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# FLUID INCLUSIONS AND RARE EARTH ELEMENTS (REE) ANALYSIS IN CALCITE VEINS: TECTONIC - DIAGENESIS INTERACTION IN THE ROSABLANCA FORMATION, MESA DE LOS SANTOS SECTOR, EASTERN CORDILLERA, COLOMBIA

# ANÁLISIS DE INCLUSIONES FLUIDAS Y DE TIERRAS RARAS (REE) EN VENAS DE CALCITA: INTERACCIÓN DIAGÉNESIS - TECTÓNICA EN LA FORMACIÓN ROSABLANCA, SECTOR MESA DE LOS SANTOS, CORDILLERA ORIENTAL, COLOMBIA

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## ABSTRACT

Studies conducted by means of petrography, cathodoluminescence, SEM, fluid inclusion and REE geochemistry in core samples from the Rosablanca Formation in the Mesa de Los Santos sector, identified two types of material: the host rock classified as Packstones and Grainstones, and veins that texturally expose three types of filling (blocky texture, blocky elongate texture, fibrous texture). Diagenesis is characterized by dissolution, carbonate cement precipitation, compaction, fracturing and fluid circulation through fractures during at least three episodes; these diagenetic processes were contemporaneous with the distensive and compressive tectonic regimes regionally dominant during the Cretaceous, Paleogene and Neogene in the study area. The fluids that generated the different types of texture inside the veins were brines that belonged to the $H_2O – NaCl – CaCl_2$ system, with salinities between 0.03 – 12.96 % wt eq NaCl, derived from the Rosablanca Formation that was deposited under oxic conditions, retaining their marine character and implying an autochthonous origin for the REE present in the veins. The conditions of entrapment for fluid inclusions during the early event were heterogeneous, arising from an immiscible mixture of brines and hydrocarbons, while in the second, they were homogeneous with later post-entrapment processes.

## RESUMEN

Los estudios mediante petrografía, catodoluminiscencia, SEM, inclusiones fluidas y geoquímicos de tierras raras (REE) en muestras de núcleo de la Formación Rosablanca en el sector de la Mesa de Los Santos, determinaron dos tipos de material: la roca caja clasificada como Packstones y Grainstones, y venas que texturalmente exponen tres tipos de relleno (agregados granulares, agregados granulares de cristales elongados, agregados fibrosos). La diagénesis está caracterizada por procesos de disolución, cementación, compactación, fracturamiento y circulación de fluidos por fracturas durante al menos tres episodios; estos procesos en el área de estudio fueron coetáneos con los regímenes tectónicos distensivos y compresivos dominantes regionalmente durante el Cretácico, el Paleógeno y el Neógeno. Los fluidos que generaron los distintos tipos de relleno en las venas fueron salmueras que pertenecieron al sistema $H_2O$-$NaCl$-$CaCl_2$ con salinidades comprendidas entre 0,03-12,96 % wt eq NaCl, derivadas de la Formación Rosablanca que fue depositada bajo condiciones óxicas reteniendo su carácter marino e implicando una procedencia autóctona de los REE presentes en las venas. Las condiciones de atrapamiento de las inclusiones fluidas durante el primer evento fueron heterogéneas a partir de una mezcla inmiscible de salmueras e hidrocarburos, mientras que, en el segundo, fueron homogéneas con procesos post-atrape posteriores.

**KEYWORDS / PALABRAS CLAVE**

Mesa de Los Santos | Rosablanca Formation | Diagenesis | Tectonics.
Mesa de Los Santos | Formación Rosablanca | Diagénesis | Tectónica.

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# 1. INTRODUCTION

The movement of fluids through different geological formations is of great importance to the diagenetic processes in sedimentary basins because; when they occur, they aid in the transfer of fluids, allowing, for example, the migration of hydrocarbons from source rocks to reservoir rocks through faults, fractures, or interconnected porosity [1]. The study of fracture opening events, as well as the minerals with which they are filled, is of great help in understanding the conditions and compositions of the fluids that circulated during diagenesis through a stratigraphic unit [2,3].

The study of the compositions, textures and growth directions of the minerals that fill the fractures can help to increase knowledge regarding the number of fluid migration events, and they can also be associated with the deformation tectonic context in which the filling events occurred [4]-[9].

In this article we discuss the results of the petrography, inorganic geochemistry (REE), cathodoluminescence and fluid inclusion analyses performed on fracture filling material belonging to the Lower Cretaceous Rosablanca Formation. The samples were taken in outcrops in Mesa de Los Santos (Eastern Cordillera, Colombia).

The aim of this study is to characterize the composition of the fluids that filled the fractures in multiple opening-filling events, and to associate them regionally with the various tectonic events relating to the Eastern Cordillera, providing new data on the history of fluid migration for the Rosablanca Formation.

# 2. THEORETICAL FRAME

## GEOLOGICAL CHARACTERISTICS OF THE STUDY AREA

### GEOGRAPHIC LOCATION

The Mesa de Los Santos sector is located in the western part of Colombia's Eastern Cordillera, in the department of Santander, approximately 60 km southeast of the city of Bucaramanga. Geographically, this region is bound to the east by the Santander Massif and to the west by the piedmont that ends in the Middle Magdalena Valley (Figure 1)

### STRATIGRAPHY

In the study area, there are outcrops of sedimentary rocks that regionally belong to the stratigraphic sequence relating to the Middle Magdalena Valley (Figure 2), and crystalline rocks that make up the basement of such sequence. The oldest rocks relate to low and medium grade metapelites belonging to the Silgará Formation of Pre-Devonian age, which was intruded in the Mesozoic by plutonic rocks from Granito de Pescadero. An uncomformity separates the rocks of the Silgará Formation from the sediments of the Jurassic and Early Cretaceous ages deposited in continental fluvial, transitional and shallow marine environments, associated with the Jordán, Los Santos, Rosablanca, Paja and Tablazo formations [11].

The Rosablanca Formation that is being studied herein, is one of the basal units relating to the Lower Cretaceous of Colombia's Eastern Cordillera and of the study area. Towards its base it is in contact with the sandstones of the Tambor Formation and towards its top, with the mudstone of the Paja Formation. According to Julivert [12] who carried out his study in the area of the Sogamoso river canyon located west of Mesa de Los Santos, this unit is approximately 318 m thick and is comprised by a set of massive limestones with interbedded marls and shales, and towards the upper part there is also a sandy level. The massive limestones are more abundant towards the base and the top of the Formation, while towards the middle part the marls and shales become more abundant.

Paleo-environmentally, the Rosablanca Formation was deposited in an environment relating to shallow platform environments [14], with energies that permitted the development of grainstone, packstone

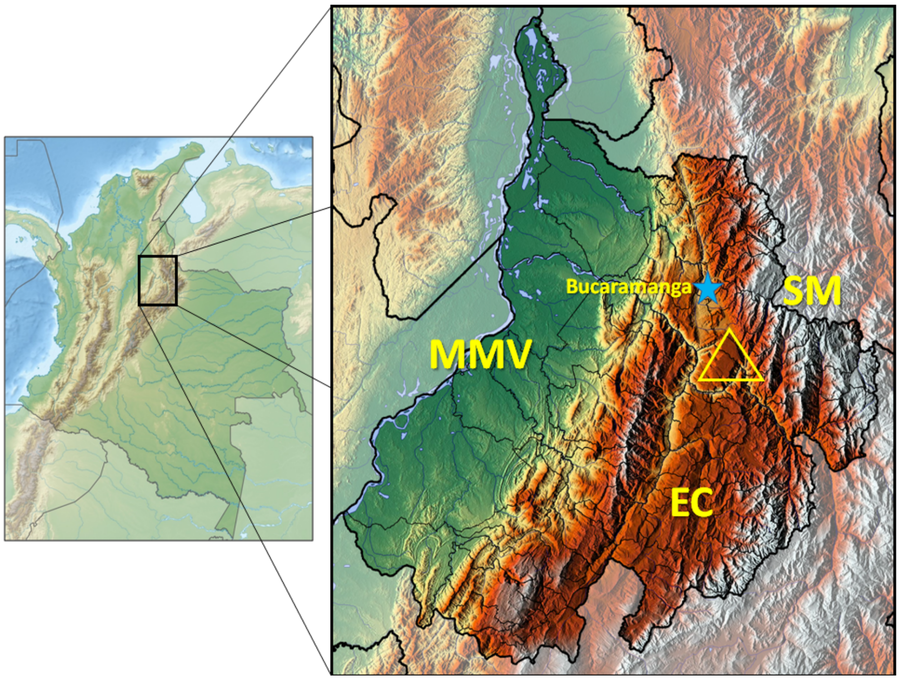


**Figure 1.** Location of the Mesa de Los Santos sector, which relates to the area enclosed within the triangle; in the Eastern Cordillera (EC), Mesa de Los Santos is located between two large domains; to the east the domain formed by the crystalline rocks of the Santander Massif (SM) and to the west the domain formed by the sedimentary rocks of the piedmont and the Middle Magdalena Valley (MMV). Image taken and modified from [10].

