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CARBONATE SEDIMENTOLOGY AND DIAGENESIS OF THE VACA MUERTA FORMATION AT PUERTA CURACO, NEUQUÉN BASIN, ARGENTINA

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RESUMEN

Sedimentología y diagénesis de los carbonatos de la Formación Vaca Muerta en la localidad de Puerta Curaco, Cuenca Neuquina

Este trabajo investiga los cambios diagenéticos sufridos por las calizas de la Formación Vaca Muerta en el perfil de Puerta Curaco con el objetivo de evaluar su relevancia para la caracterización de reservorios. Dentro de estos cambios, la precipitación, disolución y reemplazo de los carbonatos pueden modificar drásticamente propiedades tales como la fragilidad, porosidad y permeabilidad en las rocas. El análisis de microfacies de las calizas, margas y concreciones de la Formación Vaca Muerta indica que existen cantidades variables de partículas intracuencales, que incluyen bioclastos, intraclastos y peloides, tanto como cementos y reemplazos autigénicos, en el contexto de una historia de enterramiento compleja. La misma se inició durante la subsidencia térmica del Tithoniano Temprano y alcanzó profundidades máximas de alrededor de 3.3 km durante el estadío de cuenca de antepaís en el Cretácico Tardío, momento en que la Formación Vaca Muerta entró en la ventana de generación de condensado y gas.

Los análisis geoquímicos (Ca, Sr, Mg) indican que los precursores de la calcita presentes en la roca fueron aragonitay calcita con alto contenido de Mg, mientras que la calcita con bajo contenido de Mg precipitó como una fase de cemento autigénico. Los cocientes de Mn/Ca y Fe/Ca sugieren que la precipitación y recristalización de calcita se produjo a profundidades variables de enterramiento. Las diferentes tendencias en los gráficos de δ18O vsFe/Ca son coincidentes con lo anterior y además indican que las concreciones se sellaron durante la diagénesis temprana. La firma isotópica de δ18O en todas las muestras no refleja equilibrio de los microcristales de calcita con las aguas marinas poralesde la diagénesis temprana ni tampoco un equilibrio con las temperaturas diagenéticas máximas alcanzadas por la Formación Vaca Muerta. Las paleotemperaturas calculadas indican que hay una mezcla de componentes originales y autigénicos. La calcita autigénica de las calizas y margas precipitó a partir de CO2derivado de la oxidación anaeróbica de la materia orgánica en la zona de reducción de sulfatos y contribuyó a los valores ligeramente negativos que se observan en roca total. Los valores de C más positivos sugieren su origen en la zona de metanogénesis.

INTRODUCTION

Lithofacies modelling of non-conventional reservoirs is strongly linked to diagenetic processes because carbonate precipitation, dissolution and replacement can drastically modify the rock properties in limestones and marlstones. Previous studies on the Vaca Muerta Formation (Kietzmann *et al.* 2014, 2016; Guerberoff *et al.* 2015) demonstrated its complex lithofacies arrangement, with vertical and horizontal variations. The different lithofacies are the result of primary depositional processes and overprinted diagenetic transformations. This paper aims to investigate the diagenetic changes underwent by the limestones of the Vaca Muerta Formation in the Puerta Curaco section in order to assess their relevance for reservoir characterization.

METHODOLOGY

General texture, particles and grains, cement, fabric and sedimentary structures were described from polished hand samples using binocular microscope. Thin sections were analyzed by standard techniques to capture the microtextural and compositional attributes in order to define microfacies. Splinters were prepared to observe the texture of minerals in the SEM (Zeiss, SUPRA 40) and its chemical composition by EDS (Oxford Instruments) at the Centro de Microscopías Avanzadas (CMA) of the Facultad de Ciencias Exactas y Naturales (UBA).

Carbon and oxygen isotope (δ^{13}Ccarb, δ^{18}Ocarb) analyses of aliquots of powdered samples ($CaCO_3$ >10 wt.%) were conducted at the Institute of Earth Surface Dynamics of the University of Lausanne (IDYST-UNIL), using a Thermo Fisher Scientific (Bremen, Germany) Gas Bench II carbonate preparation device connected to a Delta Plus XL isotope ratio mass spectrometer, following Révész and Landwehr (2002). Samples were drilled (1 mg per sample) for stable isotopic analysis.

Rock-Eval pyrolysis methods were used to estimate TOC, source and thermal maturity of organic matter. The standard model of Rock-Eval 6 (Technologies Vinci, Rueil-Malmaison, France) uses pyrolysis in an inert atmosphere followed by oxidation, at intervals of temperature between 200°C and 850°C. Geochemical procedures were performed at the Institute of Earth Surface Dynamics of the University of Lausanne (IDYST-UNIL)

Whole rock major, minor and trace elements were measured using a portable X-ray fluorescence equipment (Thermo Fisher Scientific Niton Analyzer) at the Sedimentology Laboratory of the Departamento de Ciencias Geológicas (UBA)

GEOLOGICAL SETTING - BURIAL STORY

The entire Mendoza Group and, particularly, the VacaMuerta-Quintuco system are well exposed in Puerta Curaco locality, 30 km east from the ChosMalal city, in the northern part of the Neuquén Basin (Fig. 1) and the eastern part of the ChosMalal fold and thrust belt. The succession starts with the Tordillo Formation (Kimmeridgian-lower Tithonian?) characterized by lacustrine green siltstones and fine-grained sandstones (Gulisano, 1988). The overlying VacaMuerta Formation is characterized by a rhythmic succession of marlstones and limestones, with frequent intercalation of thin, tuffaceous beds. Its Upper Jurassic-Lower Cretaceous age derives from the ammonite biozones of Leanza and Hugo (1977) and Riccardi *et al.* (2011). It passes transitionally upward to the early ValanginianQuintuco Formation(Leanza and Hugo, 1977; Mitchum and Uliana, 1985; Aguirre-Urreta *et al.*, 1999).

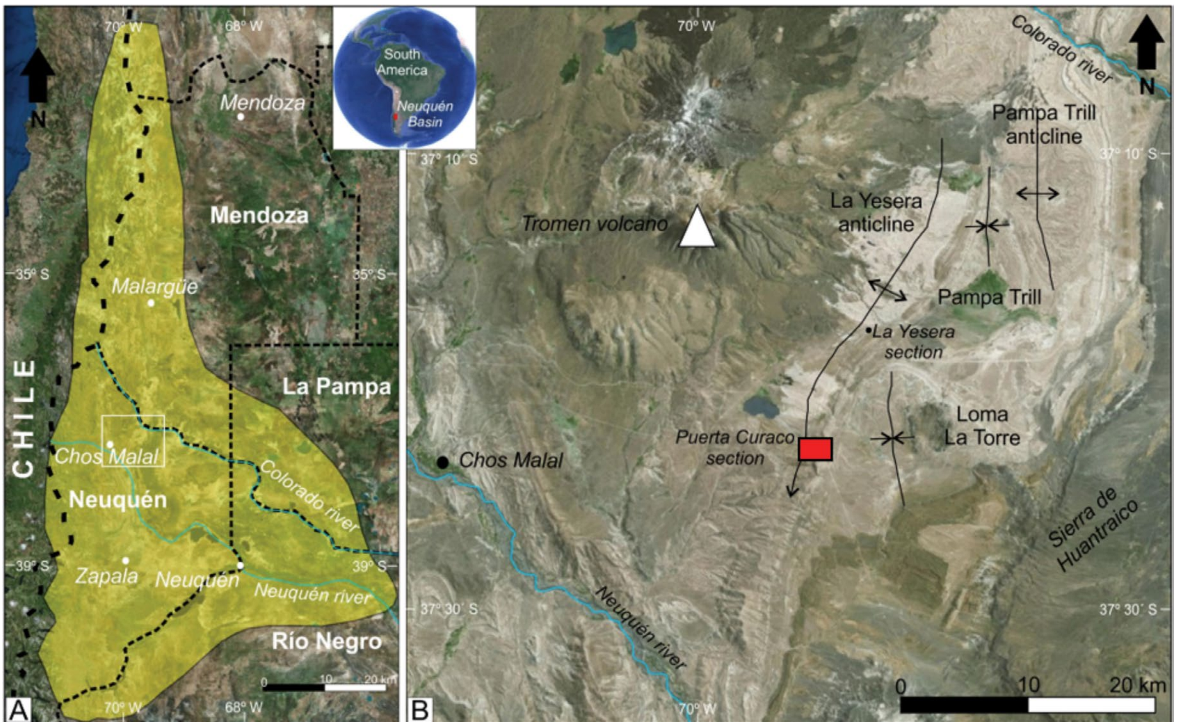

Figure 1. A) Location map of the Neuquén Basin. B) Location of the Puerta Curaco section at the La Yesera anticline.

