no son consistentes con las temperaturas obtenidas a partir de la modelización en la subcuenca de Penyagolosa (Cuenca del Maestrazgo). Según este modelo, considerando un gradiente térmico de 30ºC/km, estimado a partir de cálculos de subsidencia, la reflectancia de la vitrinita, el factor de estiramiento que tuvo lugar y la conductividad térmica durante la etapa sin-rift 2, las areniscas del Cretácico inferior habrían alcanzado cómo máximo una temperatura de enterramiento de 65ºC. Por tanto, en la Cuenca del Maestrazgo se dieron condiciones de temperaturas más altas de las típicas de una etapa de rift. A escala regional, estaría relacionado con la presencia de otros eventos de temperatura elevada como son el volcanismo alcalino básico de la Cadena Vasco-Cantábrica, el metamorfismo de Pirineos y la Cadena Ibérica y las mineralizaciones de Hg-Sb de la Cadena Ibérica.*



***Palabras clave:*** *diagénesis, transformaciones diagenéticas, indicadores térmicos, Cuenca del Maestrazgo.*


## INTRODUCTION

During the Mid and Late Cretaceous the three main geological units of the NE Iberian Peninsula, the Basque-Cantabrian Chain, the Pyrenean Mountains and the Iberian Chain, all of them developed by inversion of Mesozoic rifts during the Late Cretaceous-Paleogene, underwent some contemporaneous phenomena such as: alkali basaltic volcanism, metamorphism, thermal heating associated with high thermal gradients, and Hg-Sb bearing deposits (Salas *et al*., 2005).

This paper is focused on the Maestrat Basin, which lies in the eastern sector of the Iberian Range and

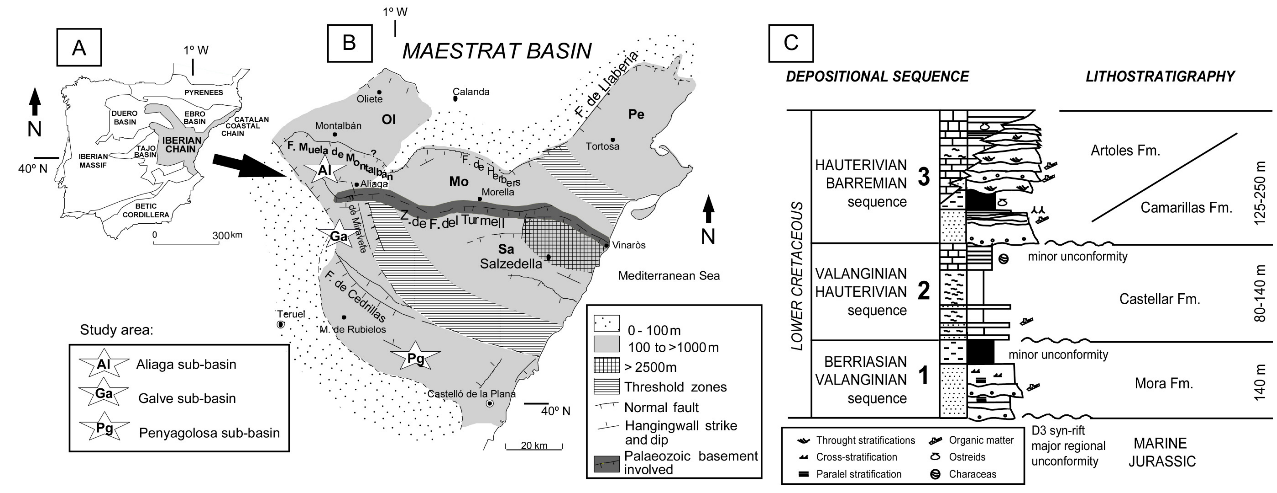


FIGURE 1. *(A) Simplified map of the Iberian Peninsula showing the main structural units; (B) Detail corresponding to the Maestrat Basin located in the Iberian Chain (modified from Salas et al., 2001). The Maestrat Basin has been subdivided into the following seven sub-basins: Oliete (Ol), Morella (Mo), Perelló (Pe), Salzedella (Sa), Penyagolosa (Pg), Galve (Ga), and Aliaga (Al). The last three sub-basins are the study area. Thickness represented corresponds to Early Cretaceous sediments; (C) Schematic stratigraphic column of the Lower Cretaceous formations showing the main unconformities (modified from Caja, 2004).*

contains almost 6000 m Mesozoic sediment (Fig. 1A and B). Syn-rift subsidence began during the Upper Oxfordian age, and was characterised by an initial period of rapid, fault-controlled syn-rift subsidence (Upper Oxfordian to Middle Albian) in a series of fault-limited blocks, followed by a post-rift interval of diminishing subsidence (Upper Cretaceous), which was in turn controlled by thermal relaxation of the lithosphere (Salas *et al*., 2001). The Maestrat Basin is divided in several sub-basins; the study area includes the western-most sub-basins, Aliaga, Galve and Penyagolosa (Fig. 1B). These sub-basins were filled during Lower Cretaceous by the so called Weald facies (Fig. 1C).