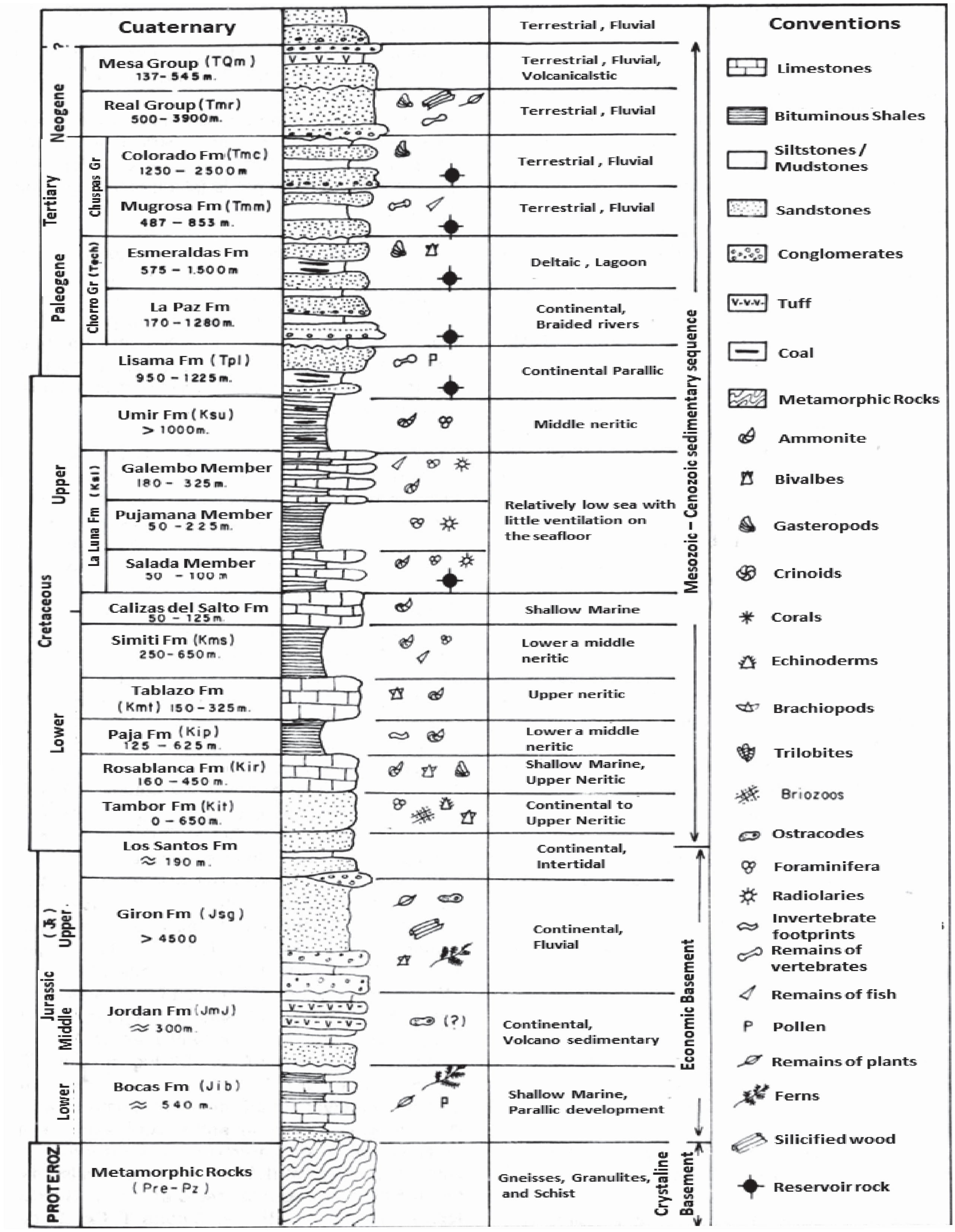


**Figure 2.** Diagram illustrating the sedimentary sequence of the Middle Magdalena Valley. In the study area, the oldest rocks are represented by the crystalline basement, overlain by units from the Middle Jurassic represented by the Jordán Formation, and from the Lower Cretaceous represented by the Los Santos, Rosablanca, Paja and Tablazo Formations. Image taken from Mojica & Franco [13].

and mudstone carbonates, as well as certain evaporitic levels [15]. Julivert [12], based on the petrographic study carried out in this unit, proposed that the deposit conditions were not constant, and the basal part of the unit was characterized by evaporite facies, implying hypersalinity and stillness in the deposit; the rest of the succession is deposited in an open and shallow environment in which the stillness (micrite, fossiliferous micrite and biomicrite deposits) and agitation (intrasparite, oosparite, intramicrite and oomicrite deposit) conditions alternate. The age of the Rosablanca Formation has been estimated as being from Hauterivian to Barremian [16].

## TECTONICS

### JURASSIC AND CRETACEOUS

The tectonic evolution of the study area (i.e. Mesa de Los Santos sector) is regionally framed within the tectonic evolution of the Middle Magdalena Valley basin and the Eastern Cordillera, especially the latter because it forms part of it. Taking into account that proposed by Mojica & Franco [13], Cooper *et al* [17] and Sarmiento [18], in the Late Triassic - Upper Cretaceous interval, distensive tectonics prevailed in which an intracontinental rift was formed, bordered by normal paleo-faults, with subsidence due to the block tectonics [19] that allowed the accumulation of the continental sediments relating to the Bocas, Girón, Jordán and Los Santos formations.

At the beginning of the Cretaceous and through the same mechanism of normal distension and faulting, a transgression took place, generating shallow marine platform environments under which the Rosablanca, Paja, Tablazo, Simití, El Salto, La Luna and Umir Formations were deposited. In the Maastrichtian at the end of the Cretaceous, the accretion of the Western Cordillera and the rise of the Central Cordillera caused a regional change in the area's tectonic regime, changing from an extensional to a compressional context [20]. In the sedimentary sequence of the Middle Magdalena Valley and in the Eastern Cordillera, this change is marked by a transition from neritic marine conditions present in the Umir Formation to the paralytic and terrestrial conditions in which the Lisama Formation was deposited [13].

Geo-tectonically, in the Middle Magdalena Valley and the Eastern Cordillera, until the Lower Cretaceous the distension was associated with an intracontinental rifting phase related globally with the separation of Gondwana and Laurasia, and the opening of the Paleo-Caribbean ocean [17,18]. In the Upper Cretaceous, this phase evolved into a retroarc basin in which the distension extended and reached its maximum extent with the deposition of La Luna Formation [20], and ended at the conclusion of the Cretaceous.