The local geological history is characterized by prolonged Jurassic-Cretaceous subsidence and two events of deformation and uplift (see Table 1; Fig. 2). The onset of deformation occurred at Albian-Cenomanian times, during the deposition of the syn-orogenic sediments of the Neuquén Group, synchronously with the initial uplift of the Andean orogeny, ~ 100 Ma (Tunik *et al.*, 2010; Fennell *et al.*, 2015, Sánchez *et al.*, 2017). Most of the contractional deformation in the ChosMalal Fold and Thrust Belt, took place during the Late Cretaceous-Paleogene and Neogene uplifting (Vergani *et al.*, 1995; Kozlowski *et al.*, 1998; Cobbold and Rossello, 2003; Ramos and Kay, 2006; Folguera *et al.*, 2007; Folguera *et al.*, 2015; Rojas Vera *et al.*, 2015; Sagripanti *et al.*, 2016, Sánchez *et al.*, 2017). In Puerta Curaco the most important uplifting episodes occurred during the Eocene and Miocene-Holocene (Table 1).

Group	Formation	Age	Beginning (Ma)	End (Ma)	Thickness (m)	Ammonite zones	Source
Miocene-recent exhumation		Miocene-Holocene	18	0	------		Ulliana y Dellapé 1981; Rojas Vera *et al.* 2015; Rodriguez 2011; Folguera *et al.* 2015; Sanchez *et al.* 2017
Paleogene exhumation		Eocene	55	40	-370		
Malargüe	**Several Units**	Early Maastrichian - Paleocene	79	55	200		Barrio 1990; Parra *et al.* 1998; Leanza 2009; Rodriguez 2011
Neuquen	**Several Units**	Cenomanian- Mid Campanian	98	79	570		Zöllner W. y Amos A. 1973; Leanza 2003; Galarza 2009; Tunik *et al.* 2010; Garrido 2011; Turienzo 2015; Rojas Vera *et al.* 2015
Early - Late Cretaceous uplift Foreland basin developement		Albian-Cenomanian	103	98	-80		Tunik *et al* . 2010
Bajada del Agrio	**Rayoso** (Rincón, Quili Malal, Pichi Neuquén and Cañadón de la Zorra Mbrs.)	Mid-Late Aptian Albian	117	103	650		Leanza 2003; Tunik et al. 2010
	Huitrín (Troncoso, La Tosca and Salina Mbrs.)	Late Barremian-early Aptian	123	117	216		Leanza 2003
Mendoza	**Agrio** (Chorreado Mbr.)	Early Barremian	125	123	30		Leanza 2003
	Agrio (Agua de la Mula Mbr.)	Late Hauterivian - Early Barremian	132,5	125	267	*Stipidiscus riccardii, Crioceratites schlagintweiti, Crioceratites diamantensis - Paraspiticeras groeberi*	Porfiri 2009; Spalletti *et al.* 2011
	Agrio (Pilmatué and Avilé Mbr)	Late Valanginian / early-late Hauterivian	134	132,5	420	*Pseudofavrella angulatiformis (Valanginiano tardío) - Holcoptychites neuquensis, Höplitocrioceras gentilii, Weavericeras vacaense*	Notta 2008; Spalletti *et al.* 2011
	Mulichinco	Mid-late Valanginian	136	134	335	*Lissonia riveroi - Olcostephanus atherstoni*	Schwarz 1999; Legarreta Pablo 2009; Leanza *et al.* 2011
	Quintuco	Early Valanginian	139,8	136	310	*Uppermost part of the Neocomites wichmanni and Lissonia riveroi zones*	Leanza y Hugo 1977; Mitchum y Ulliana 1985; Aguirre Urreta *et al* . 1999; Leanza *et al* . 2011; Kietzmann *et al* . 2016
	Vaca muerta	Early Tithonian-Early Valanginian	152,1	139,8	407	*Virgatosphinctes andesensis to lowermost part of Neocomites wichmanni*	Aguirre Urreta *et al* . 1999; Leanza y Hugo 1977; Mitchum y Ulliana 1985; Kietzmann *et al.* 2016; Capelli *et al* . 2017

Table 1. Database for burial history and calculation of Time-Temperature Index (TTI) values for the Puerta Curaco section. Age of accumulation comes mainly from ammonite zones, and thicknesses are from local and regional sources (mostly in ChosMalal fold and thrust belt).

The depositional, thermal and tectonic history was reconstructed using the Lopatin method (Fig. 2), considering an empirical average linear law between temperature and depth for the Neuquén Basin obtained from temperature measurements of 2941 wells (Sigismondi& Ramos 2008):

BHTc (°C) = 9,5967 + 0,0443 * z; with BHTc=borehole temperature (°C) and z=depth (m)

The Mendoza and Bajada del Agrio Groups accumulated during the late Jurassic – early Cretaceous thermal subsidence, before the Albian-Cenomanian uplift, which caused a slight erosion of the top of the Rayoso Formation (~80 m). The entire sequence reached its maximum burial during the foreland stage of the basin, at the time of the accumulation of the Neuquén and Malargüe Groups, that provided a thick over-burden to the column (~770 m). The greatest paleo-depth proposed by the model (see Fig. 2) for the Vaca Muerta Formation is 3325 m and is coincident with values of 3300-4000 m obtained by Eberli *et al.* 2017 using clumped isotope methods and a gradient of 25-30 °C/km. During the Paleogene and Neogene exhumations, the Neuquén and Malargüe Groups were completely eroded in the area of Puerta Curaco.

