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DOLOMITIZED TIDAL CYCLES IN THE AGUA DE LA MULA MEMBER OF THE AGRIO FORMATION (LOWER CRETACEOUS), NEUQUÉN BASIN, ARGENTINA

Maisa A. TUNIK [1], Pablo J. PAZOS [2], Agnes IMPICCINI [3], Darío LAZO [4] and María Beatriz AGUIRRE-URRETA [4]

[1]Laboratorio de Tectónica Andina, Universidad de Buenos Aires. CONICET. Actualmente en: CIMAR - Universidad Nacional del Comahue. Av. Buenos Aires 1400, Neuquén. Argentina. E-mail: maisa_tunik@yahoo.com.ar
[2]Universidad de Buenos Aires. Ciudad Universitaria, Pabellón 2, 1428 Buenos Aires. Argentina.
[3]Universidad Nacional del Comahue, Av. Buenos Aires 1400, Neuquén, Argentina.
[4]Laboratorio de Bioestratigrafía de Alta Resolución. Universidad de Buenos Aires. Ciudad Universitaria, Pabellón 2, 1428 Buenos Aires. Argentina.

Abstract: The Agrio Formation (Valanginian to early Barremian) is a siliciclastic and carbonate unit of the Neuquén Basin in west central Argentina. A conspicuous 20 m thick dolomitized section near the top of the upper Agua de la Mula Member of the Agrio Formation was identified for the first time in this unit. The analyzed section is composed of dolostones with scarce siliciclastic intercalations. A tidal flat environment with high-frequency cycles is suggested for the measured section. Petrography, SEM, X-Ray, EDAX and cathodoluminiscence analyses showed two different dolomitization processes. The first one comprises early mimetic and non mimetic dolomitization on ooids, bioclasts and early marine cements. The second one reveals precipitation of dolomite cement. The mimic dolomitization indicates that this process took place before the inversion from aragonite to calcite, or from low magnesium calcite to high magnesium calcite. The dolomitization should have been soon after the deposition. The presence of dolomite cement is probably related to a high concentration of Mg^{2+} coming from sea water flushing into highly porous sediments mixed with fresh waters from the continent. This is suggestive of a change of diagenetic environment from marine to meteoric, probably during sea level changes. A model that explains these processes is the shallow seawater dolomitization model. This model proposes that dolomitization is triggered by the drive of large amount of seawaters through the sediments.

Resumen: La Formación Agrio es una unidad clásica del Cretácico Inferior de la Cuenca Neuquina que se depositó en un ambiente de rampa carbonática con influencia mareal. Por primera vez para esta unidad se describe en el área de Mina La Continental, un espesor de casi 20 m de bancos dolomitizados. Estas rocas son *grainstones* y *packstones* con distintos tipos de dolomitización. Los análisis petrográficos, de SEM, EDAX, rayos X y de cátodoluminiscencia han permitido identificar dos procesos que llevaron a la presencia de dolomita en los sedimentos. El primero de ellos está asociado con una dolomitización de tipo mímica y no mímica de las oolitas, bioclastos y los cementos marinos (micrítico, de borde y granular). El segundo está relacionado con la depositación de dolomita primaria. La presencia de dolomitización preservando la fábrica de las oolitas, bioclastos y cemento, sugiere que la misma se desarrolló antes de la inversión de aragonita a calcita o de calcita magnesiana alta a baja, es decir que la dolomitización habría ocurrido rápidamente luego de la depositación. Asimismo, la presencia de cemento dolomítico primario estaría

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relacionada con una abundante disponibilidad de Mg^{2+} producto de la gran cantidad de circulación de aguas porales en sedimentos con buena porosidad y permeabilidad mezclado con aguas provenientes del continente e implica un cambio en las condiciones de diagénesis de marinas a meteóricas. El modelo propuesto es conocido como modelo de dolomitización de agua somera (*shallow seawater dolomitization model*), donde el agua marina que circula producto de las mareas o cambios en el nivel del mar es la portadora del Mg^{2+} necesario para la generación de la dolomita.

Keywords: Ooids, Dolomitization, Tidal environment, Agua de la Mula Member, Neuquén Basin.
Palabras clave: Oolitas, Dolomitización, Ambiente mareal, Miembro Agua de la Mula, Cuenca Neuquina.

INTRODUCTION

The Agrio Formation is an Early Cretaceous (Valanginian to Early Barremian) unit extensively exposed in the Neuquén Basin. Previous lithofacies analysis of the upper Agrio Formation suggested an open-marine ramp environment with high-frequency sedimentary cycles (Spalletti *et al*., 2001) and tidal influence (Pazos *et al*., 2007). Detailed petrographic studies of the Agrio Formation have shown several isolated dolomitized strata. In this work we present for the first time the results of the analysis of a 20-m thick dolomitized section recognized in the upper Agrio Formation (Agua de la Mula Member) at Neuquén Basin. The analyses of the dolomitized section will contribute to constrain the sedimentary environment and could constitute a new reservoir prospect for the oil industry.

Previous studies of dolostones from the Agrio Formation were performed by di Paola (1987, 1990) in the lower Agrio Formation (Pilmatué Member) in the Cerro Marucho area. This author briefly described idiotopic to subidiotopic dolostones from a fresh and mixed phreatic environment.

GEOLOGICAL SETTING

Stratigraphic Framework

The Neuquén Basin is located in west-central Argentina, mainly in the Neuquén and Mendoza provinces and is an important Meso-Cenozoic depocentre (Fig. 1). Its fill comprises more than 7000 m of continental and marine siliciclastic, carbonate, and evaporitic deposits of Latest Triassic to Late Tertiary age (Legarreta and Gulisano, 1989). During the Jurassic and Early Cretaceous, the basin formed a shallow embayment connected to the Pacific Ocean throughout a volcanic arc at its western margin. The infill of the Neuquén Basin during the Late Jurassic - Early Cretaceous is represented by both marine and continental deposits that constitute the Mendoza Group (Fig. 1). The marine Tithonian-Early Valanginian is represented by rich, organic, dark shales with calcareous nodules (Vaca Muerta Formation). During the Early Valanginian the paleogeography was complex, especially during a regressive phase when continental and volcaniclastic beds and marine shales of the Mulichinco Formation (Legarreta and Gulisano, 1989) and carbonate deposits of the Chachao Formation (Legarreta and Kozlowski, 1981) were deposited. A transgressive phase occurred in the late Early Valanginian with the accumulation of the shales and limestones of the Agrio Formation. This last unit is covered by to the evaporites and limestones of the Huitrín Formation, indicating the regression event during Barremian times.

The Agrio Formation crops out extensively from Mendoza to southern Neuquén. It was divided by Weaver (1931) into three units that are regarded as members. Two of these members have recently been named: Pilmatué for the lower Member and Agua de la Mula Member for the upper one (Leanza and Hugo 2001). Both the lower and upper members are marine. The Pilmatué Member, 600-700 m thick, is composed of thick dark shales interbedded with sandy limestones, packstones and wackestones, while the Agua de La Mula Member is composed largely of black to dark shales in the lower part and grey calcareous shales interbedded with sandy limestones in the upper part, reaching 500-600 meters. The middle Avilé Member is sandy, much thinner (20-40 m thick), and consists of light-cream colored, medium- to coarse-grained sandstones. It is fluvial and aeolian in origin, and marks a significant relative sea-level fall across the basin, providing an excellent marker horizon (Gulisano and Gutiérrez Pleimling 1988; Rossi, 2001; Veiga *et al.*, 2002). Fossil invertebrates are abundant in the Pilmatué and Agua de la Mula members, and studies on ammonoids combined with nannoplankton and palynology have provided a very good biostratigraphic framework for the whole unit that spans from the Valanginian to the Early Barremian (Aguirre-Urreta *et al.*, 2005, 2007).