### PALEOGENE AND NEOGENE

At the beginning of the Paleocene and as a consequence of the deformative advance towards the East that raised the Central Cordillera, the Middle Magdalena Valley and the Eastern Cordillera constituted a foreland basin that received sediments from the Guiana Shield and the active orogen of the Central Cordillera, with the Lisama Formation depositing itself in continental environments. Already at this time, the elevation of certain sectors of the Eastern Cordillera began taking place locally and heterogeneously [20]. In the Middle Paleocene, the Santander and Floresta massifs rose during the phase that culminates in the Paleoandean orogeny of the Early - Middle Eocene and, in the anticlinal zones formed, the erosion removes a large part of the Cretaceous sequence, while sedimentation and subsidence continue in the syncline zones more or less continuously [13], [21]-[22].

From the Upper Eocene to the Lower Miocene, the Paz, Esmeraldas, Mugrosa and Colorado Formations are deposited in continental environments in a context characterized regionally by a foreland basin constituted by the Eastern Cordillera, the Middle Magdalena Valley, the Llanero piedmont and the Catatumbo basin [20],[23]-[24] with certain sectors that locally began to rise from the Late Eocene - Early Oligocene [25,26]. During the Middle Miocene - Pliocene, the Andean Orogeny occurred, in which the old foreland basin was fractionated in the Eastern Cordillera and the Middle Magdalena Valley, Llanos and Catatumbo basins [20].

## PRIOR STUDIES

Regionally, in the Eastern Cordillera and the Middle Magdalena Valley areas, and with the object of study being the Macanal and Rosablanca Shales from the Lower Cretaceous, the authors Prada & Quintero [27], Mantilla, Tassinari & Mancini [28], and Naranjo, Duque & Moreno [29] conducted mineralogical and geochemical studies into fracture filling materials. These authors obtained data on the origin, chemical nature and paleo-temperatures of the fluids. These data were used to interpret their relationship with the genesis of emerald deposits and also to identify hydrocarbon migration events within the Rosablanca Formation.

In order to estimate the deformation events and the history of exhumation for the Macanal Formation (of Berriasian age, on the eastern flank of the Eastern Cordillera), Mora *et al* [26] integrated data on fluid inclusions, vitrinite reflectance (Ro), Apatite Fission Track (AFTA) and structural field data. With the results obtained, a model was built that integrates paleotemperatures, the exhumation of the Cretaceous units in the area, the compressional events, the migration of paleofluids and the time period for these events.

In the study area, Julivert [12] conducted petrography studies in the Rosablanca Formation in order to produce a petrological characterization of the unit, examine the correlation with the stratigraphic levels in the field and determine the paleo-environmental conditions of the deposit and how they varied throughout the deposition of the Formation. His work focused mainly on the textural, compositional and paleontological aspects.

Conde [5] and Conde, Mantilla, Naranjo & Sanchez [7] conducted a regional study on calcite veins belonging to the Rosablanca Formation, integrating samples obtained in the Mesa de Los Santos sector and in the Middle Magdalena Valley, and through the use of petrography, cathodoluminescence, fluid inclusions and rare earth geochemistry they determined regionally at least three events relating to the opening and filling of calcite veins and two hydrocarbon loading events that used fractures as migration routes.

Through chemostratigraphy, stratigraphy and petrography, Bedoya & Nomesqui [30] analyzed carbonates from the Rosablanca Formation in Mesa de los Santos and Zapatoca. The data obtained suggest that the unit was deposited in the Valanginian - Aptian lower interval in a sedimentation environment associated with a shallow platform affected by strong subsidence. Similarly, they identified diagenetic processes such as silicification, compaction and carbonate cement precipitation, proposing that carbonate sequences exhibited processes of eodiagenesis, mesodiagenesis and telodiagenesis. In addition, the petrography suggests that porosity is at a low percentage, and is of the secondary type and is fracture-related.

# 3. EXPERIMENTAL DEVELOPMENT

Four (4) core samples obtained from outcrops were analyzed, which were coded as LHR2-01, LHR2-02, LHR2-03 and LHR2-04, using petrography, fluid inclusion, SEM, cathodoluminescence and rare earth elements (REE) techniques. The analyses were focused on the limestone that constitutes the wall rock, and on the carbonates that form the filling material of the veins that cross the wall rock, reflecting uncomformity.

The exact location of the samples is not provided due to confidentiality of the information. The analyses were carried out in the laboratories of the Colombian Petroleum Institute and Universidad Industrial de Santander. For purposes of petrography and cathodoluminescence, a Nikon Eclipse E-200 transmitted light petrographic microscope and a Clmk3A / Clmk4 cathodoluminescence plate (300 - 500 µA and 12 - 15 kV) were used in order to identify minerals, cements, textures and filling events relating to the fractures or veins.

SEM analyses in the veins were performed using a Leo 1450VP electron microscope equipped with an X-ray scattering energy system (OXFORD INCA).

For the comparison between the composition of the wall rock relating to the Rosablanca Formation and the filling of the fractures through rare earth elements, data from inductively coupled plasma mass spectrometry was gathered using an ICP-MS, Perkin Elmer ELAN 6000 device.

The homogenization temperatures, salinity and chemical system of the fluids were analyzed with fluid inclusions in a Linkam THMS 600 stage. The petrography was performed using a Carl Zeiss AXIOLAB transmitted light microscope, and a Nikon Eclipse LV 100 transmitted light microscope coupled to a UV light system for the detection of fluid inclusions with hydrocarbons.

## PETROGRAPHY, SCANNING ELECTRON MICROSCOPY AND CATHODOLUMINESCENCE

### WALL ROCK

The wall rock in which the veins (with carbonate filling) are located, were classified as Packstone limestones (samples LHR2-01 and LHR2-02) and Grainstones (samples LHR2-03 and LHR2-04) using the Dunham classification system. [31].

Structurally these limestones are massive, with no stratification, lamination and sedimentary microstructures observed; texturally they are grain-supported rocks with a framework formed by particles of elongate and rounded forms comprised by intraclasts and bioclasts (which were identified as echinoderms, brachiopods and bivalves). The rock exhibits good calibration, and the contacts between the sedimentary particles are longitudinal and concave-convex due to compaction, also evidenced by the presence of styloliths (Figure 3a).

Orthochemicals such as pseudosparite and sparite appear occupying the space between the particles, and the micrite manifests itself forming bundles around the bioclasts (Figure 3b) and exhibits replacement by pseudosparite (Figure 3c). In addition, the sparite also appears as crystals, partially or fully replacing the bioclasts (Figure 3b).

The presence of oxides in the form of pseudomorphs associated with the sparite (Figure 3d) was identified in the host rock, as well as within the veins associated with calcite crystals (Figure 3e).

### CARBONATE VEINS

The fractures inside the wall rock, previously classified as Packstones and Grainstones according to Dunham [31], have thicknesses ranging between 2 mm and 2 cm, and at the textural level they are filled by the following types of crystalline aggregates (Figure 3f):

### GRANULAR AGGREGATES (BLOCKY TEXTURE - BT)

formed by inequigranular aggregates of euhedral oxides (pyrite pseudomorphs) associated with euhedral crystals to calcite anhedrals that developed syntaxially (Figure 4a and Figure 4b). The calcite appears twinned and with an undulatory extinction, it is located adjacent to the rock - fracture contact, with some of these crystals containing fragments of the host rock.

### GRANULAR AGGREGATES OF ELONGATE CRYSTALS

(Blocky Elongate Texture - BET) formed by euhedral quartz crystals (Figure 4c) associated with euhedral and prismatic crystals of calcite containing S and Mg (Figure 4d). These crystals develop syntaxially and are arranged perpendicularly with respect to the granular aggregate.

### FIBROUS AGGREGATES

(Fibrous Texture - FT) formed by calcite crystals containing S and Mg (Figure 4d). They appear as individuals with an acicular habit, forming fibrous aggregates that are arranged perpendicularly with respect to the previously described aggregates. Visually, the calcite in these aggregates is colorless with the exception of certain fibrous aggregates that exhibit a pale brown tone in parallel Nichols, and have a low to medium relief, undulating extinction, and third-order green-pink interference colors.

