DIAGENESIS OF A BIOCLASTIC OYSTER DEPOSIT FROM THE LOWER CRETACEOUS (CHACHAO FORMATION). NEUQUÉN BASIN. MENDOZA PROVINCE, ARGENTINA

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ABSTRACT: The Lower Cretaceous Chachao Formation in the Malargüe anticline area consists of wackestone, packstone, and minor grainstone and mudstone rich in benthonic fauna that were deposited in a carbonate ramp. The carbonate diagenesis in the Valanginian Chachao Formation contains many processes with conspicuous effects, including micritization, dissolution, neomorphism, and cementation. The early diagenetic process is characterized by micritization, dissolution and mineralogic stabilization of components, and earlier cement phase represented by micrite cement and isopachous calcite cement, which have petrographic characteristics consistent with precipitation in a marine-phreatic diagenetic environment. Later diagenetic phenomena include granular calcite and syntaxial cement. Both of cement types are interpreted as typical of a meteoric-phreatic environment. Concentric–zoning pattern of alternating dull, and blotchy- to bright luminescent zones is interpreted as being caused by a decrease in redox potential (Eh), under conditions of a progressive marine burial meteoric-phreatic diagenetic environment. Geochemical data (Sr^{++}, Na^{+}, Mg^{++}, Fe^{++}, Mn^{++}) and SEM features of the micrite suggest that original calcareous mud could have been calcite dominated (CDP). The $\delta^{18}O$ composition of the granular calcite cement ranging from –2.84%0 to –4.27%0 PDB and the $\delta^{13}C$ values of the cement between –2.46%0 and –3.50%0 PDB are compatible with precipitation from a fluid that evolved meteoric-phreatic composition. The high depleted $\delta^{18}O$ values of the *Gryphaea* shells can be related to the dilution of the marine water with a fresh water influx, whereas shells with the heaviest $\delta^{13}C$ isotopic compositions are probably related to the original marine signal, which suggest a closed diagenetic system for carbon.

Keywords: carbonate; diagenesis; Valanginian; Neuquén Basin; Argentina.

INTRODUCTION

By Late Jurassic to Early Cretaceous times the Neuquén Basin was a typical back-arc basin related to the Pacific South American convergent plate margin. Early in the Late Cretaceous, it became a foreland basin as a result of the beginning of the Andean uplift. Before the Late Jurassic the basement of the basin had suffered an initial rift phase which led to western marine flooding and the formation of a series of half-grabens which controlled the sedimentation.

During Late Jurassic to Neocomian times generalized thermal subsidence in the basin expanded the original sedimentation area, and during these times more than 2500 m of sediments were deposited. The sedimentation ended with Late Cretaceous to Tertiary synorogenic continental deposits, closely related to the uplift of the Andean fold and thrust belt (Manceda and Figueroa 1995; Vergani et al. 1995; Zapata et al. 1999).

The Late Jurassic-Early Cretaceous succession comprises a thick pile of marine and non-marine siliciclastic, volcanic and volcaniclastic sediments as well as carbonates and evaporites. The Valanginian inner shelf skeletal limestones rich in benthonic fauna, outcropping in the southwest of Malargüe (35° 50” S- 69°75” W) **(Fig. 1)**, formally assigned to the Chachao Formation, were carefully recently studied. Therefore and in order to investigate their diagenetic history, several features were analyzed: (a) documenting and interpreting the cement succession in intraparticle and interparticle cavities, (b) the diagenetic environment of calcite and micrite luminescence patterns (c) chemical analysis of micrite in order to know about original mineralogy of precursor lime mud, (d) the carbon and oxygen isotopic signatures of calcite granular cement and some oyster shells.

The studied section is located within the Malargüe Fold and Thrust Belt (Manceda and Figueroa 1993) which is characterized by a series of basement blocks that bound thin skinned deformation zones (Zapata et al. 1999). Major structures within this segment have been interpreted as resulting from a typical inversion of Jurassic half-grabens (Kozlowski et al. 1990; Zapata et al. 1999).

STRATIGRAPHIC FRAMEWORK

The sedimentary infilling of the Neuquén Basin records from Jurassic to Eocene times and comprised not only rifting and thermal sag deposits, but also synorogenic units related to the Andean fold and thrust belt (Legarreta and Gulisano 1989, Manceda and Figueroa 1995).

According to Legarreta et al. (1993) and Legarreta and Uliana (1991) the sedimentary column of the Neuquén Basin can be subdivided in several Mesosequences **(Fig. 2)**, on the basis of regional stratigraphic discontinuities which were largely influenced by eustatic sea level changes. Valanginian limestones of the Chachao Formation are included into the Mendoza Mesosequence. Considering the lithostratigraphical units, the Mendoza Mesosequence includes the Tordillo Formation (Kimmeridgian, fluvial, eolian and playa-lake deposits) and the Mendoza Group (Titho-Neocomian). In Southern Mendoza province, the Mendoza Mesosequence comprises black shales and limestones of the Vaca Muerta Formation (Tithonian