Sedimentologic Framework

The sedimentary succession at Mina La Continental (Fig. 1) comprises 27.4 m of dolomitic *grainstones* and *packstones* and scarce sandstones associated with mudstones. This succession belongs to the uppermost part of the Agua de la Mula Member of the Agrio Formation. Pazos *et al.* (2007) distinguished a general arrangement of sedimentary cycles based on a bed by bed analysis. Each cycle shows a thinning-upward stacking pattern that records the progradation of a tidal flat system, ranging from subtidal carbonates to almost pure siliciclastic deposits of an intertidal environment and to laminites generated under upper intertidal-supratidal conditions (Pazos *et al.*, 2007) (Fig. 2).

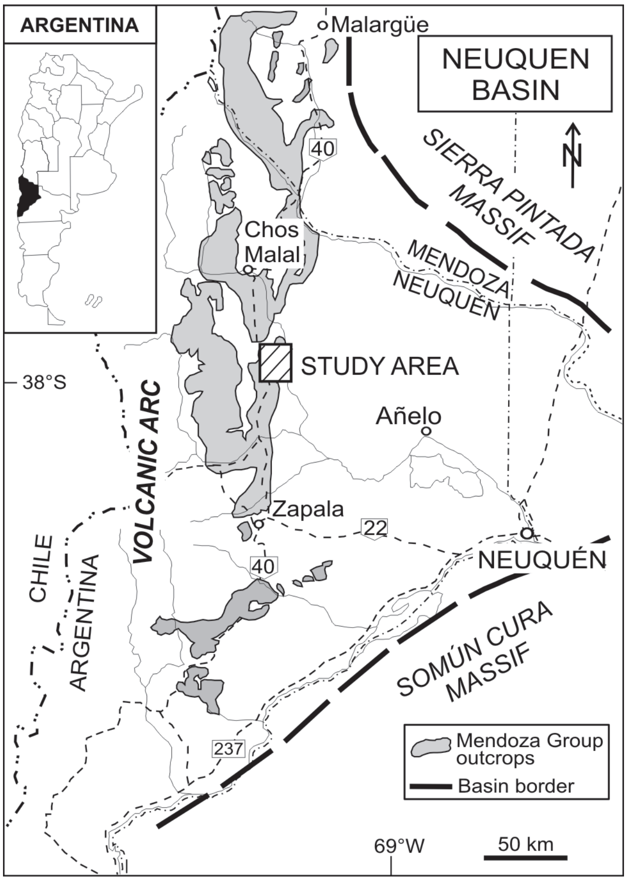


Figure 1. Location map of the study area showing the main outcrops of the Mendoza Group.

Subtidal facies. a) Brownish to gray dolomitic grainstones containing valves and ooids, or purely ooids in beds usually decimetric in thickness and sandwiched between claystone layers. These deposits indicate very shallow and agitated waters during reduced siliciclastic input. Ooids were deposited in small tidal bars during flood tidal currents. The regional and offshore palaeocurrent pattern is bipolar in this interval showing onshore unidirectional flows. b) Channeled or unconfined dolo-oolitic grainstones with small ripples, mega ripples and minor herringbone structures, cross-stratification and strongly fragmented bioclasts are also present. Reactivation surfaces are frequently observed; they are documented by the presence of tiny mud drapes not always well preserved. However, overall palaeocurrent pattern indicates less preservation of the offshore (ebb current) than the onshore (flood) part of the tidal cycle. Palaeocurrents indicate predominant flood orientation in the lower part of the succession and more variable to ebb orientations upward. Herringbone structures are rare while mud drapes are very common. These deposits record subtidal channels, high energy conditions and reworking of bioclasts in a shallow subtidal environment. c) Bioclastic accumulations or coquinas, composed of trigoniid valves, or mixtures of ooids and strongly fragmented ostreids on a siliciclastic matrix. The samples Lc2.8, Lc3, LcR, Lp, Lc4, Lc4.18 and Lc7 belong to the subtidal facies.

Lower Intertidal facies. This facies is composed of fine calcareous sandstones organized in a fining- and thinning- upward trend. This facies records sedimentation by unidirectional or oscillatory flows and settling from suspension during periods of slack waters on the tidal flat.

Bioclastic accumulations are very frequent and vary from well-packed gastropod coquinas, sometimes with fragmented ostreids and trigoniids and dolo-oolitic grainstones with scarce bioclasts. However, strongly fragmented shells and isolated gastropods are distributed in several levels of this