## FLUID INCLUSIONS

### PETROGRAPHY

Petrographic and microthermometric analyses were carried out on calcite crystals belonging to granular aggregates (BT) and granular aggregates of elongate crystals (BET) because they contain fluid inclusions of the appropriate size to be studied. The petrographic results are illustrated in Table 1.

From a petrographic point of view, the primary aqueous fluid inclusions present in the granular aggregates were grouped in fluid inclusion associations (FIA) 1 to 4 (Figure 5a, Figure 5b, Figure 5c). Morphologically they are regular, irregular, tabular and ovoid, they are monophasic (constituted by a liquid or gaseous phase) or biphasic (formed by a liquid or gas phase). Their degree of filling (volume occupied by the bubble within the fluid inclusion) is variable, and the gas bubble occupies a volume ranging between 0 to 100% of the fluid inclusion.

The primary aqueous fluid inclusions in the granular aggregates of elongate crystals, were petrographically represented by fluid inclusion association (FIA) 6 (Figure 5d, Figure 5e). These are of different sizes, with irregular and ovoid shapes, and at room temperature they are monophasic (formed by a liquid phase) and biphasic (liquid and vapor phase). Their degree of filling is less variable than in the granular aggregates, varying from 0.7 to 1 (the gas bubble does not occupy a volume greater than 30% with respect to the fluid inclusion's total volume).

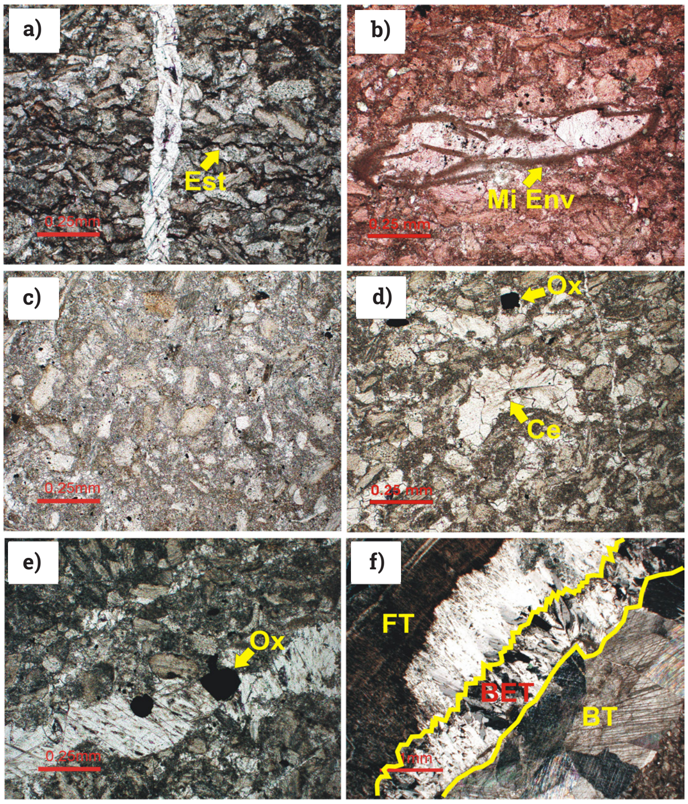


**Figure 3.** Photomicrographs at 2.5X and 10X, illustrating: (a) The effects of compaction reflected in concavo-convex contacts and styloliths in sample LHR2-01, (b). Fractured micrite covering due to compaction around a bioclaster filled with sparite in sample LHR2-03, (c) Micrite replaced by pseudosparite in sample LHR2-02, (d) and(e) Pseudomorphs of oxides associated with sparite within bioclasts and with calcite crystals in filled fractures, (f) Types of texture developed in fractures (BT: granular aggregate, BET: granular aggregates of elongate crystals, FT: fibrous aggregates).

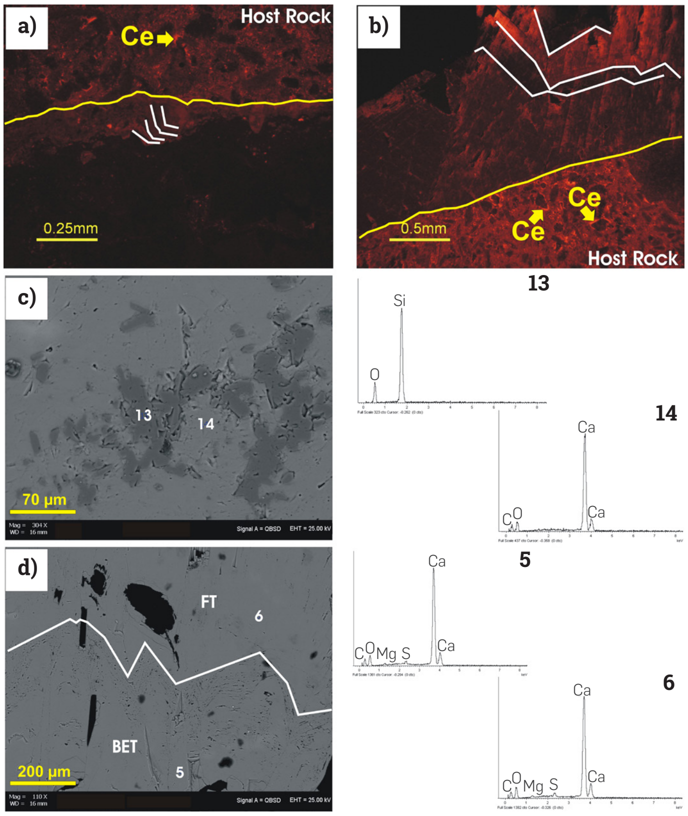


**Figure 4.** Cathodoluminescence images in samples LHR2-02 (a) and LHR2-03 (b) Illustrating the syntaxial development (white lines) of calcite crystals in granular aggregates, (c) Image from a scanning electron micrograph (SEM) in granular aggregates of elongate crystals (BET), showing quartz (13) and calcite (14) crystals with their respective compositional spectra, (d) SEM image illustrating calcite crystals, granular aggregates of elongate crystals (BET) (5) and fibrous aggregates (FT) (6) containing Mg and S as shown by their respective spectra.

**Table 1.** Characteristics of fluid inclusion associations (FIA) found in calcite crystals of granular aggregates, granular aggregates of elongate crystals and fibrous aggregates.

| Type of Fracture Filling Texture | Mineral | Fluid Inclusion association (FIA) | Location | Genetic Type | Type of Fluid Inclusion according to Nash [32] | Form | Phases | Vl/(Vl+Vv) |
|---|---|---|---|---|---|---|---|---|
| Blocky Texture | Calcite | 1 | Isolated inside crystals | PRIMARY | I | Regular | L, L + V | 0.9 to 1 |
| | | 2 | Populations inside crystals | PRIMARY | I, II | Regular | L, L + V, V + L, V | Variable (0 to 1) |
| | | 3 | Populations inside crystals | PRIMARY | I | Tabular, Irregular, ovoid | L | 1 |
| | | 4 | Lineations | PSEUDO-SECONDARY | I | Regular and ovoid | L, L+ V | 0.9 to 1 |
| | | 5 | Lineations | SECONDARY | I, II | Regular and ovoid | L, V | 0 and 1 |
| Blocky Elongate Texture | Calcite | 6 | Parallel to growth faces | PRIMARY | I | Irregular and ovoid | L + V, L | 0.7 to 1 |
| Fibrous Texture | Calcite | 7 | Parallel to fibers | PRIMARY | Not observable because these FI exhibits a small size. | | | |

In fibrous aggregates, the primary aqueous fluid inclusions were grouped in fluid inclusion association (FIA) 7 (**Figure 5f**) composed of inclusions of a very small size (<4 µm in length). Due to this factor, it was not possible to observe the phase relationships.