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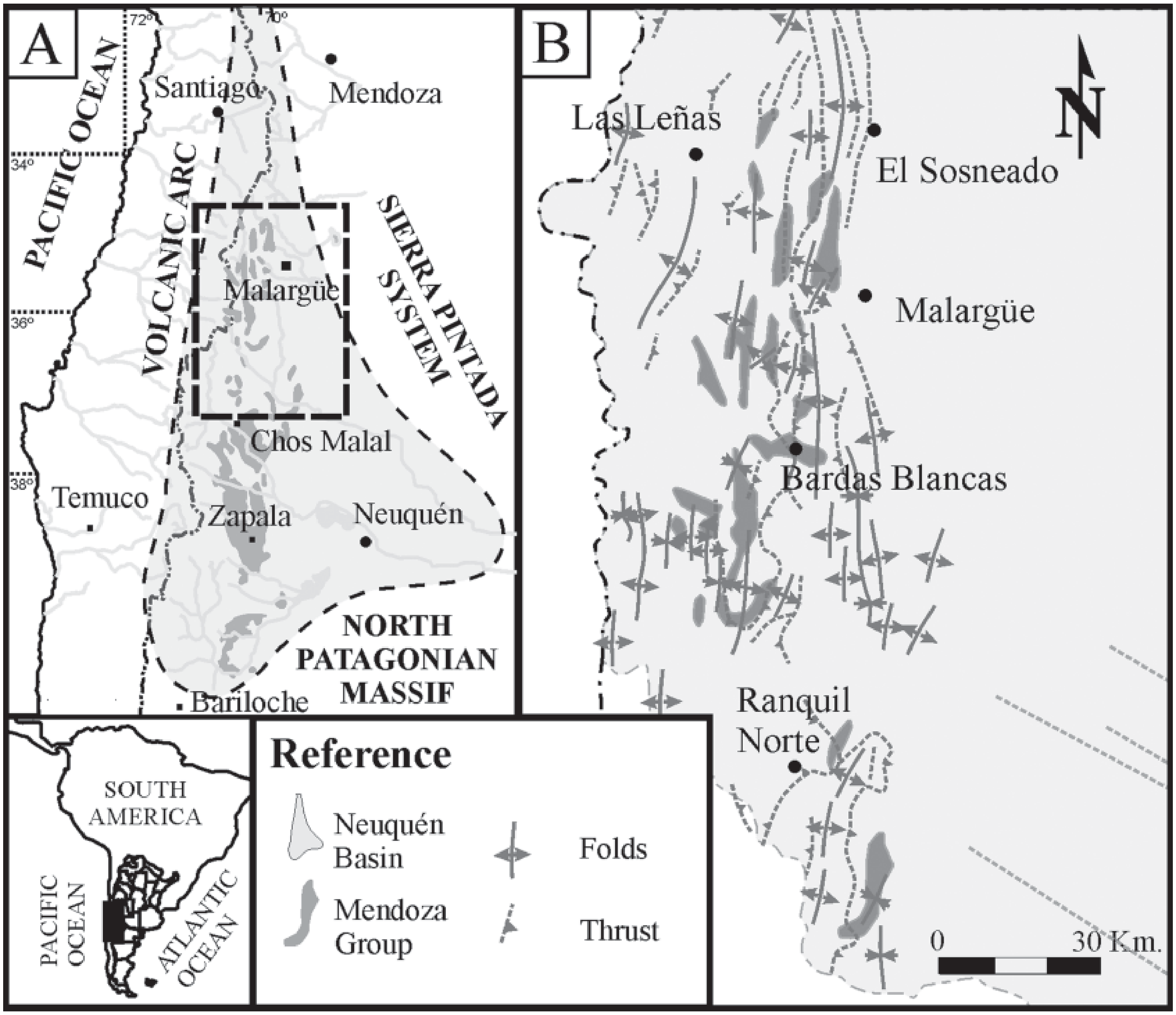
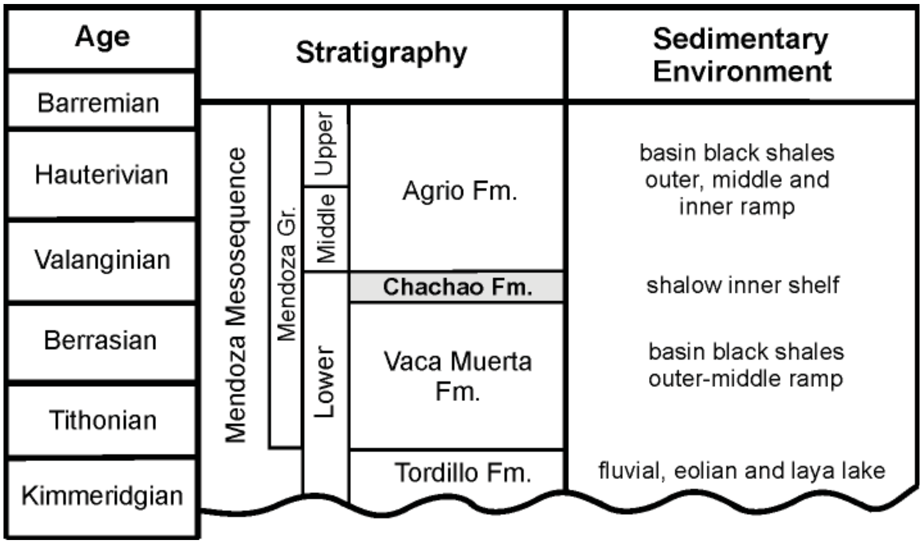


Figure 1. A. Location map of the Neuquén Basin and studied area. B. Outcrops of the Mendoza Group in the Mendoza Province.