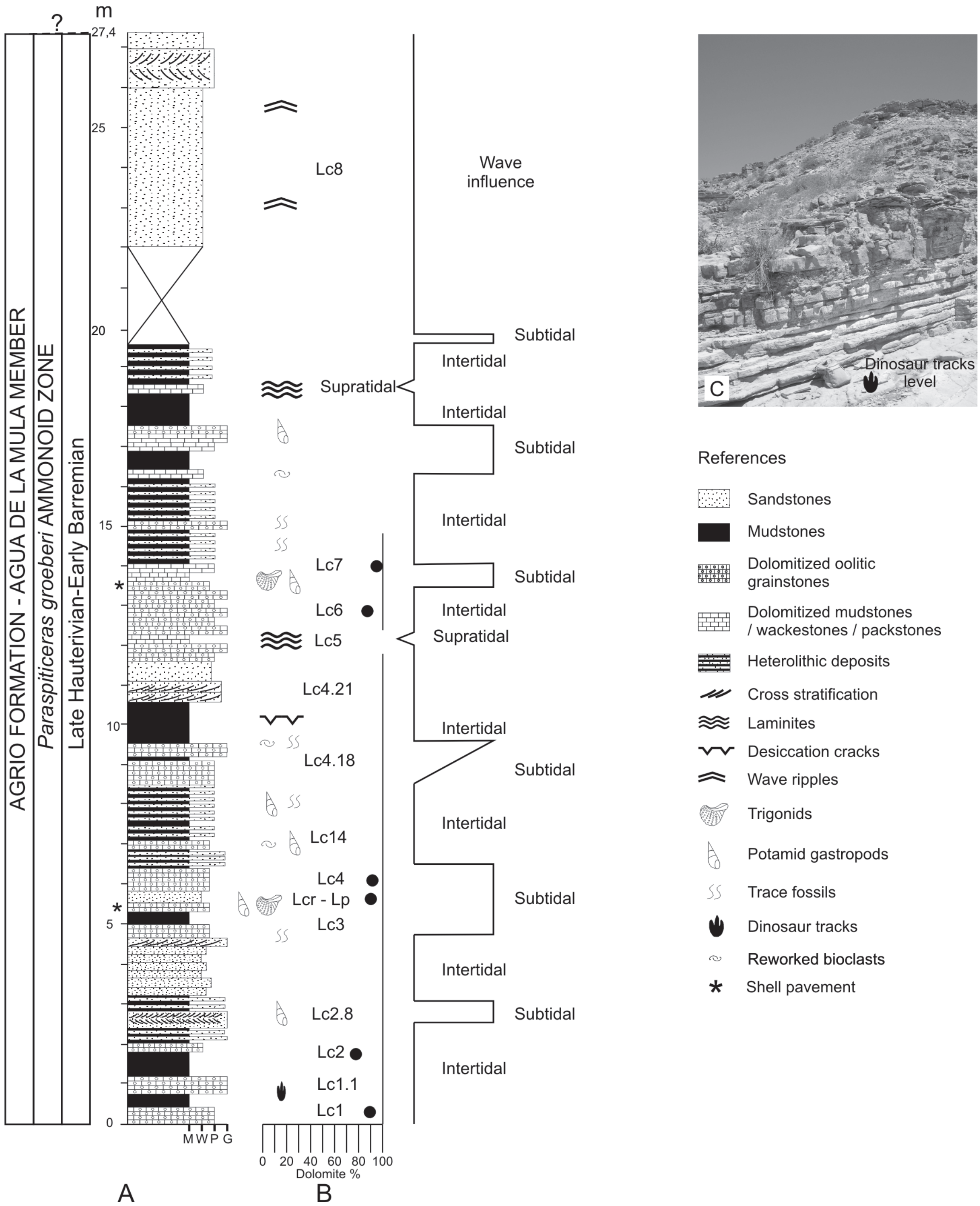


Figure 2. a) Detailed stratigraphic section of the upper part of the Agua de la Mula Member (Data from Pazos *et al.*, 2007) b) Percentage of dolomite determined by X-Ray c) Outcrop view of the of top of the Agua de la Mula Member, Agrio Formation.

facies. Locally gastropods appear in lenticular beds interpreted as small tidal channels that concentrate bioclasts mixed with reworked ooids. The samples Lc1, Lc1.1, Lc2, Lc14 and Lc6 belong to this subfacies.

Upper intertidal to supratidal facies. This interval usually records the upper part of fining-upward trends. It contains abundant calcareous mudstones and intensely bioturbated siltstones and claystones. Relictic stratification includes heterolithic ripples with asymmetric to symmetric profiles. In this upper intertidal facies mud cracks and flattened ripples and possible syneresis cracks were recognized. All these features are indicative of intermittent exposition of the mud-dominated flats, although syneresis cracks also commonly occur in the subtidal realm.

Algal-microbial mats packages 10 to 20 cm thick were identified associated with the upper intertidal facies. They are interpreted as upper intertidal to supratidal deposits. The sample Lc5 belongs to this subfacies.

Macrobenthic Assemblage and Paleoecological Implications

The analyzed macrobenthic invertebrates derive from the uppermost part of the Agua de la Mula Member of the Agrio Formation at Mina La Continental. Macrofossils are extremely scarce at this locality, but trace fossils are very common (Pazos *et al*., 2007). Although no ammonites have been collected within the studied beds, the age was established by lateral correlation of sections. The studied specimens most probably proceed from the *Paraspiticeras groeberi* zone of Latest Hauterivian-?Early Barremian age (see Aguirre-Urreta *et al*., 2007). Only two distinct shells beds have been recorded showing similar taxonomic composition (Fig. 2). Gastropods, bivalves, encrusting bryozoans, and serpulids were recorded. Gastropods are more abundant than bivalves. They represent condensed macrobenthic assemblages suggesting that environmental change was more rapid relative to net rates of sediment aggradation, and that taxa from successive habitats formed a single pavement (Kidwell and Bosence, 1991). Therefore, pavements have a relatively high degree of time-averaging due to combined erosion and omission. Most of the shells show a high degree of dissolution, abrasion, and encrustation and variable degrees of disarticulation and fragmentation. The overall taphonomic imprint suggests a parautochtonous origin with a low degree of transport.

The presence of multilamellar cheilostome masses along with serpulids on gastropod and bivalve shells are reminiscent of some occurrences of recent bryozoan-serpulid buildups associated with strong variations in salinity in lagoons (Bone and Wass, 1990; Freitas *et al*., 1994). The explosion of these buildups has been related to increased freshwater run-off and lowering of the salinity (Bone, 1991; Freitas *et al*., 1994; Taylor *et al*., 2009).

Taking these examples together with the paleoecological data of the observed gastropods and bivalves (potamids and trigonids), it seems that salinity fluctuated in the uppermost levels of the Agua de la Mula Member and that salinity decreases were able to trigger bryozoans and serpulids aggregations on bivalve and gastropod shells. This paleoecological analysis supports a tidal flat environment with mixed continental/marine waters.

PETROGRAPHY

Samples and Methods

Standard petrographic analyses of ten thin sections were performed to characterize the rock composition, paragenesis of cements, and sequence of diagenetic processes. Petrographic analyses include the description of the constituents, the amount of dolomite, dolomite type, porosity type, and diagenetic features. Thin sections were stained with a potassium ferricianide/alizarine red S solution (Dickson, 1965) for distinguishing dolomite and calcite.

Mineral identifications were made by X-Ray diffraction of the bulk sample and the clay fraction ($<2\mu$m) on seven samples (Table 1). Whole-rock samples were crushed and ground to a $<$ 200 mesh powder in a McCrone mortar. Clay mineralogy was determined via separation of the clay fraction (<2 μm) by sedimentation after overnight dispersion in distilled water, followed by centrifugation of the suspension. The clay particles were dispersed by ultrasonic vibration.

Minerals were identified using a Rigaku DMAX-2D diffractometer using Cu-K radiation, run at 40 kV and 20 mA, at the Centro de Investigaciones en Minerales Arcillosos de la Universidad Nacional del Comahue, Neuquén. Bulk rock mineralogy was analyzed from 3° to 60°2θ on unoriented powder. The clay fractions (<2 μm, air-dried, glycol-solvated and heated) were analyzed from 2° to 40°2θ, at 2° 2 /min. The X-Ray reflections were evaluated with Rigaku software.

Scanning electron microscopy (SEM) analyses were performed on 6 gold-coated freshly broken surfaces using a Philips SEM 515 microscope with an accelerating voltage of 20 kV and with an attached energy dispersive analyzer (EDAX) at the Universidad Nacional del Comahue.

Catodoluminescense analysis was carried out with a cold cathode microscope TECHNOSYN MKIII at the Laboratorio de Petrografía y Catodoluminiscencia at the Centro de Investigaciones Geológicas, La Plata.

SAMPLE #	MINERALOGY (total sample in %)
LcR	D(90), Q (6), F (4), Y (T), I (T), Py (T)
Lc1	D(91), P (4), Q (2), C (2), B (1), Y (T), Mg(T), Py (T)
Lc2	D(78), I (9), Q (5), P (4), F(3), B(1), Cl (T), Y (T), Mg(T), Py (T)
Lc4	D(91), C (9), Q (T), P (T), Y (T), Mg(T), Py (T)
Lc6	D(88), Q (8), P (2), I (2), C (T), Mg(T), Py (T)
Lc7	D(96), Q (4), P (T), Mg(T), Py (T)

Table 1. Mineralogy of selected samples analyzed by XRD. References: D: Dolomite, C: Calcite, Q: Quartz, P: Plagioclase, F: Alkali-feldspar, I: Illite, B: Barite, Y: Gypsum, Mg: Magnetite, Py: Pyrrothite, Cl: Chlorite, T: Trace.