### MICROTHERMOMETRY

The microthermometric analyses were carried out on fluid inclusions belonging to fluid inclusion associations (FIA) 1, 2, 3 (granular aggregates) and 6 (granular aggregates of elongate crystals), which showed a tendency to experience decrepitation phenomena while they were under heating or cooling.

The fluid inclusions relating to FIA 1, 2, 3 were first frozen to -150°C and then heated. During this process eutectic temperatures (Te) between -51.8 ° C and -50.8 ° C were obtained, as well as final ice melting temperatures (Tfi) between -9.1 ° C and 0°C, homogenizing to a liquid state (L + V → L) at temperatures ranging (Th) between 86.3 °C and 228.7 °C.

For granular aggregates of elongate crystals, when subjected to microthermometry the primary fluid inclusions relating to FIA 6 resulted in eutectic temperatures (Te) between -52.5 °C and -50.8 °C, final ice melting temperatures (Tfi) between -4.3 °C and -0.5 °C, homogenizing to a liquid state (L + V → L) at temperatures (Th) greater than the temperatures measured in the fluid inclusions for the granular aggregates, between 190 °C and 239.1 °C. The microthermometric results are illustrated in **Table 2.**

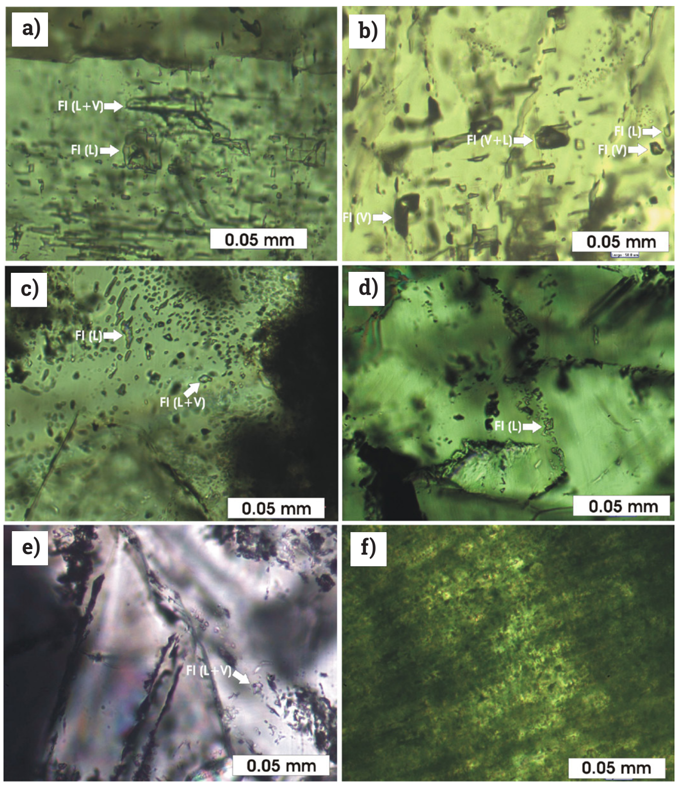


**Figure 5.** Photomicrographs at 50x illustrating: primary aqueous fluid inclusions relating to FIA 1 (a), FIA 2 (b) and FIA 3 (c) contained in calcite crystals of granular aggregates in samples LHR2-01 (a and b) , LHR2-03 (c), d and e. primary aqueous fluid inclusions (FIA 6) in calcite crystals in granular aggregates of elongate crystals (sample LHR2-04), f. primary aqueous fluid inclusions in fibrous aggregates; note their small size.

## RARE EARTH ELEMENT (REE) GEOCHEMISTRY

The analyses conducted by means of rare earth element geochemistry were performed on sample LHR2-01 (host rock, and calcite crystals belonging to the granular aggregates located inside the veins). The results in terms of the concentration of elements (ppm) and the normalization value with respect to PASS (Post Archean Australian Shale) are shown in **Table 3**, and the normalization diagram is set out in **Figure 6.** The values for the Cerio and Europio anomalies were calculated in accordance with Rollinson [33].

According to **Figure 6**, the normalization values are higher in the host rock (packstone) than in the granular aggregates (fracture filling material). In addition, the trend for the LREE is similar in both graphs, and for the HREE the trend is similar except for the Gd and Ho elements.

By taking the values for LaN, SmN, GdN and YbN as a reference (**Table 3**), the fractionation values for the REE, LREE and HREE were calculated. The results show that the fractionation of the REE in the host rock (packstone) [(La / Yb) N = 0.9621] is slightly higher than in the granular aggregates [(La / Yb) N = 0.6], while the same trend is observed for the fractionation of the HREE [(Gd / Yb) N = 1.422 host rock], [(Gd / Yb) N = 0.733 granular aggregates].

For the fractionation of the LREE, an opposite trend is observed, and in this case, the fractionation is slightly greater in the granular aggregates [(La / Sm) N = 1.125] than in the host rock [(La / Sm) N = 1.085].

In the host rock (Rosablanca Formation) the negative value for the Cerium anomaly [CeN / √(LaN * PrN) = 0.534] indicates the influence of seawater, whose REE distribution is similar to that of the modern sea [34, 35]. In this context, the negative Cerium anomaly is caused by the oxidation of $Ce^{3+}$ to the more insoluble $Ce^{4+}$ under specific pH and eH conditions [36,37,38].

In addition, this negative anomaly is indicating the incorporation of REE directly from seawater or pore water under oxic conditions [40]. The positive Europium anomaly [EuN /√(SmN * GdN) = 1.068] is not typical of seawater, and it could be caused by processes such as hydrothermal discharges in mid-oceanic ridge areas [41,42], river discharges to the sea [43] and diagenesis [44].

Considering the above, it can be suggested - in accordance with the REE diagram (**Figure 6**) and the values for the Cerium and Europium anomalies - that the host rock (Rosablanca Formation) was deposited under oxic conditions, with the REE retaining their marine nature and implying an autochthonous origin for them [28], in a palaeogeographic and paleotectonic context relating to the early Cretaceous, characterized regionally by the formation of the proto-Caribbean ocean arising from the break-up of Pangaea [45], where certain expansion centers might have been relatively close to the physiographic site where the Rosablanca Formation was deposited, thus explaining the positive anomaly for the Europium found in the host rock.

For granular aggregates (fracture filling material) the values for the Cerium and Europium anomalies gave positive values [CeN /√(LaN * PrN) = 0.871] and [EuN /√(SmN * GdN) = 2.286] respectively. This similarity in the anomalies and trends (**Figure 6**) suggests that the

**Table 2.** Results of microthermometric analyses in primary fluid inclusions for granular aggregates and granular aggregates of elongate crystals. Te = eutectic temperature, Tfi = final ice melting temperature, Th = homogenization temperature, Td = decrepitation temperature.