Age	Stratigraphy				Sedimentary Environment
Barremian					
Hauterivian	Mendoza Mesosequence	Mendoza Gr.	Upper	Agrio Fm.	basin black shales outer, middle and inner ramp
Valanginian			Middle		
			Lower	Chachao Fm.	shalow inner shelf
Berrasian				Vaca Muerta Fm.	basin black shales outer-middle ramp
Tithonian					
Kimmeridgian				Tordillo Fm.	fluvial, eolian and laya lake

Figure 2. Stratigraphic chart for the Mendoza Mesosequence (Upper Jurassic-Lower Cretaceous) in the Neuquén Basin, Mendoza Province (Modified from Legarreta and Uliana 1991).

to Berriasian), limestones of the Chachao Formation (Valanginian), and euxinic shales of the Agrio Formation (Hauterivian; Legarreta et al. 1993).

The Chachao Formation **(Fig. 3A)** grades basinwards into euxinic shales of the upper part of the Vaca Muerta Formation and it interfingers shorewards with the siliciclastic deposits of the Lomas Bayas Formation (Carozzi et al. 1981). In the northern Neuquén province this unit is stratigraphically equivalent to the Mulichinco Formation (Mombrú et al. 1978), because of the presence of the same ammonite fauna (*Olcostephanus curacoensis* and *Lissonia riveroi*, Leanza et al. 1977) in both units. The presence of *Olcosthephanus* sp. allows to date the unit as Early Valanginian (Rawson 1999).

The Chachao Formation comprises a thin succession (less than 50 meters) of shallow inner shelf skeletal limestones (mainly pelecypods packstones) widespread in the neighbourhood of the Malargüe anticline near the eastern border of the Neuquén Basin. These shell beds are composed of low-diversity molluscan fauna mostly dominated by oysters, other benthonic pelecypods (*Eryphila* sp., *Ptychomia* sp., *Pecten* sp., *Pinna* sp., *Trigonia* sp., *Cucullaea* sp.), occasional ammonites (*Olcosthepanus* sp.) and serpulids (*Sarcinella* sp., *Parsimonia* sp.). According to their biostratinomic features shell beds of the Chachao Formation have been interpreted as parautochthonous to autochthonous skeletal concentrations, mainly of sedimentologic origin (Palma and Lanés 2001). This unit has been studied by Leanza et al. (1977), Mombrú et al. (1978), Legarreta and Kozlowski (1981), Uliana et al. (1979), Legarreta et al. (1981), Carozzi et al. (1981), Palma and Lanés (1998), Palma and Lanés (2001), among others.

METHODS

Standard petrographic, cathodoluminescent and scanning electron microscopic, were used for sample analyses. Thin sections were stained with potassium ferricyanide and alizarin-red-S solutions (Dickson 1965) that allow petrographic investigations of calcite cements, matrix and skeletal components. Cathodoluminescence examination (CL) was carried out using a Technosym cold cathodoluminescent unit operating at 11-16 kV, with accelerating voltage, 200-500 µA beam current. Analyses for CL were performed in the petrography laboratory of the Complutense University of Madrid.

Different samples of *Gryphaea* (11) and granular calcite cements (6) were analysed for their carbon and oxygen stable composition at the Salamanca University Stable Isotope Laboratory (Spain). Results are expressed as per mil deviation from the Pee Dee Belemnite (PDB) international standard.

Chemical analyses (Sr^{++}, Na^{+}, Mg^{++}, Mn^{++}, and Fe^{++}) were performed by standard atomic absorption of 13 samples, which were dissolved in 1 *N* HCL and those with less than 10% insoluble residue were analysed. Some scanning electron microscopy (SEM) of micrite calcite crystal was carried out in order to infer the original mineralogy of precursor lime mud.

DIAGENESIS AND CEMENTS TYPES

The carbonate diagenesis in the Chachao Formation contains many processes with conspicuous effects, including micritization, neomorphism, dissolution, and cementation.

Micrite

Micrite is abundantly present and filling partially or totally the intraparticle and interparticle porosity. This cement is the most abundant in the Chachao Formation. On the base of their morphological features, three types of micrite can be observed: homogeneous, peloidal, and microbioclastic.

The homogeneous micrite consists of a dense mosaic of micron-size calcite crystals, while the peloidal micrite (Fig. 3B) is composed of rounded, spherical or ellipsoidal micritic aggregates. These aggregates are internally structureless, and are commonly rimmed by clear microspar. In the case of the microbioclastic micrite is possible to recognize a mixture of homogeneous micrite and silt-size skeletal debris (Fig. 3C). The micrite, whether homogeneous, peloidal or microbioclastic forms geopetal structure in special gastropods shells and serpulids.

According to Macintyre (1977, 1984) and Marshall and Davies (1981) the peloids and their clear, crystalline rimming calcite are all part of the Mg-calcite marine precipitation process. On the other hand, Chafetz (1986) concluded that such peloids may be bacterially induced marine precipitates, but in the present case we do not have evidence if the peloids are bacterially precipitated. According to Reid et al. (1990) this peloidal micrite can be considered as precipitated peloids. In fact, Macintyre (1985) concluded that Mg-calcite peloids can precipitate from seawater inside of skeletal fragments.