Mineralogy

Carbonate mineralogy was measured using X-Ray diffraction in seven powdered carbonate samples using quartz as an internal standard. Semiquantitative estimates of relative percentages of minerals from whole-rock samples were made using the intensity of the diffraction peaks by integration of the area.

Dolomite was distinguished by diagnostic reflections at 30.96, 41.14, 50.55 and 51.19°2θ (Fig. 3). The dolomite percentage, from 78% up to 96% (Fig. 2, Table 1) was determined using the relative decrease in the intensity of the peaks of X-Ray diffraction and the integration of areas of each reflection. The common accessory mineral is quartz reaching 8% and the plagioclase, found in several samples, is oligoclase. Also alkali feldspar was identified. Relative abundance of calcite was observed in sample Lc4. The clay minerals of the grainstone (Lc2 sample) consist of illite and trace of chlorite.

The dolomitized strata average 89% dolomite (n=6). Possibly, there is a stratigraphic control on dolomite distribution and abundance. The subtidal facies show higher percentages of dolomite (92.3%) than the intertidal facies (85.6%). However, the scarce number of samples must be taken into account.

Petrographic Analyses

The analyzed samples are medium to coarse-grained grainstones to packstones (Dunham, 1964) showing an important replacement by dolomite. In addition, bladed and blocky isopachous and granular void-filling dolomite are quite common. Scarce late blocky calcite was also identified. Variable amounts of siliciclastic material which increases upwards in the analyzed section were identified. According to Sibley and Gregg (1987) the samples can be classified as polimodal, planar-s dolomite with mimetic (Fig. 4a, b) or non-mimetic textures (Fig. 4c). Replacive dolomite with mimetic textures preserves the texture, fabric and crystallographic orientation of the precursor phase (Budd, 1997). Such textures are seen in the studied oolitic grainstones and in some bioclasts (Fig. 4b) and can also be called fabric-preserving dolomite. Replacive dolomite with non-mimetic texture that preserves the external outlines of the precursor grains and the depositional fabric of the host rock but not the internal structures of individual grains (Budd, 1997) can also be called non fabric-preserving dolomite. Non-mimetic dolomite was observed replacing bioclasts and filling voids in the studied samples.

The subhedral dolomite crystals have planar compromise boundaries (Fig. 4d) suggesting faceted crystal growth, which characterizes dolomite crystals formed during early diagenesis (Warren, 2000). Gregg and Sibley (1984) suggested that mosaics with planar crystal boundaries indicate growth temperatures below 50°C.

As stated by Budd (1997), the altered rock looks exactly like the precursors, and then the fact that dolomitization can only be identified by mineral stains or X-Ray analysis, as occur with the analyzed samples. Dawans and Swart (1988) and Vahrenkamp and Swart (1994) suggested that mimetic replacement of entire rocks correlated to an absence of mud, high porosity and high permeability and thus active fluid flow and faster crystal growth.

Under cathodoluminiscence, three luminescent zones can be identified (Fig. 4g, h). Zone 1 (1500 ppm Mn^{2+}) corresponds to bright orange ooids, some with bright yellow in the core. Zone 2 is identified as an early marine isopachous rim cement coating ooids with a marked luminescent. Finally, zone 3 is a cement with low to very low luminescence only observed in some samples.

Framework Grains. The oolites contain well sorted ooids with sizes ranging between 0.1 and 0.5 mm. They are micritic with thin concentric lamination and variable types of nucleus. They can be classified as Type 1 of Strasser (1986) as well rounded micritic ooids with tiny laminated cortices. The laminae consist of isometric, anhedral to subhedral crystals

1-5 μ in diameter (Figs. 4f, 6a). Rare abrasion and the good sorting of ooids suggest an autochthonous origin. Ooid nuclei are commonly composed of quartz, feldspar or more rarely dolomite or sparite. Strasser (1986) suggested a primary aragonite or high-Mg calcite composition for this type of ooids. This primary composition favored the development of mimetic replacement (Budd, 1997 and references therein). Budd (1997) also stated that this type of ooids formed in normal-marine shallow waters and can be accumulated on small sand bars under the influence of tidal currents. Data from the analyzed section of the Agua de la Mula Member support a similar conclusion.

There are two kinds of dolo-oolitic grainstones, which can be distinguished by the degree of preservation of the original oolitic textures. If the oolitic texture can be easily recognized, the dolo-oolitic grainstones are referred as fabric-preserving dolomites. If the oolitic texture has been almost completely eliminated by dolomitization but the imprint of the ooids remains discernible, the dolo-oolitic grainstones are referred as non fabric-preserving dolomites. The fabric-preserving dolo-oolitic grainstones are mainly composed of dolomitized ooids and well-rounded bioclasts. Very fine to fine blocky dolomite (0.5 - 20 μ) mainly replaces the ooids and bioclasts (Fig. 4a, e, f) while the replacements of the early marine cement occur as coarse blocky dolomite crystals having bimodal size (30 μ and 70 to 100 μ) (Fig. 4a, e). The pore-filling neighboring crystals interlock significantly reducing the intercrystalline porosity.

The non fabric-preserving dolo-oolitic grainstones to packstones are mainly composed of planar and very fine crystalline dolomite (1 a 2 μ), together with a relative important proportion of sand and silt-sized crystals. The intense dolomitization obliterated the original oolitic fabric (Fig. 4c). Also, two types of bioclast were observed, mimetically and non-mimetically replaced. Oyster (Fig. 4e) and echinoderm fragments are commonly mimetically dolomitized. Other bioclasts such as bivalve fragments show an early marine micritic envelope and a non-mimetically dolomite fills (Fig. 4a).

In sample Lc6 a subaerial exposure event is inferred. The presence of truncated ooids at the top of the bed and an iron (?) stained crust suggest al least short subaerial exposure of the grainstone,facies.