According to the reconstruction in Figure 2, the VacaMuerta Formation entered the Oil Generative Window at about 110°C in the thermal subsidence stage, during the Albian (110 m.y.B.P.); it ceased the oil generation and entered the Condensate – Wet Gas Window at about 140°C in the flexural subsidence stage, during the Santonian (83 m.y.B.P.), synchronously with the accumulation of the syn-orogenic sediments of the Neuquén Group. On the other hand, the Quintuco Formation entered the Oil Generative Window in the thermal subsidence stage, at about 100°C during the Albian (106 m.y.B.P.). It ceased the oil generation and entered the Condensate – Wet Gas Window at about 120°C at the Paleogene exhumation, during the Eocene (49 m.y.B.P.). The present-day TTI values for VacaMuerta and Quintuco Formations are 1020 and 302 respectively and correlate with Vitrinite Reflectance (Ro) values very close to 2 and 1,50 (Waples 1980), within the condensate-wet gas field. Average T max data of 507 °C from outcrop samples measurementsof VacaMuerta Formation correlates with a vitrinite reflectance value of 1.966 (Jarvie *et al.* 2001). Therefore, thermal maduration modelled from the burial history and the regional thermal regime is in good agreement with pyrolysis data. In the subsurface, a few

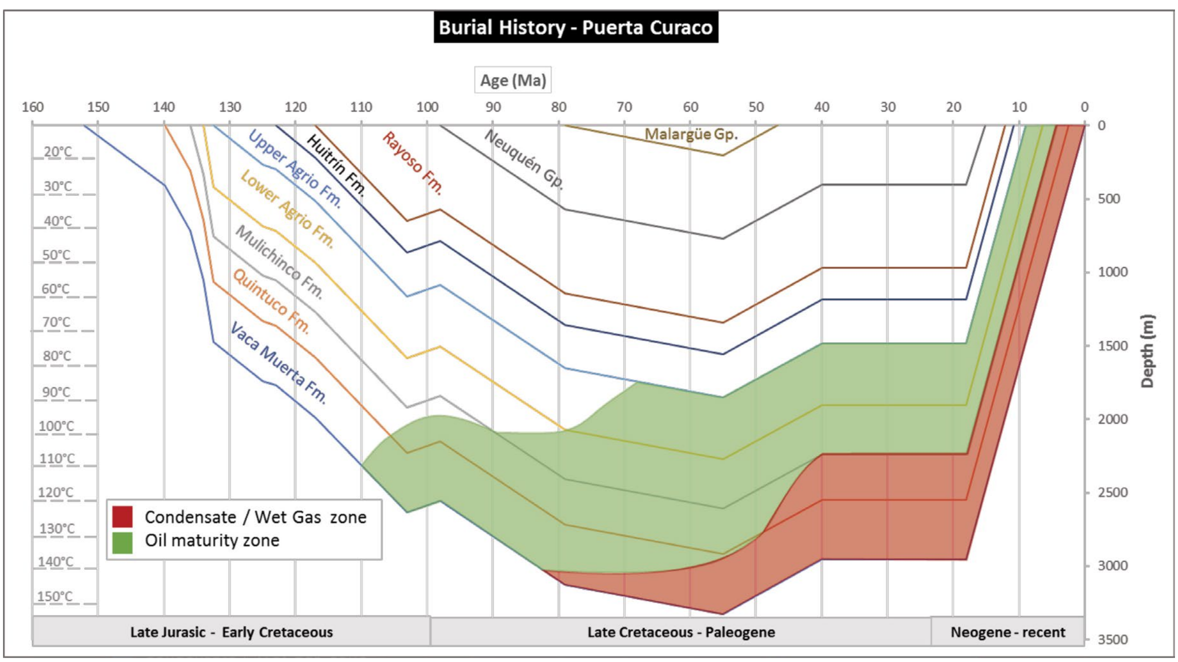

Figure 2. Burial history considering constant geothermal gradient throughout the history of the basin for Vaca Muerta Formation at Puerta Curaco. Iso – TTI lines define the Oil maturity and Condensate – Wet Gas windows for Mendoza Group (VacaMuerta to lower Agrio Formations). The rest of the units are in the immature zone.

kilometers to the east, the organic rich intervals of the Quintuco – VacaMuerta System might be currently generating wet gas – condensate (Fantín and González 2014).

PETROGRAPHICAL AND GEOCHEMICAL ANALYSIS

The Vaca Muerta Formation in Puerta Curaco is mainly composed of limestones, marls and shales, with subordinated carbonate concretions, tuffs and beefs.The heterogeneity of the rocks isexpressed in terms of different proportions of intrabasinal carbonatic, bioclastic, epiclastic and volcaniclastic particles, representing the primary input of sediments, as well as cements, authigenic minerals and other diagenetic products, representing the diagenetic contribution.A carbonate ramp paleoenvironment has been proposed for these beds (Kietzmann *et al.*, 2016).

Petrography

Microfacies and primary sedimentary processes

The most representative limestone microfacies are synthetized in Table 2 according to Dunham (1962). Different microfacies were characterized by primary elements, like texture, microfabrics, skeletal and non-skeletal carbonate particles and matrix proportion, and secondary elements like pseudomatrix and type and distribution of the carbonate cement.

Microfacies	Texture and Microfabric	Skeletal / Non-Skeletal / Terrigenous	Cement / Matrix	Distribution
Radiolaritic Wackestones (Mf1)	Matrix to grain supported. Tenuous lamination	Predominance of skeletal particles (~30%). Non-skeletal carbonate particles up to 15%. Rare terrigenous (3%).	Abundant micritic matrix and pseudomatrix composed of very fine silt pelloids with diffuse boundaries due to neomorphism (52%). Scarce organic matter and framboidal pyrite.	OUTER RAMP TO BASIN
Wackestone with terrigenous (Mf2)	Matrix supported. Without lamination	Terrigenous (10%) are more abundant than in the other microfacies. Skeletal particles (15%) and non-skeletal carbonate particles (12%).	Abundant micritic matrix (73%) with presence of framboidal pyrite.	OUTER RAMP
Intraclastic Packstones - Wackestones (Mf3)	Grain to matrix supported. Tenuous lamination	Predominance of non-skeletal particles (intraclasts) (~50%) over skeletal particles (25%). Rare terrigenous (2%)	Micritic matrix- pseudomatrix and microspar cement (22-25%), moderate proportion of framboidal pyrite	DISTAL OUTER RAMP TO BASIN
Pelloidal Packstones-Grainstones (Mf4)	Grain supported. Very well developed microlamination	Predominance of peloids (~75%). Skeletal particles up to 8%. Rare terrigenous (2%)	15% Micritic matrix in the packstones and carbonate cement (microsparite to sparite) in the Grainstones	PROXIMAL OUTER RAMP
Carbonate concretions (Mf5)	Grain supported. Very well developed microlamination	Predominance of carbonate intraclasts and peloids (~65%). Skeletal particles up to 8% . Rare terrigenous (2%)	Microspar to spar cement (25%)	PROXIMAL OUTER RAMP TO BASIN
Calcitized tuffs (Mf6)	Massive	Abundant shards and pumice fragments. Subordinated quartz and feldspar grains.	Abundant poikylotopic carbonate cement, moderate presence of clorite and framboidal pyrite	OUTER RAMP TO BASIN

Table 2. Summary of main limestone microfacies according to Catalano *et al.* (2017).

The high proportion of intrabasinal particles, including bioclasts, intraclasts, micritic peloids, and rare extra basinal terrigenous particles (<3%), reflects erosion of shallower zones above the storm wave level and subsequent transport by subaqueous flows (Kietzmann *et al.*, 2014, 2016). Fine grain-sized (from very fine silt to coarse sand) and good sorting of carbonate intraclasts with variable content of organic matter and pyrite, skeletal concentration,as well as disarticulated bivalve shells with random orientation in wackestones and packstones (Fig. 3) may indicate redeposition of storm-derived material. The microfacies are the result of the interaction of two main geological processes: fallout from suspension of fine-grained material and tempestite underflow deposition in proximal to outer ramp settings (Catalano *et al.* 2017).