The aims of this paper are to characterize diagenetic minerals present in the Lower Cretaceous sandstones that can provide paleotemperature information and obtain other paleothermal constraints (e.g. vitrinite reflectance) in order to support the existence of a regional thermal anomaly and discuss its relationship with the rift evolution.

## SAMPLES AND ANALYTICAL METHODS

Nine representative stratigraphic sections were studied in the Aliaga, Galve and Penyagolosa sub-basin from the Maestrat Basin. Sampling was focused on the Lower Cretaceous sandstones from the Mora, El Castellar and Camarillas formations (125 sandstones and 26 shale samples). Analytical methods used in this paper were: i) Petrographic and cathodoluminescence (CL) study of thin sections and modal analyses of medium-size sandstones counting up to 400 points in 49 samples; ii) X-Ray diffraction (XRD) and differential thermal analysis (DTA) on <10μm fraction of sandstone samples with relative high abundance in kaolin; iii) Scanning Electron Microscopy (SEM) in fresh-broken sandstone samples for diagenetic clay mineral identification; iv) Electron microprobe analyses and back-scattered imaging (BSE) on albite grains; v) Fluid inclusion study in quartz cements; vi) Vitrinite reflectance analyses, which include the measure of up to 100 points for each sample (4 samples from El Castellar Fm. and 1 sample from Camarillas Fm.) Vitrinite fragments with evidences of recycled origin were not observed; and vii) Burial and thermal modelization was performed using BasinMod 1D© (*Platte River Associates*). In the burial history were considered the sediments present and eroded in the Penyagolosa Sub-basin. In the thermal modelization, a thermal gradient typical for rift basins (27-30ºC/km) was assumed. For a more detailed description of samples and analytical methods see Caja (2004).

## RESULTS

### Diagenetic minerals

#### *Quartz cement*

Quartz cement occurs in all the studied sandstones (5.8% modal average in Mora Fm., 2.4% in Castellar Fm., and up to 6.3% in Camarillas Fm.) as overgrowths on detrital quartz grains. Fluid inclusions of Camarillas Fm. sandstones are characterised by a very small size (<5-35μm), with subidiomophic shapes, growing parallel to quartz cement crystal edges and at room temperature show two phases, liquid and gas. Occasionally, fluid inclusions associated to microfractures were observed. Primary liquid fluid inclusions are aqueous, with low salinity (2.5 to 6.8 wt. % NaCl) and homogenisation temperatures range from 122 to 183 ºC, mode 145ºC (Fig. 2).

#### *Fibrous illite*

Illite occurs in Mora, Castellar and Camarillas sandstones as replacement on feldspars. In the Camarillas Fm. sandstones of the Penyagolosa sub-basin, K-feldspars are completely replaced by illite and no kaolin is present. Illite in the SEM is characterised by large fibrous habit (up to 20 μm) and a subordinate lath-shaped morphology.

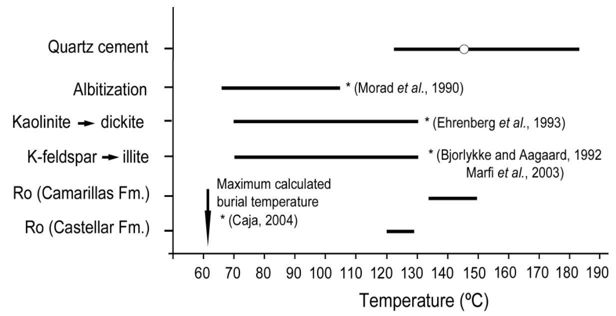


FIGURE 2. *Measured and estimated temperatures for diagenetic minerals and vitrinite reflectance. * See the reference list in the text..*

### *Kaolin*

Kaolin is present in the studied sandstones as kaolinite and dickite. Kaolinite occurs as pore filling cement and replacement on feldspar grains with a vermiform texture. Camarillas Fm. sandstones present a relative high abundance of kaolinite (average modal abundance, up to 4.1%). Dickite occurs dominantly as pore filling cement, present a blocky morphology and its presence was confirmed by XRD and DTA analyses.

### *Albitization*

Plagioclase grains in Mora Fm. sandstones are untwined, frequently euhedral-subeuhedral, clouded by tiny vacuoles and partially replaced by chlorite, kaolin or calcite. Microprobe analyses on these grains revealed a near pure albite end member composition ($Or_{0.1}$ $Ab_{99.7}$ $An_{0.2}$; average of 63 analyses). BSE imaging shows abundant micropores, aligned parallel to cleavage planes or microfractures. Under the CL, the albite grains are non-luminescent. One of the most peculiar characteristic of these albite grains is that they are albitized completely. However, no K-feldspars occur in Mora Fm. sandstones. In contrast, Castellar and Camarillas Fm. sandstones present feldspars only partially albitized. Albite occurs as patches with a near pure albite end member composition ($Or_{0.2}$ $Ab_{99.5}$ $An_{0.3}$; average values of 4 analyses), which are associated and aligned to the exfoliation planes, twins or microfractures.