| Sample | Texture present in fracture fill | Mineral | Genetic Classification | FI type [32] | Phases | VL (VL+Vv) | Te(°C) | Tfi(°C) | Th(°C) | Phase Transition | Td (°C) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| LHR2 -01 | Blocky Texture | Calcite | PRIMARY | I | L + V | 0.95 | -51.2 | -7.2 | 126.9 | L + V → L | - |
| | | | PRIMARY* | I | L + V | 0.95 | - | - | 165.3 | L + V → L | - |
| | | | PRIMARY* | I | L + V | 0.9 | - | - | 123.3 | L + V → L | - |
| | | | PRIMARY* | I | L + V | 0.95 | - | - | 170.5 | L + V → L | - |
| | | | PRIMARY | I | L + V | 0.9 | -50.8 | -6.5 | - | - | -2.1 |
| | | | PRIMARY | I | L + V | 0.9 | -51.7 | - | - | - | 20 |
| | | | PRIMARY | I | L + V | 0.9 | -50.8 | - | - | - | - |
| | | | PRIMARY | I | L + V | 0.9 | -51.2 | - | - | - | - |
| | | | PRIMARY | I | L | 1 | -50.8 | - | - | L → L | - |
| | | | PRIMARY | I | L | 1 | -51.2 | - | - | L → L | - |
| | | | PRIMARY | I | L | 1 | -51.2 | -6 | - | L → L | - |
| | | | PRIMARY | I | L | 1 | -51.2 | - | | L → L | - |
| | Blocky Elongate Texture | Calcite | PRIMARY | I | L + V | 0.95 | -51.7 | -3.4 | 239.1 | L + V → L | - |
| | | | PRIMARY | I | L + V | 0.95 | -50.8 | -0.5 | 237.9 | L + V → L | - |
| | | | PRIMARY | I | L + V | 0.9 | -52.5 | -2.2 | 222 | L + V → L | - |
| | | | PRIMARY* | I | L + V | 0.8 | - | - | 200 | L + V → L | - |
| | | | PRIMARY* | I | L + V | 0.8 | - | - | 190 | L + V → L | - |
| | | | PRIMARY | I | L + V | 0.95 | -51.6 | -1.9 | - | | 29.9 |
| | | | PRIMARY | I | L + V | 0.9 | -51.7 | -4.3 | - | | 0 |
| LHR2 -03 | Blocky Texture | Calcite | PRIMARY | I | L + V | 0.95 | -51.2 | -0.6 | 228.7 | L + V → L | - |
| | | | PRIMARY | I | L + V | 0.7 | -51.2 | 0 | 156.2 | L + V → L | - |
| | | | PRIMARY | I | L + V | 0.95 | -51.2 | -7.5 | 105.9 | L + V → L | - |
| | | | PRIMARY | I | L + V | 0.95 | - | -0.7 | 86.3 | L + V → L | - |
| | | | PRIMARY | I | L + V | 0,95 | - | -0.6 | 100.2 | L + V → L | - |
| | | | PRIMARY* | I | L + V | 0.95 | - | - | 150.5 | L + V → L | - |
| | | | PRIMARY | I | L + V | 0.95 | -51.8 | -9.1 | - | - | -5 |

**Table 3.** Concentration of rare earth elements present in the host rock and in fracture filling material (granular aggregates or blocky texture) in sample LHR2 - 01. In addition, it also illustrates the normalized concentration with respect to the PAAS according to .

| Sample (LHR2-01) | REE Concentrations | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Y | Ho | Er | Tm | Yb |
| Host rock (Packstone) | 8.351 | 9.013 | 1.561 | 6.401 | 1.307 | 0.344 | 1.759 | 0.240 | 0.748 | 11.190 | 0.320 | 0.916 | 0.123 | 0.748 |
| Fracture Filling Material (Blocky Texture) | 0.311 | 0.547 | 0.058 | 0.212 | 0.044 | 0.023 | 0.051 | 0.037 | 0.043 | 0.286 | 0.034 | 0.022 | 0.019 | 0.043 |
| PAAS (McLennan, 1989) | 32.800 | 79.600 | 8.830 | 33.900 | 5.550 | 1.080 | 4.660 | 0.774 | 2.820 | 27.000 | 0.991 | 2.850 | 0.405 | 2.820 |
| Host rock (Packstone) N | 0.255 | 0.113 | 0.177 | 0.189 | 0.235 | 0.319 | 0.377 | 0.310 | 0.265 | 0.414 | 0.323 | 0.321 | 0.304 | 0.265 |
| Fracture Filling Material (Blocky Texture) N | 0.009 | 0.007 | 0.007 | 0.006 | 0.008 | 0.021 | 0.011 | 0.048 | 0.015 | 0.011 | 0.034 | 0.008 | 0.047 | 0.015 |

| | |
|---|---|
| EuN/√(SmN*GdN) Packstone | 1.068 |
| CeN/√(LaN*PrN) Packstone | 0.534 |
| EuN/√(SmN*GdN) Fracture filling material (Blocky Texture) | 2.286 |
| CeN/√(LaN*PrN) Fracture filling material (Blocky Texture) | 0.871 |

McLennan [39], as well as the Cerium and Europium anomalies.

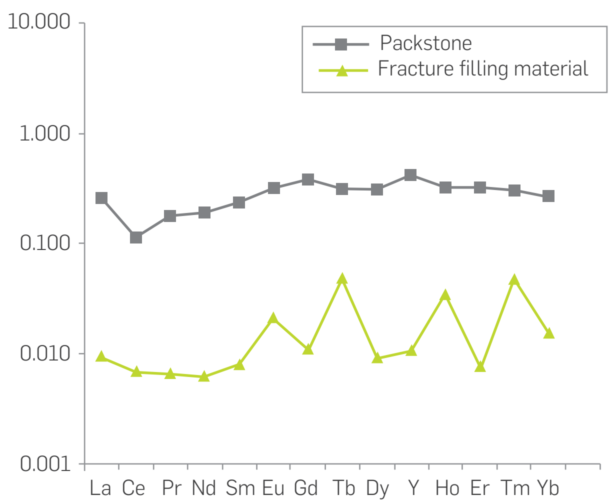


**Figure 6.** Distribution of normalized concentrations (with respect to PASS) of rare earth elements (REE) in sample LHR2-01, both in the host rock (packstone) and in the fracture filling material (granular aggregates or blocky texture).

REEs of the granular aggregates are of the same nature as the REE present in the host rock, implying their extraction from such rock. In accordance with the above point of view, it is possible that the fluids that circulated through the fractures and that later gave rise to the granular aggregates, granular aggregates of elongate crystals and the fibrous aggregates, came from the Rosablanca Formation, meaning that intra-formational fluids were involved in the diagenesis of this Unit [7,28].

# 4. RESULTS ANALYSIS

Using the various studies conducted both at a regional and local level on the Rosablanca Formation [5,7,12,29,30] as a reference, and considering the fact that four samples were studied, the results obtained in this study suggest that locally (i.e. in the Mesa de Los Santos sector), during the post-depositional history of the Rosablanca Formation, diagenesis was characterized by events of dissolution, precipitation, compaction, fracturing and fluid circulation, which were simultaneous with the tectonic regimes that the unit was subjected on a local and regional scale after its deposition.

## DIAGENESIS

The petrography indicates that the earliest diagenetic event was the precipitation of micrite around the bioclasts, followed by the dissolution of unstable particles and bioclasts (probably constituted by aragonite) and the subsequent formation of authigenic calcite (sparite - microesparite - pseudosparite) and pyrite within fragments of shells, intraclasts and as filling material in the porous space.

As the burial progressed, the compaction caused by the weight of the overlying sedimentary units generated the concavo-convex and longitudinal contacts, the reduction of primary porosity and the formation of stylolites.

The pressure exerted by the fluids of diagenetic origin gave rise to fracturing [46] and therefore an escape route for these fluids, generating a system of fractures through which the fluids circulated, and fundamentally carbonate minerals were precipitated and grew syntaxially, forming the veins. At least three filling events relating to these veins are documented in this study.

First, calcite and pyrite were precipitated forming the granular aggregates (Blocky Texture) and then calcite and quartz generating the granular aggregates of elongate crystals (Blocky Elongate Texture), and during the third event, calcite, giving rise to the fibrous aggregates (Fibrous Texture). This means that the fractures acted as escape channels suggesting that, in Mesa de los Santos, the Rosablanca Formation is able to behave like a fractured reservoir [5].

It is likely that pyrite oxidation will occur after the formation of granular aggregates due to the effect caused by the circulation of oxidizing fluids, which are probably of meteoric origin.

## RELATIONSHIP BETWEEN THE FORMATION OF VEIN FILLS AND TECTONICS

From a textural point of view, the fractures filled by various types of mineral precipitates in the Rosablanca Formation related to crack seal veins formed by the repeated fracturing and mineral precipitation, developing granular, elongate and fibrous mineral fillings [47,48].

In addition, considering that proposed by Mügge [49], granular aggregates are formed in contexts of rapid opening where the opening rate is greater than the crystalline growth rate, while elongate and fibrous textures are formed in a slow opening environment where the opening rate is slow compared to the crystal growth rate.