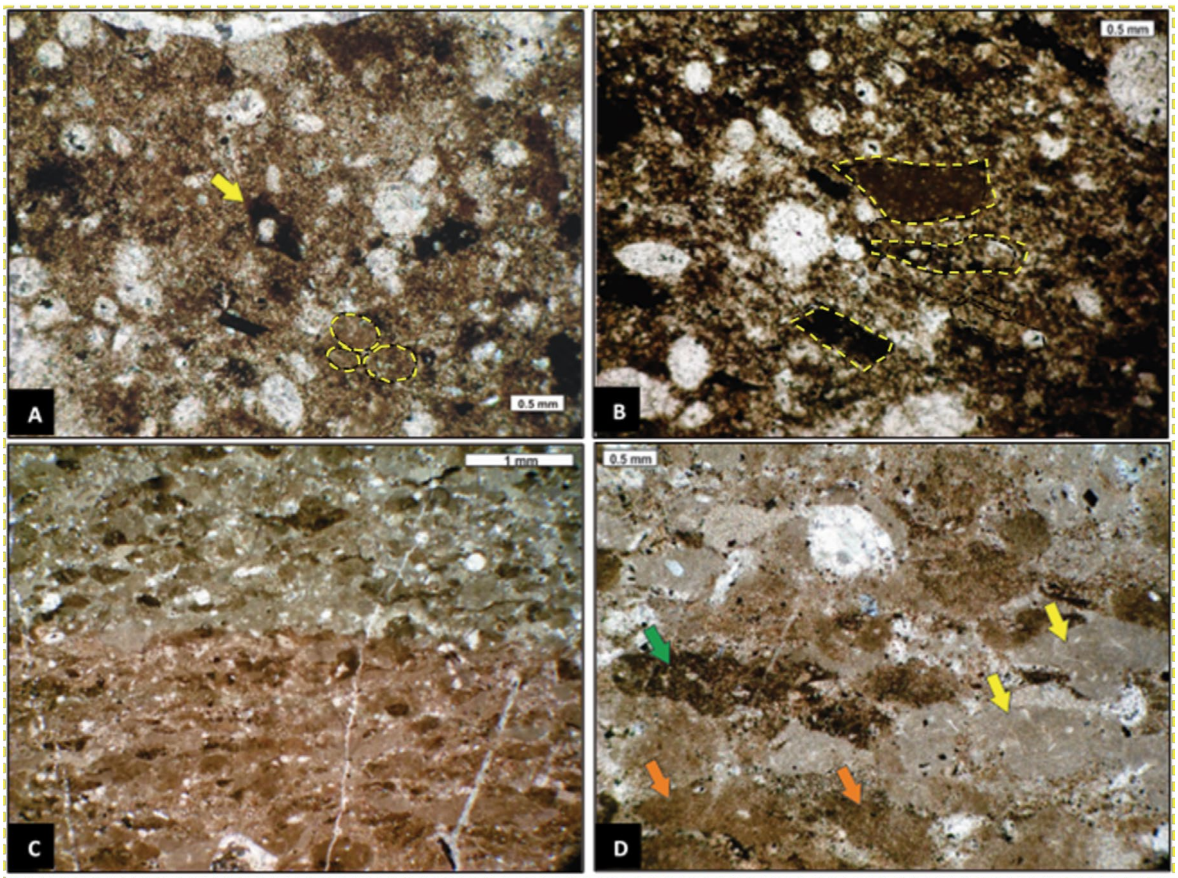

Figure 3. A) Intraclastic packstone–wackestone withgrain to matrix-supported texture composed by different types of black, angular intraclasts(yellow arrow) and brown, rounded intraclasts (dotted line). B) Intraclastic packstone with grain-supported texture composed of angular black-brownish intraclasts (dotted line). C) Peloidal packstone–grainstone with grain-supported texture and well developed microlamination. D) Peloids and intraclastswith variable proportion of micrite, organic matter and pyrite. Peloids with high content of organic matter and pyrite (green arrow); micrite peloids without organic matter (yellow arrow), and micrite peloids with moderate proportion of organic matter (orange arrows).

Diagenetic products

In wackestones, packstones and concretions, neomorphismis evidenced through the presence of graded microtexture from microsparite (0.005 mm) to sparite (0.05 mm), recrystallization of skeletal and non-skeletal particles and filling of interstices and intragranular pores particles with spar.The compaction and neomorphismaffect pellets and peloids and give rise to the formation of a carbonate pseudomatrix (Flügel 2004; Kietzmann 2011). Neomorphism makes diffuse the outlines of the carbonate non-skeletal particles difficulting their identification. Blocky spar patches replacing the matrix and fine to coarse graded mosaics (micrite to spar) can be recognized in wackestones and packstones (Fig. 4 A-B-C). In carbonate concretions, the interstices between intraclasts and peloids are filled with microspar to sparcement. Micritic silt-sized peloids partially or completely recrystallized to microspar or spar, skeletal particles filled with coarse carbonate microcrystals and pyrite aggregates are common in all microfacies. Syntaxial overgrowths (Fig. 4 D) on microcrinoid plates are rare.

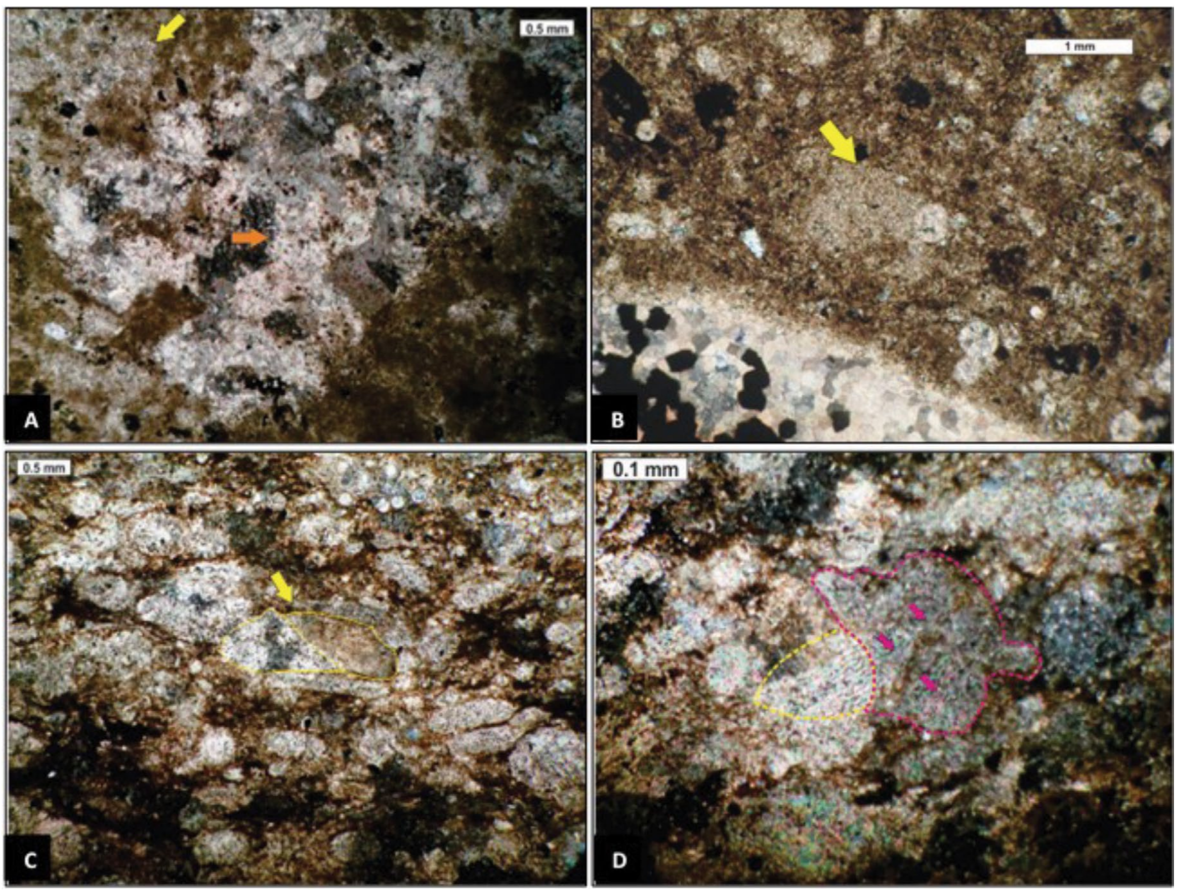

Figure 4. A) Spar recrystallization in skeletal particle (orange arrow) and microspar patches affecting the micritic matrix (yellow arrow). B) Graded microtexture from microsparite (0.005 mm) to sparite (0.05 mm) and relictic non-skeletal particle replaced by microsparite (yellow arrow). C) Peloids with spar patches (yellow arrow). D) Syntaxial overgrowth (magenta arrows) on microcrinoid plates (yellow dotted line).