The samples from Mina La Continental section

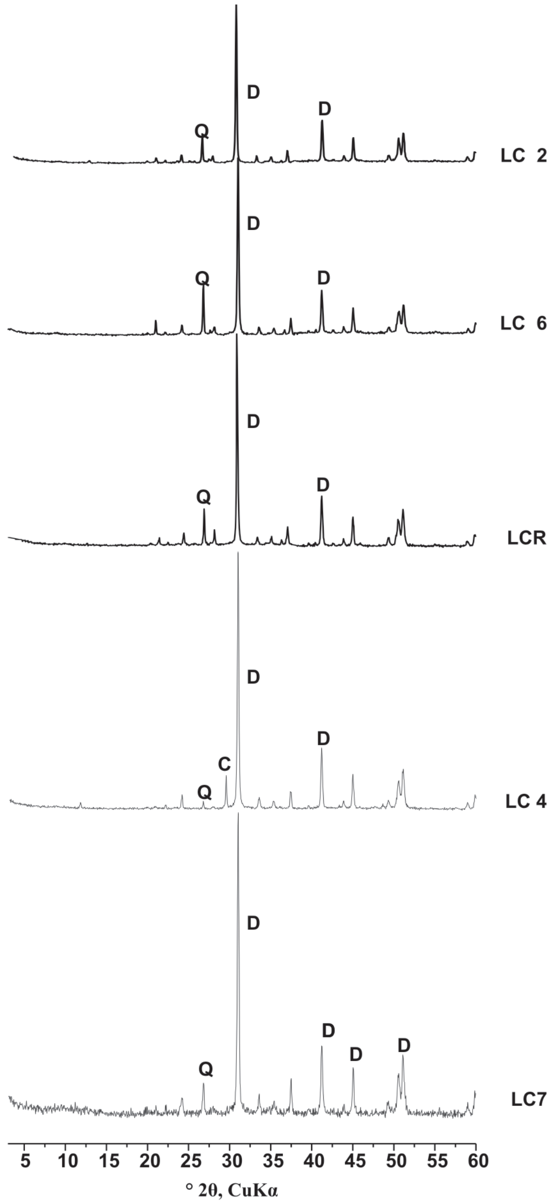
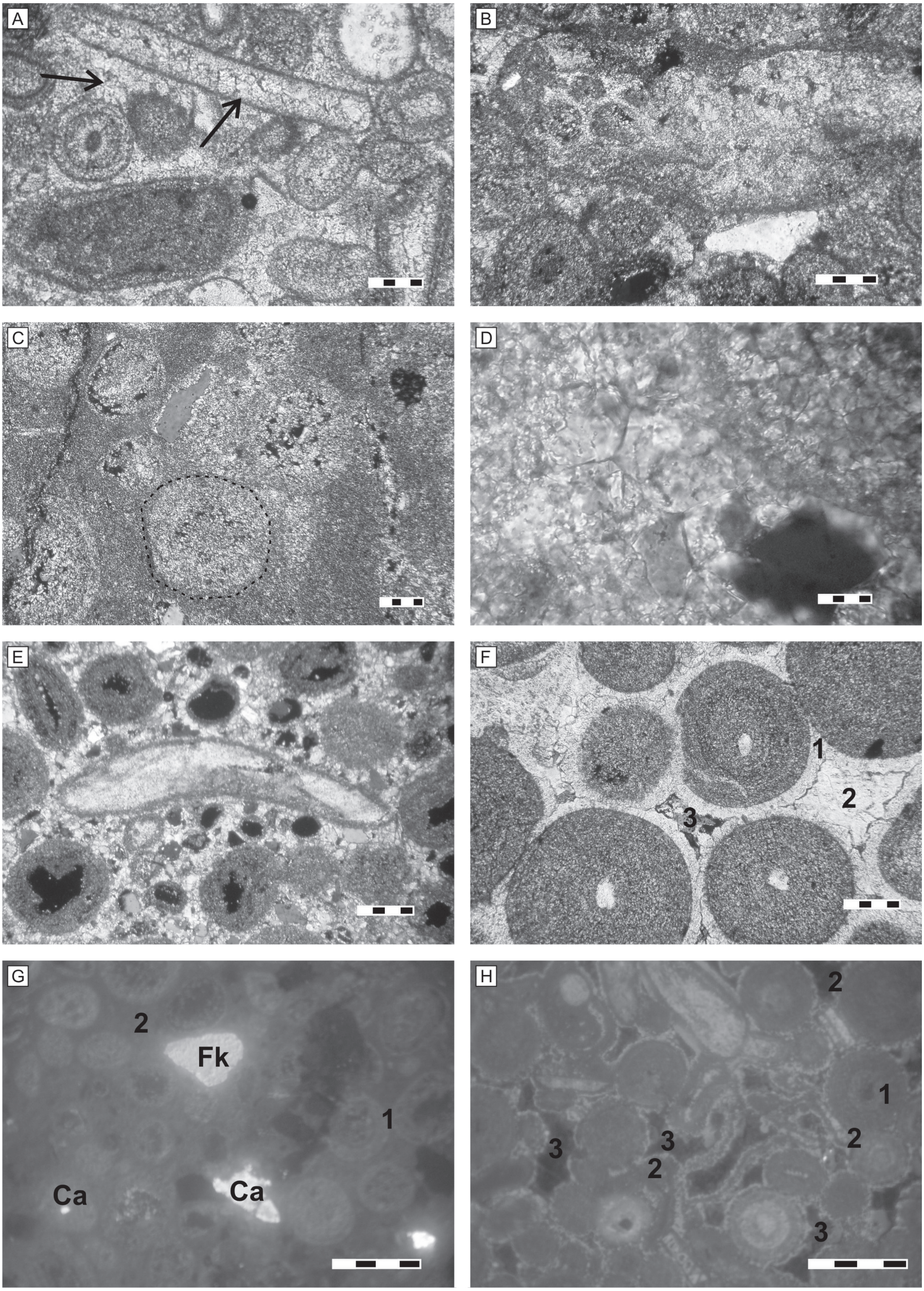


Figure 3. Representative X-Ray patterns obtained from unoriented samples. D: Dolomite, Q: Quartz, C: Calcite. Not all samples are shown.

have low oomoldic, intergranular and intragranular porosity. The presence of calcite filling the ooid molds suggests that the dissolution occurred as a late diagenetic event. The calcite also fills intergranular and intragranular pores (Figs. 4f, 5). The observed porosity is higher on the subtidal facies.

Micritization of ooid and bioclast margins is common in Mina La Continental. Micritization is believed to have occurred through microboring by photosynthetic algae and bacteria (Reid and MacIntyre, 2000).

The observed siliciclastic material is mainly monocrystaline and polycrystalline quartz, alkaline


A
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3

feldspar, scarce microcline and plagioclase with poor size-sorting and different degrees of roundness. Some feldspar shows intercrystalline porosity and/or alteration to calcite and dolomite. Rock fragments are common, mainly from volcanic lithics with pilotaxic textures. Replacive silica is frequently observed in this interval as pore-filling cement. Scarce amounts of illite were identified using SEM and X-Ray.

Compaction. Compaction includes several processes producing a reduction in the bulk volume of the rock. Mechanical compaction processes include rearrangement, deformation and breakage of grains and skeletal components. Chemical compaction is mainly limited to various categories of pressure-solution phenomena, including stylolitization (Meyers, 1980). Chemical compaction greatly controlled the textures and fabric of the ooids. Pressure-solution within grains and at grain contacts have been recognized (Fig. 4f). Less common is the presence of stylolites.

The main process that affected the samples was mechanical compaction, although it had a minor influence on the analyzed section (Fig. 4b). Some mechanical rearrangement of grains was probably produced soon after deposition but no major postdepositional grain rotation occurred.

Cementation and Void Filling. Sibley and Gregg (1987) used the term void filling instead of cement because the definition of cement states that it is made of passively precipitated crystals that grow attached to a free surface (Bathurst, 1975). Conversely, void filling includes cement and dolomite that replaced previous cement. In Mina La Continental section, void filling dolomite, dolomite cement, and late blocky calcite cement were identified through standard and cathodoluminiscence petrography.