The microbioclastic and peloidal nature of the micrite and its boring-filling character suggest that deposition of the micrite was in the marine phreatic environment. Lighty (1985) suggests that micrite precipitated from seawater, could have either aragonite or high-Mg calcite mineralogy.

Therefore, the Chachao micrite is thus interpreted as being a chemical sediment, precipitated from seawater in the pore spaces, that acts now as a cementing material similar to the high-Mg calcite cement mentioned by Reid et al. (1990).

The luminescent character of the micrite cement display dull-to blotchy orange luminescent features under CL (Fig.

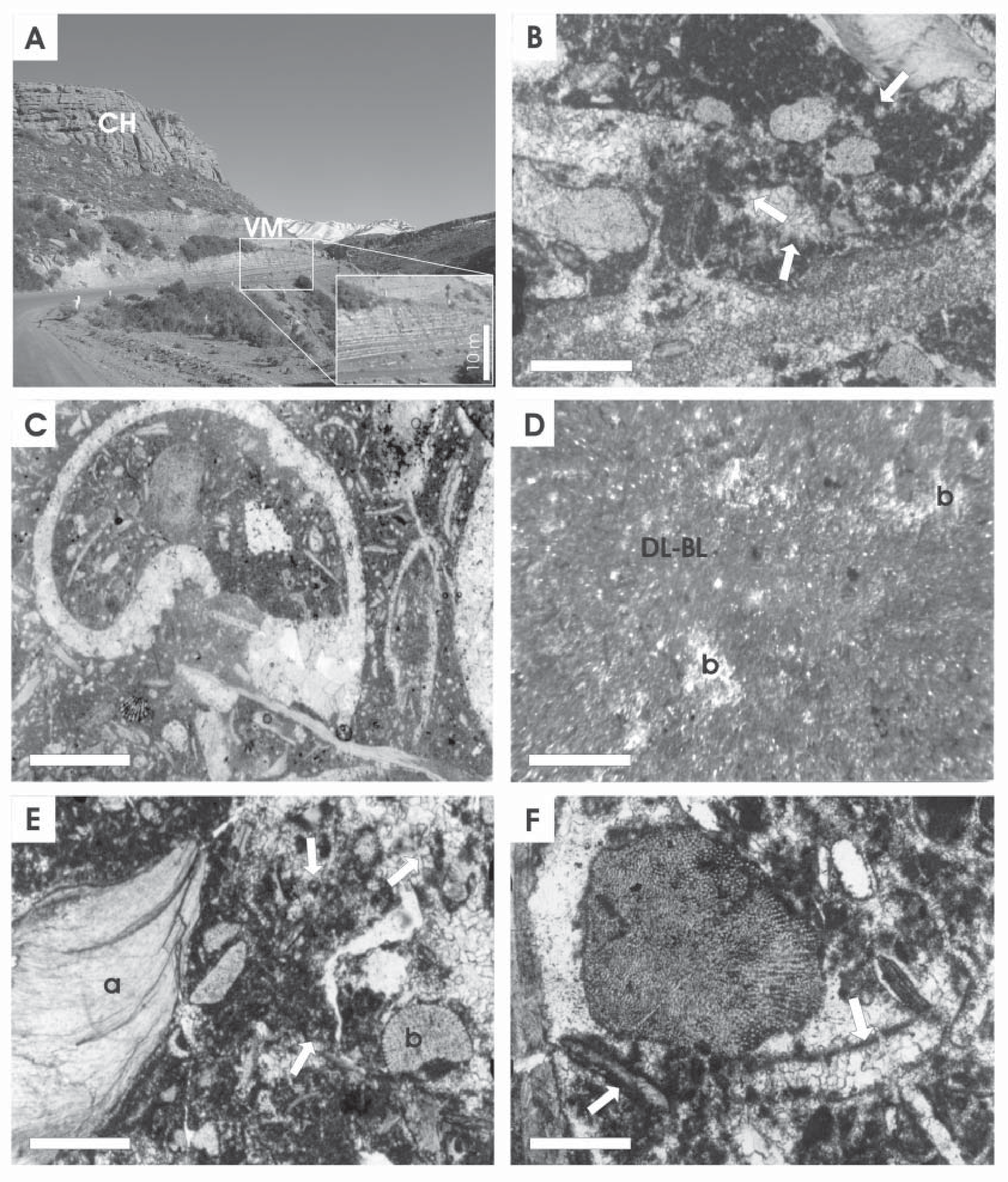


Figure 3. A. Outcrop of Chachao (CH) and Vaca Muerta (VM) formations in the Chihuido area. Malargüe anticline; B. Clotted texture of peloidal micrite (arrow) in intraparticle cavity. Scale bar is 500µm; C. Microbioclastic micrite in microcavity of a gastropod shell. Note the mixture of homogeneous micrite and fragmented small skeletal fragments. Scale bar is 500µm; D. Cathodoluminescence (CL) micrographs showing red motled micrite (DL/BL) and microspar crystals (b) with bright orange luminescent. Scale bar is 250µm; E. Bioclastic wackestone with ostreid fragment (a), echinoderm plate (b) and microspar calcite cement (arrow). Scale bar is 500µm; F. Note micritization of bioclasts. Bivalve fragments (arrow) are dissolved and the molds are filled with granular calcite cement. Scale bar is 500µm.