Carbonate concretions, packstones and grainstones of the Vaca Muerta Formation have abundant authigenic carbonate with selective to pervasive distribution and moderate to abundant amounts of framboidal pyrite aggregates (Fig. 5). Intraclastic carbonate concretions are characterized by grain supported textures, with tangential contacts between sub-spherical intraclasts (without evident signs of compaction; Fig 5 A-B). This indicates that the carbonate cement filled the open spaces in an early stage, preventing later compaction.

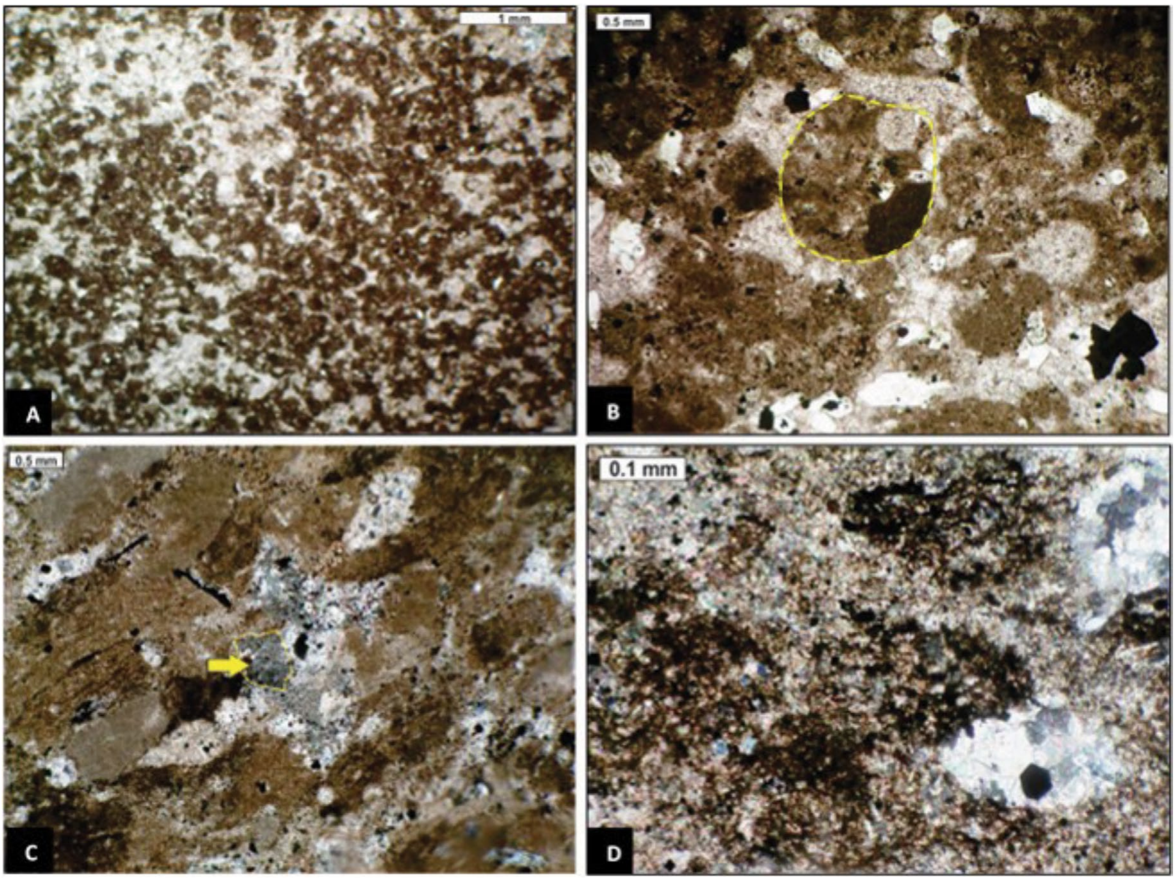

Figure 5. A) Intraclastic limestone with selective to pervasive distribution of carbonate cement (microspar to spar). In the upper left sector, the carbonate cement has obliterated the original grain-supported texture. B) Intraclasts preserving their original shape, without signs of compaction in carbonate concretions (see dotted yellow line). C) Early carbonate cement in peloidal grainstone, consisting of a sparite mosaic (crystals up to 0.3 mm) associated with framboidal pyrite aggregates. D) Microspar cementing dark intraclasts with high proportion of organic matter and pyrite.

Silica masses with prismatic aggregates and pseudo-hexagonal sections of quartz crystals (Fig. 6) are associated with cubic pyrite and small dolomite crystal in carbonate concretions. Cubic pyrite is included in the silica masses and doesn't present reaction surfaces. Terrigenous particles are rare (<3%) whereas radiolarians are abundant (up to 38% in radiolaritic wackestones, bioclastic mudstones and intraclastic packstones).

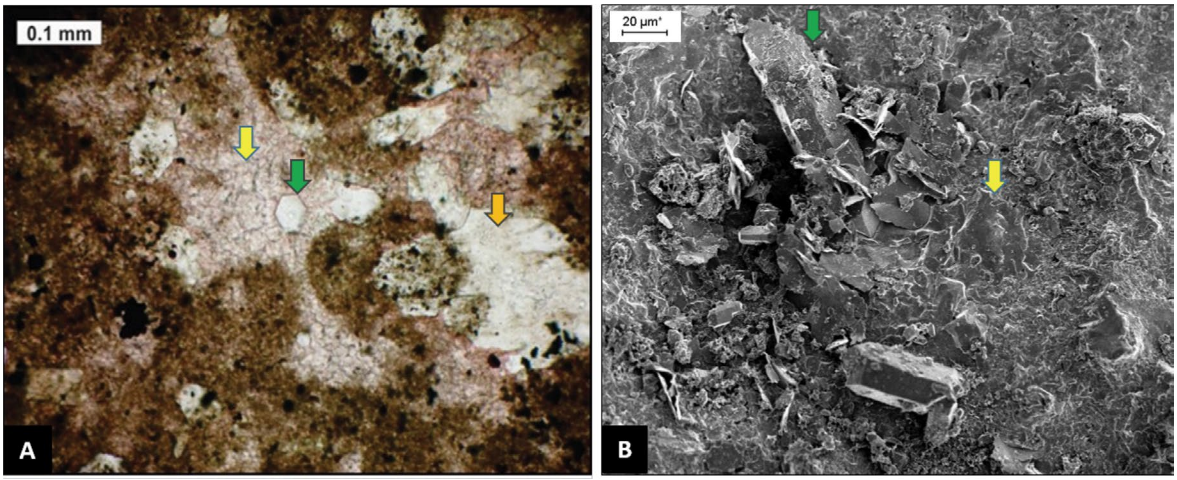

Figure 6. A) Euhedral quartz (green arrow) and prismatic aggregates of quartz (orange arrow) in interstices previously filled with carbonate cement (yellow arrow). B) SEM image of well-developed prismatic quartzcrystals (green arrow) andmicrospar to spar (yellow arrow) cement.