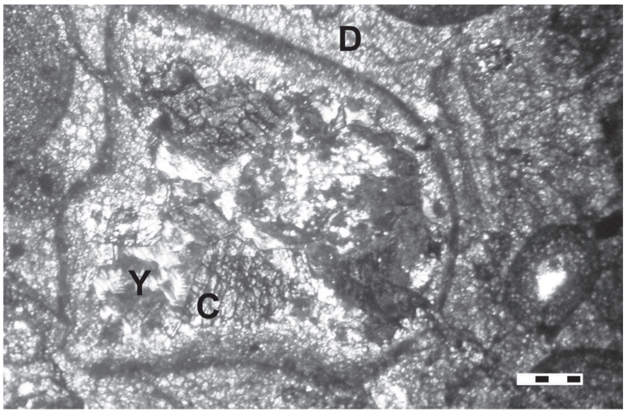

Figure 5. Late gypsum (Y) precipitation as pore-filling associated with late ferroan calcite (C). The sample is completely dolomitized (D). Sample Lc14. The scale bar is 0.1 mm. 10X. NC.

Void filling dolomite or dolomite replacement of the original marine cement. Two dolomite void filling phases were recognized in samples associated with intertidal facies: 1) an isopachous rim composed of bladed crystals that surround the ooids and bioclasts constitutes the first generation of the marine-phreatic cementation. This rim usually is developed on micritized ooids and bioclasts. The cement crystals are arranged perpendicularly to the ooid surface or fill the pore with coarse blocky spar without preferred orientation (Figs. 4a, 6b); 2) a granular pore-filling event can also be recognized. It is characterized by relatively small equidimensional pore-filling crystals. The blocky and granular dolospar also filled the aragonite bioclasts that were previously dissolved probably under meteoric-phreatic conditions (Figs. 4a, e, 5, 6a, b). The diagenetic environment in which all these void-filling dolomite crystals developed was probably meteoric-phreatic. Melim *et al*. (1995) noted that these features, both the blocky and the granular pore-filling, could also reflect burial diagenesis, but no other characteristics of this environment as poikilotopic calcite that postdated compactation, equant mosaic calcspar that post-dates microstylolites or cement that fill tectonic

Figure 4. Petrographic and cathodoluminescense thin section photomicrographs of the grainstones and packstones of Agua de la Mula Member. a) Well-sorted medium- to coarse-grained grainstones where ooids and bioclasts are dolomitized. Note the isopachous sparry dolomite as cement and replacing bioclasts (arrows). Sample Lc1. Scale bar is 0.2 mm. 10X. b) Mimetically replaced Bryozoan fragment. Sample Lc1. Scale bar is 0.2 mm. 10X. c) Oolitic grainstone non-mimetically replaced. Note the ooid ghosts. Sample Lc2. Scale bar is 0.1 mm. 10X. d) Crystal junctions. Sample: Lc1. Scale bar is 0.5 mm. CN. 20X. e) Mimetically replaced Oyster fragment. Note the preservation of the inner structure. Sample Lc6. Scale bar is 0.3 mm. CN. X10. f) Ooid dolostone with dolomite replacement of early marine cement (1), a dolomite cementation event (2) and late calcite cementation (3). Sample Lc4. Scale bar is 0.2 mm. PL. 10X. g. Microphotography under CL. Note the orange luminescence of the dolomitized cement and ooids and also the presence of calcite (Ca) and feldspar (Fk). Sample Lc2. Scale 0.25 mm X10. h) 3 types of luminescence: 1. ooids 2. dolomitized cements 3. dolomitic cement. Sample Lc4 Scale bar is 0.7mm. X4.

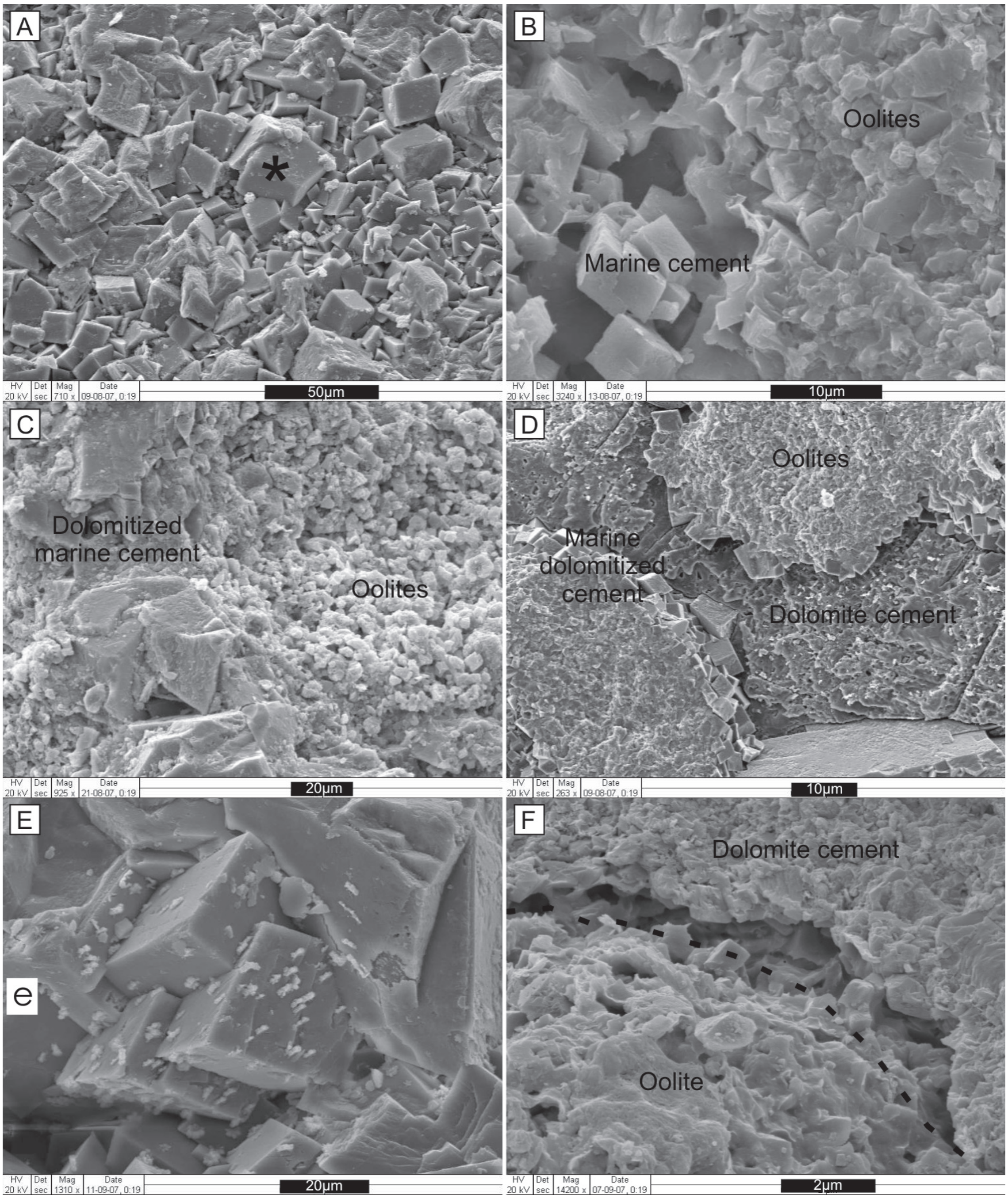

Figure 6. SEM photomicrographs of the Agua de la Mula Member dolomites. a) Euhedral dolomite crystals replacing a bioclast (*indicates location of EDAX analysis). Sample Lc6-3. b) Euhedral finely crystalline dolomite replacing both ooids and cement. Note the two modes of the dolomite crystals. Sample Lc2b-5. c) Contrast between euhedral void-filling dolomite and finely crystalline dolomite that replaces the ooids. Sample LcR-2. d) Dolomitized ooids with sizes contrasting between euhedral dolomite cement and euhedral dolomitized ooid and dolomitized marine cement. Sample Lc4-12. e) Limpid dolomite cement showing a well developed crystal form. Sample Lc4-9. f) Ooid and dolomite cement, EDAX analyses (Table 2) show that the dolomite cement has more Mg^{2+} than the ooid. Sample Lc7-5.

fractures were recognized on the samples.