3D) and their origin is related to diagenetic alteration. Micrite cement is an unstable mineral phase in diagenetic process, thus it has been patchily neomorphosed to microspar (Fig. 3D) and partially has been leached out and formed secondary pores.

Microspar

Microspar calcite crystals appear like a mosaic of anhedral crystals, which contain impurities of clay minerals probably along the irregular intercrystalline boundaries (Fig. 3E). The contact between the turbid micrite crystals and the slightly clear microspar calcite crystals appears gradual thus suggesting a neomorphic origin for microspar (Bathurst 1975). During neomorphism, the loss of Sr^{++}, Na^{+} and the gain of Mn^{++} should be greatest in the meteoric-phreatic zone (Wagner and Mattheus 1982). The microspar calcite cement exhibits a bright orange luminescent characteristics (Fig. 3D).

Micritization

Most skeletal carbonate grains are affected by intensive micritization and some of them (e.g., mollusc fragments) show microboring holes. Micritization of the outer shell and infilling of the molluscs with carbonate cements took place prior to dissolution of the shell (Fig. 3F). Micritization is considered to be an important process in modern marine phreatic environments (Longman 1980). It is important to point out that most micritization occurs near the sediment-water interfase (Kobluk and Risk 1977) but it may be also continue in water depths (May and Perkins 1979). The luminescent character of the micrite envelopes display a bright orange luminescent feature under CL **(Fig. 4B)**.

Isopachous Cement

The isopachous calcite cement is bladed, finally crystalline, inclusion-rich, light brown under plane-polarized light, and show an ondulose extinction. It mostly appear on the outer and inner surfaces of micritized bioclasts, forming an isopachous coating of variable size (Fig. 4A). Isopachous calcite cement is not widely distributed, and is overlain by either micrite or granular calcite. This cement appear in many cases leached, indicating a primary metastable mineralogy (Tucker and Wright 1990).

The isopachous nature of this calcite phase indicates precipitation in the marine-phreatic environment where all the pore spaces are filled with marine water. According to Harris et al. (1985) and James and Choquette (1990a) their inclusion-rich suggest precipitation from marine water. Under CL, the isopachous cement is non-luminescent. (Fig. 4B).

Granular Calcite

The granular calcite is entirely non-ferroan composition. Cement crystals are generally equant and increase in size from pore boundary toward pore centre (Fig. 4A,C). Crystals have sharp to slightly curved intercrystalline boundaries. Under cross-polarized light, the clear calcite shows straight extinction.

This cement filled both intergranular and intragranular pores. Most aragonitic molluscs are represented by molds that are either filled with granular calcite, but some others molluscs are filled with micrite or peloidal micrite, where occasionally occurs as a geopetal structure.

The precipitation of these cement occurred after a period of dissolution, where gastropods and some pelecypods valves have been dissolved. Many of them show dark micritic rims enclosing the central zone of granular calcite filling the fabric.

The granular calcite cement appears to be the last cement generation and has petrographic characteristics of meteoric-phreatic origin (Longman 1980; Scoffin 1987; James and Choquette 1990b). Granular calcite cement overly the cloudy isopachous calcite cement.

The granular calcite cement have variable luminescence, from dull luminescent red/orange (DL) to blotchy luminescent area (BL) and followed by brightly yellow luminescent zone (BY) zoning pattern (Fig. 4B). Oyster shells can appear with preserved original structure or filled with granular calcite crystals (Fig. 4C), which reveals similar luminescent zoning pattern (Fig. 4D).

Syntaxial Cement

Syntaxial overgrowth is represented by small crystals growing coaxially on echinoderm fragments (Fig. 4E). Development of syntaxial cement has restricted distribution. On the presence of micritization, syntaxial overgrowth is absent. This cement may originate in various marine and freshwater environments, as well as under burial conditions (Maliva 1989). The luminescence is quite similar to the granular calcite: dull luminescent red/orange (DL) to blotchy luminescent area (BL) and followed by brightly yellow luminescent zone (BY) (Fig. 4F).

INTERPRETATION AND DISCUSSION

The interpretation of the sedimentologic, petrographic, and cathololuminesce data in conjunction with data from analogous studies, indicates a complex diagenetic history for the Valanginian deposits. It has been assumed that cathodoluminescence in carbonate rocks is mainly derived from the incorporation of manganese into the calcite lattice, with the ion commonly acting as a cathodoluminescence quencher (Meyer 1974; Fairchild 1983). It is important to point out that luminescence is not only controlled by the