C and O stable isotopes and their interpretation

The $\delta^{13}C$ values in marls and limestones (Fig. 7) range between 0 to -4 ‰ (PDB), whereas in concretions they range between 2 and 7 ‰ (PDB). The isotopic signature of the bulk rock is the result of a mixture of different proportions of original and diagenetic mineral phases (see Figs. 3-4-5 and Table 2). Bioclasts of marine organisms together with other carbonate particles, authigenic cements and secondary replacements may contribute to the final isotopic values of the rock in different proportions.

In the case of the carbonate concretions, the authigenic phases are more abundant (see Figs. 5-6 and Table 2). Consequently the contribution of diagenetic C is more important than in limestones. In addition, the concretions show little evidence of compaction and probably grew during the early diagenesis. The more positive C isotopic composition points to an origin in the methanogenesis zone (early diagenesis) in which the positive isotopic composition of the CO_2 released by the methanogenous bacteria precipitated forming the authigenic carbonate phases (see Figs. 5-6) in the calcite concretions.

On the other hand, the limestones show a C isotopic composition which is a mixture of the original primary components (bioclasts, peloids, intraclasts, etc) with $\delta^{13}C$ values probably close to 0 and authigenic mineral carbonate phases with a negative isotopic signature provided by the oxidation of organic matter within the rocks during diagenesis.

The isotopic signature for $\delta^{18}O$ in marlstones, limestones (Fig. 8) is between -10 to -7 ‰ PDB. In the carbonate concretions the values range between -10 and -12 ‰ PDB. Once again, the O isotopic composition is the result of the mixture of several carbonate mineral phases. Carbonate concretions have lower $\delta^{18}O$ ratios than marl-limestones. The fact that the carbonate concretions show more abundant authigenic phases and more negative O signature indicates they originally had a lower O signature than the limestones/marls. These conditions were held through diagenetic changes in which re-equilibration of the O isotopes at higher T for both concretions and limestones didn't erase the original difference.

Estimates of diagenetic paleotemperatures considering an isotopic composition of diagenetic fluids analogous to that of the Tithonian sea water ($\delta^{18}O$= -1 ‰ SMOW, Ditchfield *et al.*, 1994; Scasso *et al.*, 2005) were accomplished with an equilibrium fractioning for the oxygen isotopes expressed by the following equation (Irwin *et al.* 1977):

$$T = 16.9 - 4.21(\delta c - \delta w) + 0.14(\delta c - \delta w)^2; \ \delta c = \delta^{18}O \ (PDB) \text{ and } \delta w = \delta^{18}O \ (SMOW)$$

Calculated paleotemperatures for limestones and marls range between 65.5 C°- 49,6 C° and for carbonate concretionsrange between 76.5 C°-57 C°. The thermal-burial history modelled by Lopatin´s method and other diagenetic indicators as Rock-Eval Pyrolisis data, suggest these temperatures are lower than the maximum temperature underwent by the rocks of the Vaca Muerta Formation.

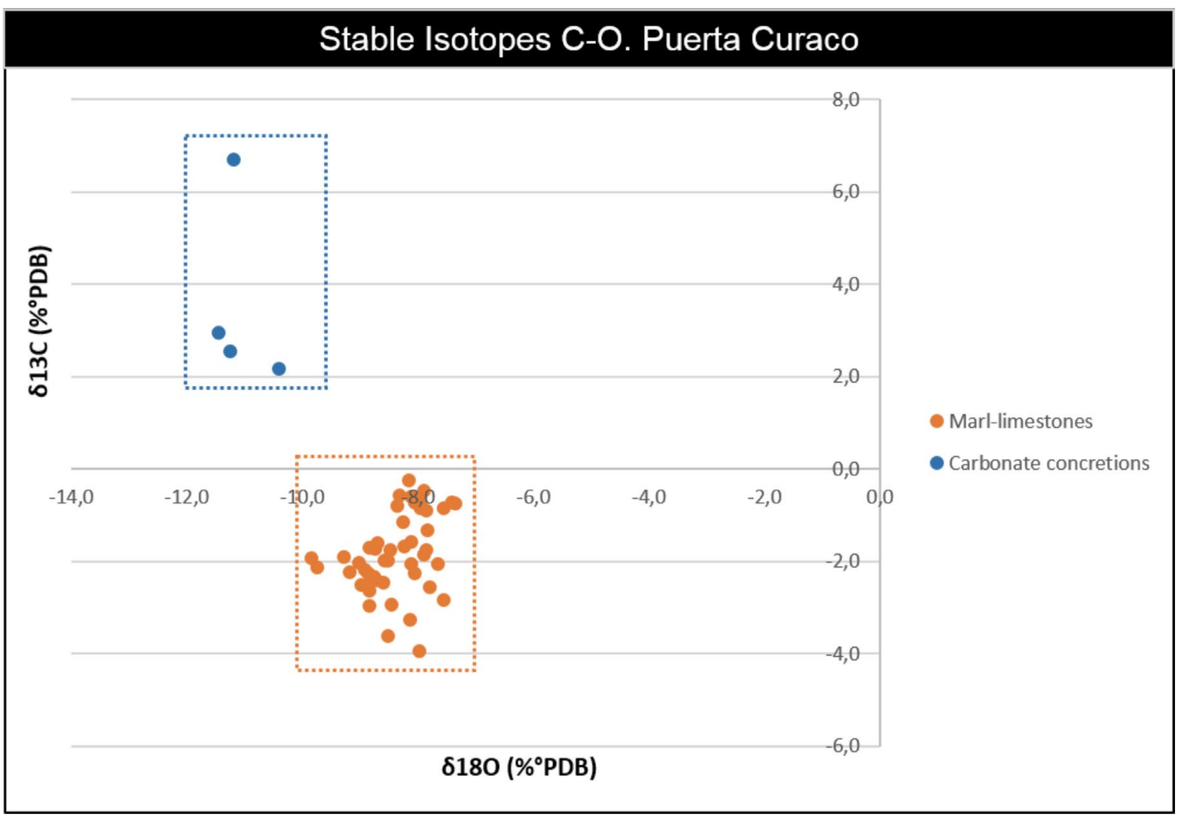

Figure 7. Stable isotopes C-O for marl-limestones and carbonate concretions.

Trace Elements and their meaning

Marls, limestones and concretions of Puerta Curaco have been measured at all intermediate compositions between 1 to 250 mmol/mol Mg/Ca and 0,15 to 1.62 mmol/mol Sr/Ca (Fig. 8), Plots of Sr and Mg normalized to Ca are useful for discriminating between aragonite, low magnesium calcite (LMC) and high magnesium calcite (HMC), (Carpenter *et al.*, 1991; Hasiuk and Lohmann 2008). In Fig. 8 three areas can be differentiated: “Area 1” with composition from 0 to 6 mmol/mol Mg/Ca and 0.4 to 1.65 mmol/mol Sr/Ca, “Area 2” with composition from 38 to 100 mmol/mol Mg/Ca and 0.15 to 1 mmol/mol Sr/Ca and “Area 3” with composition from 146 to 250 mmol/mol Mg/Ca and 0.13 to 0.83 mmol/mol Sr/Ca.

Samples from Area 1 show higher Sr/Ca and lower Mg/Ca ratios, consistent with aragonitic precursors. Samples belonging to Area 2 have values between HMC and aragonite, so mixing between abiotic marine calcite and biotic aragonite precursors can be assumed. The high Mg contents in samples from Area 3 (dolomitized limestones) are explained by dolomite precipitation in early diagenesis.