The void-filling dolomites have common properties under cathodoluminiscence (light orange luminescence with 2800 to 2100 ppm Mn^{2+}) and are easily recognized (Fig. 4g, h). The replacement of the original cement is common in the subtidal and the intertidal facies.

Isopachous and blocky dolomite cement. Isopachous and blocky dolomite cement (Figs. 4f, 6f) was

		Mg%	Ca%	Total	Edax made on:
Intertidal	Sample Lc2-b8	41,81	58,19	100	Dolomitized cement
Intertidal	Sample Lc2-b8	51,5	48,5	100	Dolomitized cement
Intertidal	Sample Lc2b-12	49,3	50,7	100	Ooid
Intertidal	Sample Lc6-3	48,37	51,63	100	Dolomitized shell
Subtidal	Sample Lc7-5	53,55	46,45	100	Ooid
Subtidal	Sample Lc7-5	45,78	54,22	100	Dolomitic cement
Subtidal	Sample Lc4-1	53,15	46,85	100	Dolomitic cement
Subtidal	Sample Lc4-3	65,85	34,15	100	Ooid

Table 2. Relative % of Ma and Ca from the EDAX analysis on selected samples.

recognized specially on the samples associated with the subtidal facies. The dolomite cement is differentiated from the void-filling dolomite by the textural details of the dolomite crystals (Kaldi and Gidman, 1982) such as: 1) rhombs are euhedral and clear of inclusions, 2) there are no relic structures such as those expected in replacement crystals, 3) grains originally composed of micrite (*e.g.* pellets) are not altered to dolospar, 4) contacts between dolomite rhombs and micrite envelopes are sharp, 5) the margins of the dolospar coincide with the original surface of the particles, and 6) the intercrystalline boundaries of euhedral dolomite are planar.

Under cathodoluminiscence this cement is clearly recognized by its dark orange lower luminescence to no luminescence (Fig. 4h). The diagenetic environment under which the isopachous dolomite cements formed was probably one where meteoric waters mixed with sea water (Kaldi and Gidman, 1982). The isopachous and blocky dolomite cement is associated with the samples of the subtidal facies.

Blocky calcite. Pore-central, ferroan blocky calcite spar cement (Fig. 4f) occludes remaining pores and moulds. It is very scarce in sample Lc1 but quite common in sample Lc4 and also in sample Lc14 (Fig. 5). This calcite is also reveled though X-Ray (Fig. 3 and Table 1) and clearly from cathodoluminiscence (bright yellow). It is interpreted as late diagenetic and possibly deep burial in origin, such as seen in other limestones (Oldershaw, 1971; Bathurst, 1975). In some samples (Lc14) the presence of gypsum was observed as a late pore-filling cement (Fig. 5). The emplacement of gypsum during later stages of dolomitization is common in seawater or chemically altered seawater (Machel, 2004). This fact could be proved with future stable isotopes analysis. This blocky calcite cementation is found both in the intertidal and in the subtidal facies.

Porosity. It was originally suggested that dolomitized rocks generally have better reservoir properties than limestones because, during certain dolomitization conditions, two moles of calcite are converted to one mole of dolomite, leading to a net increase in porosity (Beaumont 1837; Weyl, 1960; Murray, 1960). However, several subsequent workers have demonstrated that other factors such as the features of the precursor sediment (Lucia and Major, 1994), subsequent leaching (Purser *et al.*, 1994) and cementation (Moore and Heydari, 1993) may govern porosity changes during dolomitization (Swart *et al.*, 2005).

The observed porosity in the studied samples is variable. Some of them have low porosity, mainly interparticle, while others have quite good oomoldic porosity and partial dissolution on the ooid nuclei and laminae. For the analyzed section of the Agua de la Mula Member we propose an early complete dolomitization conditioned by the precursor rock type that prevented the expected increase in pore size during dolomitization. In fact, Lucia (1999) argued that when the precursor limestone is a grainstone or a packstone there is not increase of the pore size. As the sizes of the grains of the grainstones and packstones are much larger than the dolomite crystals, the growth of dolomite rhombs does not have a significant effect on the porosity of the rock (Moore and Heydari, 1993). Nevertheless, dissolution after dolomitization is the main factor to develop secondary porosity and the analyzed samples showed no visible latter dissolution.

SEM and EDAX Analyses

Under SEM, textures of the dolomite from the intertidal and subtidal facies were characterized. The intertidal dolomite is characterized by two dolomite

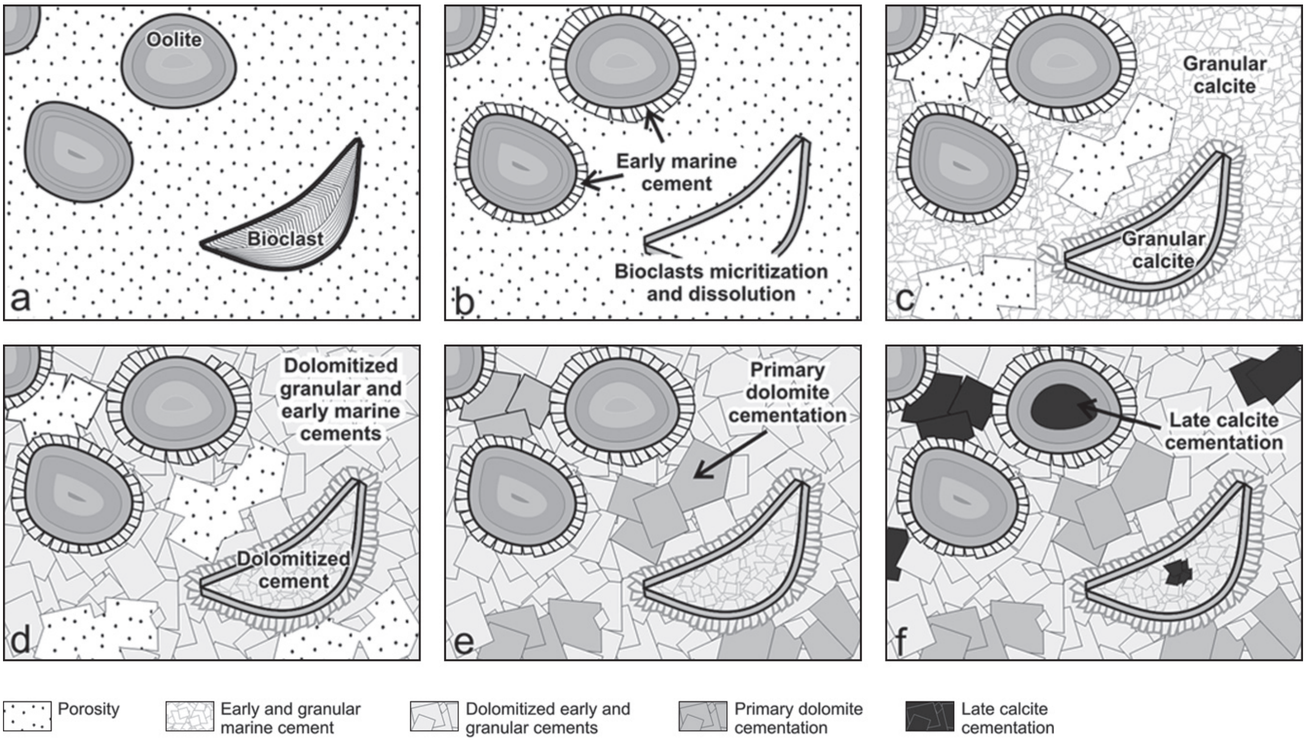

Figure 7. Schematic diagrams showing the summary of the cementation phases and diagenesis stages identified for Mina La Continental dolomites.