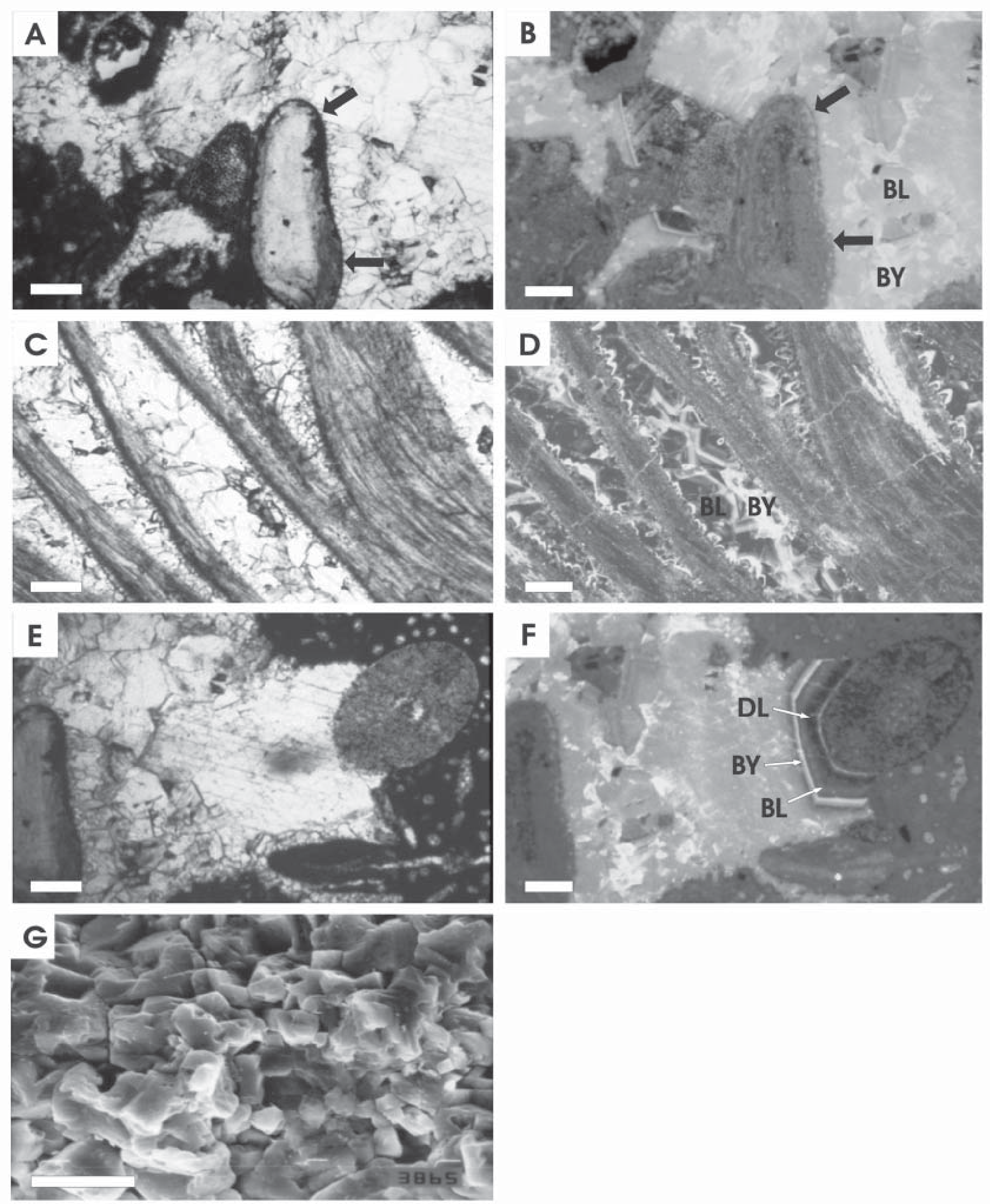


Figure 4. A. Transmitted light of originally aragonite bivalve and early isopachous calcite cement (arrow). Scale bar is 250µm; B. Red luminescent micrite envelope of aragonite bivalve. Dull or non-luminescent isopachous calcite cement (arrow). Note the bright luminescent granular calcite cement (BY) and blotchy luminescent cement (BL). Scale bar is 250µm; C. Transmitted light of granular calcite cement inside of open foliated structure of oyster shell. Scale bar is 250µm.; D. Bright-luminescent (BY) and blotchy luminescent (BL) granular calcite cement inside of open foliated structure of oyster shell. Scale bar is 250µm. E. Transmitted light of syntaxial rim cement on echinoid fragment. Scale bar is 250µm; F. Close view of E: Note the complex dull (DL) to blotchy (BL) and bright luminescent (BY) zones of syntaxial rim cement on echinoid fragment. Scale bar is 250µm; G. Scanning electron micrographs of micrite crystals. Note the unpitted surface crystals. Scale bar is 10µm.

variations in the Mn^{++} and the Fe^{++} fluid concentrations, but also by crystals growth rates (Reeder and Grams 1987).

The bright orange luminescence of micrite envelopes and micrite cement suggest that both should have had the same initial composition, probably high magnesium calcite. Alternatively the luminescence might be interpreted as having formed in the same way and at the same time on the basis of their similarity in luminescent pattern; this might be produced by diagenetic alteration, as well as the luminescent features of the microspar calcite cement.

The isopachous cement on skeletal and non-skeletal particles is generally interpreted as typical of a marine phreatic environment, where all the pore spaces are filled with marine water (Harris et al. 1985; Prezbindowski 1985; James and Choquette 1990a). The isopachous cement and their non-luminescent features, together with the fact they occur as the first stage cement before compaction, would indicate a marine phreatic origin (Frank et al. 1982; Grover and Read 1983).