Moreover, granular aggregates precipitate from fluids in contexts with zero or insignificant deformation at the time of crystallization, generating free - face growth, while elongate and fibrous aggregates crystallize in a context with the presence of deformation, generating contact growth [50].

Finally, according to Cox [51,52], granular aggregates are related to extensional fractures that are formed in the plane $\sigma1$-$\sigma2$ ($\sigma1$- $\sigma3$ <T), while the elongate and fibrous aggregates are related to extension-shear fractures in which the angle formed between the axis $\sigma1$ and the plane of the fracture is usually 0 <$\alpha$ <25° (4 <$\sigma1$- $\sigma3$ <5.7T). Also, taking into account Urai & Williams [53], Aghib, Giorgetti & Wilson [54] and Ribak-Ostrowska *et al* [55], the elongate and fibrous aggregates can form syntectonic veins reflecting tectonic control, possibly related to horizontal shortening and folding episodes.

Taking into account the above, one could consider that, in the Mesa de Los Santos sector, the diagenesis processes (through to the formation of granular aggregates (Figure 7) occurred when the unit was deposited locally and buried under a dominant distensive geotectonic context during the Cretaceous, not only in Mesa de Los Santos, but also in the Middle Magdalena Valley and in the Eastern Cordillera where this unit is also located [17,18].

The precipitation of granular aggregates of elongate crystals and fibrous aggregates inside the Rosablanca Formation was able to occur when the sedimentary sequence deposited in the Mesa de Los Santos sector began to experience compressive forces, likely related to the beginning of the basin tectonic inversion since the Paleocene (Figure 8).

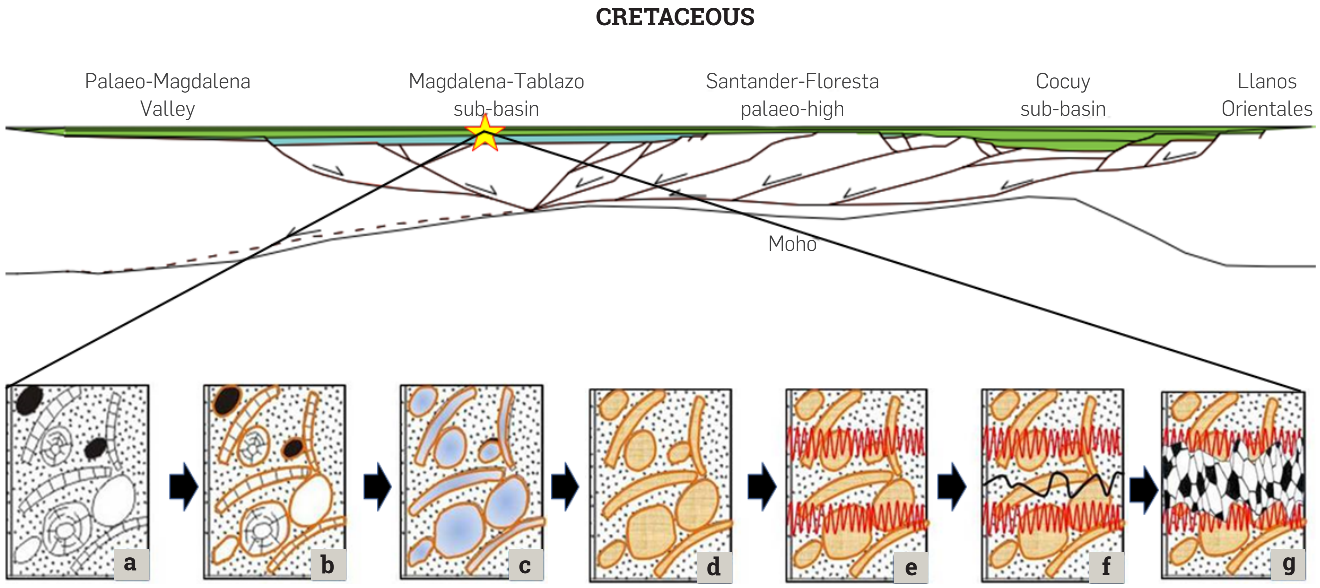


**Figure 7.** Diagram illustrating the sequence of diagenetic processes experienced by the Rosablanca Formation in the area of Mesa de Los Santos (star) (a) beginning of diagenesis, (b) development of micrite, (c) dissolution, (d) precipitation of orthochemicals, e) compaction and styolite formation, (e) fracturing, (f) generation of granular aggregates (BT). These processes occurred locally, influenced regionally by a distensive context that was predominant in the Cretaceous. Modified image from Sarmiento [18].

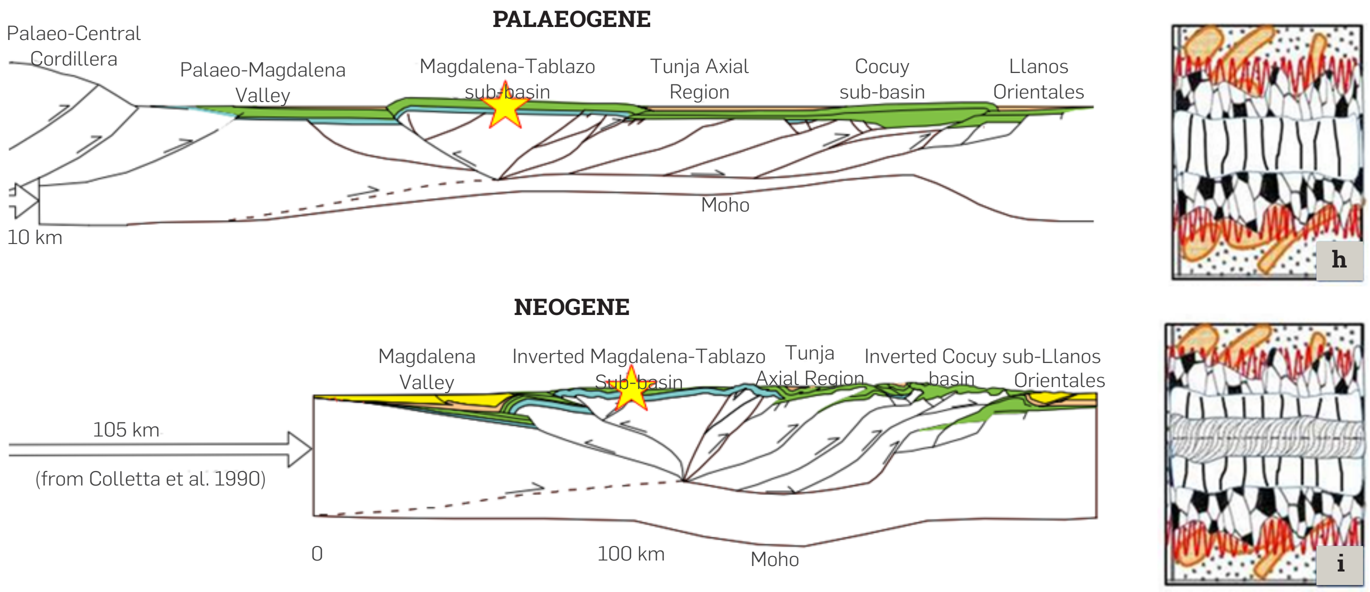


**Figure 8.** Diagram illustrating the interior of the Rosablanca Formation in Mesa de Los Santos (star): (h) the formation of granular aggregates of elongate crystals and (i) the formation of fibrous aggregates within veins. At a local level, these processes were likely influenced regionally by compressive processes associated with tectonic inversion and the elevation of the Santander Massif. Modified image from Sarmiento [18].