crystal modes, one from 0.5 to 5 μ and the other one from 10 to 30 μ (Figs. 6a, 6b) where the small dolomite crystals correspond to the ooid replacement and the other mode to cement and the replacement of bioclasts. The cathodoluminiscence suggests that they have similar chemical composition, so the fluids that dolomitized the ooids and the cement had similar composition and probably correspond to one early-diagenetic event. The subtidal facies are characterized by three modes of dolomite crystal sizes. The first one corresponds to the dolomitized ooids (0.5 to 5 μ), the second one to the dolomitized marine cement (10 to 20 μ), and the last one to the dolomite cement (40 to 100 μ). The dolomite replacement and the dolomite cement show crystals with clear developments of rhombs (Figs. 6c, 6d, 6e). The cathodoluminiscence suggests that the dolomitic cement has a different composition than the dolomitized marine cement, probably with more Fe that quenched the luminescence.

Table 2 shows the data obtained from EDAX that support these results. We are aware the EDAX analyses are semi-quantitative, but they can be used to compare the composition of the different components (*e.g.* Misik, 1993; Mastandrea *et al.*, 2006). The two cementation phases (early marine and dolomitic) developed from different pore waters.

DISCUSSION

The genesis of dolomite has been and is still one of the most studied problems in sedimentary petrology (see Choquette and Hiatt, 2008; Machel, 2004; Warren, 2000; Budd, 1997 and references therein). Several models of dolomitization have been developed: evaporative pumping, seepage-reflux, mixing zone, burial, and seawater models (*e.g.* Morrow, 1982; Land, 1985; Machel and Mounjoy, 1986; Hardie, 1987; Tucker and Wrigh, 1992; Purser *et al.*, 1994; Warren, 2000). Also dolomite formation by microbial activity has been demonstrated (Vasconcelos *et al.* 2006). Up to now, the seawater dolomitization model is accepted as the most likely explanation for dolomites within carbonate platforms (Saller, 1984; Tucker and Wright, 1992; Vahrenkamp and Swart, 1994; Mazzullo *et al.*, 1995; Wheler *et al.*, 1999; Kırmacı, 2008). But it is necessary to mention that the seawater dolomitization model is not an independent model. Rather the various possibilities of dolomitization by seawater form a group of models that have seawater in common as the principle source of Mg (Machel, 2004). Also, as recently stated by

Choquette and Hiatt (2008) the "dolomite problem" may narrow down to the chemistry and controls of dolomite micro and macrocementation.

Dolomites formed in different diagenetic environments can be recognized by their petrography, spatial distribution, geochemical and isotopic signatures (Kırmacı, 2008). This paper shed some light on the dolomites on the Agrio Formation and only petrography and spatial distribution of framework grains, cements and its relationships were analyzed. Additional geochemical and isotopic analyses will provide more information.

The dolomitization of the top of the Agua de la Mula Member took place after deposition and marine cementation and before of precipitation of sparry calcite. The sequence of events (Fig. 7) based on the textural and petrographic characteristics is: 1) formation of mimetic and non-mimetic dolomite from early marine cementation and bioclasts (Fig. 7a-d), during the driven of large amounts of seawater through the sediments 2) precipitation of limpid dolomite cement (Fig. 7e), during mixed waters with more meteoric conditions, and 3) precipitation of late sparry calcite cement (Fig. 7f).

The early development of the dolomitization is based on the very good preservation of the ooids (Corsetti *et al*., 2006), cement fabrics and cathodoluminiscence data. The oolitic inner structure and its sedimentological aspects suggest an aragonite or high-Mg calcite original composition and an autochthonous origin. Also the oolites petrographic evidences indicate that the mimetic dolomitization must have occurred before the conversion of aragonite to calcite or of high-magnesium calcite to low-magnesium calcite. Some bioclasts, aragonitic in origin, were dissolved before and filled with blocky calcite which was then dolomitized.

Based on the diagenetic events and the proposed tidal flat origin, we suggest that the dolomitization occurred under a seawater dolomitization model or shallow subtidal dolomitization model. In this model, normal marine waters are involved; large volumes are flushed through shallow sediments by tides or sea level rises, thus providing large volumes of Mg^{2+} for dolomitization (Patterson and Kinsman, 1982; Carballo *et al*., 1987; Mazzullo *et al*., 1995). The mixing of waters from the continent with the sea water contributed to the early dolomitization of the marine cements and ooids (Pierre *et al*., 1984; Hardie, 1987; Montañez and Read, 1992). The presence of early diagenetic dolomite cement is suggestive of the change of diagenetic environment from marine to meteoric in the presence of metastable carbonates (Kaldi and Gidman, 1982) and might form during sea-level-driven events (Choquette and Hiatt, 2008)

CONCLUSIONS

Sedimentological and petrographic characteristics indicate that the dolo-oolitic grainstones at the uppermost section of the Agua de la Mula Member in Mina La Continental were originally deposited in a shallow marine environment with agitated waters, tidal influence and temporary subaerial exposition.

Two different dolomitization processes affected the sedimentary succession. The first one is very common on the intertidal facies but is also found on the subtidal facies; it generates two different void-filling events and the mimetic dolomitization of the ooids and some bioclasts. The first dolomite void filling is a blocky marine event that surrounds the ooids and bioclasts and the second one fills the interparticular space. The fabric-preserving dolomite that developed on the samples suggests that the dolomitization must have occurred before the inversion of aragonite to calcite or high-Mg calcite to low-Mg calcite. The non-mimetic dolomite observed in some bioclasts is indicative of a low-Mg calcite composition in origin or early dissolution of the bioclasts. The presence of mimetic dolomite in this subfacies may therefore reflect an early marine cementation and rapid dolomitization that should have occurred soon after deposition.

The second dolomitization process took place extensively on subtidal facies and it was identified by its textural characteristics as *in-situ* dolomite cementation.

The dolomitization events did not produce an increase of the net porosity of the grainstone probably due to the precursor grainstone lithology and an early marine cementation together with rapid dolomitization and dolomite cementation. A latter and scarce cementation event is a pore-filling ferroan calcite and gypsum.

All the characteristics listed above allowed us to propose a shallow subtidal dolomitization model for the upper section of the Agua de la Mula Member of the Agrio Formation in the studied locality. This model is related to a very early development of the dolomitization in the diagenetic succession and a strong influence of the texture of the precursor limestones. The precipitation of the dolomite cement observed in the analyzed samples was probably produced by sea level changes.

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