The granular calcite cement has variable luminescence according to distinct pattern of zoning, which represent phases of crystal growth. In fact, each zone represents the precipitation of calcite from pore waters with different chemical composition (Meyers 1991; Machel 2000) from dull light brown/red luminescent (DL) to blotchy luminescent area (BL) and followed by brightly yellow luminescent (BY) zone. A quite similar patron of luminescence was observed in syntaxial overgrowth and in some dissolution cavities.

These variations in the luminescence characteristics are probably cause by episodic incorporation of Mn^{++}. Irregular boundaries between alternating zones suggest either rapid changes during temporal interruption of crystal growth.

The dull/blotchy/bright CL transition is generally interpreted as being caused by a decrease in redox potential (Eh), under conditions of progressive marine burial meteoric-phreatic diagenetic environment (Drever 1982; Grover and Read 1983).

This zonation in luminescence suggests geochemical variations within pore fluids system. This bright yellow luminescence of granular calcite cements were probably precipitated under suboxic conditions (Frank et al. 1982).

In general, the sediments originated as shallow marine were altered by meteoric water, mainly in a phreatic realm during a first stage of diagenesis. This second stage of diagenesis is interpreted to have occurred in a meteoric-phreatic realm.

CHEMICAL ANALYSIS OF MICRITE

In order to know about original mineralogy of precursor lime mud 26 chemical analysis were carried out. It is important to point out that modern carbonate muds are usually formed by physical and biochemical precipitation of aragonite and high–Mg calcite in sea water or by abrasion and desintegration of carbonates grains. During diagenesis these metastable minerals are transformed into stable carbonates with increase of crystal size due to aggrading neomorphism (Bathurst 1975).

According to Lansemi and Sandberg (1984, 1993) the microfabric and composition of micrites may be related to the original mineralogy of precursor lime mud. Aragonite precursor micrites (ADP micrites) are characterized by a coarser microfabric than the calcite dominated precursor micrites (CPD). Under SEM, APD micrites display aragonite relics and pitted crystals surfaces, whereas CDP micrites show an absence of aragonite relics and unpitted crystals surfaces. In our case, we observed that micrite are characterized by an unpitted crystal surfaces and absence of aragonitic relics (Fig. 4G). These observations indicate that the original mineralogy of micrite might be calcite-dominated, which can be supported by their low Sr^{++} contents.

The Sr^{++} concentration ranges from 320-720 ppm, with an average of 492 ppm suggesting that the micrite was originally Mg-calcite rather than aragonite, since transformation of aragonite to calcite is usually associated with the release of Sr^{++} (Lansemi and Sandberg 1984).

Sr^{++} concentrations from modern marine magnesian calcite are greater than 800 ppm, whereas aragonite cements can contain 8,000-10,000 ppm Sr^{++} (Tucker and Wright 1990; Major and Wilber 1991; Carpenter and Lohmann 1992), but in our case the Sr^{++} content of the micrite cements is low (average of 492 ppm). The strontium concentration is related probably to changes in the mineralogical composition of original components, and suggests calcitic rather than aragonitic original mineralogy (e.g., Lansemi and Sandberg 1984). These authors suggest an average of 800 ppm of Sr^{++} for original aragonitic micrites, while calcitic micrites have values just around of 400 ppm of Sr^{++}. According to SEM features as well as geochemical data (Sr^{++}) the original calcareous mud could have been calcite dominated (CDP).

The Na^{+} concentration ranges from 94-383 ppm, with an average of 192 ppm and indicates a loss of Na^{+} (Land and Hoops 1973). The lower concentration of Na^{+} together with decreasing of Sr^{++} is normal during the meteoric diagenesis (Land and Hoops 1973; Randazzo et al. 1983). The lost of Na^{+} concentration through the influence of meteoric waters (Folk and Land 1975) could favour the dolomite formation.

The Mg^{++} concentration ranges from 1688-7055 ppm, with an average of 2973 ppm. High values of Mg^{++} concentrations are related to a specific level of the stratigraphic section which appear dolomitized. Dolomites display finely to medium planar-e crystals, and are basically iron-free. Under transmitted light, dolomite crystals are clear to slightly cloudy. Many dolomite crystals show evidence of dissolution (Palma and Matheos 1997).

The Fe^{++} concentration (260-490 ppm) is attributed to the incorporation of Fe^{++} during the transformation of Mg-calcite to calcite (Richter and Füchtbauer 1978) and probably to the presence of some impurities in the micrite such as clays and iron oxide.

The Mn^{++} concentration ranges from 154-497 ppm with an average of 352 ppm is attributed to the diagenetic modification of the micrite during meteoric diagenesis (Pingitore 1978). Diagenetic modification as consequence of oxidizing seawater are known to contain slow concentrations of Mn^{++} and Fe^{++} (James and Choquette 1990a).