Considering that Mesa de Los Santos is relatively close to the Santander Massif and that, according to Mojica & Franco [13], it was raised in the Middle Paleocene, and that in the study area only the Lower Cretaceous sedimentary sequence is preserved, it can be suggested as a hypothesis that the precipitation of the granular aggregates of elongate crystals and the precipitation of the fibrous aggregates within the Rosablanca Formation in Mesa de Los Santos could be related to the progressive elevation of the Santander Massif, at least since the Middle Paleocene, and that it experienced its greatest pulses during the paleo-Andean orogeny in the Middle Eocene and during the Andean Orogeny in the Middle Miocene [20].

## PHYSICOCHEMICAL CHARACTERISTICS OF THE FLUIDS THAT CIRCULATED THROUGH THE FRACTURES

Data on fluid inclusions and rare earth elements (REE) geochemistry, suggest that the fluids that circulated through the fractures in the Rosablanca Formation in Mesa de Los Santos and generated the granular aggregates and granular aggregates of elongate crystals, were made up of intra-formational brines derived from the host rock (Rosablanca Formation), composed of the $H_2O - NaCl - CaCl_2$

system with salinities ranging between 0.03 - 12.96% wt eq NaCl using the equation from Potter, Clynne, & Brown [56].

GRANULAR AGGREGATES:
It is interpreted that these intraformational fluids circulated at minimum temperatures of between 100 °C - 150 °C (Figure 9). Considering the variability in the degree of filling observed in the primary fluid inclusions for granular aggregates and the significant range of homogenization temperatures obtained, one can consider that, in accordance with Goldstein & Reynolds [57] and Goldstein [58], these data represent heterogeneous conditions of entrapment for a system possibly composed of an immiscible mixture of hydrocarbons and brines.

Although no hydrocarbon fluid inclusions were detected in granular aggregates, Conde [5] and Conde, Mantilla, Naranjo & Sanchez [7] reported minimum entrapment temperatures of 65 °C - 88 °C from primary hydrocarbon fluid inclusions contained in calcite crystals belonging to granular aggregates in veins of the Rosablanca Formation in the Alfa 1 well (Middle Magdalena Valley).

In addition, Mantilla *et al* [59] report the existence of hydrocarbons in the spaces between fluorite crystals and within microfractures associated with the Pescadero Granite, which is located near the study area, and they propose that these hydrocarbons came from the Rosablanca Formation, which reached thermal maturity conditions between 60 °C - 100 °C.

This makes it possible to suggest that the granular aggregates precipitated from an immiscible mixture of hydrocarbons and brines, implying the existence of an event involving the generation and migration of hydrocarbons derived from the Rosablanca Formation in the Mesa de Los Santos area, as a result of which the unit reached thermal maturity conditions due to burial.

GRANULAR AGGREGATES OF ELONGATE CRYSTALS:
the data obtained by microthermometry seem to indicate minimum trapping temperatures between 190 °C and 230 °C (Figure 9) for the fluids that generated this type of filling. Additionally, no associated hydrocarbon fluid inclusions were detected. However, this data should be regarded with caution, as the following must be considered:

a) the temperatures are very high for a sedimentary system and the petrographic analysis showed no evidence of deep diagenesis, or even features such as the development of incipient foliation.

b) it was difficult to find biphasic fluid inclusions because most are monophasic, and those that were measured by means of microthermometry showed a tendency towards decrepitation.

c) Petrophically, biphasic primary fluid inclusions (L + V) were observed for this type of filling, and the degree of filling exhibited little variability associated with monophasic fluid inclusions (L), with frequently irregular shapes and evidence of necking down.

If we consider that proposed by Goldstein & Reynolds [57] and Goldstein [58], the petrographic and microthermometric data would represent homogeneous entrapment conditions from a system formed by low temperature brines in a liquid state, and after formation these fluid inclusions experienced post-trapping processes.

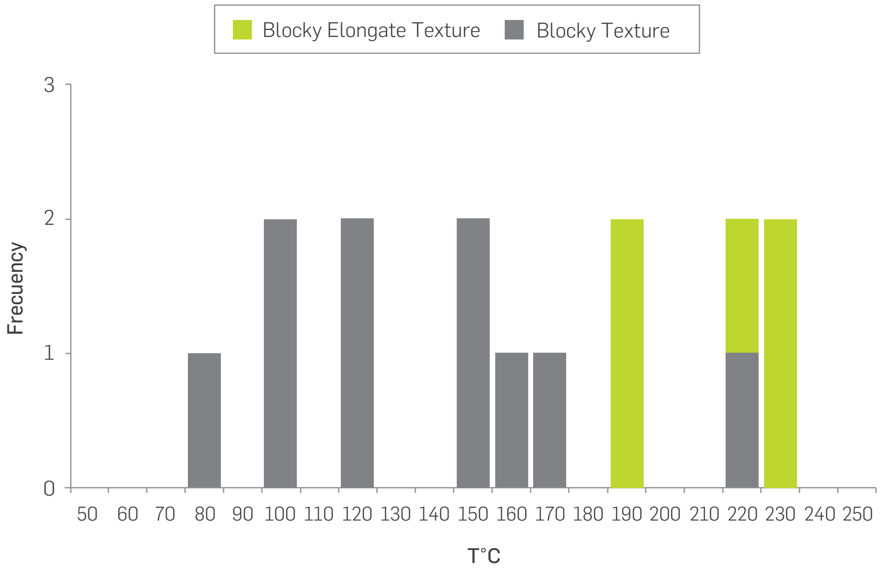


**Figure 9.** Distribution of homogenization temperatures obtained from primary fluid inclusions belonging to vein filling material (granular aggregates and granular aggregates of elongate crystals).

## CONCLUSIONS

In the Mesa de Los Santos, the petrographic study of core samples belonging to outcrops from the Rosablanca Formation shows that the wall rock is classified as Packstones and Grainstones, and the veins are texturally formed (mainly) by carbonates that constitute three types of filling: granular aggregates, granular aggregates of elongate crystals, and fibrous aggregates.

In the study area, the diagenesis of the Rosablanca Formation involved dissolution events, cement precipitation, compaction, fracturing, opening and fluids migration during at least three events in which the following precipitated consecutively: granular aggregates, granular aggregates of elongate crystals, and fibrous aggregates.

The diagenetic events relating to dissolution, cement precipitation, compaction, fracturing in the wall rock, and the formation of the granular aggregates inside the veins, all happened locally and regionally in a distensive geotectonic context that was dominant during the Cretaceous in the area of Mesa of Los Santos.

The formation of granular aggregates of elongate crystals and fibrous aggregates occurred under a compressive tectonic regime linked to the initial stages of tectonic inversion, in the study area. The elevation of the Santander Massif could have influenced the formation of fillings of this type (at least since the Middle Paleocene).

The fractionation of REE and HREE in the host rock is greater than in the fracture filling material. Moreover, regarding fractionation of LREE, the opposite trend is observed. In addition, the values for the anomalies relating to Cerium and Europium suggest that the Rosablanca Formation was deposited under oxic conditions, retaining its marine nature and implying an autochthonous origin for the REE.

For the fracture filling material, the similarity in the trend for Cerium and Europium and the standardized REE diagrams indicate that the granular aggregates and probably the granular aggregates of elongate crystals (together with the fibrous aggregates) precipitated from fluids that came from the Rosablanca Formation, entailing the circulation (through fractures) of fluids of intraformational origin.

The fluids responsible for the formation of granular aggregates and granular aggregates of elongate crystals, were intraformational brines from the Rosablanca Formation, composed of the $H_2O$ – NaCl – $CaCl_2$, with salinities ranging between 0.03 - 12.96% wt eq NaCl.

During the formation of the granular aggregates, there was an event involving the migration and loading of hydrocarbons generated by the Rosablanca Formation, as a result of which it entered conditions of thermal maturity due to burial. The granular aggregates precipitated from heterogeneous conditions in a system formed by an immiscible mixture of brines and hydrocarbons.

The granular aggregates of elongate crystals precipitated from low temperature fluids formed by brines in a liquid state. After entrapment the fluid inclusions experienced post-trapping processes.

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