Shallow marine carbonate sediments are composed predominantly of aragonite and HMC (Tucker and Wright 1990), while LMC indicates burial diagenesis (Flugel 2004). Several types of skeletal particles in the Vaca Muerta Fm. are made of HMC (i.e. bivalves, echinoderm plates, etc). Other are of aragonitic composition (i.e. foraminifera, bivalves, calcispheres,

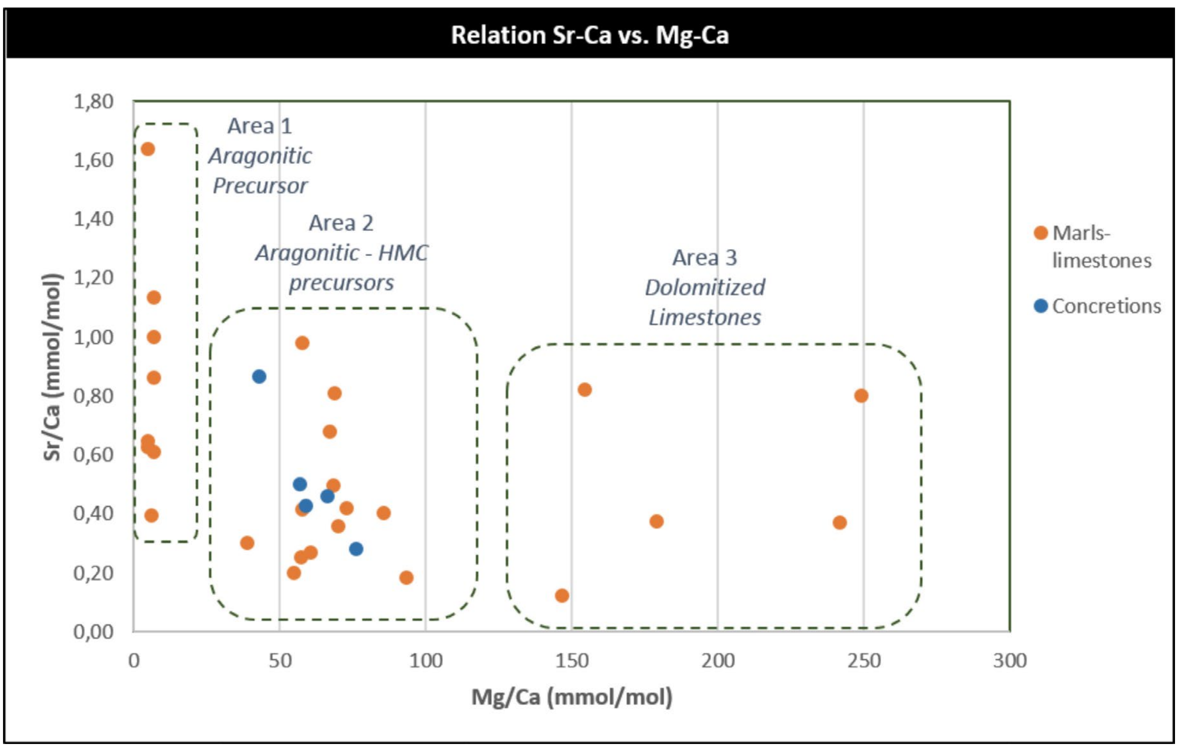

Figure 8. Different areas are identified in Puerta Curaco limestones and concretions: Aragonitic precursor (Area 1), Aragonitic – HMC precursors (Area 2) and Dolomitized Limestones (Area 3).

nannoplankton). Besides, shoal water micritic carbonate resulting from bioclast erosion, abiotic marine calciteand diagenetic neomorphism could contribute to the heterogeneity of carbonate composition.

Figure 9A shows that marls-limestones of Puerto Curaco have values of Fe/Ca ranging between 3 to 70 mmol/mol and Mn/Ca between 0 to 12 mmol/mol. Concretions have lower values of Fe/Ca and Mn/Ca than limestones, ranging between 2 to 5 mmol/mol and 1.5 to 2.7 mmol/mol respectively, Mn has strong affinity with carbonates. As there is not a good correlation between Fe content (ppm) and pyrite abundance, we assume that most Fe is in the carbonates together with the Mn. The wide range of Fe/Ca values in marls-limestones represent mixing of calcite microcrystals precipitated in the sulfate reduction zone (Fe free carbonates) and calcite microcrystals precipitated in deeper burial conditions (ferroan calcites). Lower Fe/Ca values in concretions reflect original components and early carbonate cementation, probably associated to the lower part of the sulphate reduction zone, where the concentration of Fe is low due to previous precipitation of pyrite.

The marls-limestones show one trend of increasingly negative values of $\delta^{18}O$ as the Fe/Ca ratio increasesup to 100 mmol/mol (Fig. 9B). The other trend includes the limestones-marls and the concretions and shows relatively constant Fe/Ca ratios while $\delta^{18}O$ values becomes increasily negative. The relation Fe/Ca has been suggested to increase with burial diagenesis (Choquette and James 1990). Accordingly, the first trend is interpreted as the result of increasingly-deep burial diagenesis. The Fe/Ca ratio is relatively constant in the second trend because in this case cementation sealed the pores of the marls-limestones and concretions during the early digenesis leaving less or no place for later calcite precipitation.

DISCUSSION

The limestones, marls and carbonate concretions of the Vaca Muerta Formation have variable amounts of intrabasinal carbonate particlestransported by subaqueous flows and storm suspension clouds (Kietzmann *et al.*, 2014, 2016; Catalano *et al.* 2017) and diagenetic carbonate mineral phases (cements, replacements). Carbonate concretions are characterized by grain supported textures, with high sphericity intraclasts (without evident signs of compaction) and pervasive distribution of early carbonate cement with framboidal pyrite. Marls-limestones exhibit intrabasinal particles with signs of compaction and selective distribution of carbonate with framboidal pyrite. In the first case, carbonate cement filled the open spaces in an early stage, preventing later compaction. Precipitation of authigenic phases changed the mechanical behavior of the rocks during diagenesis. Carbonate concretions and heavily cemented and recrystallized limestones underwent less compaction and became more fragile than marls and limestones, which developed marked fissility and were plastically deformed.