OXYGEN AND CARBON COMPOSITIONS

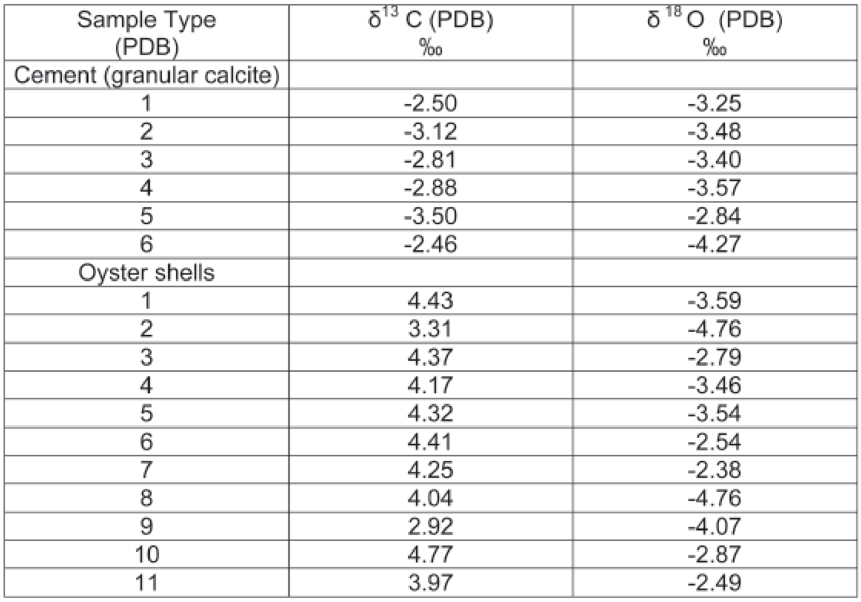
Samples from granular calcite cements and from the oysters valves were analysed for their oxygen and carbon isotopic composition **(Table 1)**. The $\delta^{18}O$ values of the granular calcite cements ranges from –2.84%0 to –4.27%0 PDB and the $\delta^{13}C$ values vary between –2.46%0 and –3.50%0 PDB. These cements are interpreted to be products of early meteoric-phreatic diagenesis (Veizer 1992). The fauna shows a wide range of preservation state. Oysters may be represented either by entire or fragmented shells, left/right valves sorting and preferred orientation. Valves for analysis were picked out under binocular microscope in order to avoid dissolution and growth of calcite crystals, inside cavities and between laminae of the shell structure. Out of these areas the shell structure appeared preserved. Studied valves are composed of low-magnesian calcite as demonstrated by x-ray diffraction (Dodd and Stanton 1981). The $\delta^{13}C$ content of the analysed oyster samples varies between 2.92 %0 and 4.77%0, while $\delta^{18}O$ composition mainly ranges from about –2.38 %0 to –5.22 %0.

The lighter $\delta^{18}O$ values can be explained by the dilution of the marine water with a fresh water influx. The narrow range of positive values of $\delta^{13}C$ from well preserved calcitic (LMC) oyster shells are probably related to the original marine signal, which suggests a closed diagenetic system for carbon (Kaufman and Knoll 1995). Investigations on modern molluscs have demonstrated that carbon isotopic composition of the shells is controlled by different parameters (Killingley and Berger 1979; Krantz et al. 1987). The $\delta^{13}C$ content could be related to physiological growth changes, so that the $\delta^{13}C$ enrichment shows in the oyster shells may be related to a disequilibrium effects (Krantz et al. 1987). On the other hand the $\delta^{13}C$ results in the oyster shells show more positive values than other oysters of similar age (Krantz et al. 1987). According to this it is difficult to explain this result but might be due to environmental fractionation or diagenetic alteration.

CONCLUSIONS

The diagenesis of the Valanginian Chachao Formation can be summarized as follows: Marine cements in the Chachao Formation occur as micrite and isopachous cements. Fabric neomorphism and chemical reequilibration of micrite

Table 1. Carbon and oxygen composition of granular calcite cement and of the oyster shells. Isotopes values are reported relative to PBD standard.



Sample Type (PDB)	$\delta^{13}C$ (PDB) ‰	$\delta^{18}O$ (PDB) ‰
Cement (granular calcite)		
1	-2.50	-3.25
2	-3.12	-3.48
3	-2.81	-3.40
4	-2.88	-3.57
5	-3.50	-2.84
6	-2.46	-4.27
Oyster shells		
1	4.43	-3.59
2	3.31	-4.76
3	4.37	-2.79
4	4.17	-3.46
5	4.32	-3.54
6	4.41	-2.54
7	4.25	-2.38
8	4.04	-4.76
9	2.92	-4.07
10	4.77	-2.87
11	3.97	-2.49

cements occurred as consequence of influence of meteoric water. Low Sr^{++} content (average 492 ppm) and SEM feature of the micrite argue that the original calcareous mud could have been calcite dominated (CDP).

Leaching and neomorphism (microspar) occurred when meteoric waters flowed through Chachao sediments during shallow burial. Cathodoluminescence reveals fine scale oscillatory zonation within granular calcite cement. Concentric–zoning pattern of alternating dull, and blotchy- to bright luminescent zones is interpreted to result from varying Mn^{++}/Fe^{++} ratio, and interpreted as being caused by a decrease in redox potential (Eh), under conditions of progressive marine burial meteoric-phreatic diagenetic environment.

The depleted $\delta^{13}C$ and $\delta^{18}O$ of the analyzed granular calcite cement can be related to influences of phreatic meteoric water. Griphaeids isotope data indicate that most of the shells have been altered by meteoric water, with depleted oxygen content, whereas shells with the heaviest $\delta^{13}C$ isotopic composition are probably related to the original marine signal, this suggesting a closed diagenetic system for carbon.

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