### *Barite and saddle dolomite*

Barite occurs as isolated, idiomorphic and elongated crystals in Camarillas Fm. sandstones precipitating in the pores. Barite cement abundance is very low and in Mora and Castellar formations was not observed. Textural relationships with adjacent cements indicate that barite precipitated after or during quartz cement precipitation.

Saddle dolomite also occurs in Camarillas Fm. sandstones. The small size of fluid inclusions prevented the homogenisation temperature measure.

## Vitrinite reflectance

Vitrinite reflectance was measured in mudstone samples from Castellar and Camarillas formations. Obtained data show a unimodal distribution and low dispersion of values. Average values of vitrinite reflectance in Castellar (up to 0.98%, n=4) and Camarillas (average 0.82%Ro, n=1) formations range from 0.82 to 0.98. These values correspond to burial temperatures of 119 to 134 ºC and hydrothermal temperatures of 125 to 150ºC (after Barker and Pawlewicz, 1994; Fig. 2).

## DISCUSSION AND CONCLUSIONS

The measured homogenisation temperatures in quartz cement are consistent with the development of other diagenetic processes, from which it was impossible to obtain direct paleotemperatures: i) the presence of fibrous illite replacing K-feldspars completely (Camarillas Fm.) has been reported to commence at 70ºC and is a pervasive process above 130ºC (Bjorlykke and Aagaard, 1992). The precipitation of authigenic illite in the Jurassic and Cretaceous sandstones of the Western Desert (Egypt) ranges from 117 to 140ºC and postdated quartz, barite and bitumen entrapment (Marfil *et al.*, 2003); ii) the transformation of kaolinite to dickite is considered a process that begin at 70-90ºC and the complete transformation is reached when temperature is over 90-130ºC (Ehrenberg *et al.*, 1993); iii) diagenetic albitization is commonly observed in sandstones buried around 2200 m and 65ºC. It has been reported that the process of albitization is completed for sandstones buried over 3400 m and 105ºC (Morad *et al.*, 1990); and iv) saddle dolomite and barite are minerals commonly associated to Pb-Zn-Cu ore deposits (Mississippi Valley Type) reported in the Penyagolosa sub-basin and related with the circulation of hydrothermal fluids (Grandia *et al.*, 2003).

The burial and thermal model of Penyagolosa sub-basin (Caja, 2004) reveals that Castellar and Camarillas formations were buried around 1600 m of depth and reached a maximum temperature of 62ºC (i.e. Ro ~ 0.4; Barker and Pawlewicz, 1994). However, the "calculated" model do not permit explain the obtained vitrinite values and the diagenetic paragenesis occurring in the Lower Cretaceous sandstones (Fig. 3). If the "calculated" model is constrained with the obtained vitrinite reflectance values, then Castellar and Camarillas formations would have reached a temperature of 128-151ºC, which is consistent with all the diagenetic minerals and transformations observed. This thermal gradient value exceed 30ºC/km, which is estimated by subsidence analysis, vitrinite reflectance, the stretching factor of the rift basin, the related surface heat flow and thermal conductivity values during syn-rift stage 2 (Salas *et al.*, 2005). Thus, homogenisation temperatures obtained from diagenetic minerals present

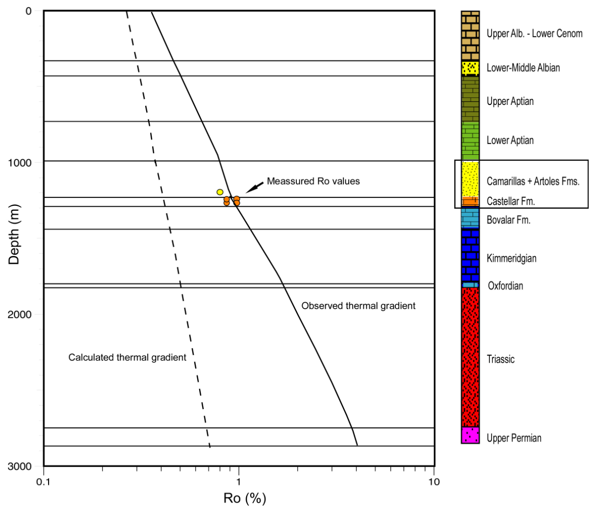


FIGURE 3. *Depth (m) versus vitrinite reflectance (Ro, %) for Penyagolosa sub-basin (modified from Caja, 2004). Note that the "calculated" and the observed thermal gradient are different. Vitrinite reflectance values reveal conditions of relative high temperature in the Maestrat Basin, which are consistent with the homogenisation temperatures measured and diagenetic paragenesis observed..*

in the studied Lower Cretaceous sandstones and vitrinite reflectance values reveal conditions of relative high temperature in the Maestrat Basin. These thermal anomaly is consistent with the existence other high-temperature events, such as alkali basaltic volcanism, metamorphism, thermal heating associated with high thermal gradients, and Hg-Sb bearing deposits have been reported in the Basque-Cantabrian Chain, the Pyrenean Mountains and the Iberian Chain. This regional thermal anomaly event could be related with a hot spot which is currently located offshore opposite San Sebastian developed in relation to the opening of the oceanic North Atlantic and Bay of Biscay basins (Salas *et al*., 2005).

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