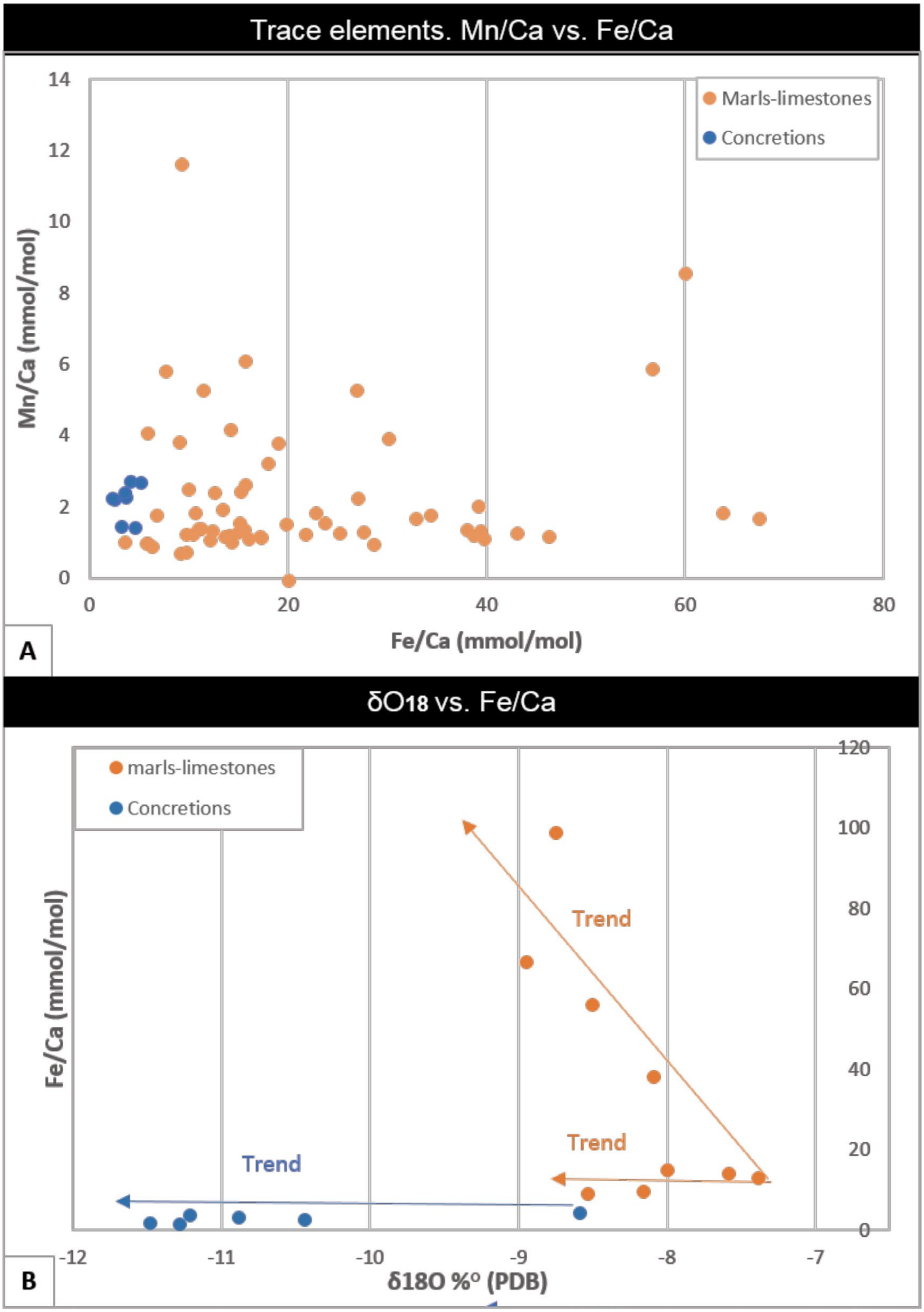

Figure 9. A) Relation between Fe/Ca and Mn/Ca for marls-limestones and concretions. B) Relation between Fe/Ca and $\delta^{18}O$ratios for marls-limestones and concretions.

Ca, Sr and Mg analysis in limestones, marls and concretions highlight the possible carbonate precursors in microfacies with a high degree of neomorphism, indicating a mixing of primary marine and autighenic carbonate signatures in bulk rocks (compare with Hasiuk *et al.* 2016). Carbonate concretions, packstones and grainstones of the Vaca Muerta Formation, have abundant authigenic carbonate with selective to pervasive distribution and moderate to abundant amounts of framboidal pyrite aggregates. The rocks with abundant authigenic carbonate show lower Fe content, suggesting that calcite microcrystals precipitated at an early diagenetic stage in the sulfate reduction zone (Irwin *et al.*, 1977; Scotchman 1989; Reid *et al.*, 2008). Deeper burial authigenic calcite tend to be enriched in Fe and Mn (Choquette and James 1990; Hasiuk *et al.*, 2016). Marls and limestones with high values of Fe/Ca indicate that they have greater contribution of calcite microcrystals precipitated in conditions of deeper burial.

Values of $\delta^{18}O$ for marlstones, limestones and concretions are considerable lower than -2 ‰ (PDB). The isotopic signature of $\delta^{18}O$ of all samples (-12 to -7 ‰ PDB) does not reflect an equilibrium of calcite microcrystals with pore marine waters in the first meters below the marine-sediment interface, under early diagenetic conditions (e.g. Hudson 1977; Mozley and Burns 1993; Hasiuk *et al.*, 2016). These values reveal that calcite was at least partially re-equilibrated at deeper burial diagenetic conditions. For this reason,paleotemperatures calculated from $\delta^{18}O$ must be considered as minimum temperatures.

Since neomorphismand cementation has occurred at different diagenetic stages in the thermal-burial history, the oxygen isotope values for marls, limestones and carbonate concretions are the result of the mixing of original and authigenic components. Carbonate concretions have more negative $\delta^{18}O$ ratios than marls-limestones, because they have a higher contribution of diagenetic cements than marls-limestones.

Carbon dioxide (CO_2) derived from oxidation of organic carbon should reflect the isotopic composition of organic matter, with $\delta^{13}C$ values ranging between -20 to -25‰ PDB (Irwin *et al.* 1977; Curtis and Coleman 1986,Scasso and Kiessling 2001, Gontharet *et al.*, 2007). However, $\delta^{13}C$ ratios for marl-limestones range between 0 to -4 ‰ PDB. The slightly negative values represent mixing between original primary components (bioclasts, peloids and intraclasts) with $\delta^{13}C$ values probably close to 0 and authigenic mineral carbonate phases with a negative isotopic signature provided by oxidation of organic matter during diagenesis.

Considering petrography and geochemical data of Puerta Curaco concretions, they started to grow at shallow depths, near the water-sediment interface in the sulfate reduction zone. As bacterial methanogenesis reactions become more important in the fermentation zone, CO_2 dissolved in pore water becomes heavier, and $\delta^{13}C$ values are generally positive. Carbon isotopic composition for carbonate concretions range between 2 and 6.9 ‰ PDB. The more positive C isotopic composition indicates an origin during early diagenesis from carbon dioxide (CO_2) derived by methanogenesis reactions.

CONCLUSIONS

Microfacies analysis of the limestones, marls and concretions of the Vaca Muerta Formation show variable amounts of intrabasinal carbonate particles (including carbonate bioclasts and detritus, intraclasts and peloids) and authigenic cements and replacements. The later were formed during early diagenesis at the beginning of Vaca Muerta sedimentation (Early Tithonian – thermal subsidence stage) to the deeper burial diagenesis and up to the foreland stage (with maximum paleo-depths close to 3.3 km) when Vaca Muerta Formation had entered in condensate-gas window. Thermal maturation modelled from the burial history and the regional thermal regime is in good agreement with pyrolysis data.

Carbonate neomorphism and cementation, from early through deep burial diagenesis, impact on reservoir properties as rock fragility, porosity and permeability.

On the basis of geochemical analysis (Ca, Sr, Mg) aragonite and HMC are regarded as the carbonate precursors. LMC was precipitated as an authigenic cement phase.

Mn/Ca and Fe/Ca ratios suggest precipitation and recrystallization of calcite at variable burial depths. Different trends in marls-limestones and concretions in the plots of $\delta^{18}O$ vs. Fe/Ca also suggest variable burial diagenesis for the carbonates and early-diagenetic sealing for the pores in the concretions.

The isotopic signature of $\delta^{18}O$ of all samples reflect neither the equilibrium of calcite microcrystals with pore marine waters in the first meters below the marine-sediment interface, nor re-equilibration at the highest temperatures reached by the Vaca Muerta Formation during its thermal history. Calculated paleotemperatures suggest mixing of original and authigenic carbonate phases and partial re-equilibration. Carbonate concretions have more negative $\delta^{18}O$ ratios than marls-limestones because they have a higher contribution of diagenetic cements.

CO_2 derived from anaerobic oxidation of organic carbon in the sulfate reduction zone precipitated as early diagenetic carbonate cements and contributed to the slightly negative $\delta^{13}C$ values observed in bulk rocks. The more positive C isotopic composition exhibited in the concretions, suggest its origin in the methanogenesis zone.

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